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Effects of oxygen plasma treatment on domestic Aramid fiber III surface properties

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Abstract. The effects of oxygen plasma treatment on Domestic Aramid Fiber III (DAF III) surface properties were investigated in this work. The fiber surface chemical composition, surface morphology, surface roughness and surface wettability before and after oxygen plasma treatment were characterized by X-ray Photoelectron Spectroscopy (XPS), Atomic Force Microscopy (AFM) and Dynamic Contact Angles Analysis (DCAA), respectively. The results showed that oxygen plasma treatment improved the fiber surface chemical activities, changed surface morphologies, enhanced surface roughness and improved surface wettability by oxidative reactions and plasma etching. The total free energy increased from 49.8 mJ/m2 to 62.73 mJ/m2 after oxygen plasma treatment.

1. Introduction

The domestic aramid fibers, developed type of para-aramid fibers manufactured in China, which is spun from poly-(polyamide benzimidazole-co-p-phenylene terephthalamide) have widely potential application as reinforcement material in the fields of aviation, automobile, shipbuilding due to its high strength, high module and high temperature resistance[1-2]. However, because of its smooth and chemical inert fiber surfaces, which limit its application in composite system [3] Thus, it is necessary to modify the fiber surface. Compared with some other modification methods, such as chemical and physical methods, low temperature plasma treatment offers several advantages such as the selection modification of only the outer atomic layers of the substrate, the selection of the desired functional groups and the minimization of thermal degradation and so on [4-7].

The aim of this work is to investigate the effects of oxygen plasma treatment on domestic aramid fiber III surface properties. The fiber surface chemical composition, surface morphology, surface roughness and surface wettability before and after oxygen plasma treatment were analyzed by X-ray photoelectron spectroscopy (XPS), Atomic Force Microscopy (AFM) and Dynamic Contact Angles Analysis (DCAA), respectively.

2. Experimental

2.1 Materials

Aramid fibers III (polyheteroarylene-co-p-phenyleneterephthalamide) were supplied by China Bluestar Chengrand Chemical Co. Ltd for surface modification. The fibers were cleaned successively with acetone and distilled water and then dried in a vacuum oven for 3 h at 110 °C before further analysis.

Plasma was excited by an inductive coupling radio frequency generator (13.56 MHz). Oxygen was kept at a flow rate of about 20-30 SCCM. The operation pressure was set at 30 Pa. The fiber samples

were treated for 25 min with plasma treatment power of 200 W. Then the samples before and after plasma treatment were kept in a constant temperature and humidity box.

2.2 Characterization

Surface chemical composition of DAF III before and after oxygen plasma treatment was determined by X-ray photoelectron spectroscopy (XPS) (ESCALAB 250, Thermo). The Non-Linear Least Squares Fitting (NLLSF) program with a Gaussian-Lorentzian production function was used for curve fitting of C1s spectra.

Surface morphology and roughness of DAF III fiber before and after oxygen plasma treatment was characterized by AFM (Multimode 3D, Veeco) in non-contact mode. Fiber surface morphology images were recorded with scanned areas of 16 square micron. (4 μm ×4 μm).

Surface wettability of DAF III fiber before and after oxygen plasma treatment was characterized by DCAA (Dataphysics, KRüSS).

3. Results and Discussion

3.1 XPS analysis

Figure 1 shows the XPS results of aramid fiber III before and after oxygen plasma treatment. The relative content of these three elements including C, N and O and the ratios of N/C and O/C are given in Table 1. It is found that fiber surface carbon, nitrogen and oxygen element contents are 77.1%, 6.5% and 16.4% for untreated fiber sample, respectively. The ratios of N/C and O/C are 0.08 and 0.21, respectively. After plasma treatment, these three element contents experience different changes. The surface carbon element content decreases sharply to 70.7%, surface nitrogen experiences obviously increasing to 12.4% and surface oxygen element content increases a little to 16.9%. Meanwhile, the ratios of N/C and O/C increase to 0.17 and 0.24, respectively. This result proved that oxygen plasma treatment can change fiber surface chemical composition which is beneficial for improving the chemical bonding in composite system.

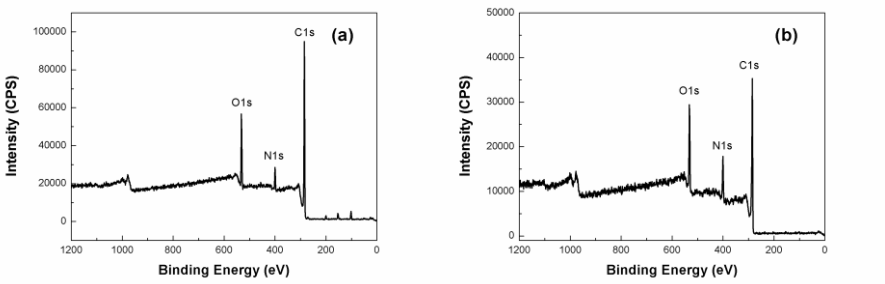

Figure 1. XPS of aramid fiber before (a) and after (b) oxygen plasma treatment.

Table 1. Element analysis of DAFIII

Samples	Element content (%)			N/C	O/C
	C (%)	N (%)	O (%)		
Untreated	77.1	6.5	16.4	0.08	0.21
Plasma treated	70.7	12.4	16.9	0.17	0.24

3.2 Surface morphology observation

Figure 2 shows the two-dimensional topographies AFM images of aramid fiber before and after oxygen plasma treatment. Meanwhile, the root mean square roughness (R_q) and the arithmetic mean roughness (Ra) are given in Figure 3. The surface of the untreated fibers as shown in Figure 2(a) is smooth and the root mean square roughness (R_q) and arithmetic mean roughness (Ra) were 46.5 nm and 42.3 nm, respectively. As seen from Figure 2(b), it is found that the surface turn to be rougher and surface roughness values R_q and Ra reach to 49.6 nm and44.2 nm, respectively. The AFM results confirm that oxygen plasma etching can change the fiber surface morphology and increase fiber surface roughness on a microscopic scale.

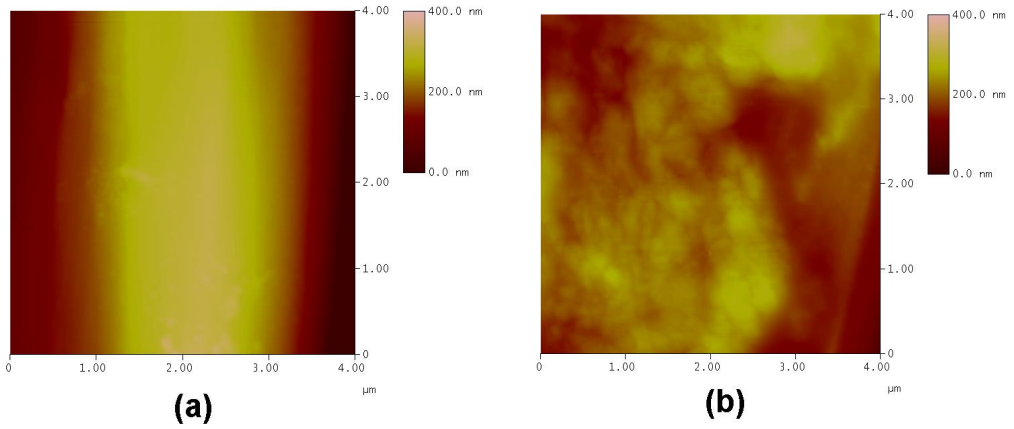

Figure 2. AFM observation of aramid fiber before (a) and after (b) oxygen plasma treatment.

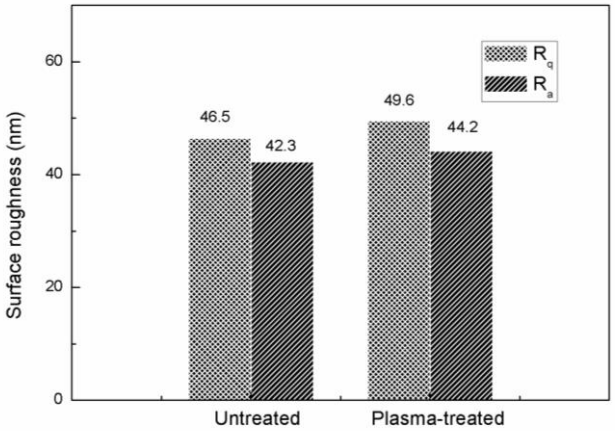

Figure 3. Surface roughness Rq and Ra before and after oxygen plasma treatment

3.3 Surface wettability

Surface wettability is measured by dynamic contact angles with water (W) and diiodomethane (DIM). The results are shown in Table 2. Surface free energy are calculated by equations in Ref.[7] It is found that the contact angles of water decreases from 70.30 °to 37.23 °and the contact angles of DIM increases from 30.96 ° to 57.64 °after oxygen plasma treatment. Figure 4 illustrates the results of surface polar component (γ^p) , surface dispersive component (γ^d) and surface total free energy (γ_s). For the untreated samples, these three values were 6.08 mJ/m^2, 43.82 mJ/m^2 and 49.90 mJ/m^2, respectively. After plasma treatment, the γ^p and γ_s increase to 32.79 mJ/m^2 and 62.73 mJ/m^2, respectively. Meanwhile, the γ^d decreases to 29.93 mJ/m^2 and 43.3 mJ/m^2. This results may be explained by fiber surface chemical activities and etching effects after oxygen plasma treatment, which together improved surface wettability.

Table 2. Contact angles with water (W) and diiodomethane (DIM) of aramid fiber before and after oxygen plasma treatment

Samples	$\theta_a(W)$	$\theta_a(DIM)$
Untreated	70.30 (1.2)	30.96 (2.4)
Plasma treated	37.23(1.1)	57.64 (3.1)

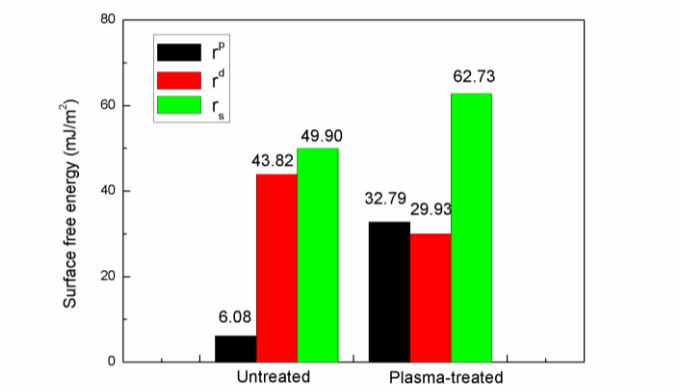

Figure 4. Surface free energy before and after oxygen plasma treatment

4. Conclusion

The XPS results showed that oxygen plasma treatment changed fiber surface chemical activities. AFM observation showed that fiber surface morphologies were changed and the fiber surface roughness were enhanced DCAA results illustrated that fiber surface wettablity was improved. The total free energy increased from 49.90 mJ/m^2 to 62.73 mJ/m^2 after oxygen plasma treatment.

Acknowledgments

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References

[1]. Liu D D, Hu, YY H, Zhang F F. Interfacial reinforcement of domestic aramid fiber III/PTA composites using azide-containing benzimidazole coupling agent. Acta Mater Composite Sinica, 34(2017) 336-344.
[2]. Zhang S H, He G Q, Liang G Z. Comparison of F-12 aramid fiber with domestic armid fiber III on surface feature. Appl Surf Sci. 256(2010) 2104-2109.
[3]. Xing L X, Liu, L, Huang Y D. Enhanced interfacial properties of domestic aramid fiber-12 via high energy gamma ray irradiation. Composites Part B. 69(2015)50-57.
[4]. Yang S J. Yin H,. Two atmospheric-pressure plasma sources for polymer surface modification. Plasma Chem Plasma Process, 2007; 27(1) :23-33.
[5]. Wang C X, Du M, Lv J C. Surface modification of aramid fiber by plasma induced vapor phase graft polymerization of acrylic acid. I. Influence of plasma conditions. Appl Surf Sci , 349(2015)333-342.
[6]. Wang J, Chen P, Li H.The analysis of Armos fibers reinforced poly(phthalazinone ether sulfone ketone) composite surfaces after oxygen plasma treatment. Surf Coat Tech. 202(2008): 4986-4991.
[7]. Chen P, Wang J, Wang B C. Improvement of interfacial adhesion for plasma-treated aramid fiber-reinforced poly(phthalazinone ether sulfone ketone) composite and fiber surface aging effects. Surf Interface Anal. 41(2009) 38-43.