Available online at www.sciencedirect.com
ScienceDirect
Applied Surface Science 254 (2008) 2882–2888
applied surface science
www.elsevier.com/locate/apsusc

Studies on surface modification of poly(tetrafluoroethylene) film by remote and direct Ar plasma

Wang Chen[a,b], Chen Jie-rong[a,*], Li Ru[b]

[a] School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an 710049, China
[b] College of Textile and Materials, Xi'an Polytechnic University, Xi'an 710048, China

Received 6 June 2007; received in revised form 13 October 2007; accepted 13 October 2007
Available online 22 October 2007

Abstract

Poly(tetrafluoroethylene) (PTFE) surfaces are modified with remote and direct Ar plasma, and the effects of the modification on the hydrophilicity of PTFE are investigated. The surface microstructures and compositions of the PTFE film were characterized with the goniometer, scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). Results show that the remote and direct plasma treatments modify the PTFE surface in morphology and composition, and both modifications cause surface oxidation of PTFE films, in the forming of some polar functional groups enhancing polymer wettability. When the remote and direct Ar plasma treats PTFE film, the contact angles decrease from the untreated 108–58° and 65.2°, respectively. The effect of the remote Ar plasma is more noticeable. The role of all kinds of active species, e.g. electrons, ions and free radicals involved in plasma surface modification is further evaluated. This shows that remote Ar plasma can restrain the ion and electron etching reaction and enhance radical reaction.

Keywords: Remote and direct Ar plasma; Poly(tetrafluoroethylene); Surface modification

1. Introduction

Surface modification of polymers by plasma treatment is industrially attractive, as the technique is simple, easy to implement, reliable, no pollution, and cost effective [1–5]. Many studies [6,7] have been reported using various plasma-based approaches and process gases, which about investigations of plasma surface modification technologies, the effects of plasma treatment, the nature of the plasma environment, and the mechanisms that drive the plasma–surface interaction. Plasma treatment affects the polymer surface to an extent of several hundred to several thousand angstroms. The bulk properties of polymers, therefore, remain unchanged. Apart from being a surface-sensitive modification technique, plasma treatment does not give rise to toxic waste problems as in the case of chemical treatment. Plasma containing electrons, ions, and radicals can interact with polymer surfaces and modify their chemical and physical properties. The plasma is capable of exerting four major effects [1,8–10], that is, surface cleaning, surface ablation or etching, surface cross-linking, and modification of the surface chemical structure, both in situ and on subsequent exposure to the atmosphere. These effects depend on the presence of active species in plasma. However, so far researches on plasma surface modification have merely been limited to a mixed atmosphere constituted solely by active species [11–15]. How great is the contribution of the different active species to surface modification?

Plasma is a mixture of electrons, ions, and radicals. These species disappear in processes of the electron–positive ion recombination, the positive ion–negative ion recombination, and the radical–radical recombination. The rate constant of these reactions is in the order of 10^{-7} and 10^{-33} cm^3/s, respectively [16]. Therefore, radicals can possess extremely longer lifetime than electrons and ions. Taking advantage of the different lifetime of various active particles such as electrons, ions and free radicals, these active particles are separated in a special plasma field and the super pure and high free radical concentration is attained at the position away from the plasma discharge region. This is the concept of a remote plasma treatment [9,10,17,18], that is, the concentration of the ion and

* Corresponding author.
E-mail address: jrchen@mail.xjtu.edu.cn (J.-r. Chen).

0169-4332/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2007.10.029

electron is relatively low and the concentration of free radicals is relatively high in remote Ar plasma. The article studies the effects of remote and direct Ar plasma surface treatment on poly(tetrafluoroethylene) (PTFE) films in terms of changes in surface wettability and surface chemistry. The surface properties are characterized by the water contact angle measurement, scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). Finally the mechanism is analyzed, and the role of all kinds of active species, e.g. electrons, ions and free radicals involved in plasma surface modification is further evaluated.

2. Experimental

2.1. Materials

The PTFE films used in this study are supplied by Fuxing Fluorin Chemical Works Ltd. (China). Films of 25 mm × 50 mm are Soxhlet-extracted with acetone for 24 h to remove any surface impurities. Clean films are dried under vacuum at ambient temperature (22 °C) and stored in a desiccator before use. Diiodomethane used is of analytical grade. Deionized water is used in all experiments.

2.2. Remote plasma treatment

A self-designed reactor is used for the remote and direct Ar plasma treatments of the PTFE samples, as shown in Fig. 1. The reactor includes four parts—gas inlet, a reaction chamber, a gas exhaust, a power supply and a matching network (SY-500W power supply and SP-matcher made in Micro-electronics Center, the Chinese Academy of Sciences). The reaction chamber is a Pyrex glass tube (45 mm in diameter, 1000 mm long), where inductance-coupling discharge is applied. The Pyrex glass tube has a copper coil (nine turns) for the energy input radio frequency (RF) power (13.56-MHz frequency). The RF power is adjusted by a power controller (SP-III model). The PTFE films are positioned at a constant distance of 0 (direct Ar plasma treatment) and 40 cm (remote Ar plasma treatment) from the center of the copper coil and exposed to the Ar plasma. First, the air in the reactor is displaced with argon. Afterward, the reactor is evacuated to approximately 1.3×10^{-2} Pa, and then the argon is introduced into the Pyrex glass tube with a flow rate of 10–50 cm^3/min adjusted by a mass flow controller. The total pressure of the plasma chamber is adjusted by the mass flow controller and kept for 5 min. The argon flow of 10, 20, 30, 40 and 50 cm^3/min corresponds to about the argon pressure of 13.3, 25.6, 34.5, 41.5 and 49.7 Pa, respectively. Then the plasma was generated at a RF power of 30–180 W and the film is exposed to the plasma for a time of 25–200 s. The purity of argon is more than 99.99%.

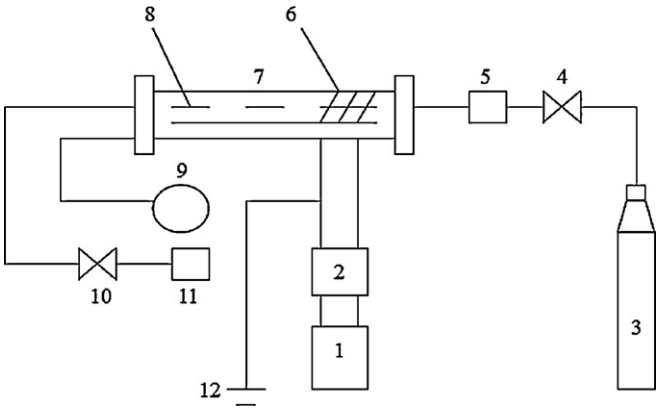

Fig. 1. Schematic structure of plasma reactor: (1) RF generator; (2) matching system; (3) gas bottle; (4) valve; (5) mass flow meter; (6) inductance coil; (7) reaction chamber; (8) sample; (9) vacuum gauge; (10) electromagnetic valve; (11) vacuum pump; (12) ground protection.

2.3. Contact angle measurements

The static contact angles, characterizing surface wettability, are measured immediately after finishing the plasma treatment experiments to minimize the changes in the surface properties. The contact angles of water on the PTFE film surface treated with the remote and direct Ar plasmas are measured by the sessile drop method using a contact angle meter with a goniometer (Chengde, China; model JY-82). The readings are stabilized and taken 50 s after dropping. To lessen the effect of gravity, the volume of each drop is regulated to about 0.2 mL by a micro-syringe. The measurement is carried out at a 20 °C and humidity of 45% RH. The averaged value of the angles of both sides of each drop is counted as one measurement. Each contact angle is determined from an average of 10 measurements with a standard deviation of 1°.

2.4. Surface free energy measurement

The measurement of the contact angle between water and a film surface is one of the easiest ways to characterize the hydrophilicity of a film. When water is applied to the surface, the outmost surface layers interact with the water. A hydrophobic surface with low free energy gives a high contact angle with water, whereas a wet high-energy surface allows the drop to spread, that is, gives a low contact angle.

The untreated films, the remote and direct plasma-treated films are analyzed for their hydrophilic properties by carrying out water and diiodomethane contact angle measurements. The liquids used in measuring the contact angle of the film are shown in Table 1. Wu [19] thought that the surface free energy (γ) could be separated into a dispersing parameter (γ^d) and a polar parameter (γ^p). This procedure leads a harmonic mean equation to the Young equation. γ, γ^d, and γ^p can be calculated by solving the system of equations as follows:

$$\gamma_1(1+\cos\theta_1) = \frac{4\gamma_1^p\gamma_s^p}{\gamma_1^p+\gamma_s^p} + \frac{4\gamma_1^d\gamma_s^d}{\gamma_1^d+\gamma_s^d},$$

$$\gamma_2(1+\cos\theta_2) = \frac{4\gamma_2^p\gamma_s^p}{\gamma_2^p+\gamma_s^p} + \frac{4\gamma_2^d\gamma_s^d}{\gamma_2^d+\gamma_s^d},$$

$$\gamma_s = \gamma_s^d + \gamma_s^p$$