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CHARACTERIZATION OF DYNAMIC WETTING OF PLASMA-TREATED PTFE FILM

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Polytetrafluoroethylene (PTFE) has been increasingly used in many industries due to its low frictional coefficient and excellent chemical inertness. The surface properties of PTFE are of importance in various applications. The surfaceproperties of PTFE can be modifiedby different techniques. In this study, PTFE film was treated in oxygen plasma for improving surface wettability. The effects of plasma treatment on dynamic wetting behavior were characterized using Scanning Probe Microscopy (SPM), Fourier transform infrared spectroscopy (FTIR), and dynamic contact angle (DCA) measurements. SPM observations revealed the etching effect of the plasma treatment on the film. The introduction of hydrophilic groups by plasma treatment was detected by FTIR. The roughened and functionalized surface resulted in the change in both advancing and receding contact angles. Advancing and receding contact angles were significantly reduced, but the contact angle hysteresis was obviously increased after plasma treatment.

Keywords: Dynamic; plasma treatment; PTFE; AFM; contact angle.

1. Introduction

Polytetrafluoroethylene (PTFE) is a type of thermoplastic, with outstanding chemical resistance, low coefficient of friction, high continuous use temperature, and high oxygen index.[1] PTFE in the form of film has received a lot of attention due to its variety of applications.[2] The chemical inertness and the poor wettability of PTFE films have limited its applications in the sorption and adhesion areas. Various techniques have been adopted to modify PTFE films to improve the wettability of the material, such as ion implantation,[3] grafting copolymerization,[4] and plasma treatment.[5] Surface modification by plasma treatment has opened up new possibilities in relation to wettability and adsorption of various materials.[6]

Contact angles are commonly used to characterize the wettability of a material. Contact angle is routinely measured based on the static contact angle method.[7] In various dynamic processes, such as sorption, desorption, drying, and coalescence, however, static contact angle is not sufficient to understand the wetting behavior of different materials. Dynamic contact angles are needed to analyze the wetting behavior of a material. 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

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hysteresis. Contact angle hysteresis affects the liquid adsorption and/or retention processes of a material.[8]

In this study, PTFE films were treated in oxygen plasma for improving surface wettability. The effect of plasma treatment on wetting behavior of the films was characterized using dynamic contact angle measurements. The changes in surface morphology and chemistry were also examined using Scanning Probe Microscopy (SPM) and Fourier transform infrared spectroscopy (FTIR).

2. Experimental

2.1. *Materials*

Films used in this study were Polytetrafluoroethylene (PTFE). The PTFE films had an average thickness of 40 μm. The film samples were first washed in ethanol and rinsed twice in distilled water and then they were dried at 50°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 80 W for 30, 60, and 90 s, respectively.

2.2. *Surface morphology and film stability*

The SPM used in this study was CSPM4000 produced by Benyuan Company. The scanning mode used was contact mode in this study, and the scanning range was set at a size of 15.0 μm × 15.0 μm. All samples were scanned at room temperature in the atmosphere.

The stability of the PTFE film after plasma treatment was analyzed by tensile testing. The tensile tests were made using BZ2.5/TNIS Zwick universal testing machine.

2.3. *Fourier transform infrared spectroscopy*

The surface chemistry of the film was examined by Fourier Transform InfraRed (FTIR) spectrometer. The Fourier transform infrared (FTIR) tests were conducted on a Perkin-Elmer 1720X Attenuated total reflection- Fourier transform infrared (ATR-FTIR) spectrometer. The spectra were recorded with Harrick ATR attachment using KRS-5 crystal (50 × 10 × 2 mm) at an incident angle of 45° and 25 reflections. The spectral resolution was 4 cm^{-1}.

2.4. *Dynamic contact angles*

The dynamic contact angles of PTFE films were measured using a CDCA-100F, produced by Camtel Ltd in the UK. PTFE films were cut into a size of 1 cm × 4 cm for the dynamic contact angle testing.

3. Results and Discussion

3.1. *SPM observation and film stability*

A series of images obtained by SPM reveal the evolution of the film surface, as presented in Fig. 1. The untreated PTFE film shows a relatively smooth surface with clear particle-like structures, as illustrated in Fig. 1(a). The effect of oxygen plasma treatment on the surface morphology of the PTFE film is presented in Figs. 1(b), 1(c), and 1(d). Oxygen plasma treatment for 30 s obviously etches the surface of the PTFE film, as shown in Fig. 1(b). Oxygen plasma treatment for 60 s further roughens the surface of the PTFE film, as displayed in Fig. 1(c). The plasma treatment for 90 s causes the degradation of the film surface due to the etching effect, resulting in the formation of the aggregation structures on the film surface, as exhibited in Fig. 1(d).

Table 1 shows the change in surface roughness during the plasma treatment. It can be clearly observed that plasma treatment significantly alters the surface roughness of the PTFE film. The surface roughness is increased as the plasma treatment time is extended.

The surface of the film was significantly roughened after the plasma treatment, but the film's tensile strength just dropped about 15% from 28 MPa for the untreated sample to 24 MPa for 90 s treatment. Thus, the film still remained highly stabile after the plasma treatment for 90 s.

3.2. *FTIR analysis*

The FTIR–ATR spectra of the surface of PTFE are shown in Fig. 2. The main absorption band of the untreated PTFE film situated at about 1400–1100 cm^{-1} is composed of the two peaks at 1200 and 1150 cm^{-1}, which are assigned to the C–F structure

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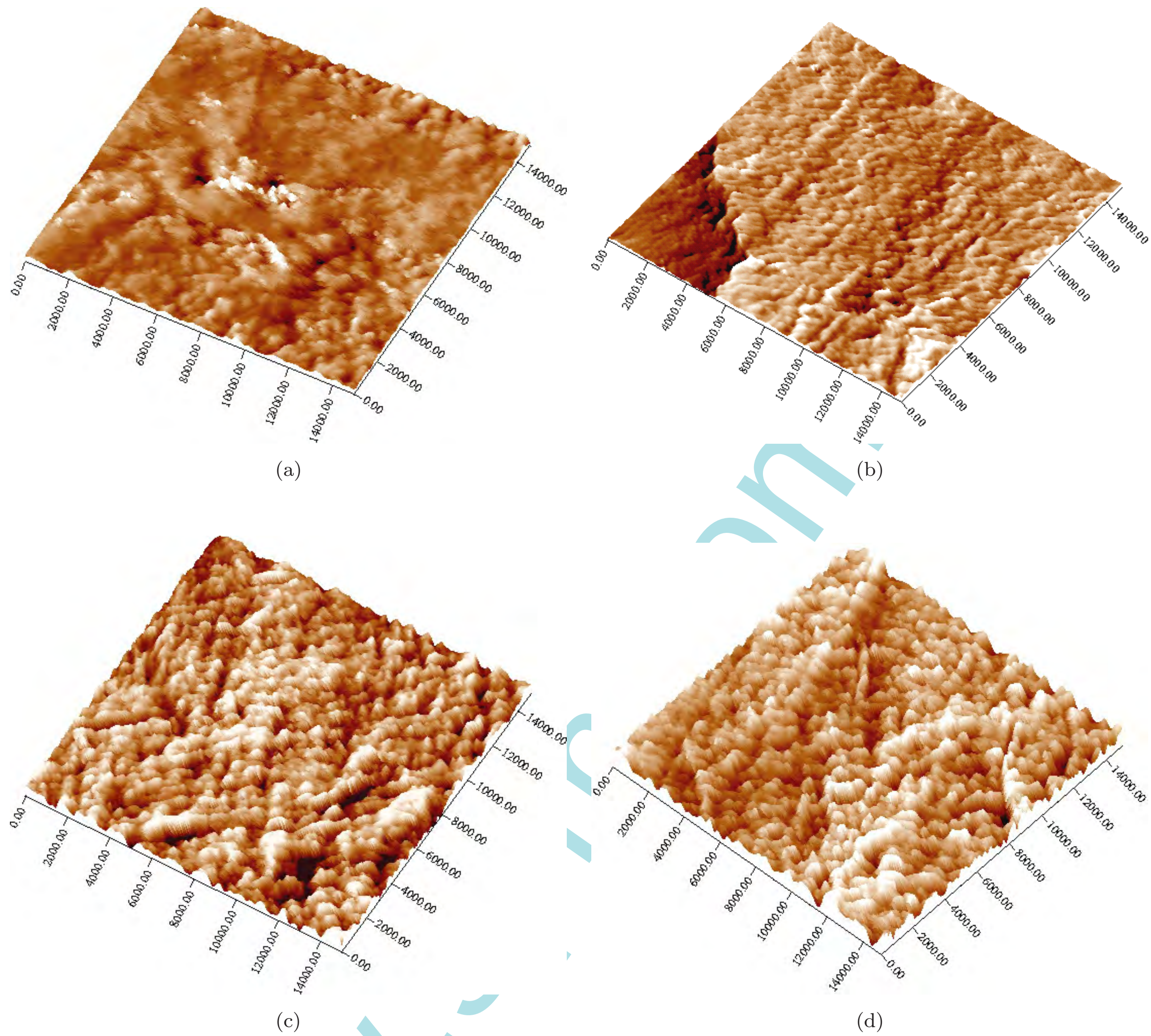


Fig. 1. AFM images of PET film: (a) untreated; (b) plasma treated for 30 s; (c) plasma treated for 60 s; (d) plasma treated for 90 s.

Table 1. Surface roughness of PTFE film.

Treatment duration (s)	0	30	60	90
Surface roughness (nm)	10.5	18.7	25.4	29.7

of the PTFE film. The plasma treatment leads to the appearance of new adsorption peaks at 1720 cm^{-1}, which can be attributed to the C=O stretching band in COOH carboxyl groups. It is also observed that the concentration of carbonyl functional group is increased with the increase in treatment time, as exhibited in Fig. 2. The FTIR examination reveals the introduction of hydrophilic groups on the surface of the PTFE film, which will lead to the improvement

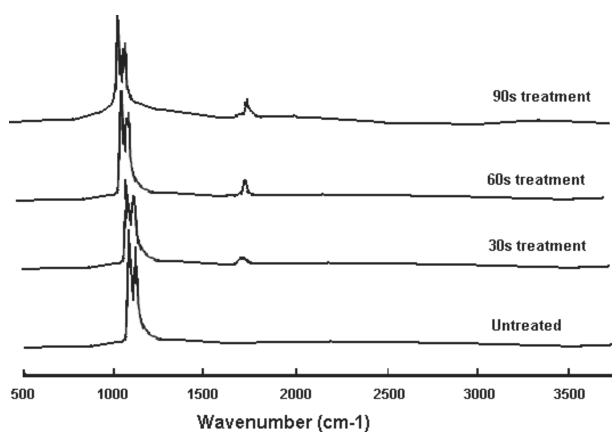


Fig. 2. FTIR spectra of PET film.

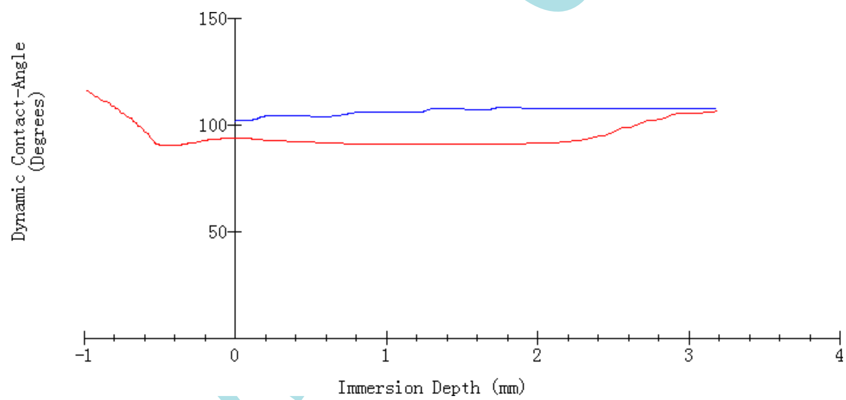
in surface wettability. The dynamic contact angle measurements examine the change in surface wetting behavior induced by plasma treatment.

3.3. *Dynamic wetting*

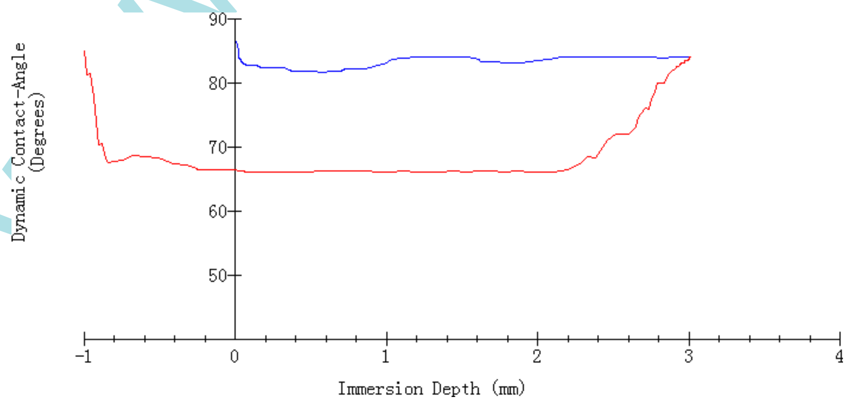
The PTFE film shows high contact angles before plasma treatment, as indicated in Fig. 3(a). The advancing contact angle of the film is about 103° and the receding contact angle is about 92°, indicating hydrophobic properties of the film surface. There is an obvious hysteresis of about 11° between the advancing contact angle and receding contact angle. The hysteresis is attributed to the surface roughness of the film, as revealed in Fig. 1(a).

Figure 3(b) clearly indicates the decrease of the advancing and receding contact angles of the PTFE film treated by oxygen plasma for 30 s. The advancing and receding contact angles are reduced to about 83° and 65°, as presented in Fig. 3(b). The decrease in both advancing and receding contact angles is caused by the formation of hydrophilic groups on the PTFE film surface revealed by the FTIR analysis. The exposure to plasma for 60 s causes further decrease in the contact angle of the PTFE film, as presented in Fig. 3(c). The advancing and receding contact angles are reduced to about 65° and 38°. The hysteresis is increased to about 27°. The rougher surface is contributed to the increase in the contact angle hysteresis, as illustrated in Fig. 1(c). The advancing and receding contact angles are further reduced to about 58° and 26° as the duration of the treatment is extended to 90 s, as shown in Fig. 3(d). The contact angle hystersis is increased to 32°.

It is found that both advancing and receding contact angles are reduced very fast in the initial treatment, but the prolonged treatment seems not to reduce the contact angles as fast as the initial treatment.

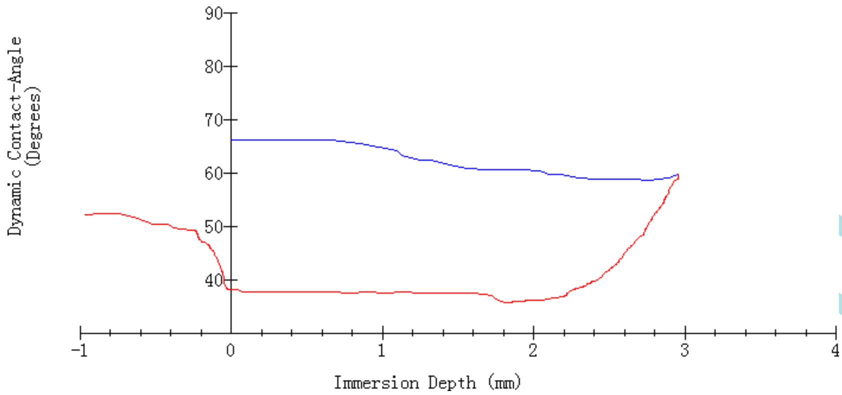


(a)

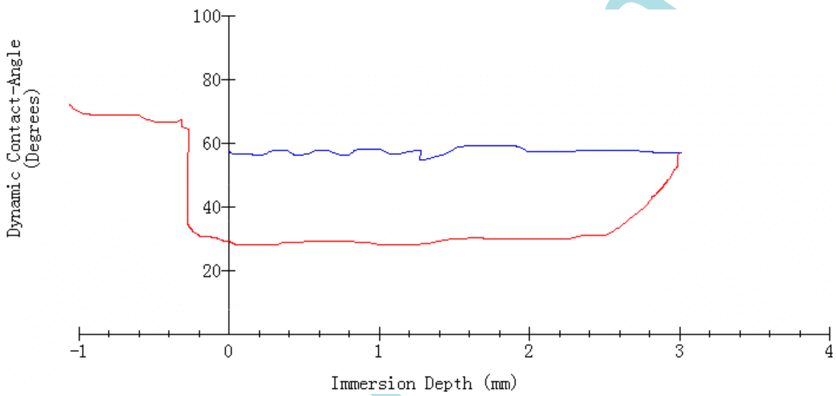


(b)

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



(c)



(d)

Fig. 3. (*Continued*)

4. Conclusions

This study has revealed that oxygen plasma treatments significantly altered the surface of the PTFE film. The surface wettability of the film was considerably improved by oxygen plasma treatment. Oxygen plasma treatments introduced the polar groups on the film surfaces and so reduce the advancing and receding contact angles of the films. The contact angle hysteresis of plasma-treated PTFE films was found to be altered by the roughening of the film surface. Dynamic contact angle measurements revealed the dynamic wetting behavior of the PTFE film treated by oxygen plasma.

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