Formed high hydrophilic/hydrophobic contract surface on a PET substrate by ECR SF$_6$ plasma

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Abstract: A simple method for producing high hydrophilic/hydrophobic contrast surface on flexible substrate has been presented. In this method, we used a mask and controls the distance of the mask to substrate under electron cyclotron resonance (ECR) sulfur hexafluoride (SF$_6$) plasma atmosphere. The hydrophilic and hydrophobic surfaces can be one step formed on treated poly (ethylene terephthalate) (PET) film, and the difference in water contact angle between the hydrophilic and hydrophobic regions is over 100 degree.

Keywords: Hydrophilic; hydrophobic; X-ray photoelectron spectroscopy (XPS); PET.

1. Introduction

Low pressure plasma is a popular technique for the surface modification of polymers because the processes involved are solvent-free and dry, these processes are precisely controllable. Moreover the consumption of chemicals is extremely low and need for sterilization of the products is eliminated. It is now well established that the low pressure plasma treatment creates physical and chemical changes such as etching, cross-linking, grafting of chemical functionalities and polymerization [1-5], usually without varying its bulk properties. Sulfur hexafluoride (SF$_6$) plasma is commonly used to etch a variety of materials during the fabrication of semiconductor devices [6]. It is also used as a potential method for modifying polymer surface characteristics such as wettability and adhesion [7,8].

In our current investigation, electron cyclotron resonance (ECR) was used to generate sulfur hexafluoride (SF$_6$) plasma, which was in turn used to modify the surface of the polyethylene terephthalate (PET) samples. SF$_6$ plasma is commonly used to etch a variety of materials during the fabrication of semiconductor devices [9]. It is also used as a potential method to modify polymer surface characteristics such as wettabillity and adhesion [10,11]. This study has demonstrated that SF$_6$ plasma can result in relatively hydrophobic and hydrophilic surfaces that are in-situ formed on a PET substrate. In the proposed method, we place the mask onto the surface PET substrate and control the distance of the mask to the substrate in order to prepare the hydrophilic and hydrophobic surface. The surface properties of the plasma-treated PET films were characterized by contact angle measurement, x-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM).

2. Experimental

The commercial PET films with a thickness of 188 m (DuPont Teijin Films, USA) are treated in ECR SF6 plasma with a 2.45 GHz frequency microwave source (Plasmalab 80 plus, Oxford Instruments). A schematic diagram of the apparatus is shown in Fig. 1. The gas is admitted into the source chamber using a flow controller, and the application of microwave power generates glow discharge.

![Fig. 1. Schematic of the electron cyclotron resonance plasma treatment apparatus.](image)

The downstream plasma extended to the processing chamber is used for the surface modification. The operating pressure is maintained at 0.67 Pa with a gas flow rate of 12 sccm during the treatment procedure. The PET surface was shielded by a mask, and the mask-to-substrate distance (Dms) varied from 0.2 mm to 1.5 mm. The plasma treatment times were varied between 1 and 15 min, while power was fixed at 200 W.

The contact angles of water on the PET surface were measured at room temperature using the sessile drop
Results and discussions

The water contact angles as a function of the SF6 plasma treatment time are shown in Fig. 2. All PET films were treated at a working pressure of 0.67 Pa, a Dms of 0.6 mm, and an MW power of 200W. “Unshielded” means that the surface is not covered by a mask, while “shielded” refers to the opposite. Fig. 2 shows that the water contact angles of the “unshielded” surface were nearly constant when the plasma treatment time was longer than 3 min. It is 74° with the water contact angle of the untreated PET film. For the “shielded” surface, the water contact angle decreases radically with the increase in plasma treatment time and reaches a minimum value (below 5°) at a plasma treatment time of 5 min. Then the water contact angle decreases with an increase in time. A high contrast surface was obviously obtained after plasma treatment within 5–7 min of treatment time range at a power of 200W. The difference in water contact angle between the hydrophilic and hydrophobic regions is large, as indicated by the differential water contact angle of 100° between the two regions.

Fig. 2. The water contact angles as a function of the SF6 plasma treatment time.

Fig. 3 shows the water contact angles as a function of Dms at a pressure of 0.67 Pa and a treatment time of 5 min. The figure indicates that the measured water contact angle decreased drastically with an increase in Dms, and was reduced to the lowest value (below 5°) when the distance was between 0.4 mm and 0.6 mm. Subsequently, the water contact angle increased radically with an increase in Dms.

To further study surface property, the surface chemical composition analyses of the treated and untreated PET films were carried out using XPS. Table 1 shows the atomic percentage of PET as a function of Dms at a pressure of 0.67 Pa and a treatment time of 5 min. It was 0.38 with an O/C ratio for the untreated PET. The data indicate the F/C and O/C ratios depending on the increasing distance with fluorine and oxygen concentration. As shown in Table 1, the F/C ratio increases from 0.66 to 1.09, while Dms increased from 0.2 mm to 2.4 mm. XPS analysis reveals that the main effect of the plasma treatment is fluorine grafting on the polymer surface. The concentration of fluorine increased with the increase in distance, which might explain why it is more difficult for the activated species such as F, SF3-, and SF5- to pass through a smaller distance. Therefore, the smaller distance has a lower F% than the larger one.

![Fig. 3. The water contact angles as a function of mask-to-substrate distance at a pressure of 0.67 Pa and a treatment time of 5 min.](image-url)

<table>
<thead>
<tr>
<th>Item</th>
<th>untreated PET</th>
<th>Mask shielded area</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1s)</td>
<td>72.7</td>
<td>49.3</td>
</tr>
<tr>
<td>O(1s)</td>
<td>27.3</td>
<td>18.2</td>
</tr>
<tr>
<td>F(1s)</td>
<td>0.0</td>
<td>32.4</td>
</tr>
<tr>
<td>C/O</td>
<td>0.38</td>
<td>0.37</td>
</tr>
<tr>
<td>F/C</td>
<td>0.00</td>
<td>0.66</td>
</tr>
</tbody>
</table>
Fig. 4 shows the water contact angles for the differently treated samples as a function of aging time. The water contact angle of the “unshielded” and “shielded” Dms was 0.6 mm, with the sample being nearly a constant after 168 h. The water contact angle for the Dms of the 1.2 mm samples showed a rapid decrease for about 2 h, and then stabilized below 5°. Nevertheless, for the Dms of the 0.2 mm samples, the water contact angle still remained to have a low value after about 96 h. At a condition of 0.67 Pa, 5 min, and Dms of 0.6 mm, the hydrophilic/hydrophobic contrast was the highest. Therefore, this condition was determined to be the optimum for SF6 plasma and was used in the remaining analysis.

![Image](image1)

Fig. 4. The water contact angles for the differently treated samples as a function of aging time.

Fig. 5 illustrates the root-mean-square surface roughness (RMS) and morphology of the untreated and plasma-treated PET films at a treatment time of 5 min, with a distance of 0.6 mm. The untreated PET film shows an RMS of 0.9 nm. For the “unshielded” and “shielded” surfaces, the RMS was 1.1 nm and 1.4 nm, respectively. The wettability of the substrate depends on several factors, such as surface roughness.[14] An increase in roughness on the hydrophilic surface decreases the contact angle, whereas increasing the roughness does the opposite. As compared to the roughness of the untreated PET film surface, there is no significant difference expect for a slight difference in the morphology of the surface. Therefore, the AFM measurement results on the roughness effect can be disregarded without strongly influencing the change in surface property. The chemical composition varies in the polymer surface as caused by the plasma treatment, which leads to wettability changes.

4. Conclusion

A simple method for producing a high hydrophilic/hydrophobic contrast surface on a flexible substrate by ECR SF6 plasma has been demonstrated. This is achieved using a mask and by controlling the distance of the mask to the substrate. At the optimum parameters of the SF6 plasma, the “shielded” surface after plasma treatment exhibited a super hydrophilic property, that is, the water contact angle is lower than 5°. Meanwhile, the F/C ratio is 0.88, and the O/C ratio is 0.36. On the other hand, for the “unshielded” surface, the water contact angle increases to 113 ± 0.5°, the F/C ratio increases to 1.09, and the O/C ratio decreases to 0.32. This high hydrophilic/hydrophobic contrast surface can be patterned as a flexible substrate for fluid devices and simple biochip arrays applications. The advantage of this method is the elimination of the need for conventional photolithography.

![Image](image2)

Fig. 5. AFM pictures of the PET surfaces: (a) untreated, plasma-treated PET (b) without a mask shielded, and (c) with a mask shielded (the mask-to-substrate distance is controlled at 0.6 mm).
Acknowledgement

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References