Surface modification of polymeric materials by plasma immersion ion implantation

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Available online 1 July 2005

Abstract

Polymer surfaces typically have low surface tension and high chemical inertness and so they usually have poor wetting and adhesion properties. The surface properties can be altered by modifying the molecular structure using plasma immersion ion implantation (PIII). In this work, Nylon-6 was treated using oxygen/nitrogen PIII. The observed improvement in the wettability is due to the oxygenated and nitrogen (amine) functional groups created on the polymer surface by the plasma treatment. X-ray photoelectron spectroscopy (XPS) results show that nitrogen and oxygen plasma implantation result in C–C bond breaking to form the imine and amine groups as well as alcohol and/or carbonyl groups on the surface. The water contact angle results reveal that the surface wetting properties depend on the functional groups, which can be adjusted by the ratio of oxygen–nitrogen mixtures.

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PACS: 52.77.Dq; 68.47.Mn; 79.60.Fr; 61.82.Pv; 81.05.Lg

Keywords: X-ray photoelectron spectroscopy; Nylon-6; Functional groups; Wettability; Ion implantation

1. Introduction

Polymeric materials have unique properties such as low density, light weight, and high flexibility and are widely used in various industrial sectors. However, the inert nature of most polymeric materials creates challenges in many
applications that demand specific surface characteristics such as those required by inking and printing processes, wetting and adhesion for coatings, biomaterials, and certain types of composite materials. Hence, surface modification of polymeric materials plays an important role in that selected surface properties can be optimized while the favorable bulk attributes of the materials can be retained. Therefore, various surface modification techniques such as chemical oxidation [1], flame [2], grafting [3,4], laser [5], UV irradiation [6] and plasma treatments [7–9] have attracted much attention. In particular, the surface wetting and adhesion properties of modified polymers are the subject of many studies and much work has been devoted to the enhancement of the metal–polymer and polymer–polymer adhesion as well as dyeing and printing on polymers. Examples of specific applications include aluminum–polycarbonate adhesion [10], copper–polyimide adhesion in microelectronics [11], polyethylene and polyester substrates used in photographic films [12], and polyolefins for printing and painting [13].

The use of energetic ions and activated species in the plasma immersion ion implantation (PIII) process introduces deeper ion penetration than conventional surface treatments and can give rise to special functional groups on the polymeric surfaces. This may help reducing the aging effects and degradation of the functional groups or chains as compared to low-energy surface treatment. The degree of improvement depends on the polymers as well as the nature of the plasma and the treatment conditions. In this study, we investigate the effects of nitrogen and oxygen plasma immersion ion implantation on the chemical and physical changes on the surface of Nylon-6. The surface chemical changes are examined by X-ray photoelectron spectroscopy (XPS) and the surface wetting properties are evaluated by measuring the water contact angle using the sessile drop method.

2. Experimental

Nylon-6 disks with a diameter of 32 mm and thickness of 3 mm were first polished to a shiny finish and then washed with distilled water before loading into our plasma immersion ion implanter [14–16]. Nitrogen or a nitrogen–oxygen mixture was fed into the vacuum chamber to a working pressure of $8 \times 10^{-2}$ Pa. The plasma was ignited by a 13.56 MHz radio frequency inductively-coupled plasma source (RF-ICP) using an input power of 1000 W. The samples were pulse-biased to $-40$ kV with a pulse width of 15 $\mu$s and repetition rate of 100 Hz. The implantation current was about 1 A per pulse and according to previous experiments conducted under similar conditions, the sample temperature was below 150 $^\circ$C under the conditions short pulse width and low repetition rate. The experimental conditions are listed in Table 1.

X-ray photoelectron spectroscopy (XPS) was performed on the Physical Electronics PHI-5600 using the monochromatic AlK$_{\alpha}$ radiation operated at 14 kV and 350 W. The photoelectron takeoff angle was 45°. To compensate for surface charging, all binding energies were referenced to the aliphatic C 1s neutral carbon peak at 284.6 eV. To investigate the implantation induced surface chemical changes, the C 1s, N 1s and O 1s core level spectra were recorded. The XPSPEAK version 4.1 software (developed by R.W.M. Kwok, Chinese University of Hong Kong) was used for peak fitting. This program employs Newton’s method for optimization as well as Shirley background subtraction and Gaussian–Lorentzian function for peak fitting. Static contact angle measurements were performed by the sessile drop method on a JY-82 contact angle goniometer at ambient humidity and temperature. The test liquid was doubly distilled water and five drop measurements were taken on each specimen to yield a statistical average.
3. Results and discussion

Plasma immersion ion implantation is an effective method to enhance the surface wetting property of polymers and the surface properties of the treated Nylon-6 are highly dependent on the treatment conditions and the plasma species. Nylon-6 is a thermoplastic with characteristic amide groups in the backbone carbon chain that is six carbons long. When it is subjected to high energy ion bombardment, reactive defects are created on the surface resulting in hydrogen abstraction, C–C bond breaking, and incorporation of reactive nitrogen and oxygen species to form amine \([>C–NH_2]\), alcohol \([R–CH_2–OH]\), and/or carbonyl \([C=O]\) groups. Bond breaking in the chain leads to two fragments that can form various functional groups on the surface according to the following sequences:

\[
\begin{align*}
R–CH_3–CO–NH–CH_2–R' & \rightarrow R–CH_2^+ \\
+ R'–CH_3–NH–CO^+ \\
R–CH_2^+ & \rightarrow R–CH = N–H \text{ or } R = CH–NH_2, \\
R–CH_2^+ & \rightarrow R–CH_2–OH, \\
\text{and/or} \\
R–CH_2^+ & \rightarrow R–CH = O.
\end{align*}
\]

It should be noted that the formation of the imine group \([-CH=N–H]\) and amine terminal group \([-CH–NH_2]\) can be explained by hydrogen abstraction from the polymer chains.

To evaluate plasma implantation induced surface chemical changes on Nylon-6, XPS measurements were performed. The C 1s core level spectra can be deconvoluted into four components: C–C at \(BE = 284.6\) eV, C–N at \(BE = 285.4\) eV, C–O or C–OH at \(BE = 286.1\) eV, and CONH at \(BE = 287.7\) eV. After PIII, the asymmetric C 1s peak shifts toward a high binding energy in all the treated samples. It implies that the polymer chains have been broken and the functional groups on the surface have been rearranged and re-established. In the nitrogen plasma-implanted sample, the intensity of C–N peak is higher than that of the control, whereas the intensity of the C–O and C–OH peaks measured from the nitrogen and oxygen co-implanted samples increases gradually according to the gas mixture.

The deconvoluted peak areas of the functional groups are compared to the peak area of carbon-to-carbon (C–C) bonding and the calculated results are displayed in Table 2. As expected, the relative ratio of C–N to C–C group dramatically increases from 0.26 to 0.43 in the nitrogen-implanted sample. On the other hand, by adjusting the relative ratio of oxygen to nitrogen in the mixed gas PIII experiments, change of C–N to C–C and considerable increase of C–O, C–OH to C–C ratios with respect to those of the control can be observed. These results suggest that different plasma species preferentially generate different functional groups on the polymer surface. Fig. 1 shows the N 1s core level spectra acquired from the control and plasma-implanted samples. The N 1s peak can be decomposed into three components. The first component at \(BE = 399.1\) eV can be assigned to the amine group \([R–NH_2]\), the second component at \(BE = 400.0\) eV to the imine group \([C=NH]\), and the third component at \(BE = 401.3\) eV to the amide group \([R–CO–NH_2]\). After ion bombardment, the binding energy of the nitrogen peaks shifts slightly toward lower energy, indicating that more amine and imine groups are formed on the polymer surface.

The wetting properties of the control and plasma-implanted samples are determined using the sessile water drop method by measuring the contact angle between the sample surface and water surface and the results are listed in Table 3. In contrast to the contact angle of 66.08° observed on the control sample, the contact angles markedly diminish after plasma implantation. Sample # 4 implanted using a high ratio of oxygen.

### Table 2

Relative peak area ratios of various functional groups to carbon-to-carbon bonding as acquired from the C 1s core level of XPS spectrum

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Relative ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>#2</td>
</tr>
<tr>
<td>C–N/C–C</td>
<td>0.26</td>
</tr>
<tr>
<td>C–O, C–OH/C–C</td>
<td>0.15</td>
</tr>
<tr>
<td>CONH/C–C</td>
<td>0.15</td>
</tr>
</tbody>
</table>
mixture exhibits the greatest improvement in the hydrophilicity. The enhancement of the wetting properties can be explained by the formation of polar functional groups thereby increasing the surface free energy of the polymer surface and leading to enhanced adhesion and wetting due to better interaction with water molecules. Comparing the roles of the various newly-formed surface functional groups, the amide group is relatively not reactive and therefore may not contribute much to the adhesion and wetting improvement. The increase of the imine, amine, alcohol, and carbonyl groups on the plasma-implanted surface appears to be the main reason for the wetting enhancement. Our results also indicate that nitrogen implantation produces mainly imine and amine groups on the Nylon surface while a gas mixture of nitrogen and oxygen in the plasma creates preferentially more alcohol and/or carbonyl groups. Since alcohol and carbonyl groups are more polar that the imine and amine groups, better wetting properties can be achieved in the mixed-gas plasma treatment. Overall, it is clear that plasma immersion ion implantation can result in dramatic change in the surface chemistry of polymers by introducing favorable functional groups. Coupled with high-energy ion bombardment, sufficient bond breaking and desorption of low molecular weight species occur thereby producing a different chemical structure that gives rise to the enhanced surface properties.

4. Conclusion

Plasma immersion ion implantation has been performed on Nylon-6 to change the surface chemistry and enhance the wetting properties. XPS results show that the amounts of the polar functional groups such as imine, amine, alcohol and carbonyl groups increase after high-energy ion bombardment. The dominant functional groups can be adjusted by choosing the appropriate gas species in the plasma generation. The water contact angle results reveal that the more polar groups (alcohol > amine > amide) give rise to better wetting properties.

Acknowledgements

The work was jointly supported by Hong Kong Research Grants Council (RGC) Competitive Earmarked Research Grant (CERG) No. CityU 1137/03E, City University of Hong Kong Strategic Research Grant No. 7001642, as well as National Natural Science Foundation of China under Grant No. 10345003, No. 50373007 and No. 30400109.
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