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Dynamic wetting behavior of plasma treated PET fibers

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Abstract

Polyethylene terephthalate (PET) fibers have been increasingly used in textile industries for a variety of applications ranging from filtration, composites, tissue engineering and electronic textiles. The surface properties of these polymer fibers are of importance in various applications. The surface properties of PET fibers can be modified by different techniques. In this study, PET fibers were treated in oxygen plasma for improving surface wettability. The effects of plasma treatment on dynamic wetting behavior were characterized using atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and dynamic contact angle measurements. The plasma treatment roughened the fiber surface revealed by atomic force microscopy (AFM). The introduction of functional groups was detected by XPS. The roughened and funtionalized surface resulted in the change in advancing and receding contact angles. Both advancing and receding contact angles were significantly reduced, but the contact angle hysteresis was increased after plasma treatment.

Keywords: Plasma treatment; Polyethylene terephthalate; Contact angle; Hysteresis; AFM; XPS

1. Introduction

Fibers are basic elements of textile materials. Natural fibers have dominated the textile market for thousands of years, but the new developments in chemical fiber industry have significantly changed the industry [1]. The use of chemical fibers has been expanding from modern apparel, home furnishings, medicine, aeronautics, energy industry to high performance applications.

For industrial uses, manufactured fibers have been increasingly used to replace traditional materials in applications from super-absorbents, to artificial organs, to construction materials for space programs. The dominant fibers used in technical textiles include olefin fibers, PET fiber and rayon fibers [2].

Since polyester fiber has a lot of special characteristics, such superior strength and resilience, it has become one of the most important materials in various industries. For the applications of PET fibers in sorption related industries, PET materials have to be modified to improve the wettability of the materials. Surface modification by plasma treatment has opened up new possibilities in relation to wettability and adsorption of textile materials [3]. Plasma is a low-temperature glow discharge or a low-pressure partially ionized gas consisting of large concentrations of excited atomic, molecular ionic, and free radical species. Plasma surface treatment causes changes to a limited depth; bulk properties of even the most delicate materials remain unchanged [4].

The wettability of materials can be characterized by contact angle. The contact angle, the angle formed at the intersection of the solid and the fluid interfaces, is routinely evaluated based on the static contact angle [5]. In various dynamic processes, however, static contact angle is not sufficient to characterize the wetting behavior of different materials. Dynamic contact angles are divided into advancing and receding contact angles, which are defined as the contact angles measured when the three phase line is in controlled movement by wetting the solid by the liquid or by withdrawing the liquid over a pre-wetted surface, respectively. The difference between advancing contact angle and receding contact angle forms contact angle hysteresis. Contact angle hysteresis affects the liquid adsorption and/or retention processes of a material [6].

In this study, polyethylene terephthalate (PET) fibers were treated in oxygen plasma for improving surface wettability. The effect of plasma treatment on wetting behavior of the fibers was characterized using dynamic contact angle measurements. The changes in surface morphology and chemistry were also

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examined using atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Materials

Fibers used in this study were polyethylene terephthalate (PET). The PET fibers had an average diameter of 28 μm. The fiber samples were first washed in ethanol followed by twice rinses in distilled water and then they were dried at 40 °C in an oven.

Plasma treatment was performed in a HD-1A vertical laboratory plasma treatment machine. The treatment was carried out using oxygen at a pressure of 15 Pa. Each sample was treated at 50 W for 30, 60 and 90 s, respectively.

2.2. Surface characterization

2.2.1. AFM observation

Scanning probe microscope (SPM), particularly in the form of atomic force microscopy (AFM) provides new tools for examining nanostructures [7]. The AFM used in this study was CSPM4000 produced by Benyuan Company. The vertical resolution of the machine is 0.1 nm, while the horizontal solution is 0.2 nm. The scanning mode used was contact mode in this study, and the scanning range was set at a size of 5.0 μm × 5.0 μm. All samples were scanned at room temperature in atmosphere.

2.2.2. X-ray photoelectron spectroscopy

The XPS used in this study was an ESCA 300 (Scienta Instruments). The XPS utilizes photoionisation and energy-dispersive analysis of the emitted photons to monitor the composition of the surface region of the sample. The experiments were carried out using a monochromatised Al Kα X-ray source (1486.7 eV) at 15 kV and 10 mA. The wide scan spectra for identification of elements were obtained over the range 0–1000 eV, using a pass energy of 150 eV. The same pass energy was also used in obtaining the high-resolution spectra.

2.2.3. Dynamic contact angles

The dynamic contact angle measurement of individual fiber was performed using a CDCA-100F produced by the Camtel Ltd. in the UK, The dynamic contact angles were determined by Wilhelmy technique [8], where a solid sample was immersed and withdrawn into and out from a liquid while simultaneously measuring the force acting on the solid sample at 20 °C. The advancing and receding contact angles could then be determined from the obtained force curve.

3. Results and discussion

3.1. Surface morphology

The AFM images of 5.0 μm × 5.0 μm in Fig. 1 reveal the surface structures of the PET fibers. The series of images show the change in surface morphology of the PET fibers before and after plasma treatment. The groove-like structures of the untreated PET fibers are clearly observed by AFM examination, as illustrated in Fig. 1a. They are formed by the fibril structure of the polymer fiber. It can also be seen from the AFM image that the fibrils are oriented in the direction of the fiber axis. These fibril structures are formed during the fiber drawing processing. The effect of oxygen plasma treatment is presented in Fig. 1b–d. The surface of the PET fiber is obviously roughened after the plasma treatment for 30 s, as shown in Fig. 1b. The fibril structure is not visible any more and aggregate structures with various sizes can be seen on the fiber surface. The different sizes of the aggregates indicate the uneven effect of the surface etching by plasma

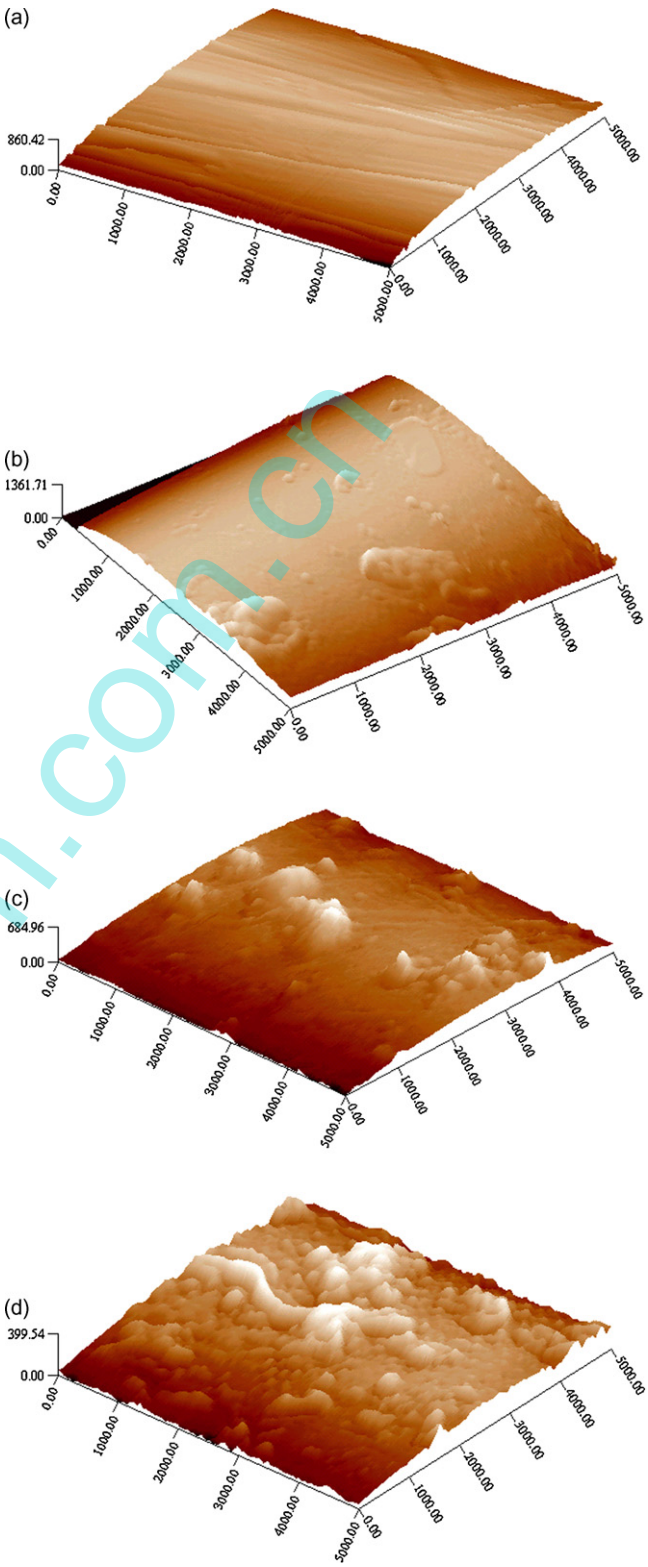

Fig. 1. AFM images of PET fiber: (a) untreated; (b) plasma treated for 30 s; (c) plasma treated for 60 s; (d) plasma treated for 90 s.

treatment. Oxygen plasma treatment for 60 s further roughens the PET fiber surface, resulting in the formation of the pit-like structures on the fiber surface as displayed in Fig. 1c. The plasma treatment for 90 s causes the degradation of the fiber surface due to the etching effect, as exhibited in Fig. 1d.

Table 1
Surface roughness and hysteresis

Treatment conditions	Gas: oxygen; power: 50 W and working pressure: 15 Pa			
Duration of treatment (s)	0	30	60	90
Surface roughness (nm)	12.3	35.6	44.7	52.2
Hysteresis (°)	17	28	35	N/A

The evolution of the surface morphology is also confirmed by surface roughness analysis using the AFM software. The fiber has an average roughness of 12.3 nm due to the fibril structures. Plasma treatment significantly alters the surface roughness, as presented in Table 1. It is shown that the increase in the treatment time leads to the increase in surface roughness.

3.2. Surface chemistry

The surface chemistry of the PET fibers examined by XPS is presented in Fig. 2. XPS C1s spectrum of the untreated PET fibers is composed of three main peaks. They are assigned to C–C and C–H at 285.0 eV, C–O at 286.5 eV and O–C=O at 289.0 eV, as displayed in Fig. 2a. C1s spectra for the PET fibers treated for 30 s is shown in Fig. 2b. The additional C=O peak appears in the spectrum. This confirms the formation of functional groups on the fiber surface after the oxygen plasma treatment. It is also found that the introduction of C=O peak is made at the expense of the C–C bounds and C–H bounds, as revealed in Fig. 2b. Obvious increase of C=O peak is also observed in the XPS analysis for the fibers treated longer than 30 s.

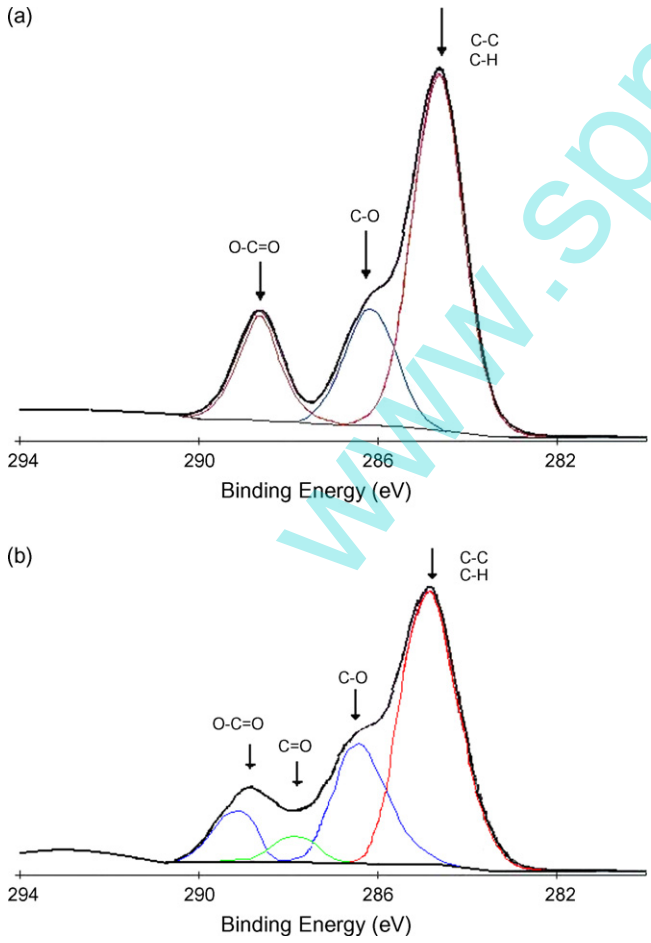

Fig. 2. XPS spectra of PET fiber: (a) untreated; (b) plasma treated for 30 s.

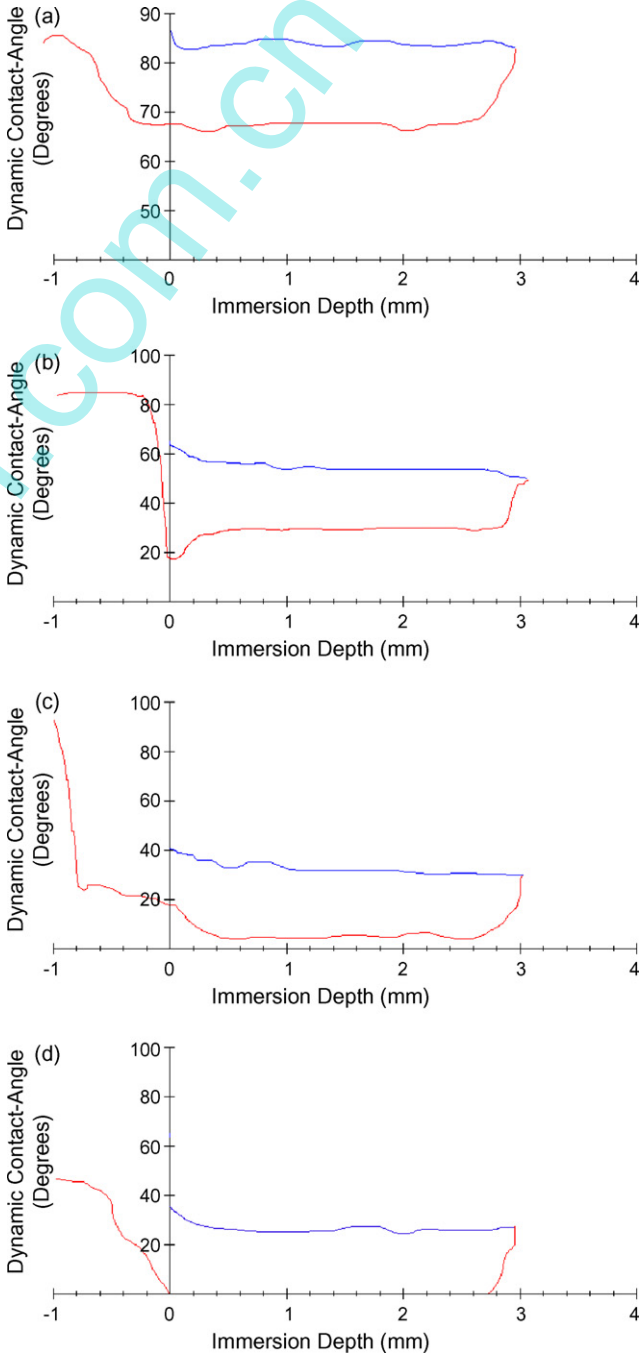

Fig. 3. Dynamic contact angles of PET fiber: (a) untreated; (b) plasma treated for 30 s; (c) plasma treated for 60 s; (d) plasma treated for 90 s.

3.3. Dynamic contact angles and hysteresis

The effect of plasma treatment on surface wettability is revealed by dynamic contact angle measurement. It can be seen from Fig. 3a that the untreated PET fiber has an average advancing contact angle of about 85° and receding contact angles about 68°. There is an obvious hysteresis between the advancing contact angle and receding contact angle. The hysteresis is about 17°, as presented in Table 1. This hysteresis is attributed to the surface roughness of the fibril structures [9].

The plasma treatment significantly alters the surface wetting behavior of the PET fibers. Fig. 3b clearly indicates the decrease of the advancing and receding contact angles of the PET fiber treated for 30 s. The advancing contact angle is reduced to about 58° from 85° and the receding contact angle is dropped to 30° from 68°. The decrease in both advancing and receding contact angles is caused by the formation of hydrophilic groups on the PET fiber surface confirmed by the XPS analysis. It is observed that the hysteresis is increased from about 17° for the untreated fibre to 28° for the fibre treated for 30 s. The increase of contact angle hysteresis is attributed to roughening of the fibre surface by plasma treatment [10], as shown in Fig. 1b and Table 1.

The plasma treatment for 60 s causes the further decrease of contact angle of the PET fibre, as presented in Fig. 3c. The advancing and receding contact angles are lowered to about 40° and 5°. The hysteresis is increased to about 35°. The rougher surface is contributed to the increase in the contact angle hysteresis. The increase of surface roughness from 12.3 to 44.7 nm leads to an obvious increase up to 35° in the contact angle hysteresis, as indicated in Table 1. The advancing contact angle does not drop very much as the duration of the treatment is extended to 90 s, as shown in Fig. 3d. The receding contact angle is too low to be detected. It can be seen that the prolonged treatment seems not to significantly reduce the contact angles, but the longer treatment can cause the decomposition of the fiber surface, as shown in Fig. 1d.

4. Conclusion

Oxygen plasma treatments significantly improve the wettability of the PET fibers. Oxygen plasma treatments introduce the polar groups on fiber surfaces and so reduce the advancing and receding contact angles of the PET fibers. The contact angle hysteresis of plasma treated PET fibers is found to be altered by roughening of the fiber surface. Dynamic contact angle measurement provides new insight into the behaviors of individual fibers, which will help researchers and engineers to development functional textiles with better performance based on the fundamental understanding of the wetting properties of textile materials.

Acknowledgements

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