Biocompatibility of polymer surfaces treated in SO₂ or H₂S plasma

A. Vesel, M. Modic and M. Mozetic
Jozef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia

Abstract: Polymer polyethylene terephthalate (PET) was treated in RF plasma in order to incorporate sulphur functional groups. Plasma was created either in SO₂ or H₂S gas. Surface chemical modification was studied by X-ray photoelectron spectroscopy. While SO₂ plasma caused functionalization of the PET surface with –SOₓ functional groups, H₂S plasma caused functionalization with non-oxidized sulphur groups –SH₂. Thrombogenicity of the plasma treated polymer surfaces was tested as well. High platelet adhesion was observed for both plasma treated surfaces.

Keywords: H₂S and SO₂ plasma, PET polymer, plasma treatment, surface modification, platelet adhesion

1. Introduction

Gaseous plasma treatment is often applied for surface modification of polymers used in biomedical applications. An example is surface modification of vascular grafts for improving their hemocompatible properties. Normally, plasma is used only as an initial step for further grafting the surface with molecules having antithrombogenic properties. Nevertheless, it was also shown that remarkable decrease in platelet adhesion can be obtained by using oxygen plasma treatment only [1]. According to the literature, sulphur-containing functional groups may be antithrombogenic as well [2-4]. Therefore, we decided to study the hemocompatibility properties of polymer surfaces treated in sulphur-containing plasma created either is SO₂ or H₂S gas.

2. Experimental section

PET foil with the thickness 0.25 mm from Goodfellow was used. The foil was cut to discs with a diameter of 1 cm. Experiments were performed in a Pyrex tube (80 cm long and 4 cm in diameter). A coil of 6 turns was mounted in the centre of the tube. Plasma was created by an RF generator coupled to the coil via a matching network. The generator operated at the standard frequency of 13.56 MHz and its power was set to 150 W. The discharge chamber was pumped with a rotary pump operating at a nominal pumping speed of 80 m³ h⁻¹. Either H₂S or SO₂ gas was leaked to the experimental system. Pressure was set to 30 Pa. The samples were placed in the middle of the coil. They were treated for 30 s.

Samples were characterized before and after plasma treatment by X-ray photoelectron spectroscopy (XPS). Hemocompatibility of the plasma treated samples was tested by studying platelet aggregation using confocal microscope.

3. Results and discussion

In Table 1 is shown surface composition of the samples before and after plasma treatment. In the case of SO₂ plasma treatment, the oxygen concentration has increased slightly. Furthermore, approx. 4 atomic % of sulphur was found as well. The amount of sulphur on the surface was much higher in the case of H₂S plasma treatment, where approx. 40 atomic % of sulphur was detected, while the concentration of oxygen on this sample was lower than in the case of untreated or SO₂-plasma treated sample.

Table 1. Surface composition of plasma treated samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>O</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET untreated</td>
<td>73.5</td>
<td>26.5</td>
<td></td>
</tr>
<tr>
<td>PET + SO₂ plasma</td>
<td>65.6</td>
<td>30.3</td>
<td>4.2</td>
</tr>
<tr>
<td>PET + H₂S plasma</td>
<td>45.6</td>
<td>14.0</td>
<td>40.4</td>
</tr>
</tbody>
</table>

To get more knowledge about the surface functional groups incorporated to the surface during plasma treatment, high-resolution XPS spectra were recorded and are shown in Fig. 1. In the case of SO₂ plasma treatment, the intensity of peaks due to C-O and O=C-O groups has increased after treatment (upper figure). This result leads to the conclusion, that in the case of SO₂ plasma we have both surface oxidation as well as incorporation of sulphur species to the surface. Sulphur peak S2p is positioned at about 170 eV, which means that oxidized sulphur species SOₓ are formed on the surface (bottom Fig. 1).

The situation is completely different in the case of H₂S plasma treatment. In this case, the intensity of the peak due to O=C-O groups has not changed after the treatment. The intensity of C-O peak has virtually increased, but this is actually due to overlapping with the peak due to C-S bonds that appears between the main C-C peak and C-O peaks. This is in agreement with Table 1, where huge sulphur content and low oxygen content was found for this sample. Not all sulphur is bonded to the surface. As shown by AFM images (not shown here) sulphur also agglomerates on the surface. Contrary to the sample treated in SO₂ plasma, where SOₓ species were found on the surface, the sulphur on H₂S-plasma treated sample is not bonded to oxygen atoms (Fig. 1 bottom) but rather to carbon and hydrogen (-SH₂ groups).
After both plasma treatments, the samples were tested for their hemocompatibility properties. Tests were performed 4 h after plasma treatment. The samples were incubated with platelet-rich plasma for 1 h. In Fig. 2 are shown images of polymer surfaces with adhered platelets recorded with optical microscope. For the untreated PET sample we can see that the surface is fully covered with platelets and only small uncovered parts are observed (upper figure). For the sample treated in SO₂ plasma (middle figure) and H₂S plasma (bottom figure) we can observe similar finding. Also in this case the surface is fully covered with platelets. So therefore, treatment of PET polymer in sulphur containing plasmas did not improve hemocompatibility properties of the surface.

4. Conclusions
Treatment of PET polymer in SO₂ plasma resulted in surface functionalization with SOₓ groups, while treatment with H₂S plasma resulted in surface functionalization with –SH₂ groups. Both plasma treatments did not reduce thrombogenicity of the polymer surface.

Fig. 1. Comparison of XPS high-resolution peaks for carbon (top) and sulphur (bottom) for different plasma treatment conditions.

Fig. 2. Platelet adhesion on untreated PET (top) and treated in SO₂ (middle) and H₂S (bottom) plasma.

5. References

6. Acknowledgements
This research was financially supported by the Slovenian Research Agency ARRS (project L7-6782).