



Short Communication

Surface and wettability property analysis of CCF300 carbon fibers with different sizing or without sizing

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ABSTRACT

To analyze the role of sizing on carbon fibers and the mechanism of adhesion in CF/polymer matrix composites, scanning electronic microscopy (SEM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and dynamic contact angle analysis (DCAA) were selected to characterize the different properties between two types of sizings on carbon fiber CCF300. The results of surface roughness obtained from SEM and AFM images showed that the sizings smooth the surface of CCF300. In addition, the percentage of surface polar functional groups on sized CCF300 decreased slightly after sizing. In another hand, the total surface energy and the polar component of surface energy of the sized CCF300 decreased slightly compared to the unsized CCF300, and the J4 sizing has the more influence.

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1. Introduction

Carbon fibers are widely used as reinforcements in composites, especially in advanced composites [1–4]. Mechanical properties of composites primarily depend on the fiber and matrix properties. However, the fiber/matrix interfaces also play an important role in controlling some of the mechanical properties of composites, such as interlaminar shear strength and impact strength. A strong interface can transfer the load efficiently from the matrix to the fiber, resulting in stronger composites. A universal method to increase the fiber/matrix adhesion is surface treatment included oxidation in plasmas, oxidation in air, electrochemical oxidation, and oxidation in nitric acid or phosphoric [5–10]. Surface treatment increasing in the surface polarity or active sites for van der Waals linking and hydrogen bonding can improve the interfacial adhesion between the fiber and surrounding polymer matrix [8–12]. After surface treatment, the fibers are generally sized or coated with a polymer layer [13–15]. The function of sizing is still controversial. Some scholars consider that the purpose of sizing is to insert a polymer between the carbon fiber and the polymer matrix and to use the properties of sizing to control the level of fiber/matrix adhesion [16–18]. Others consider that sizing material usually does not promote adhesion but is present to prevent fiber damage during fiber handling in filament winding, prepregging and weaving operations [19,20]. Otherwise, sizing has also been reported to improve the wetting of fiber by the matrix resin so as to protect its reactivity [21].

This research aims at analyzing whether the sizing agent would increase the surface roughness, numbers of surface reactive groups and wettability of the carbon fiber, therefore enhancing the interface properties of composite, while reducing the friction and preventing fiber damage during subsequent textile processing. The surface morphology and surface roughness of unsized and sized carbon fibers were obtained by scanning electronic microscopy (SEM) and atomic force microscopy (AFM). The surface composition and surface functional groups of fibers were examined by X-ray photoelectron spectroscopy (XPS). Wettability studies were carried out by the dynamic contact angle analysis (DCAA).

2. Materials and experimental

Polyacrylonitrile based carbon fibers CCF300 produced by Wei-Hai TuoZhan fiber Co. Ltd. in China was used without and with J4 and A436 emulsion-type sizings. Whether sizing or not, all the carbon fibers in this research were had been subject to electrochemical oxidation surface treatment before leaving the factory. The main ingredients of sizings are modified epoxy resin. The J4 sizing was obtained commercially from Toho in Japan and the A436 sizing was supplied by Fudan University.

The unsized and sized CCF300 were analyzed using a Thermo VG ESCALAB250 X-ray photoelectron spectrometer (XPS). The spectra were collected using a Mg K α X-ray source (1253.6 eV) with a power of 300 W. The XPS data were fitted according to Gaussian–Lorentzian function.

The SEM images of CCF300 with or without sizing were characterized by a LEO 1530 field emission scanning electronic microscopy.

Atomic force microscopy (AFM) measurements were performed with a solver P47 pro instrument manufactured by NT-MDT Co. in

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Russia. A single carbon fiber was fastened to a steel sample mount with double sided tape. All images were collected in air using the tapping mode with a silicon nitride probe. Roughness analysis was carried out from the images obtained over a $3\ \mu\text{m} \times 3\ \mu\text{m}$ area.

The surface energy (including dispersive γ_s^d and polar γ_s^p components) measurements were performed on the carbon fibers using a DCAT21 Dynamics Contact Angle Analyzer manufactured by Data Physics Co. Four fibers about 20–25 mm were first bonded to a double sided tape with proportional spacing and trimmed on one side of fibers. Then the assembly was hung on the arm of the electronic balance. The DCAA experiments were preformed at a motor speed of $8\ \mu\text{m/s}$ and the fiber immersion depth of 5 mm with deionized water, ethylene glycol and diiodomethane, respectively, as the wetting medium. The liquids used and their surface free energies are listed in Table 1. Ten separated results of tested fiber samples were averaged to obtain one representative value. The advancing contact angle was used to calculate the fiber surface energy according OWRK equation in SCAT software package supplied by DataPhysics.

3. Results and discussion

3.1. Surface topography

Figs. 1 and 2 show the SEM and AFM images of unsized and sized CCF300, respectively. SEM and AFM images consistently reveal that the sizing changes the surface topography on a microscopic scale. The sizing increases fiber surface smoothness and the longitudinal streaks on sized fibers become shallower, which resulted from streaks on fiber surface were covered during the sizing process. Increasing the fibers surface roughness could enhance the mechanical interlocking [22]. Therefore, the smooth surface of the samples after sizing has negative effect on mechanical interlocking.

Table 2 summarizes the results of the roughness analysis of unsized and sized fibers as obtained from the AFM images. The results indicate that the mean surface roughness value (Ra) is 88.493 nm for the unsized CCF300 carbon fiber. The AFM images of sized carbon fibers show a slight decrease in roughness compared to the unsized carbon fiber. The Ra for the J4 and A436 sized carbon fibers

Table 1
Surface free energy characteristics of the liquids.

Liquid	Source	Purity	γ_s^d (mJ/m ²)	γ_s^p (mJ/m ²)	γ_s^T (mJ/m ²)
Deionized water	–	–	28.25	43.35	71.50
Ethylene glycol	Jinke in Tianjin	AR	31.19	16.27	47.46
Diiodomethane	J&K Chemical Ltd.	AR	49.24	0	49.24

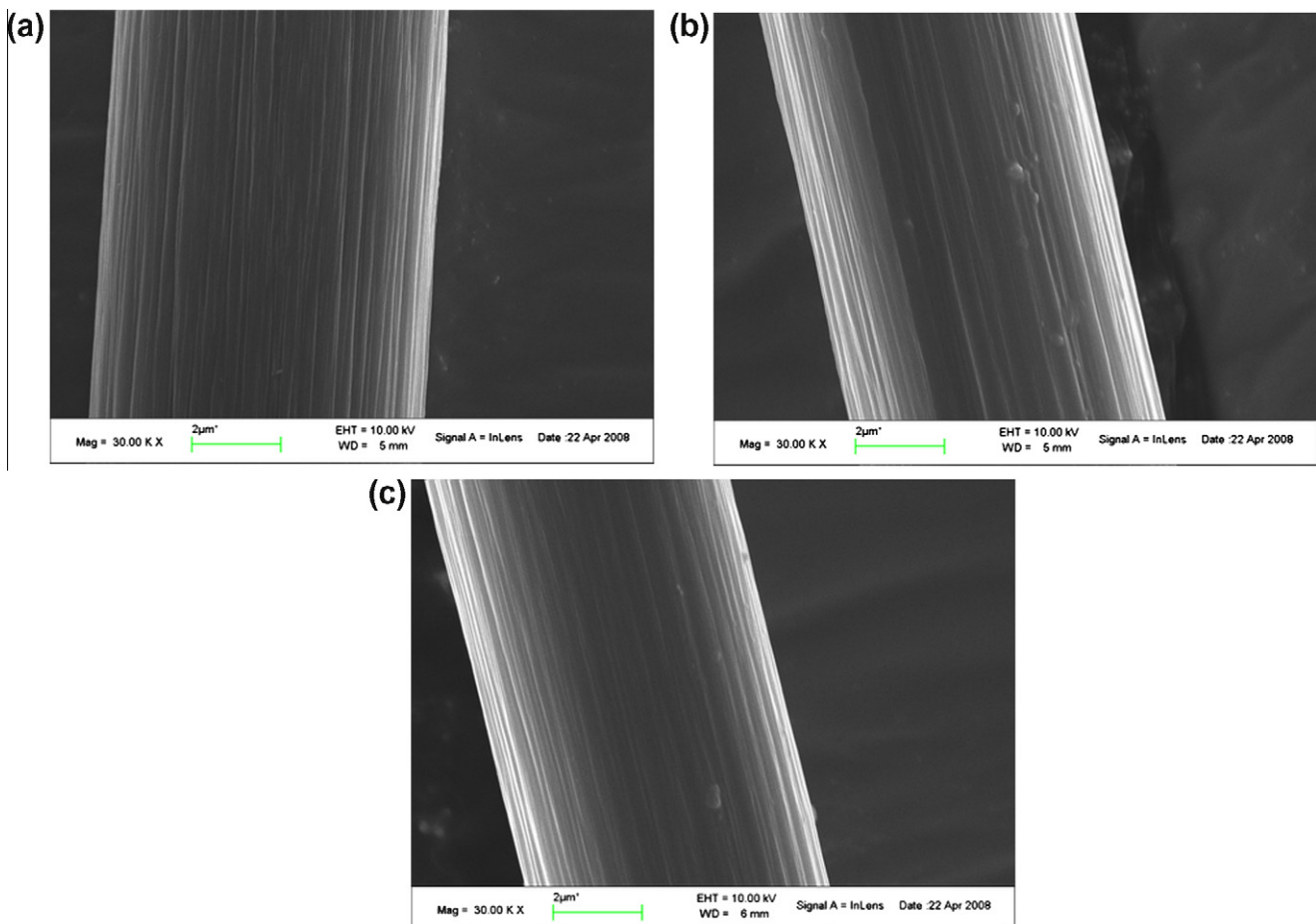


Fig. 1. SEM images of carbon fibers surface. (a) Unsized CCF300; (b) sized CCF300 with J4 sizing; (c) sized CCF300 with A436 sizing.

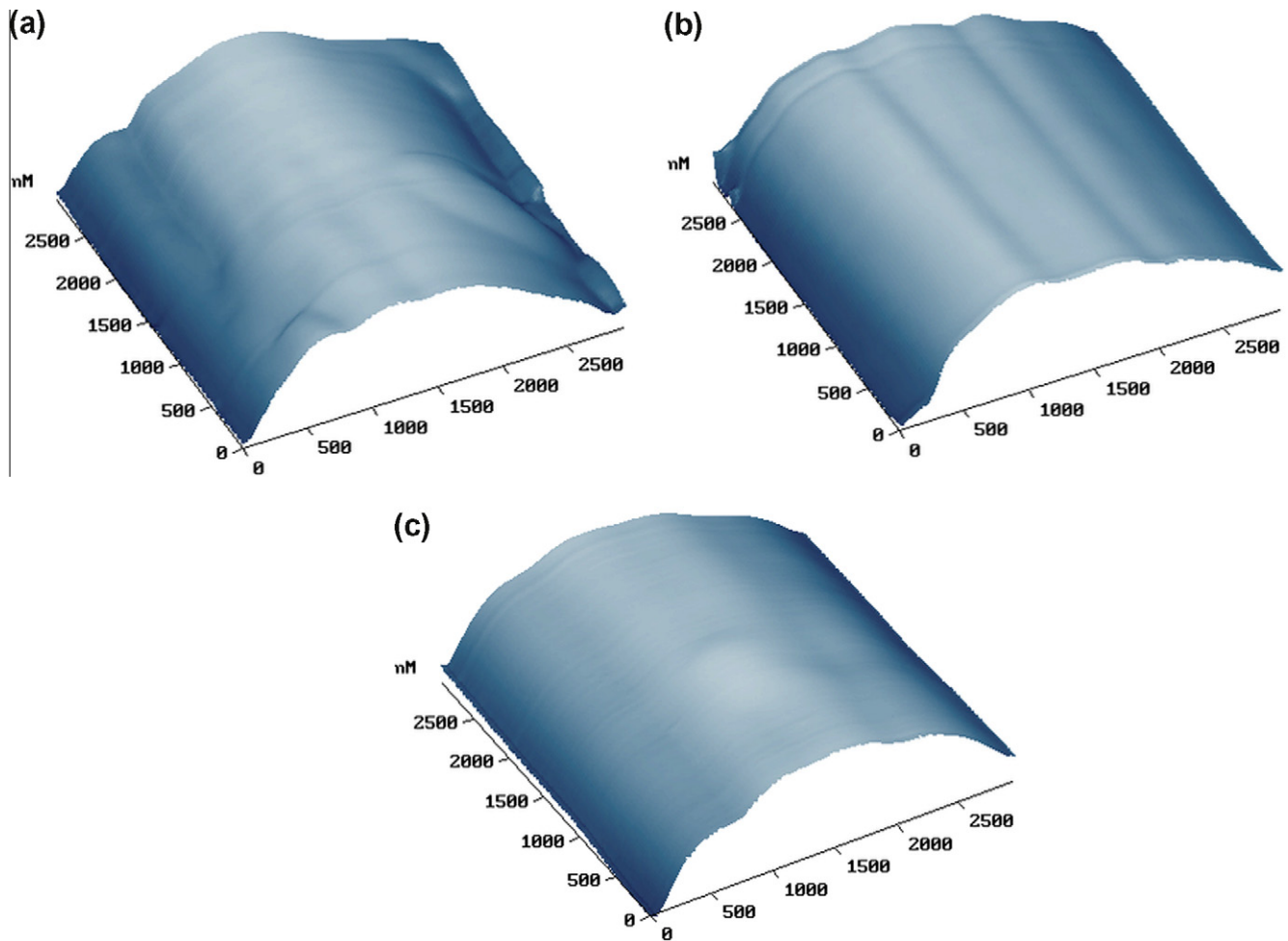


Fig. 2. AFM images of carbon fibers surface. (a) Unsized CCF300; (b) sized CCF300 with J4 sizing; (c) sized CCF300 with A436 sizing.

Table 2
Surface roughness of unsized and sized CCF300 carbon fibers.

Samples	Ra (nm)	RMS (nm)
Unsized CCF300	88.493	109.446
Sized CCF300 with J4 sizing	71.698	99.257
Sized CCF300 with A436 sizing	58.877	77.016

decreased slightly from 88.493 nm to 71.698 nm and from 88.493 nm to 58.877 nm, respectively. It may be a disadvantage to interfacial adhesion between carbon fibers and a matrix resin by decreasing the surface area (decreasing roughness) which may provide less points of contact between the fiber and the matrix.

3.2. Surface composition

The surface composition of unsized and sized carbon fibers was determined by XPS and the results are given in Table 3. Values of

the binding energy (BE) and the atomic concentration (AC) are listed for each photopeak. The unsized CCF300 surface is composed of carbon, oxygen, nitrogen, sulfur and silicon. The J4 and A436 sized CCF300 carbon fibers contain these same elements except nitrogen.

Fig. 3a–c shows typical XPS C1s fitting curve spectra for unsized and sized CCF300 carbon fibers. The percentages of functional groups (C–OH or C–OR; C=O) on unsized and sized carbon fibers were estimated from these fitting curve C1s photopeaks and are listed in Table 4. Values of the binding energy (BE) and the percent contribution (PC) of each curve fitting photopeak to the total C1s photopeak are summarized in Table 4. The functional groups C–OH and C=O were detected on all unsized and sized carbon fibers. The percentage of functional groups containing oxygen decreased for both J4 and A436 sized carbon fibers when compared to the unsized carbon fiber, because the CCF300 carbon fiber had obtained electrolytic surface treatment to increase amount of surface active functional groups containing oxygen before sizing in

Table 3
XPS surface composition of unsized and sized CCF300 carbon fibers.

Samples	C1s		O1s		N1s		S2p		Si2p		O/C
	BE (eV)	AC (%)	BE (eV)	AC (%)	BE (eV)	AC (%)	BE (eV)	AC (%)	BE (eV)	AC (%)	
Unsized CCF300	285.0	67.25	532.6	20.2	400.9	3.17	168.6	1.32	103.2	8.06	0.30
Sized CCF300 with J4	285.0	75.81	532.7	18.81	–	–	168.9	1.32	102.6	4.05	0.25
Sized CCF300 with A436	285.0	72.73	533.0	20.3	–	–	170.2	1.74	102.8	5.23	0.28

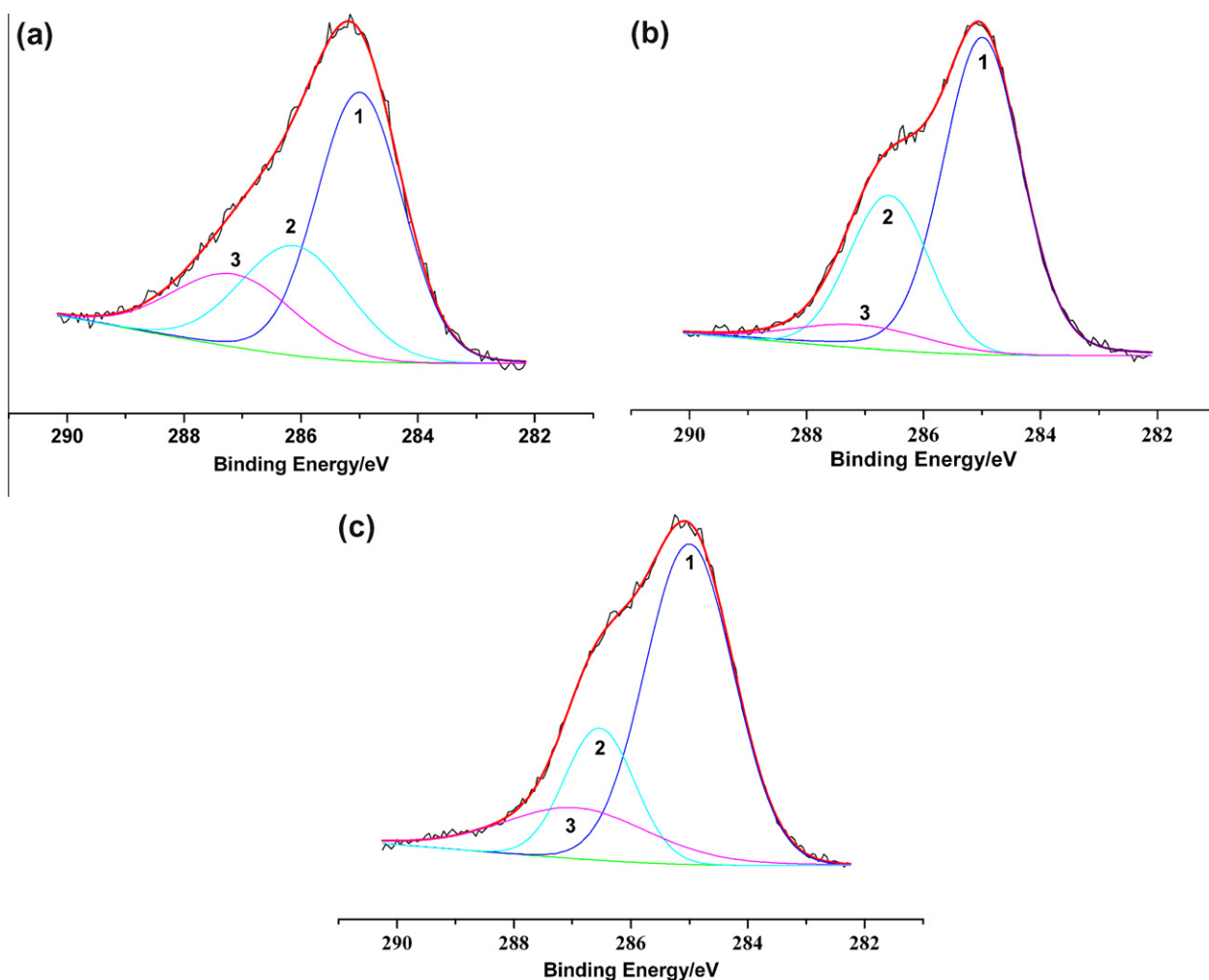


Fig. 3. Curve fitting C1s photoelectron peaks of carbon fibers. (a) Unsized CCF300; (b) sized CCF300 with J4 sizing; (c) sized CCF300 with A436 sizing.

CCF300 carbon fiber production line. The covered sizing layer with less active functional groups containing oxygen on the carbon fibers will decrease numbers of the surface active sites. Meanwhile, it is generally accepted that the functional groups containing oxygen are acidic [23,24], and the acidic filler have better adhesion

strength with epoxy matrix than those of basic fillers for Lewis acid-basic interactions since the polar component of the epoxy resin is basic [8,10,25]. So, it is reasonable that the decreased functional groups containing oxygen on sized carbon fibers are disadvantage to the fiber/matrix adhesion. It has been suggested

Table 4
XPS C1s curve fitting results of unsized and sized carbon fibers.

Samples	Peak 1		Peak 2		Peak 3	
	—C—C or —C—H		—C—OH or —C—OR		—C=O	
	BE (eV)	PC (%)	BE (eV)	PC (%)	BE (eV)	PC (%)
Unsized CCF300	285.0	53.43	286.2	26.66	287.2	19.91
Sized CCF300 with J4	285.0	63.38	286.6	29.33	287.1	7.29
Sized CCF300 with A436	285.0	62.12	286.5	20.10	287.0	17.78

Table 5
Carbon fiber surface energies and contact angles in different liquids.

Samples	Contact angle (°)			OWRK surface energy (mN/m)		
	Deionized water	Glycol	Diiodomethane	γ_s^T	γ_s^d	γ_s^p
	Unsized CCF300	55.80	32.99	40.05	47.54	29.88
Sized CCF300 with J4	76.09	42.41	36.40	41.02	35.40	5.62
Sized CCF300 with A436	61.58	39.57	26.19	46.18	33.57	12.61

that the surface treatment surface treatment has more pronounced effect on improving the interfacial strength than the sizing in Refs. [13,26].

3.3. Surface free energy analysis

The surface free energy is a strong gage of solid surface, and adhesion strength between fibers and matrix is predominantly affected by the surface free energy of fibers [25]. The total surface energy (γ_s^T) of the fibers was estimated as sum of the dispersive or London component (γ_s^d) and the polar components (γ_s^p) [27]. Owens and Wendt [28] consider that the interfacial tension of solid/liquid contact phase can be formulated by the following equations:

$$\gamma_{sl} = \gamma_s + \gamma_l - 2(\gamma_s^d \gamma_l^d)^{1/2} - 2(\gamma_s^p \gamma_l^p)^{1/2} \quad (1)$$

$$\gamma_s = \gamma_s^d + \gamma_s^p, \quad \gamma_l = \gamma_l^d + \gamma_l^p \quad (2)$$

By applying the Young's equation, the following equation can be deduced:

$$\gamma_l(1 + \cos \theta) = 2(\gamma_s^d \gamma_l^d)^{1/2} + 2(\gamma_s^p \gamma_l^p)^{1/2} \quad (3)$$

$$\cos \theta = F/P\gamma_{sl} \quad (4)$$

where subscript *s*, *l* and *sl* are the shortening of solid, liquid and solid/liquid interface, respectively, θ is the contact angle at solid/liquid interface, *F* is the wetting force at the solid/liquid interface, *P* is the wetting perimeter. Measured wetting forces from DCAA were used to calculate contact angles θ from Eq. (4), knowing γ_{sl} and *P*.

According OWRK method, measured contact angles of two types of liquid (knowing γ_l , γ_l^d , γ_l^p) on fiber surface, respectively, then the dispersive (γ_s^d) and the polar (γ_s^p) components of the fiber surface energies were calculated from Eq. (3). The results for the surface energies, contact angles in different liquids of unsized and sized carbon fibers are presented in Table 5. It is clear that the total surface energy decreases slightly and the dispersive component (γ_s^d) increases slightly for sized carbon fibers CCF300, respectively. However, there is a distinct decrease in the polar component (γ_s^p) for the two types of sized carbon fiber when compared to the unsized fiber.

The percentage of surface functional groups containing oxygen on the unsized fiber is higher than ones on sized fibers as shown in Fig. 4. So, the decrease in total surface energy and its polar component appears to be due to the decrease in the percentage of surface polar functional groups (C—OH or C—OR; C=O) for both sized fibers. In fact, an approximately linear relationship can be obtained between polar component of the surface energy and oxygen content

(the O/C atomic ratio) on the surface of carbon fibers [11]. The polar component is a governing factor in the adhesion between the fibers and the epoxy matrix [25], because the percentage of surface active functional groups (C—OH or C—OR; C=O) increases the possibility of forming a chemical bond between fiber and matrix [24–26]. Meanwhile, an increase in the surface polarity or active sites for van der Waals linking and hydrogen bonding can improve the interfacial adhesion between the fiber and the surrounding polymer matrix, leading to better stress transfer from the matrix to the fiber materials [11,29]. Therefore, the decreased surface energy, especially the polar component of surface energy on carbon fiber's surface after sizing suppresses surface wettability or even decreases the interfacial adhesion between fiber and matrix possibly.

4. Conclusions

The results of this study revealed that the surface characteristics of carbon fiber significantly changed after sizing. The SEM and AFM images showed that both the size of streaks on the sized carbon fibers and surface roughness decreased. XPS results proved that the amount of surface functional groups containing oxygen and the ratio of oxygen to carbon decreased. Dynamic contact angle analysis results indicated that the sized carbon fibers had a lower total surface energy and the polar components of surface energy decreased as well, compared with the unsized carbon fiber, which proved the XPS result of the decrease on the amount of surface functional groups containing oxygen after sizing.

Surface roughness, surface active functional groups and surface energy are of great importance to adhesion of carbon fiber/matrix interface. The decreases on the surface roughness, amount of surface active functional groups and surface energy contributed negative effect to adhesion of carbon fiber/matrix interface. All the results indicated that the main role of sizing was not to increase the interfacial adhesion between fiber and matrix, and the sizing for carbon fiber could serve a lubricant to prevent fiber damage during subsequent textile processing such as weaving and prepreg processing [19,20], while being compatible with the matrix resin and not obviously decreasing the fiber/matrix interface adhesion.

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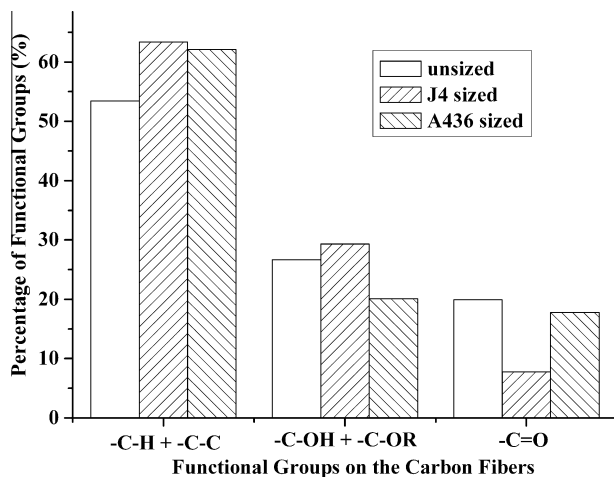


Fig. 4. The percentage of functional groups of unsized and sized CCF300 carbon fibers.

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