THERMAL DEFUNCTIONALIZATION OF AN OXYGEN-PLASMA-TREATED POLYETHERSULFONE

TERMIČNA DEFUNKCIONALIZACIJA POLIMERA POLIETERSULFONA, OBDELANEGA V KISIKOVI PLAZMI

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The phenomenon of spontaneous decay of oxygen-rich functional groups on the surface of a polymer was studied with high-resolution X-ray photoelectron spectroscopy (XPS). Samples of smooth poly(ether-sulfone) PES foils were exposed to a highly non-equilibrium oxygen plasma created in an electrodeless RF discharge. After receiving a dose of about 1×10^{24} m^{-2} oxygen atoms the surface of the polymer became saturated with oxygen-rich functional groups such as C–O, C=O, COO$^-$. The XPS survey spectra showed an increase in the oxygen concentration from the original mole fractions 21 % to more than 42 %, while the high-resolution C1s spectra showed that the carboxyl group prevailed. The samples were heated in the XPS chamber for different periods and characterized in-situ right after the heat treatment. It is shown that the functional groups decay spontaneously with time and their concentration decreases below the detection limit after annealing at 200 °C for 8 min.

Keywords: oxygen plasma, polymer, functionalization, defunctionalization, thermal stability, activation, deactivation

Z metodo rentgenske fotoelektronske spektroskopije (XPS) smo raziskovali proces spontanega razpada kisikovih funkcionalnih skupin na površini polimera. Vzorce folije PES smo izpostavili visoko neravnovesni kisikovi plazmi, ustvarjeni v brezelektrodni radiofrekvenčni razelektritvi. Po izpostavitvi vzorcev kisikovi plazmi, kjer je bila prejeta doza kisikovih atomov okoli 1×10^{24} m^{-2}, se je površina vzorca nasitila z različnimi funkcionalnimi skupinami, kot so C–O, C=O, COO$^-$. Iz preglednih XPS-spektrov smo ugotovili, da je koncentracija kisika na površini narasla iz prvotnih molskih deležev 21 % na 42 %, medtem ko smo iz visokoločljivih spektrov ogljika ugotovili, da prevladuje karboksilna skupina. Plazemsko obdelane vzorce smo nato po kemijski analizi v posodi XPS in-situ segrevali različno dolgo, jih ohladili in še enkrat pomerili površinsko sestavo. Ugotovili smo, da funkcionalne skupine s časom spontano razpadajo. Po 8 min gretja pri 200 °C pade njihova koncentracija pod detekcijsko mejo.

Ključne besede: kisikova plazma, polimer, funkcionalizacija, defunkcionalizacija, termična stabilnost, aktivacija, deaktivacija

1 INTRODUCTION

Polymer materials are nowadays widely used in practical life and science. The surface properties of selected polymers are often not adequate so they should be modified prior to specific applications. The basic property of a polymer is its hydrophilicity. Most polymers are moderately hydrophobic. If it is necessary to make them more hydrophobic, the surface is functionalized with nonpolar functional groups, typically fluorine-rich functional groups.[1–4] Together with the high surface roughness, the polymers can be made superhydrophobic which means that the contact angle of a water drop approaches 180°. On the other hand, it is sometimes necessary to make polymers more hydrophilic. A standard procedure is the functionalization of a surface with polar functional groups – usually oxygen-rich functional groups such as carboxyl, carbonyl, hydroxyl, etc. Surprisingly enough, a combination of a high concentration of these functional groups and a very rough surface, which is due to an intense etching of a polymer surface,[5–8] often leads to a superhydrophilic character of the polymer.[9] Namely, the contact angle of the water drop becomes immeasurably low. In practice it means that the contact angle is below a few degrees.

There are many methods for the surface functionalization, but it seems that the nowadays treatment with non-equilibrium gaseous plasma prevails. Plasma treatment often assures for rapid functionalization.[10] While atmospheric plasmas are increasingly popular, low-pressure plasmas are still more applicable because they assure for a rather uniform treatment of the arbitrary samples with a complex shape. Plasma treatment is nowadays widely used also on the industrial scale. A phenomenon that is known to many researchers, but often neglected in relevant literature, is a slow loss of hydrophilicity.[11–13]

Highly hydrophilic properties of polymer materials are usually obtained by applying weakly ionized, highly reactive oxygen plasma. There are numerous reports on the functionalization of different materials with an oxygen-plasma treatment, including polyethylene terephthalate[9,14,15], polyethersulphone[16], polystyrene[17], polyvinylchloride[18], polymethyl methacrylate[19], cellulose[20,21], etc. While many authors use plasma as a black box (i.e., they do not measure the plasma parameters but present the results on the functionalization as a function of discharge parameters), there are also reports in the literature about a precise determination of both plasma parameters and the surfaces of plasma-treated

materials.[22,23] A decent scientific paper would typically include a flux of positively charged oxygen as well as neutral oxygen atoms on the surface of a polymer, and a characterization with XPS and/or SIMS and AFM and/or SEM. In fact, quite a few scientific papers include all these data. There are many papers studying the ageing effects (especially with the water-contact-angle measurements)[9] but, on the other hand, very few papers address the ageing phenomenon, i.e., a spontaneous decrease in the concentration of functional groups induced with thermal effects. In the present paper we address these phenomena. The decay of the functional groups was studied in-situ in the XPS chamber in order to minimize the number of possible effects.

2 EXPERIMENTAL WORK

Samples of the commercially available PES foils with pretty smooth surfaces were prepared as follows. The freshly packed foils were unpacked, cut into small pieces and mounted to a plasma system to be functionalized. The plasma system has been described to details elsewhere.[9] For the sake of the completeness of the paper let us just summarize the properties. Plasma is excited with an electrodeless RF discharge at variable power and oxygen pressure. In the case of our latest experiment we used a rather low RF power of about 100 W. At the pressure of 75 Pa the density of the charged particles was about 8×10^{15} m^{-3}, while the density of the neutral oxygen atoms was orders of magnitude larger at a value of about 4×10^{21} m^{-3}. The samples of PES foil were exposed to the plasma with such parameters for 3 s. The resultant flux of the neutral oxygen atoms was about 6×10^{23} m^{-2} s^{-1} and the received dose of the atoms in 3 s was close to 2×10^{24} m^{-2}. Such a large dose of the neutral oxygen atoms assures for a saturation of the polymer surface with the oxygen-rich functional groups as has been already shown in another paper[9].

The plasma-treated samples were exposed to air for a short time and mounted into the XPS instrument (TFA XPS Physical Electronics). The XPS (X-ray photoelectron spectroscopy) measurement was performed as follows: a plasma-treated sample was first analyzed to see its chemical composition after the plasma treatment. Then the sample holder in the XPS chamber was heated, in a short time, to 200 °C to study the thermal stability of the functional groups formed during the plasma treatment. The sample was kept at this temperature for a certain time (1 min and 8 min) and the holder was cooled down to room temperature before the XPS characterization of the treated sample.

During the XPS measurement the sample was excited with the X-rays with a 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 survey-scan spectra were made at a pass energy of 187.85 eV and with a 0.4 eV energy step. The high-resolution spectra of C1s were made at a pass energy of 23.5 eV and with a 0.1 eV energy step. The concentration of the elements was determined using MultiPak v7.3.1 software from Physical Electronics, which was supplied together with the spectrometer. The high-resolution spectra were fitted using the same software. The curves were fitted with the symmetrical Gauss-Lorentz functions. A Shirley-type background subtraction was used. Both the relative peak positions and the relative peak widths (FWHM) were fixed in the curve-fitting process.

3 RESULTS

Small pieces of foils were treated with the oxygen plasma in order to get the surface saturated with the oxygen-rich functional groups. Several samples were tested, but the differences between particular samples treated under the same conditions were minimal. The XPS survey spectra of the selected samples are shown in **Figure 1**. The lowest curve refers to the untreated sample and the other curves refer to the sample treated by plasma, the sample treated by plasma and heated at 200 °C for 1 min and the sample treated by plasma and heated for 8 min at the same temperature. From **Figure 1** it can be estimated that the plasma treatment caused an increase in the oxygen concentration, while the thermal treatment caused a decrease in the oxygen concentration on the plasma-treated samples. The quantitative values of the surface composition for all four cases are presented in **Table 1**. As expected, the concentration of oxygen on the plasma-treated sample is much larger than on the original sample. The O/C ratio is increased by almost a factor of 3. The values of the oxygen concentration on the samples treated by plasma and then heated in the
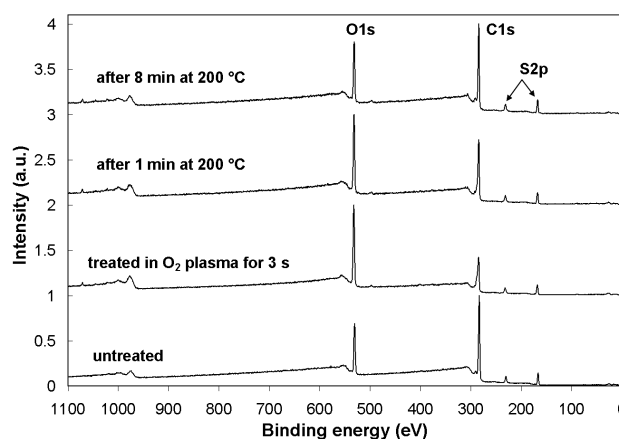

Figure 1: Comparison of the XPS survey spectra of an untreated polymer, a polymer treated in oxygen plasma for 3 s, a polymer treated in plasma and heated at 200 °C for 1 min and the one heated at 200 °C for 8 min

Slika 1: Primerjava preglednih spektrov XPS neobdelanega polimera, polimera obdelanega v plazmi 3 s in plazemsko obdelanega polimera, ki je bil za 1 min ter 8 min segret na 200 °C
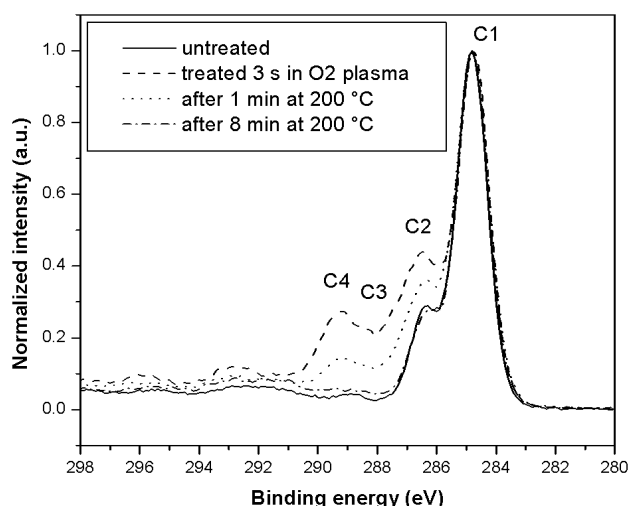
Figure 2: Comparison of the high-resolution C1s spectra of the untreated and treated PES polymers
Slika 2: Primerjava visokoločljivih spektrov ogljika C1s neobdelanega in obdelanega polimera PES

Table 1: Surface compositions of the untreated and treated PES polymers
Tabela 1: Površinska sestava neobdelanega in obdelanega polimera PES

Sample	C	O	S	O/C
untreated	73.8	21.1	5.1	0.29
treated for 3 s in O$_2$	52.0	42.3	5.7	0.81
after 1 min at 200 °C	61.3	33.4	5.4	0.54
after 8 min at 200 °C	69.8	24.6	5.6	0.35

Table 2: Concentrations of different chemical states of carbon atoms on the untreated and treated PES polymers
Tabela 2: Deleži različnih kemijskih stanj atomov ogljika na neobdelanem in obdelanem polimeru PES

Sample	C1 C-C C-S	C2 C-O	C3 C=O	C4 COO$^-$
untreated	82.7	17.3		
treated for 3 s in O$_2$	55.5	24.5	7.3	12.7
after 1 min at 200 °C	71.1	21.3	2.1	5.5
after 8 min at 200 °C	84.2	15.8		

XPS chamber are more interesting. Table 1 shows that the oxygen concentration drops substantially even after 1 min of heat treatment. After 8 min of heat treatment the oxygen concentration becomes so low that any speculation about the ratio between O and C for these samples and the untreated sample would not be fair.

Figure 2 represents the high-resolution C1s peaks for the selected samples. From this figure one can conclude that any difference between the untreated sample and the sample treated with oxygen plasma and heated for 8 min is below the detection limit of our device. On the other hand, the high-resolution C1s peak for the sample treated in the oxygen plasma for 3 s is completely different. The quantification of these results is summarized in **Table 2**. From this table we can see that the majority of the

oxygen is incorporated into the surface layer of PES in the form of carboxyl groups. It is interesting that the decay of a particular functional group during the heat treatment is not very selective. Within the experimental error one cannot conclude weather any of the newly formed functional groups decays faster than the other groups. It is only possible to conclude that the thermal decay is pretty effective.

Finally, it is worth mentioning that the original concentration of sulphur is preserved after the oxygen-plasma treatment and also after the heating experiments. This is an indication that the original structure of the polymer is preserved and oxygen is bonded practically only on the carbon atoms of the phenyl ring.

4 CONCLUSIONS

The experiments on the ageing of a plasma-functionalized PES showed a spontaneous decrease in the functional groups during the heat treatment. The temperature of 200 °C was found suitable for the effective decay of the functional groups. Since the experiments were performed in an ultra-high vacuum in the XPS chamber the decay of the groups cannot be explained with the environmental effects. The two possible explanations (either a diffusion of oxygen inside the polymer or a thermal desorption from the surface) should be taken into account. However, it is not possible to draw the final conclusion from the experimental results presented in this paper.

Acknowledgements

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