Available online at www.sciencedirect.com
SCIENCE DIRECT
ELSEVIER
Polymer Testing 25 (2006) 22–27
POLYMER TESTING
www.elsevier.com/locate/polytest

Material Properties

Dynamic contact angles and morphology of PP fibres treated with plasma

Fenglin Huang [a], Qufu Wei [a,*], Xueqian Wang [b], Wenzheng Xu [a]

[a] *School of Textiles and Clothing, Southern Yangtze University, Wuxi 214122, People's Republic of China*
[b] *Anhui University of Technology & Science, Wuhu 24100, People's Republic of China*

Received 19 August 2005; accepted 27 September 2005

Abstract

Low-temperature plasma treatment is a kind of environmentally friendly surface modification technology, which has been widely used to modify various materials in many industries. In this study, cold gas plasma was used to treat polypropylene (PP) fibres. The effects of plasma treatment on the surface morphology and wettability of the fibres were characterized using atomic force microscopy (AFM) and dynamic contact angle measurement. The AFM observations revealed the changes in the surface morphology of the fibres caused by plasma treatment. The dynamic contact angles (DCA) were measured based on the Wilhelmy principle. The DCA technique was able to examine the advancing contact angles and receding angles of the fibres. The study revealed that the plasma treatment could considerably reduce both advancing contact angle and receding angle of polypropylene fibre. The surface roughness was the main reason for reducing the receding contact angle, while the advancing contact angle was more related to the surface properties of the fibres.

Keywords: Polypropylene; Plasma; Contact angle; Morphology; AFM

1. Introduction

Polypropylene fibres have such excellent properties as low specific weight (0.91 g/cm^3 only), high strength (42–53 cN/Tex), and good resistance to acids and alkalis, and they also possess good thermal resistance and anti-bacterial properties. PP fibres have been widely used in sports wear and industrial textiles, such as for filtration, composites, biomaterials and electronics. In these applications, the surface properties of the fibres are particularly important. The poor wettability (only 0.05% at 20 °C) [1] and dying ability have, however, limited the application of these fibres in garments and other industries.

It is of importance to improve the wettability of PP fibres for many applications. Chemical treatment has been traditionally used to modify fibre materials but it has some disadvantages, such as influence on bulk properties and environmental pollution. As a type of environmentally friendly physical surface modification technology, plasma treatment can also be used to treat textile materials. Plasma treatment is a simple process without any pollution. Moreover, plasma modification only takes place on the uppermost surface of fibres and will not change the bulk properties [2,3].

As is well known, plasma treatment has two sorts of effect on fibres surface; one is physical etching, using

* Corresponding author.
E-mail address: qfwei@sytu.edu.cn (Q. Wei).

0142-9418/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymertesting.2005.09.017

an inert gas such as argon etc. to modify the surface; the other is chemical graft, inducing some polar radicals, such as oxygen and nitrogen etc., to functionalize the surfaces of fibres.

A lot of literature has been published on the plasma treatment for improving surface polarity as well as wettability [2–4]. In this work, PP fibres were treated with oxygen and argon plasma respectively. The treated fibres were characterized using atomic force microscopy (AFM) and dynamic contact angle measurement.

2. Experiment

2.1. Materials

The PP fibres used in this study were spun from a melt extrusion machine supplied by Extrusion Systems Limited (ESL). Details of the extrusion equipment are provided elsewhere [5]. The PP resin used was HF445J B-29037 (kindly supplied by Borealis), with a melt flow index of 19.0 g/10 min. The spinning conditions are detailed in Table 1.

2.2. Plasma treatment

Plasma treatment was performed in a HD-1A vertical plasma treatment machine. Since the fibres used were produced without any spin finish, they can be directly put into a container with simple cleaning. During the plasma treatment, the control of treatment power was very important, considering the low melting point (165–173 °C) of the fibres. The treatment was performed with oxygen and argon at a pressure of 15 Pa. Each sample was treated at 35 and 75 W for 30 and 60 s, respectively.

Table 1
Polypropylene fibres

Chips	MFI18-HF445
Quenching air speed (%)	50
Hole size of spinneret (mm)	0.4
Barrel 1 temperature (°C)	215
Barrel 2 temperature (°C)	225
Barrel 3 temperature (°C)	230
Spinning temperature (°C)	230
Winding speed (m/min)	100
Metering pump speed (rpm)	3
Spin finish	0

2.3. AFM observation

AFM is the one of the effective tools to examine the microstructures of fibres. It is able to scan materials without any special preparation at normal temperature and pressure [6]. The AFM used in this study was CSPM3300 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.

2.4. Dynamic contact angle measurement

The wettability of materials can be characterized by contact angle. The testing methods for contact angle can be divided into two categories; one is the static drop micro-observation [7–9], while the other is the dynamic testing method. However, the first method has many disadvantages as it can only acquire static contact angles. As a smooth transition area exists between the solid and a liquid, it is difficult to precisely measure contact angles by the static approach. In this study, the dynamic testing method based on the Wilhelmy principle was used.

Wilhelmy's theory [10] on testing the surface and interface tension has been widely used by chemists to study the characteristics of the interfaces among the solid, liquid and vapour. Because of hysteresis of the contact angle, the Yong eq. is not able to explain the dynamic behaviour of surface wettability. The dynamic contact angle measurement, known as the Wilhelmy technique, is specially designed to explore the dynamic process of wetting. When a solid is dipped into a liquid, the liquid will ascend (hydrophilic) or descend (hydrophobic) along the vertical side of the solid. The Wilhelm method measures the pull force or the push force, the wetting force, to measure contact angles.

The dynamic contact angle measurements were performed using a CDCA-100F produced by Camtel Ltd. in the UK. If the dimensions of a sample are $w \times t$ (width × thickness) and it is submerged to a height h, then the forces (F) acting on the sample can be expressed as:

$$F = \text{Weight} - \text{Upthrust} + \text{Interfacial tension}$$

$$= (\rho_p lwt)g - (\rho_L hwt)g + 2(wt)\sigma \cos\theta \qquad (1)$$

Where ρ_p is the density of sample, ρ_L is the density of liquid used and l is the length of the sample.

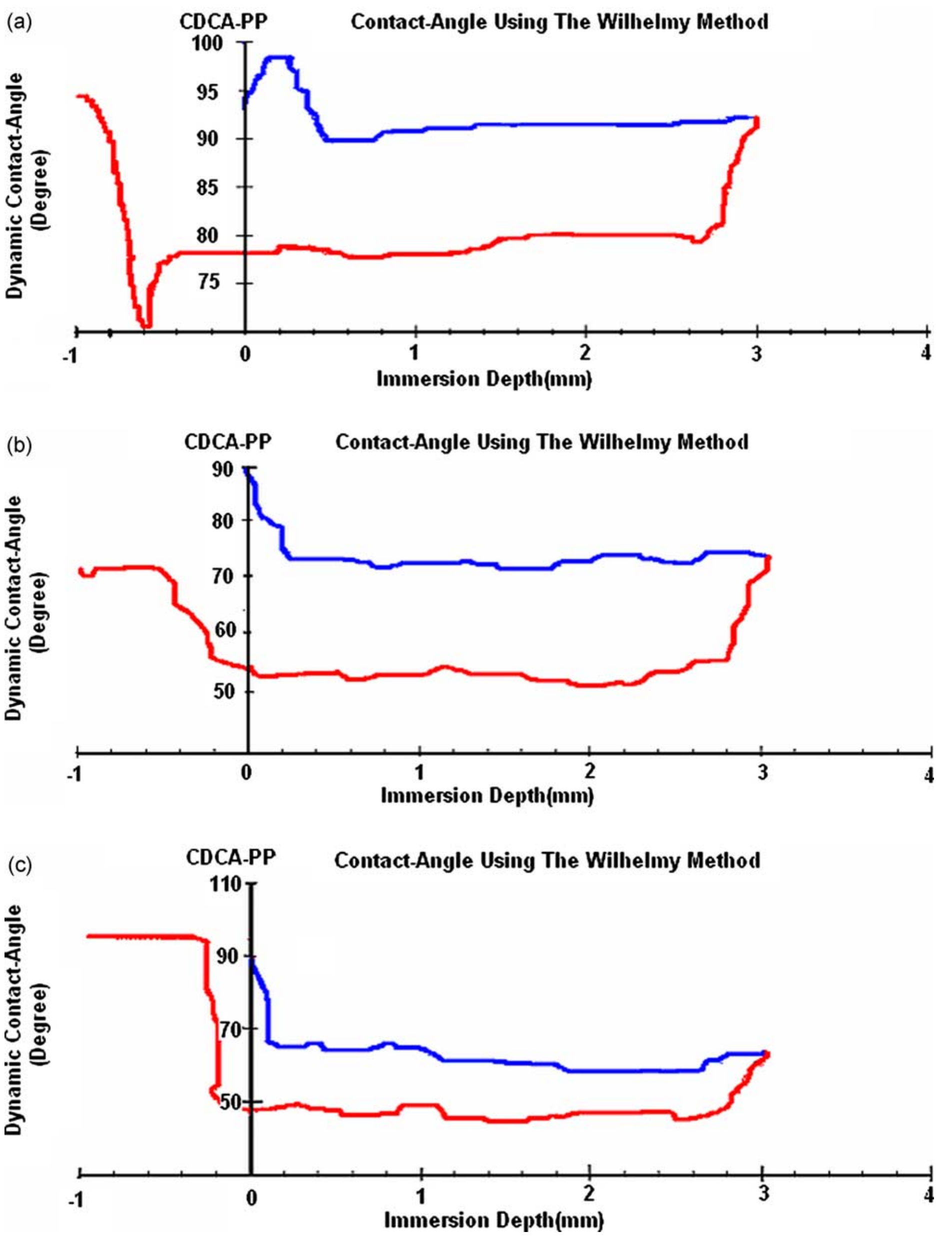

Fig. 1. Advancing and receding contact angles of PP fibres: (a) untreated; (b) argon plasma treated for 30S; (c) oxygen plasma treated for 30S (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

Before making any measurements, the balance is tared (zeroed) which eliminates the weight term. So the eq. can be rewritten as:

$$F = -(\rho_L hwt)g + 2(wt)\sigma\cos\theta \quad (2)$$

Extrapolation to zero depth eliminates the buoyancy effect (Upthrust, Fb), that is using forces at zero immersion to calculate advancing and receding angles (Fig. 1). The relationship between F and θ becomes:

$$F = 2(wt)\sigma\cos\theta \quad (3)$$

3. Results and discussion

3.1. AFM

The PP fibres without plasma treatment appear to be smooth, but in the AFM, the lines and the roughness of the surface can be clearly shown, which is one of the reasons causing the hysteresis of the contact angle of the untreated sample ($\theta_a - \theta_r = 11.8°$). As shown in Fig. 2(a), the height of the lines ranges from 30 to 353 nm. Oxygen plasma treatment etches the surface of PP fibres, forming aggregates on the surface as illustrated in Fig. 2(b). The AFM image also reveals the size of aggregates in the range between 10 and 314 nm. While using argon plasma treatment, the etching effect makes the surface of the fibres even rougher, as shown in Fig. 2(c). Fig. 2(d) reflects the effect of the treatment time. The longer exposure to the plasma, the rougher the surface becomes. It can be seen from Fig. 2(d) that almost all the surface is etched and the etching effect makes the height of the surface fall by 10–716 nm.

3.2. Dynamic contact angle

The results of testing the samples treated by different gases separately are listed in Table 2. From these results, it can be concluded that the advancing and receding contact angles are both considerably reduced after treatment by oxygen or argon. The receding contact angles are reduced to about 20° after treatment for 60 s. The results also show that the oxygen plasma treatment reduces the advancing contact angle more effectively than the argon plasma treatment under the same conditions. It is shown in Table 2 that the advancing contact angle is reduced from 91.0 to 43.8° ($\theta_{ar} = 47.2°$) when fibres are treated with oxygen plasma for 60S.This can be attributed to the grafting effect of oxygen plasma as well as the etching [6].

3.3. Discussion

Contact angle represents the wettability of fibres, but the hysteresis of contact angle makes the relationship between wetting and contact angle more complicated. Some literature believed that

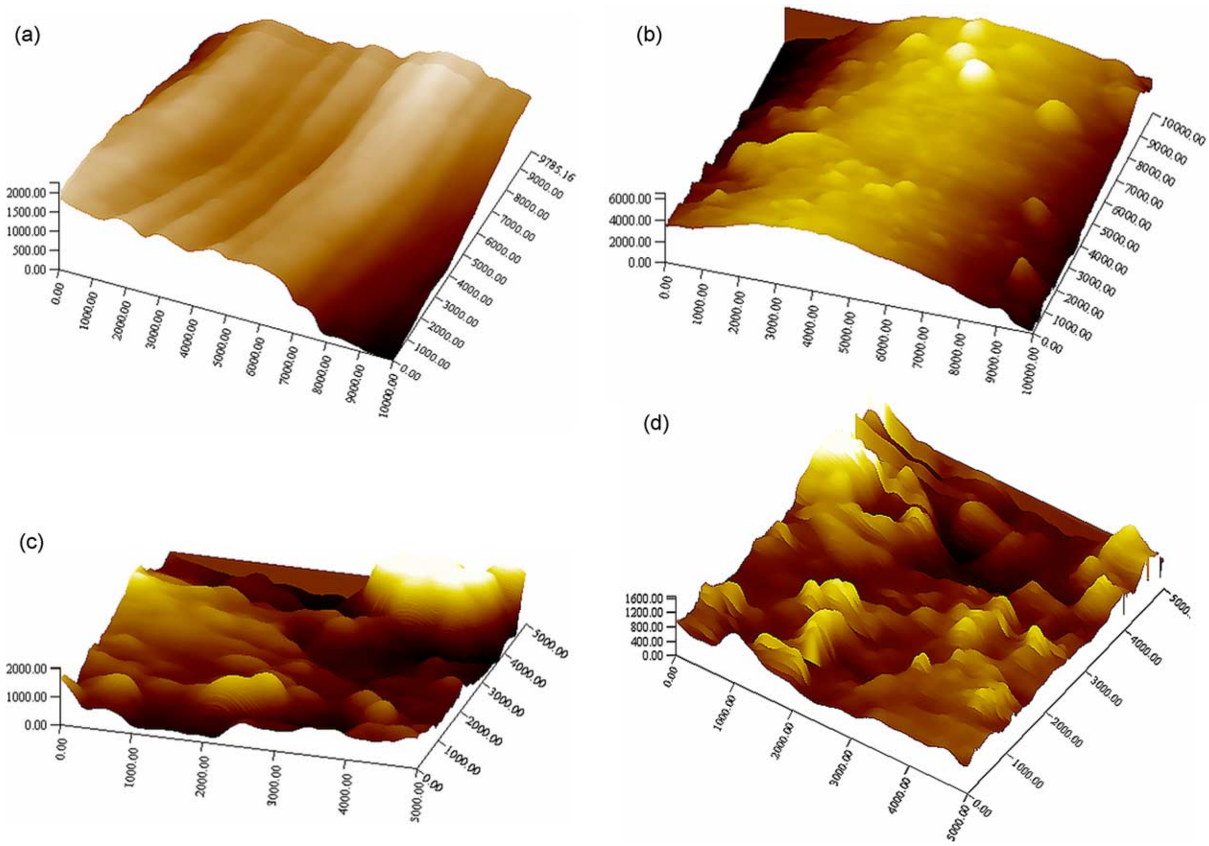

Fig. 2. AFM images of PP fibres (a) untreated; (b) oxygen plasma treated for 30 s; (c) argon plasma treated for 30 s; (d) argon plasma treated for 60 s.

Table 2
The advancing contact angle and receding contact angle (power is 30 W, pressure is 15 Pa)

gas	Time					
	0 s (untreated)		30 s		60 s	
	θ_a	θ_r	θ_a	θ_r	θ_a	θ_r
O_2			68.5	49.0	43.8	23.0
Ar	91.0	80.2	72.2	54.3	54.6	22.2

contact angle is determined not by the equilibrium of surface free energy, but by the balance of surface forces [11]. Some researchers also attributed the hysteresis to the roughness of a surface completely, considering that the advancing and receding contact angles are both influenced by surface roughness [12]. Other scholars pointed out that the hysteresis has some relationship with the properties of the liquid used [13].

In this experiment, we have found that surface roughness is only one of the main reasons causing the hysteresis, especially for the receding contact angle. In fact, the water molecules should overcome the forces of chemical bonds when adsorbing or leaving the surface of fibres. However, the forces in the two processes are different. The difference is also one reason for the hysteresis of contact angles.

Surface roughness appears to have much more influence on the receding contact angle. After treatment with argon for 60 s, the receding contact angle of the PP fibres reduces from 80.2 to 22.2°, while oxygen plasma treatment produces more effect on the advancing contact angle. After treatment with oxygen for 60 s, the advancing contact angle of the PP fibres reduces from 91.0 to 43.8°.

The original fibres with only polypropylene still show obvious hysteresis, $\theta_{ar}=\theta_a-\theta_r=10.8°$, because of the surface roughness as illustrated in Fig. 2(a). After the plasma treatment with any gas, the hysteresis is increased. This phenomenon is more significant when using argon, and the hysteresis increases from 10.8 to 17.9°(30 s) or even to 32.4° (60 s), because the surface roughness has much more influence on the receding contact angle. While using oxygen, the hysteresis is much lower than that of argon treated fibres. This can be attributed to the significant decrease of advancing contact angle after the oxygen plasma treatment. The introduction of hydrophilic groups onto the fibre surface by oxygen plasma treatment is believed the main reason for the decrease of advancing contact angle.

4. Conclusion

This study has evaluated the contact angles of the treated and untreated PP fibres using a dynamic measurement technique based on the Wilhelmy principle. The study has revealed that the plasma treatment can considerably reduce the contact angle and significantly improve the wettability of PP fibres, while the hysteresis is more obvious after treated with either oxygen or argon. The surface morphology can be examined using AFM on the nanoscale. The AFM observations have revealed the etching effect on the surface roughness of the fibre. AFM has been proven to be a powerful tool in the examination of surface morphology. After analyzing the factors influencing the contact angles, it has been concluded that the surface roughness is the main reason for reducing the receding contact angle, while the advancing contact angle is more related to the surface properties of the fibres.

Acknowledgements

The authors wish to thank the financial support by Southern Yangtze University (2004LYY005).

References

[1] Yao Mu, Zhou Jingfang, Huang Shuzhen, Textile Material, China Textile Press, Beijing, 1997, p. 208.
[2] Marian McCoM, et al. Atmospheric pressure plasma modification of textile surfaces: nylon 66, polypropylene, and ultra high modulus polyethylene, 2th AUTEX Conference 6 (2002) 313
[3] Peter P. Tsal, Surface modification of fabrics using a one—atmosphere glow discharge plasma to improve fabric wettability, Text. Res. J. 5(1997) 359.
[4] IoanI. Negulescu, et al., Characterizing polyester fabrics treated in electrical discharges of radio-frequency plasma, Text. Res. J. 1(2000) 1.
[5] R.D. Yang, R.R. Mather, A.F. Fotheringham, Int. Polym. Process. 14 (1999) 60.
[6] Q.F. Wei, Surface characterization of plasma-treated polypropylene fibres, Material Characterization 52 (2004) 231–235.
[7] B.J. Carroll, The accurate measurement of contact angle, phase contact areas, drop volume, and laplace excess pressure in drop on-fibre systems [J], J. Colloid Interf. Sci. 57 (3) (1976) 488–495.

[8] Tammar S. Meiron, Abraham Marmur, I. Sam Saguy, Contact angle measurement on rough surfaces, J. Colloid Interf. Sci. 274 (2004) 637.
[9] C.N.C. Lam, R.H.Y. Ko, et al., Dynamic cycling contact angle measurements: study of advancing and receding contact angles, J. Colloid Interf. Sci. 243 (2001) 208.
[10] J. Wilhelmy, Ueber die abhangigkeit der capillaritats-constanten des alkohols von substanz und gestalt des benetzten festen korpers, Ann. Physik. 119 (1863) 177–217.
[11] A.W. Physical Chemical of Surface, Beijing:Science Press, Beijing, (1984) p. 351.
[12] Xiaodong Wang, Xiaofenand Peng, Buxuan Wang, Contact angle hysteresis and hysteresis tension on rough solid surface, Chinese J. Chem. Eng. 12 (5) (2004) 615.
[13] C.N.C. Lam, N. Kim, D. Hui, D.Y. Kwok, M.L. Hair, The effect of liquid properties to contact angle hysteresis, Colloids Surf. A Physicochem. Eng. Asp. 189 (2001) 265.