SURFACE MODIFICATION OF POLYMER POLYETHYLENE TEREPHTHALATE WITH PLASMAS CREATED IN DIFFERENT GASES

MODIFIKACIJA POVRŠINE POLIMERA POLIETILEN TEREFTALATA S PLAZMO, USTVARJENO V RAZLIČNIH PLINIH

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Plasma is often used for a surface functionalization of polymer materials. Various functional groups can be formed on a polymer surface depending on the processing gas used for creating a discharge. In this work we present a comparison of different gases including Ar, O_2, CO_2, CF_4, N_2, NH_3, H_2 and SO_2 for a surface modification of polymer polyethylene terephthalate (PET). The surface of the plasma-treated polymer was analysed with X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). The results revealed significant differences in the sample morphology and roughness and, especially, in the chemical surface composition of the plasma-treated samples.

Keywords: polymer-surface modification, plasma treatment, XPS, AFM

Plazma se pogosto uporablja za funkcionalizacijo površine polimernih materialov. Na površini polimera lahko tvorimo različne funkcionalne skupine, odvisno od tega, v katerem plinu ustvarimo razelektritev (plazmo). V prispevku predstavljamo primerjavo različnih plinov, kot so Ar, O_2, CO_2, CF_4, N_2, NH_3, H_2 in SO_2, za modifikacijo polimera polietilen tereftalata (PET). Površino plazemsko obdelanega polimera smo preučevali z metodama rentgenske fotoelektronske spektroskopije (XPS) in mikroskopa na atomsko silo (AFM). Ugotovili smo pomembne razlike v morfologiji, hrapavosti in še posebej v površinski sestavi različno obdelanih vzorcev.

Ključne besede: modifikacija polimerne površine, plazemska obdelava, XPS, AFM

1 INTRODUCTION

Polymer materials are nowadays used in many different applications like in medicine, food-packaging industry, automotive industry, etc. Since a polymer surface is quite hydrophobic and inert, it is often necessary to modify its surface properties. In medicine a polymer surface must be modified in order to change antibacterial properties, improve cell adhesion and proliferation, improve or prevent protein adhesion and alter the surface antithrombogenic properties of body implants.[1–4] Another application is a development of special cellulose fabrics for wound dressings with better sorption and antibacterial properties.[5,6] In the case of the food-packaging industry there is a need to use plasma treatment for a better adhesion of special antibacterial coatings to polymer surfaces to extend the lifetime of meat products.[7] In the automotive industry, plasma is often used for a surface activation before metallization or painting.[8]

One of the methods commonly used for a surface modification is a plasma treatment. Plasma treatment is a very quick and efficient method. Normally, a few seconds of treatment are enough to cause a significant surface modification, i.e., a surface functionalization, thus increasing the surface hydrophilicity.[9] Longer treatment times cause slow etching of the materials which can lead to the changes in the surface morphology and even to the formation of a nanostructured surface.[9] Plasma can be created in various gases and this allows enormous potential applications of plasma for different purposes, since it is possible to graft different functional groups onto a surface depending on the type of the processing gas. In this way we can also get different surface hydrophilicity or we can even make the surface more hydrophobic than the original polymer surface.[10]

Among the available appropriate gases, oxygen plasma or a mixture with argon plasma is used most often. We can find numerous papers about the treatment of different polymers in oxygen plasma.[11–13] Carbon-dioxide plasma was also used instead of oxygen, especially for grafting carboxylic groups, although it is doubtful if carbon-dioxide plasma really causes a higher quantity of carboxylic groups than oxygen.[14] Nitrogen or ammonia plasmas are used to form nitrogen functional groups which can be important for various biomedical applications. It was also reported that ammonia plasma produces more amino groups on a surface than nitrogen plasma.[15,16] Some researchers also used a mixture of nitrogen and hydrogen instead of ammonia plasma.[17] Sulphur-dioxide plasma is very interesting as it can be used to graft oxidized sulphur species to a polymer surface.[18] Some attempts were performed to use this plasma to make a polymer surface antithrombogenic.[19,20]

Since different authors used different polymer materials and different plasma equipment, it is difficult to compare the results obtained by different authors. Therefore, in this paper we show a systematic comparison of different gases used for a surface modification of polymer polyethylene terephthalate (PET) like: oxygen, carbon dioxide, sulphur dioxide, hydrogen, nitrogen, ammonia, argon and tetrafluoromethane.

2 EXPERIMENTAL WORK

2.1 Sample preparation

Samples of semi-crystalline polymer polyethylene terephthalate (PET) from Goodfelow Ltd. were treated in plasmas created in different gases. The following commercially available gases were used: oxygen (O_2), carbon dioxide (CO_2), sulphur dioxide (SO_2), hydrogen (H_2), nitrogen (N_2), ammonia (NH_3), argon (Ar) and tetrafluoromethane (CF_4). The samples of the PET polymer were exposed to the glowing part of plasma and treated with two pulses, each with a duration of 0.5 s. The thickness of the polymer foil was 250 μm.

The plasma reactor was composed of a discharge tube made from Quartz glass. The length of the tube was 80 cm and the diameter was 4 cm. A coil of 6 wounds was mounted into the centre of the tube. A rather large distance between the coil and the grounded flanges was applied in order to minimize the capacity coupling. Plasma was created with an RF generator coupled to the coil via a matching network. The generator operated at the standard frequency of 13.56 MHz. The nominal power was set to 700 W. The discharge chamber was pumped with a Roots pump with a nominal pumping speed of 400 m^3 h^{-1} backed by a two-stage oil rotary pump with a pumping speed of 80 m^3 h^{-1}. A commercially available gas was added into the discharge chamber through a flow controller. The pressure was measured with an absolute vacuum gauge. The pressure was fixed to 30 Pa.

2.2 Sample characterization

After the plasma treatments the surface chemical compositions of the samples were determined with X-ray photoelectron spectroscopy (XPS), while the surface roughness and morphology were studied with atomic force microscopy (AFM).

The samples were analysed with a TFA XPS Physical Electronics XPS instrument. The base pressure in the XPS analysis chamber was about 6×10^{-8} Pa. The samples were excited with X-rays over a spot area 400 μm with the monochromatic Al $K_{\alpha1,2}$ radiation at 1486.6 eV. The photoelectrons were detected with a hemispherical analyzer positioned at an angle of 45° with respect to the normal to the sample surface. The energy resolution was about 0.5 eV. The survey-scan spectra were made at a pass energy of 187.85 eV and 0.4 eV energy step. The

high-resolution spectra were made at a pass energy of 23.5 eV and 0.1 eV energy step. The concentration of the elements on the polymer surface was determined using the MultiPak v8.1c software from Physical Electronics, supplied with the spectrometer.

An AFM (Solver PRO, NT-MDT, Russia) was used to characterize the surface topography of the samples. All the measurements were done in a semi-contact mode using golden silicon probes NSG10 tips (NT-MDT, Ireland) with a resonance frequency of 140–390 kHz and a force constant of 3.1–37.6 N m^{-1}. The size of the images was 2 μm × 2 μm.

3 RESULTS AND DISCUSSION

Table 1 shows the surface compositions of polymer PET after the treatments in the plasmas created in different gases and **Figure 1** presents high-resolution carbon C1s spectra for all the treatments. From **Table 1** we can see that oxygen concentration on the polymer increased with all the gases containing oxygen, i.e., O_2, CO_2 and SO_2. Furthermore, oxygen concentration on the polymer surface is practically the same for all three gases. It can be concluded that the plasmas created in all three gases supply a huge amount of oxygen atoms to the polymer surface causing the maximum surface functionalization according to the available free sites on the surface.[21] This is also reflected in the high-resolution spectra of carbon C1s peaks shown in **Figure 1** that look quite similar. In all the cases we observe an increase in the intensity of the peaks due to C-O and O=C-O groups. In the case of the SO_2 plasma we also found small amounts of sulphur on the surface which was oxidized as well (not shown here). The C-S bond cannot be clearly resolved from the carbon C1s peak since it is positioned quite close to the main C-C peak.

Table 1: Surface compositions of PET samples treated with different gases (in amount fractions, x/%)
Tabela 1: Površinska sestava vzorcev PET, obdelanih z različnimi plini (v množinskih deležih, x/%)

Gas type	C	O	N	S	F
control	74.0	26.0			
Ar	79.0	20.1	0.9		
O_2	65.7	34.3			
CO_2	65.8	34.2			
SO_2	64.0	34.6		1.4	
CF_4	40.0	1.2			58.8
N_2	66.7	15.5	17.9		
NH_3	79.5	12.9	7.5		
H_2	90.4	9.6			

Oxygen concentration was slightly decreased after the treatment in the Ar plasma, followed by the N_2 and NH_3 plasmas. The lowest amount of oxygen was found after the treatment in the H_2 plasma and, especially, after the treatment in the CF_4 plasma, where huge amounts of fluorine (more than amount fraction $x = 58$ %) were
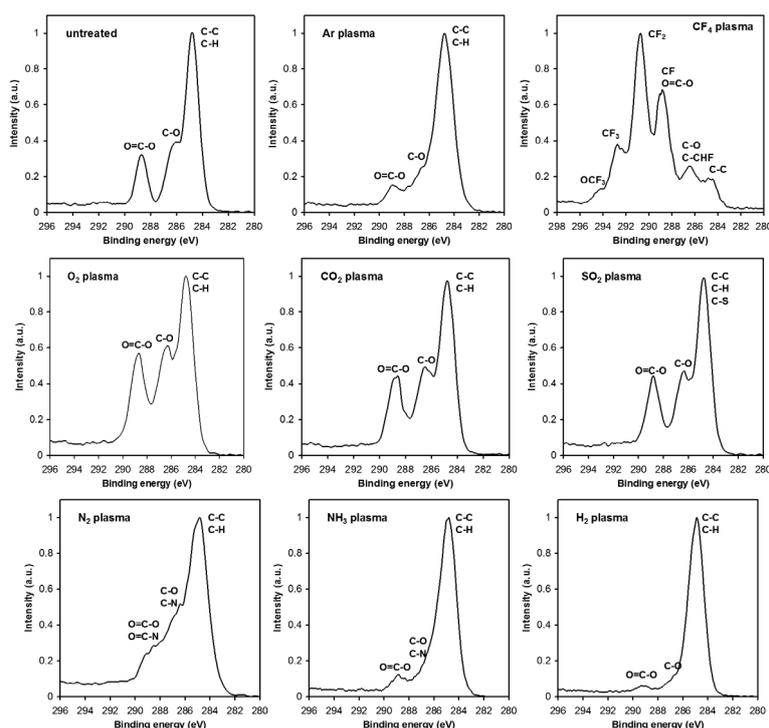
Figure 1: High-resolution XPS spectra of carbon C1s peaks of PET samples treated with different gases
Slika 1: Visokoločljivostni XPS-spektri ogljika C1s vzorcev PET, obdelanih z različnimi plini

found as well. The spectrum of the carbon C1s peak after the CF_4 plasma treatment is very different from all the other spectra (**Figure 1**). The formation of different fluorine-containing functional groups like CF_3, CF_2 and CF causes a big shift in the binding energy and can be, therefore, clearly observed in the spectrum. On the contrary, in the case of the polymer treated with nitrogen-containing plasmas like N_2 and NH_3 the peaks overlap with the oxygen groups (C-O and O=C-O) due to nitrogen functional groups (C-NH_2, O=C-NH_2). Nevertheless, **Table 1** clearly shows substantial amounts of nitrogen on the polymer surface, especially in the case of the N_2 plasma. The reason, why the peaks in the case of the NH_3 plasma are not as distinct as in the case of the N_2 plasma, is lower nitrogen and oxygen amounts.

The carbon spectrum after the treatment in the H_2 plasma is also interesting because very low amounts of oxygen were found in it. Obviously, hydrogen causes a reduction of the existing functional groups on the polymer and, therefore, the main peak prevails due to C-C, C-H bonds. Also, in the case of the Ar plasma we observed that the intensity of the peaks had decreased due to C-O and O=C-O groups, typical for an untreated polymer. Since Ar is chemically inert it cannot cause a functionalization but rather a polymer etching or cross-linking.

Other features worth discussing are the surface roughness and morphology. According to **Table 2**, the roughness of the untreated sample is about 1.2 nm. The roughness only slightly decreased after the treatment in the CF_4, NH_3 and H_2 plasmas, while for the other plas-

mas like Ar and N_2 it remained (within the experimental error) nearly the same. A slight increase in the surface roughness was observed only in the cases of the O_2 and CO_2 plasmas, which is due to etching.[9] Here we should note that the reason for such small differences in the surface roughness between different polymers is a very low treatment time (1 s). If the treatment time was longer, the difference in the surface roughness would be much higher. Especially high surface roughness was found in the case of the SO_2 plasma. According to **Figure 2**, this is due to a formation of some large features on the surface, which can be sulphur-containing "droplets" that always form on the walls of the discharge chamber when

Table 2: Surface roughness of PET samples treated with different gases. The roughness was measured on the areas of 5 μm × 5 μm or 3 μm × 3 μm.
Tabela 2: Površinska hrapavost vzorcev PET, obdelanih z različnimi plini. Hrapavost smo merili na dveh različno velikih področjih 5 μm × 5 μm ali 3 μm × 3 μm.

Gas type	Roughness (nm) measured on 5 μm × 5 μm	Roughness (nm) measured on 3 μm × 3 μm
control	1.2	1.2
Ar	1.1	0.9
O_2	1.9	1.9
CO_2	1.6	1.6
SO_2	14.1	13.2
CF_4	0.8	0.7
N_2	1.3	1.2
NH_3	0.8	0.8
H_2	0.6	0.6
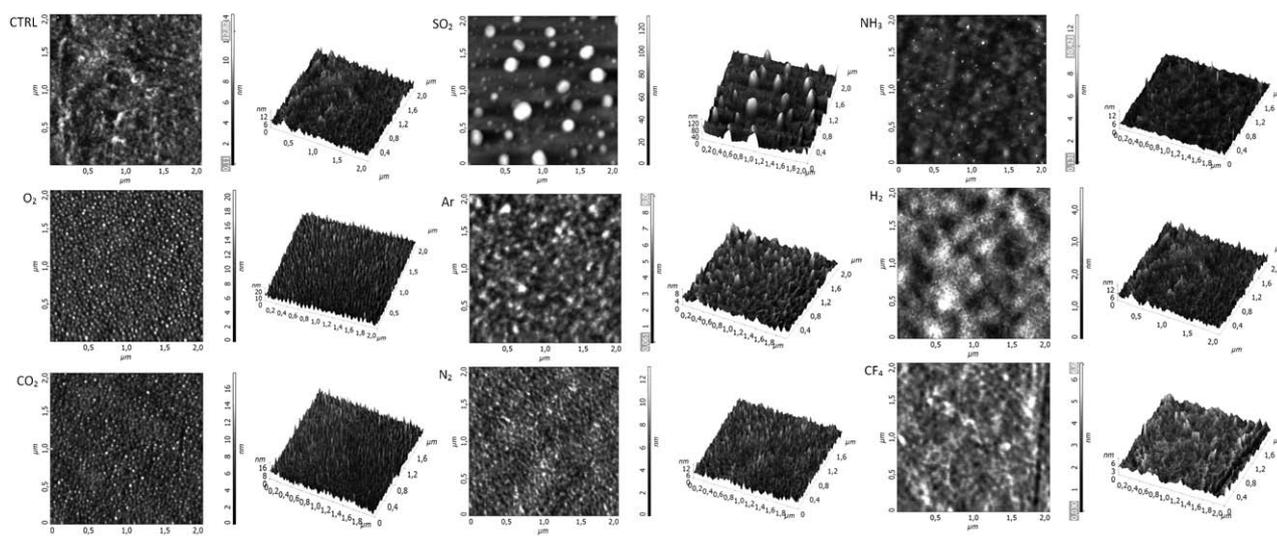
Figure 2: AFM images of PET samples treated with different gases. The image size is 2 μm × 2 μm.
Slika 2: AFM-slike PET-vzorcev, obdelanih z različnimi plini. Velikost slike je 2 μm × 2 μm.

using the SO_2 gas. **Figure 2** also shows that the O_2 and CO_2 plasmas cause a formation of a fine-grain nanostructured surface due to etching.[22] Contrary to the O_2 and CO_2 plasmas, the Ar plasma does not show such a fine surface structure – in this case, the peaks formed on the surface are much wider and smaller. On the other hand, the CF_4, N_2, NH_3 and H_2 plasmas do not show a formation of any particular features at all and the surfaces are much more indistinct. Also, the surface roughness of these samples changes only slightly.

4 CONCLUSIONS

The surface of a PET polymer was modified in the plasmas created in various gases. When using oxygen-containing plasmas like O_2 and CO_2, similar results were obtained regarding the surface chemical composition and morphology. Namely, for both plasmas similar oxygen concentrations were found on the surface which resulted in a formation of oxygen functional groups with similar concentrations. The roughness of both plasma-treated surfaces increased and a formation of nanostructured surfaces was observed.

When using the hydrogen plasma, the original oxygen concentration of the polymer significantly decreased and the intensity of oxygen functional groups was also significantly reduced. As expected, the hydrogen plasma had just the opposite effect from the oxygen plasma. Also, no significant changes in the surface roughness and morphology were observed for the sample treated in the hydrogen plasma.

The argon-plasma treatment slightly reduced the amount of oxygen on the surface. Nevertheless, the shape of the carbon peak changed, indicating a modification of the existing functional groups and a formation of new groups. The surface morphology also slightly changed,

indicating chain scission, slight etching and a redistribution of atoms on the surface.

The fluorine plasma resulted in a strong surface fluorination, since huge amounts of fluorine were found. The surface roughness and morphology did not change significantly. In fact, this surface looks similar to the one treated in the Ar plasma.

When using the N_2 plasma, we observed more nitrogen on the surface than in the case of the NH_3 plasma. In both cases the oxygen concentration was lower than on the virgin, untreated sample. The roughness and morphology did not change significantly. The morphology of the sample treated in the NH_3 plasma is similar to the one treated in the H_2 plasma.

The treatment with the SO_2 plasma was very interesting. The oxygen concentration on the surface after the plasma treatment was similar to the ones obtained with the O_2 and CO_2 plasmas. Furthermore, small amounts of sulphur were found as well. Significant spherical spots were observed on the surface and, consequently, an enormous increase in the surface roughness was recorded.

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