

## MODIFIKACIJA POLIMERA POLIETILEN NAFTALAT Z OBDELAVO V KISIKOVI PLAZMI

### MODIFICATION OF A POLYETHYLENE NAPHTHALATE POLYMER USING AN OXYGEN PLASMA TREATMENT

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*Prejem rokopisa – received: 2009-03-09; sprejem za objavo – accepted for publication: 2009-08-25*

We have studied the surface modification of a polyethylene naphthalate (PEN) foil with an oxygen plasma. The samples of PEN were treated in an inductively coupled RF plasma with a frequency of 27.12 MHz and at an output power of about 200 W. The gas pressure was 75 Pa. The samples were exposed directly to the glow region of the plasma. The samples were treated for different periods, ranging from 3 s to 60 s. Chemical changes in the surface composition after the plasma treatments were studied using high-resolution XPS (X-ray Photoelectron Spectroscopy), while the wettability was determined by water-contact-angle measurements (WCA). The untreated surface was hydrophobic with a water contact angle of about 90°. After 10 s of treatment the surface became very hydrophilic, with a contact angle of only about 3°. The oxygen concentration was increased from an initial mole fraction 21 % to about 35–38 %, depending on the treatment time. The surface oxidation resulted in the formation of different chemical bonds between the carbon and the oxygen, e.g., C=O, O–C–O, O–C=O and –C(=O)–O–C(=O)–.

Key words: XPS, PEN, PET, polymer, plasma, oxygen, modification, surface, functionalization, hydrophilic

V članku opisujemo modifikacijo površine polimera PEN (polyethylene naphthalate) s kisikovo plazmo. Plazmo smo generirali z induktivno sklopljenim radiofrekvenčnim generatorjem s frekvenco 27,12 MHz in izhodno močjo okoli 200 W. Tlak kisika je bil 75 Pa. Vzorci polimera PEN so bili izpostavljeni plazmi različno dolgo časa: od 3 s do 60 s. Spremembe v kemijski sestavi površine smo ugotavljali z metodo XPS (rentgenska fotoelektronska spektroskopija), spremembe v omočljivosti površine pa z meritvijo kontaktnega kota vodne kapljice. Ta je bil na neobdelani površini 90°. Po 10-sekundni obdelavi v kisikovi plazmi je površina polimera postala močno hidrofilna s kontaktnim kotom le okoli 3°. Pri še daljših izpostavah plazmi je bil kontaktni kot še manjši, tako da je bil že pod mejo merljivosti. Iz XPS-meritev izhaja, da je koncentracija kisika na površini narasla od začetnih molskih deležih 21 % na 35–38 %, odvisno od časa obdelave. Posledica vezave kisika na površino polimera je nastanek novih funkcionalnih skupin, kot npr. C=O, O–C–O, O–C=O in –C(=O)–O–C(=O)–.

Ključne besede: XPS, PEN, PET, polimer, plazma, kisik, modifikacija, površina, funkcionalizacija, hidrofilčen

## 1 INTRODUCTION

Polymer materials are known to be hydrophobic. They have very poor adhesion properties and wettability. Therefore, they must be modified before applications like printing, painting, coating, to improve the biocompatibility, etc. One of the most promising methods for modifying the surface properties of polymer materials is plasma treatment.<sup>1–9</sup> Plasma treatment is an ecologically suitable method and it is replacing the traditional wet chemical techniques, which can involve harmful chemicals. Plasma treatment affects only the first few nanometers of a material without changing the bulk properties.<sup>1</sup> It is a very quick method, because usually for surface functionalization only a few seconds of treatment are necessary. Using a treatment in a plasma of different gases we can achieve a wide range of surface wettability, from moderate hydrophilicity to significant hydrophobicity. This hydrophobicity can be achieved by a treatment in plasma created in halogens, while for achieving the hydrophilicity of the surface it is best to use an oxygen plasma. In some applications, especially biological, when we want to coat the substrate with proteins or DNA, for example, a nitrogen or ammonia

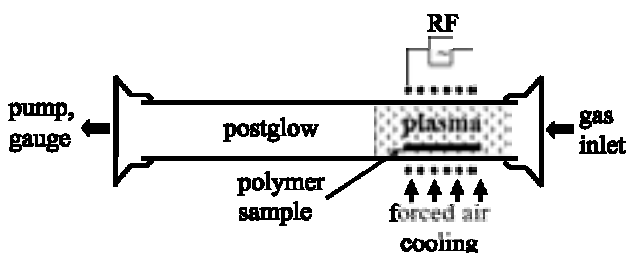
plasma is more desirable than an oxygen plasma.<sup>2</sup> It should be noted that plasma treatment does not produce a unique functionality on a polymer surface. Typically, a distribution of several different functional groups is produced. Some of the functional groups may be important and some may actually be detrimental. Thus, it is desirable to determine which of the functional groups is important for a given application and to attempt to shift the distribution in favour of a specific functionality by changing the plasma gas or other plasma parameters.<sup>3</sup> In an oxygen plasma different functional groups, like C–O, O–C–O, C=O, O=C–O, or even more exotic groups, can be produced on the surface.<sup>3–6</sup> When the polymer is exposed to plasma the first effect that appears at the polymer surface is actually just removing of contaminants, which may also lead to improved wettability. With a further treatment time the insertion of oxygen atoms from the plasma into the polymer surface appears to lead to the formation of various functional groups that change the surface wettability. With a prolonged treatment time, etching of the surface occurs, which leads to an increased surface roughness and changes in the surface morphology.

In the present paper we present a study on the functionalization of polymer PEN (Polyethylene Naphthalate (Teonex®)) by low-pressure radio-frequency (RF) oxygen plasma. The surface of the treated polymer was characterized by applying XPS (X-ray Photoelectron Spectroscopy) and WCA (Water Contact Angle) measurements. According to a literature review, a modification of the polymer PEN has already been studied by using RF nitrogen plasma<sup>10</sup> and atmospheric-pressure microwave<sup>8</sup> and RF<sup>9</sup> plasma. The authors found that the polarity of the PEN surface increased 10 times, but the contact angle on the treated surface was still relatively large (21.7°).<sup>9</sup>

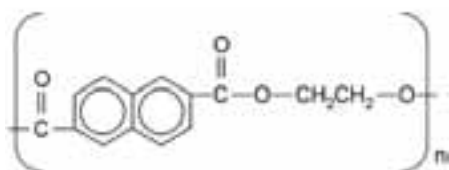
## 2 EXPERIMENTAL

### 2.1 Plasma modification

The samples of polymer Teonex® Polyethylene Naphthalate (PEN) were treated in the experimental system shown in **Figure 1**. The chemical structure of the PEN is shown in **Figure 2**. The system is pumped with a two-stage oil rotary pump with a pumping speed of 16 m<sup>3</sup>/h. The discharge chamber is a Pyrex glass cylinder with a length of 50 cm and an inner diameter of 3.6 cm. The plasma is created inside the discharge chamber with an inductively coupled RF generator, operating at a frequency of 27.12 MHz and an output power of about 200 W. The plasma's parameters are measured with a double Langmuir probe and a catalytic probe. The Langmuir probe is placed into the discharge chamber, while the catalytic probe is mounted in the afterglow chamber. Commercially available oxygen is leaked into the discharge chamber. The pressure is measured with an absolute vacuum gauge and is adjusted during continuous pumping using a precise leak valve. During our experiments the pressure was fixed at 75 Pa, where the



**Figure 1:** The plasma chamber for treating the samples  
**Slika 1:** Plazemski sistem za obdelavo vzorcev



**Figure 2:** Chemical structure of PEN  
**Slika 2:** Kemijska struktura PEN

density of the oxygen atoms was the highest. Using these discharge parameters an oxygen plasma with an ion density of  $8 \times 10^{15} \text{ m}^{-3}$ , an electron temperature of 5 eV, and a density of neutral oxygen atoms of  $4 \times 10^{21} \text{ m}^{-3}$  was obtained.

### 2.2 XPS characterization

The samples were exposed to air for a few minutes after the plasma treatment and then mounted in the XPS instrument (TFA XPS Physical Electronics). The base pressure in the XPS analysis chamber was about  $6 \times 10^{-10}$  mbar. The samples were excited with X-rays over a 400- $\mu\text{m}$  spot area with monochromatic Al K $_{\alpha 1,2}$  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 0.6 eV. Survey-scan spectra were made at a pass energy of 187.85 eV, while for C1s and O1s individual high-resolution spectra were taken at a pass energy of 23.5 eV and a 0.1-eV step. Since the samples are insulators, we used an additional electron gun to allow for surface neutralization during the measurements. The spectra were fitted using MultiPak v7.3.1 software from Physical Electronics, which was supplied with the spectrometer. The curves were fitted with symmetrical Gauss-Lorentz functions. The peak width (FWHM) was fixed during the fitting process. The main C 1s peak was shifted to 284.8 eV.<sup>11</sup> A Shirley-type background subtraction was used.

### 2.3 Contact angle measurements

The wettability was examined immediately after the plasma treatment by measuring the water contact angle with a demineralised water droplet of volume 3  $\mu\text{L}$ . Homemade apparatus equipped with a CCD camera and a PC computer was used to take high-resolution pictures of the water drop on the sample surface. Each determination was obtained by averaging the results of five measurements. The relative humidity (45 %) and temperature (25 °C) were monitored continuously and were found not to vary significantly during the contact-angle measurements. The contact angles were measured by our own software, which enables the fitting of the water drop on the surface in order to allow a relatively precise determination of the contact angle. The results of the water-contact measurements are shown in **Table 1**.

**Table 1:** Contact angles of a water drop (WCA) on the surface of the PEN foil

**Tabela 1:** Kontaktni kot vodne kapljice na površini folije PEN

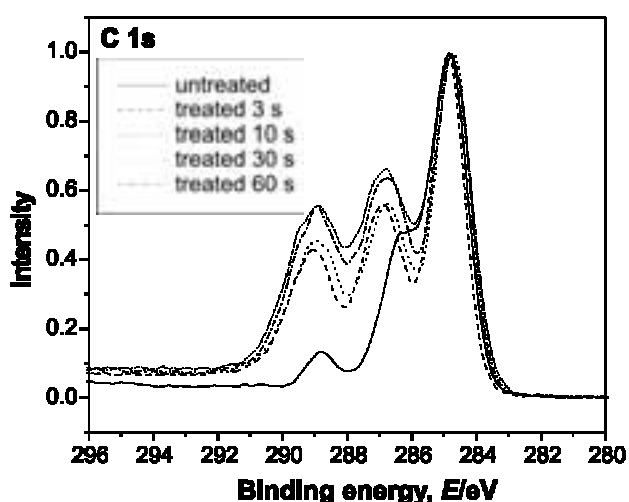
Sample	WCA (°)
untreated	88° – 95°
treated for 3 s	11° – 14°
treated for 10 s	≈ 3°
treated for 30 s	Not measurable
treated for 60 s	Not measurable

### 3 RESULTS

**Figure 3** shows a comparison of the carbon C 1s peaks for samples of PEN polymer that were exposed to plasma for different times. We can see a large difference in the intensity of the high-energy peaks between the untreated polymer and the one treated for 3 s. With treatment times longer than 3 s the difference is less pronounced, indicating surface saturation with oxygen.

The surface composition of the untreated and treated samples is shown in **Table 2**. We can see that after plasma treatment the oxygen concentration increased from the mole fraction 21 % to 35 % or to 38 % for 3 s or 60 s of treatment, respectively. The other elements N, Na, S and Si that were also found on the surface are impurities.

**Figure 4** shows the detailed structure of the carbon C 1s peak for the untreated sample. The peak consists of three sub-peaks belonging to the  $-C=C$  bond (C1), to the  $C-O$  bond (C2) and to the  $O=C-O$  bond from the ester group (C3). **Figure 5** shows an example of a carbon peak for a sample treated for 3 s. This peak consists of five sub-peaks. In comparison with the untreated sample two new sub-peaks are observed: C23, corresponding to the  $C=O$  or  $O-C-O$  bond; and C4, which according to its very high binding energy, corresponds the



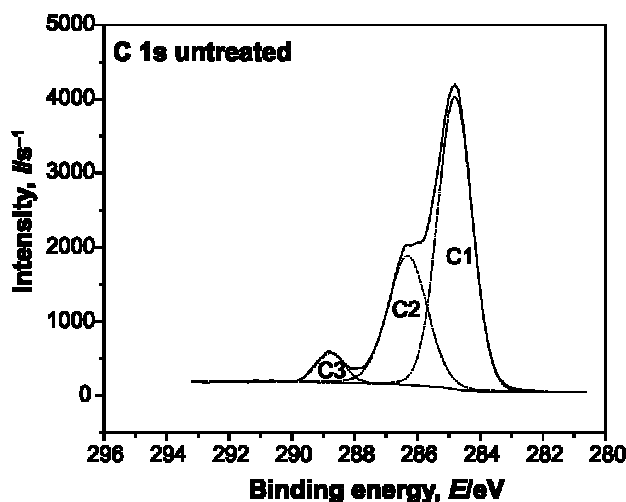
**Figure 3:** Comparison of high-resolution XPS peaks of carbon C1s peaks for different treatment times.

**Slika 3:** Primerjava visokoločljivih XPS-spektrov ogljika za različne čase obdelave

**Table 2:** Surface composition of PEN samples at different treatment times (in mol fractions, x/%)

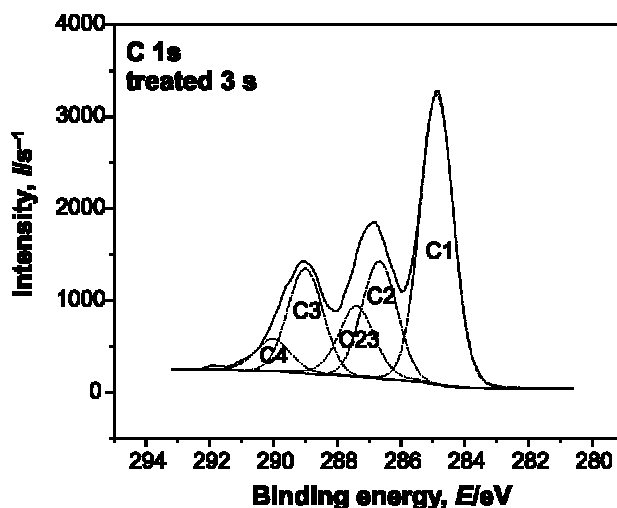
**Tabela 2:** Sestava površine vzorcev polimera PEN v odvisnosti od časa obdelave v plazmi (v molskih deležih, x/%)

Sample	C	O	N	Na	S	Si
untreated	74.9	21.0	1.9	1.1	0.8	0.4
treated for 3 s	63.8	35.0	0.8	/	/	0.4
treated for 10 s	62.6	36.5	/	/	0.1	0.9
treated for 30 s	61.7	37.2	0.6	/	/	0.5
treated for 60 s	58.1	38.3	/	2.1	0.4	1.0



**Figure 4:** Carbon C 1s peak of untreated PEN sample with three sub-peaks

**Slika 4:** Ogljikov vrh C 1s neobdelane folije PEN s tremi podvrhovi



**Figure 5:** Carbon C 1s peak of PEN sample treated in plasma for 3 s with five sub-peaks

**Slika 5:** Ogljikov vrh C 1s plazemsko obdelane (3 s) folije PEN s petimi podvrhovi

$-C(=O)-O-C(=O)-$  group. Similar functional groups were also observed on other PEN samples treated for longer times. **Table 3** summarizes the concentrations of the different types of functional groups that were obtained for the PEN samples for different treatment times.

### 4 DISCUSSION

From the XPS results shown in **Table 3** we can see that the concentration of the sub-peak C1 belonging to the  $-C=C$  bonds from the aromatic rings decreased after the plasma treatment. We can conclude that the oxygen atoms probably destroy the aromatic rings by scission of the  $-C=C$  bonds, which leads to opening of the aromatic rings. Furthermore, the concentration of the sub-peak C2

**Table 3:** Concentration of functional groups at the PEN surface versus treatment time**Tabela 3:** Koncentracija funkcionalnih skupin na površini folije PEN v odvisnosti od časa obdelave v plazmi

	Peak designation	C1	C2	C23	C3	C4
	Binding energy (eV)	≈284.8	≈286.4	≈287.3	≈288.9	≈290.0
	Assigned functional group	C-C, C=C	C-O	C=O O-C-O	O=C-O	
Sample	untreated	64.4 %	30.1 %	/	5.5 %	/
	treated 3 s	45.9 %	22.1 %	9.1 %	18.0 %	5.0 %
	treated 10 s	44.3 %	18.2 %	12.3 %	20.3 %	4.9 %
	treated 30 s	40.4 %	14.0 %	19.1 %	17.7 %	8.9 %
	treated 60 s	40.4 %	10.6 %	21.5 %	19.3 %	8.3 %

belonging to the C–O ether bond decreased as well. Therefore, not only the carbon atoms from the aromatic rings, but also carbons from the ether part of the PEN are attacked by oxygen atoms from the plasma. The oxidation of these carbon atoms resulted in the formation of C=O, O–C–O, O=C–O and –C(O)–O–C(O)– bonds. We can see that the concentration of these groups increases with the increasing treatment time, especially for the C=O, O–C–O and –C(O)–O–C(O)– groups, while for O=C–O an increase in the concentration is less pronounced, except in first 3 s of the treatment.

The incorporation of new, oxygen functional groups to the PEN surface resulted in an increased surface wettability. As shown in **Table 1**, the water contact angle on the untreated PEN surface was about 90°. Such a surface is hydrophobic with poor wettability. After 10 s of treatment the surface became very hydrophilic with a contact angle of only about 3°. At longer treatment times, the contact angle was so small that it was below the detection limit. In this case, the water drop completely wetted the polymer surface.

Here it is also worth mentioning the plasma treatment of the polymer PET (Polyethylene Terephthalate).<sup>6</sup> This polymer is similar to PEN, but it has only one aromatic ring. In the case of the PET polymer, the wettability of surface after the treatment was lower (less hydrophilic) than for the PEN. Namely, after 10 s of treatment of the PET, the water contact angle decreased from an initial 74° to 15°, while perfect wettability was achieved for treatment times longer than 60 s. The same was also found by Gonzales et al.<sup>9</sup> The concentration of oxygen at the PET surface was a little higher: 39 % and 42 % for 3 s and 60 s of treatment, respectively. The surface oxidation of the polymer PET resulted mostly in the formation of only C=O, O–C–O and O=C–O bonds.<sup>9</sup>

## 5 CONCLUSIONS

We have shown that by an appropriate treatment of the polymers PEN and PET in plasma it is possible to change the hydrophobic surface to a very hydrophilic one, which was proved by water-contact-angle measurements. For such a modification, usually a few seconds of treatment in a low-pressure oxygen plasma are adequate. Treatment in an oxygen plasma resulted in the incorporation of oxygen atoms from the plasma into the polymer surface, leading to the formation of different chemical bonds between the carbon and oxygen atoms, e.g., C=O, O–C–O, O=C–O and –C(=O)–O–C(=O)–, which are responsible for the observed changes in the surface wettability.

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