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Modification of PET surface by nitrogen plasma treatment

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Abstract. A study on nitrogen plasma functionalization of polyethyleneterephthalate (PET) is presented. The samples of PET foils were exposed to a weakly ionized, highly dissociated RF nitrogen plasma with an electron temperature of 5 eV, a density of positive ions of the order of 10^{15} m^{-3} and a density of neutral nitrogen atoms of the order of 10^{21} m^{-3} . The pressure was 75 Pa and a discharge power was 200 W. The PET-samples were exposed to plasma and its afterglow from 3 s to 10 s. After the treatment the surface was analysed by XPS (X-ray photoelectron spectroscopy). XPS results showed appearance of new functional groups like amine and amide.

1. Introduction

Polyethyleneterephthalate (PET) is often used for applications in packaging, electronic and biomedical industries. One problem associated with PET is its hydrophobic surface and thus pore adhesiveness. Therefore it must be modified prior to application in order to achieve hydrophilic character. This is becoming important in biomedical applications, where it is used for human implants such as vascular grafts, prosthetic heart valves and for endothelial cell growth [1-2]. For modifying the surface the most promising technique is a plasma treatment. Plasma has been successfully applied in different technologies like etching, functionalization and sterilization [3-4]. Usually oxygen plasma is used. By treatment of polymer in oxygen plasma different functional groups like C-O, C=O, O=C-O or even more exotic groups can be produced [5]. In biomedical applications other functional groups containing nitrogen are important because of their compatibility with different organic molecules like proteins and DNA. If we want to introduce nitrogen containing functional groups into the surface, the polymer must be treated in a nitrogen plasma or its mixture. NH₃ plasma may be used as well [6-7]. In this paper, we present a study on functionalization of PET foil by treatment in weakly ionized, highly dissociated, low-pressure RF nitrogen plasma and its afterglow. The changes in surface chemistry were studied by using X-ray photoelectron spectroscopy (XPS).

2. Experimental

Experiments were performed with a PET foil (DuPont) with the thickness of $125 \,\mu$ m. The foil was cut to pieces with a size of $1x1 \text{ cm}^2$. The samples were treated in the system which was pumped with a two-stage oil rotary pump with a pumping speed of $4.4x10^{-3} \text{ m}^3$ /s. There was a trap filled with the molecular sieves between the pump and a discharge chamber in order to prevent contamination of the chamber with the oil vapor. The discharge chamber was a Pyrex cylinder with a length of 60 cm and an inner diameter of 3.6 cm. The plasma was created with an inductively coupled RF generator, with a frequency of 27.12 MHz and an output power of 200 W. The plasma parameters were measured with a double Langmuir probe and a catalytic probe [8]. Commercially available nitrogen was leaked into the chamber by a precise leak valve. The pressure was 75 Pa. At these parameters, a nitrogen plasma with

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an ion density of the order of 10^{15} m⁻³, an electron temperature of 5 eV, and a density of neutral atoms of the order of 10^{21} m⁻³ was obtained. The samples were treated in a nitrogen plasma (in glow region) or its afterglow for 3 s and 10 s.

After the treatment the PET surface was analyzed with an XPS instrument TFA XPS Physical Electronics. The base pressure in the chamber was about 6×10^{-8} Pa. The samples were excited with X-rays over a 400-µm spot area with a 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 0.5 eV. Survey-scan spectra were made at a pass energy of 187.85 eV, while for C 1s, O 1s and N 1s individual high-resolution spectra were taken at a pass energy of 23.5 eV and a 0.1 eV energy step. Since the samples are insulators, we used an electron gun for surface neutralization. All spectra were referenced to the main C 1s peak which was assigned a value of 284.8 eV [9]. The concentration of different chemical states of carbon in the C 1s peak was determined by fitting the curves with symmetrical Gauss-Lorentz functions. The spectra were fitted using MultiPak v7.3.1 software from Physical Electronics, which was supplied with the spectrometer. A Shirley-type background subtraction was used. Both the relative peak positions and the relative peak widths (FWHM = 1.2 eV) were fixed during fitting.

3. Results and discussion

The surface composition of PET is shown in table 1. Already after 3 s of the treatment in plasma about 10 at.% of nitrogen was detected on the surface. The sample which was exposed to plasma for 10 s showed a little higher concentration of nitrogen (14 at.%) in comparison with the one treated just for 3 s. This is reasonable as the concentration of new elements that are incorporated to the surface usually increases with the increasing treatment time. Interesting is a comparison of PET treated in plasma for 3 s with the one treated in afterglow for the same period. In this case only about 3 at.% of nitrogen was detected on the surface. To explain this discrepancy we must consider the role of different plasma radicals. PET treated in afterglow was exposed to neutral nitrogen atoms only. Contrary the sample treated in plasma was exposed to nitrogen ions as well to other excited and metastable particles that can transfer their energy to the surface. Ions for example can cause bond breakage and formation of free radicals which can lead to the increased reaction probability with the nitrogen atoms. This gives a higher concentration of nitrogen in the surface of a sample treated in plasma as compared with the one treated in afterglow. Oxygen concentration was increased slightly. An increase of oxygen concentration does not necessarily reflects the amount of oxygen bonded to the surface as the samples were exposed to air prior to XPS analyses. The apparent increase of the oxygen concentration can be also due to removal of the surface contamination or to the presence of oxidizing species (oxygen, water) in the plasma reactor, since it is well known that oxygen functionalities are always incorporated into the surface of the samples treated in nitrogen plasma [10].

Sample	С	0	N
Untreated	73.1	26.9	
Treated in nitrogen plasma for 3 s	61.7	28.0	10.3
Treated in nitrogen plasma for 10 s	58.8	27.1	13.7
Treated in nitrogen afterglow for 3 s	67.0	29.9	3.1

Table 1. Surface composition of the PET foll before and after the plasma treatment	Table 1	1. Surface	composition	of the PE	T foil before	and after the	plasma treatment
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For more detailed analysis of the chemical changes induced during the plasma treatment of PET high resolution XPS spectra were recorded. The comparison of the C 1s, O 1s and N 1s spectra is shown in figure 1. After the treatment the C 1s peak considerably changed (figure 1a), while the comparison of O 1s peaks (figure 1b) showed only slight changes. To get information about the presence of different functional groups the C 1s spectra were fitted with the several curves.

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Binding e

ergy (eV)



The C 1s spectra were fitted with the minimum number of curves which were necessary to get the best fitting. An example is shown in figure 2a for the untreated PET and in figure 2b for PET treated in plasma for 3s. All the results are summarized in table 2. The C 1s peak of untreated PET composed of three peaks: peak (A) belonging to C-C and C-H bond, peak (B) belonging to C-O and peak (C) belonging to O=C-O bond [9]. In all cases after the treatment a new peak (D) is observed at a binding energy of 287.4 eV, which can be attributed to amide carbon atoms in O=C-N group. The peak (A) decreased after the treatment and peak (B) increased. The expected position of the C-N bond from amino group (~285.8 eV) which should be between (A) and (B) is not shown, since it is difficult to distinguish from the peak (A) or (B) [10]. Therefore the increase of the (B) peak is correlated to the appearance of amino groups. The appearance of other nitrogen containing functional groups like C=N or C = N can not be excluded as well. Relevant literature reports different data for binding energies of these peaks which are positioned quite close together: C-N (285.5 eV – 286.3 eV) C=N (285.5 eV – 286.6 eV), C = N (286.7 eV – 287.0 eV) [10-13] and this makes the interpretation of XPS spectra very difficult and quantification impossible. Also, the individual peaks for these carbon-nitrogen species overlap with their carbon-oxygen counterpart.



Figure 2. Curve fitting of the C 1s peaks of: (a) untreated sample, (b) sample treated in plasma for 3 s.

A decrease of the peak (A) can be due to replacement of hydrogen atoms from benzene ring with amino groups (C-NH₂) or even hydroxyl (-OH) groups. As shown in figure 1b the intensity of the ester type oxygen O-C-O (left peak) decreased after the treatment in comparison with the carbonyl oxygen C=O (right peak). This suggests that nitrogen plasma causes a disruption of ester functional group in PET as reported also by Dai [14] and Riccardi [15]. Therefore it is difficult to explain the increased

component (C) in the C 1s peak of treated PET (figure 1a, table 2) that should correspond to ester group (O=C-O). If plasma cause a scission of polymer chain at the ester group, than the (C) peak should decrease after the treatment as observed by Inagaki [4]. This indicates that probably more complex nitrogen structures like O=C-N-C=O (imide) were formed which appear at the similar binding energies as O=C-O [16]. However, the examination of N 1s spectra (figure 1c) shows that the N 1s peak is composed of a single relatively broad symmetric peak that can correspond to at least three different nitrogen states. Here we should note that the energies in plasma are sufficient to break polymer bonds, resulting in rearrangement of the surface. These rearrangements may even produce new functionalities without incorporation of new species. It was reported that braking of ester-type carbon-oxygen bond in polyester can lead to the formation of carbonyl groups and hydroxyl or ether groups, whereas braking of the ether-type carbon-oxygen bond can produce carboxyl groups [16].

Sample	A (284.8 eV)	B (286.4 eV)	C (288.8 eV)	D (287.4 eV)
_	C-C	C-O, C-N	O=C-O	O=C-NH ₂ , C=O
Untreated	67.7 %	17.9 %	13.3 %	-
Treated in nitrogen plasma for 3 s	48.5 %	23.1 %	23.2 %	5.2 %
Treated in nitrogen plasma for 10 s	46.9 %	24.5 %	23.3 %	5.2 %
Treated in nitrogen afterglow for 3 s	62.5 %	18.3 %	14.9 %	4.2 %

Table 2. Concentration of chemical groups in the untreated and treated PET foils.

4. Conclusions

Functionalization of PET foil after treatment in nitrogen plasma and its afterglow was studied. XPS was used for monitoring the surface chemical modifications after the plasma treatment. The results showed that the samples were covered with new functional groups both in plasma and afterglow region in already 3 seconds of the treatment time. It is difficult to estimate the amount of different surface groups, since XPS does not easily differentiate between the various nitrogen groups which are present on the surface. Detailed analysis of the carbon C 1s peak showed an evidence of appearance of amine and amide groups, although other nitrogen containing groups like imin can not be excluded.

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