MODIFICATION OF PET-POLYMER SURFACE BY NITROGEN PLASMA

MODIFIKACIJA POVRŠINE PET-POLIMERA Z DUŠIKOVO PLAZMO

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Low pressure weakly nitrogen plasma was applied for incorporation of nitrogen-containing functional groups onto poly(ethylene terephthalate) – PET polymer. Nitrogen plasma was created in an electrode-less radiofrequency discharge at the nominal power of 200 W and the frequency of 27.12 MHz. Nitrogen molecules entered the discharge region were highly excited, partially dissociated and weakly ionized. Transformation into the state of plasma allowed for creation of chemically reactive particles with a high potential energy while the kinetic energy remained close to the value typical for room temperature. The chemical reactivity allowed for rapid functionalization with nitrogen-rich functional groups. The appearance of these groups was monitored by X-ray photoelectron spectroscopy – XPS. The polymer surface was quickly saturated with nitrogen indicating that the modification was limited to an extremely thin surface film.

Keywords: poly(ethylene terephthalate), nitrogen plasma, surface modification, functional groups, X-ray photoelectron spectroscopy

Nizkotlačno, šibko ionizirano dušikovo plazmo smo uporabili za površinsko modifikacijo polimera polietilen tereftalat z dušikovimi funkcionalnimi skupinami. Plazmo smo vzbujali v brezelektrodni visokofrekvenčni plinski razelektritvi z generatorjem, ki deluje pri koristni moči okoli 200 W in osnovni frekvenci 27,12 MHz. Dušikove molekule, ki vstopijo v plinsko razelektritev, se vzbudijo v visoka vzbujena stanj, delno disociirajo in šibko ionizirajo. Transformacija plina v stanje plazme omogoča nastanek kemično reaktivnih delcev z veliko potencialno energijo, medtem ko ostane njihova kinetična energija blizu vrednosti, ki je značilna za plinske molekule pri sobni temperaturi. Velika kemijska reaktivnost dušikove plazme omogoča hitro funkcionalizacijo površine PET-polimera z dušikom bogatimi funkcionalnimi skupinami. Ta pojav smo spremljali z rentgensko fotoelektronsko spektroskopijo. Polimerni vzorci so postali hitro nasičeni z dušikom, iz česar je mogoče sklepati, da je funkcionalizacija omejena na zelo tanko plast prav ob površini vzorcev.

Ključne besede: poly(ethylene terephthalate), dušikova plazma, modifikacija površine, funkcionalne skupine, rentgenska fotoelektronska spektroskopija

1 INTRODUCTION

Polymer materials are widely used not only in industry but also in biomedical applications. A polymer which is of particular interest in biomedical applications is poly(ethylene terephthalate) – PET. The structural formula is presented in **Figure 1**. PET is supplied in variety of forms from bulk pieces through thin foils to fabrics. Perforated foils are often used as the first layer of plasters, while artificial blood vessels are made from knitted material. The PET material has excellent chemical and mechanical properties and expresses reasonably good bio-compatibility. The latter property, however, is not always adequate since un-specific interaction with body fluids is often observed. It is therefore desirous to modify the surface properti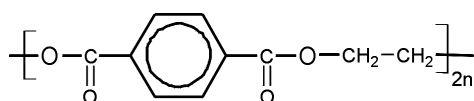es of PET before specific applications. The modification can be performed by a variety of wet chemical treatments, but such procedure often does not yield optimal results.

A popular technology for modification of polymer surface properties is treatment by gaseous plasma.[1–14] The surface properties of PET polymer can be modified using oxygen plasma treatment (to make it more hydrophilic),[15–21] or fluorine plasma (to obtain excellent hydrophobicity).[22–23] Such treatments have been applied, but it seems that in some cases they do not allow for optimal modification of surface properties. This is especially the case when optimal interaction with proteins is required. In such cases other types of plasma should be used. In the present paper, modification of PET by nitrogen plasma is addressed.

2 NITROGEN PLASMA

Plasmas of diatomic gases are often used in order to modify surface properties of polymer and other materials. It has been shown that oxygen molecules dissociate in plasma forming highly reactive atoms.[24–27] Similar effects were observed in hydrogen plasma.[28–35] Nitrogen, however, behaves much different in an

Figure 1: Structural formulae of poly(ethylene terephthalate)
Slika 1: Strukturna formula polietilen tereftalata

electrical discharge. This is due to a particular property of excited states as well as collision phenomena. In oxygen plasma, for instance, the probability for super-elastic collisions between vibrationally excited molecules and neutral atoms is huge, while in nitrogen it is negligible. This particular phenomenon allows for extremely high vibrational temperature of molecules in nitrogen plasma.

Appearance of highly vibrationally excited molecules is not the only particularity of nitrogen plasma. Nitrogen molecules also have a variety of electronically excited states and most are metastable. Plasma, created in nitrogen, is therefore a rich source of excited nitrogen molecules that are chemically pretty reactive. Some common excited states are presented in **Figure 2**.

3 EXPERIMENTAL

Samples of PET foils were treated in nitrogen plasma. The reactor has been described to details elsewhere.[15,36,37] Due to the completeness of the paper let us just summarize the most important features of the experimental system. The system comprises a discharge chamber, a vacuum pump, gas feeding system, radio-frequency generator and an optical spectrometer. The discharge chamber is a borosilicate glass tube (Schott 8250) with the length of 60 cm and the outer diameter of 4 cm. It is connected to kovar rings on both sides, and the rings are welded to standard FK 40 flanges. Rubber gaskets are used for vacuum seals. The discharge chamber is pumped on one side with a two stage oil rotary pump with the nominal pumping speed of 28 m^3/h. The pressure is measured with an absolute vacuum gauge. Nitrogen is leaked continuously on the other side of the discharge tube through a manually adjustable needle valve. The valve is connected to a nitrogen flask via a copper tube. The vacuum system is often exposed to ambient atmosphere and never baked so the ultimate pressure is several Pa. The residual atmosphere contains mostly water vapour. Plasma is created in the discharge
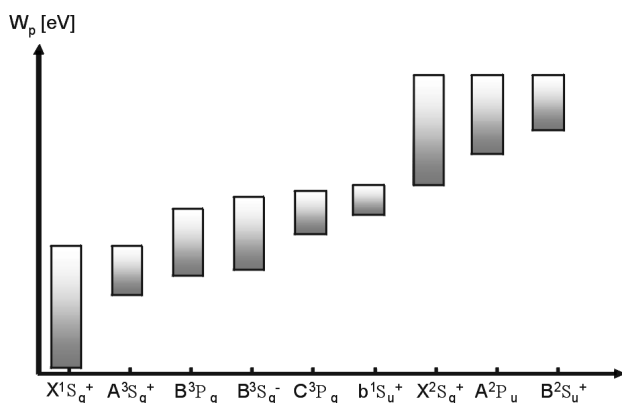

Figure 3: A typical optical spectrum of nitrogen plasma
Slika 3: Značilen optični spekter dušikove plazme

chamber by radiofrequency generator with the nominal power of 700 W and the fundamental frequency of 27.12 MHz. A coil of 14 turns is wound up the discharge chamber and connected directly to the generator. Since no matching network is applied between the generator and the coil, the matching is rather poor so it was estimated that the forward power was only about 200 W [38–42]. Both inductive and capacitive components are present in the discharge. The glowing plasma fills the entire volume in the discharge tube at low pressure, but at high pressure it is limited to a small volume inside the coil. At the pressure of 75 Pa the plasma is at its optimal condition so the samples are usually treated at this pressure. An optical spectrometer of rather poor resolution is used to monitor the plasma radiation from about 300 nm to 1000 nm. The best sensitivity of the spectrometer is between 400 nm and 800 nm where the borosilicate glass is pretty transparent.

Commercially available PET foils were cut to small pieces and exposed to plasma for (3, 10 and 30) s. No cleaning or other pretreatments were performed prior to exposure to plasma, but handling was careful so any presence of foreign material is unlike. Samples were

Figure 2: Some excited states of nitrogen molecule. The width of the states is due to vibrationally excitation
Slika 2: Nekatera vzbujena stanja dušikove molekule. Širok razpon po potencialni energiji je posledica vibracijskih vzbujenih stanj
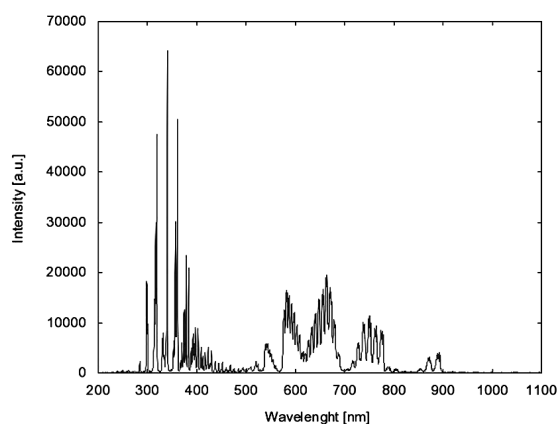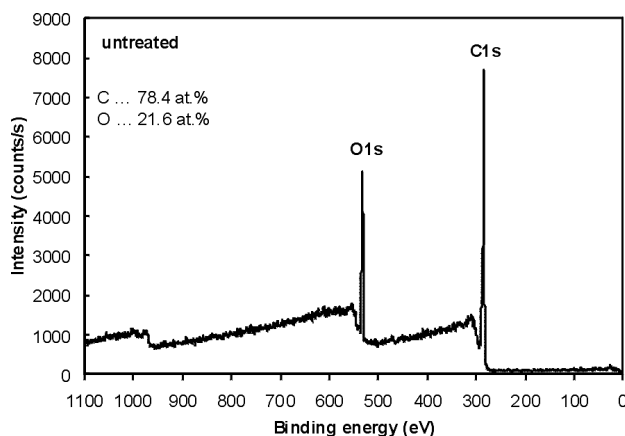

Figure 4: XPS survey spectrum of an untreated sample
Slika 4: Pregledni XPS-spekter neobdelanega vzorca

Figure 5: XPS spectrum of the sample treated with nitrogen plasma for 3 s
Slika 5: XPS-spekter vzorca, ki je bil obdelan z dušikovo plazmo 3 s
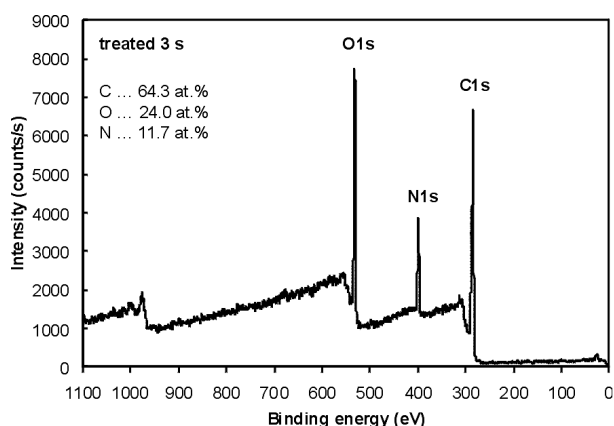

Figure 7: XPS spectrum of the sample treated with nitrogen plasma for 30 s
Slika 7: XPS-spekter vzorca, ki je bil obdelan z dušikovo plazmo 30 s

analyzed by X-ray photoelectron spectroscopy (XPS). We used our spectrometer AvaSpec 3648 from Avantes.

The surface of the plasma treated PET samples was analyzed with an XPS instrument TFA XPS Physical Electronics. The base pressure in the XPS analysis chamber was about 6×10^{-8} Pa. The samples were excited with X-rays over a 400-μm spot area with a monochromatic Al $K_{\alpha1,2}$ 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. Survey-scan spectra were made at a pass energy of 187.85 eV a 0.4 eV energy step, while for C1s 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 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. A Shirley-type background subtraction was used. Both the
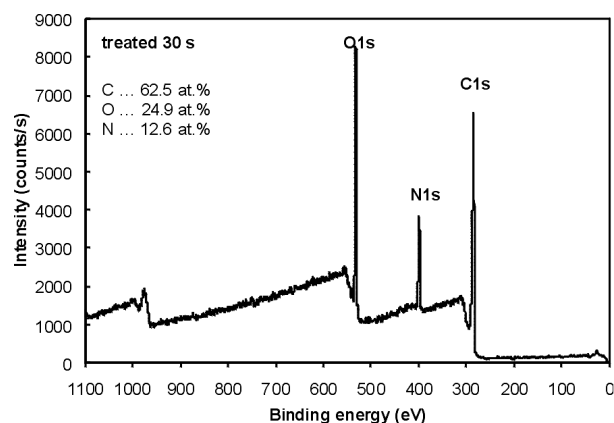
relative peak positions and the relative peak widths (FWHM) were fixed in the curve fitting process.

3 RESULTS

Optical spectra of nitrogen plasma were measured during treatment of the samples. The spectra did not change noticeably during the treatment indication pretty poor interaction of plasma with the samples. A typical spectrum is shown in **Figure 3**.

Samples were characterized by XPS before and after plasma treatment. A typical survey spectrum for untreated sample is presented in **Figure 4**, while **Figures 5, 6 and 7** represent spectra measured for samples exposed to nitrogen plasma for (3, 10 and 30) s, respectively. The survey spectra allow for quantification of the composition in the surface layer from which photo-electros can reach the detector. The elemental composition in atomic percent is given in boxed text placed in each spectrum presented in **Figures 3 – 7**.

4 DISCUSSION

The treatment of PET samples by nitrogen plasma caused interesting modification of the surface layer that is worth discussing. First, and most significant effect, is appearance of nitrogen. The spectrum of untreated sample, presented in **Figure 4**, is free from nitrogen. Only carbon and oxygen are presented and the concentration (79 % C and 21 % O) is close to the theoretical value for bulk poly(ethylene terephthalate). Even a 3 s long exposure to nitrogen plasma causes a pretty large concentration of nitrogen atoms at about 12 % (**Figure 5**). The appearance of nitrogen is a consequence of interaction between reactive particles generated in plasma and surface atoms. Namely, nitrogen molecules in the thermally equilibrium gas at room temperature do not interact chemically with PET. A question arises, which particles are responsible for breaking of surface chemical bonds and formation of functional groups containing
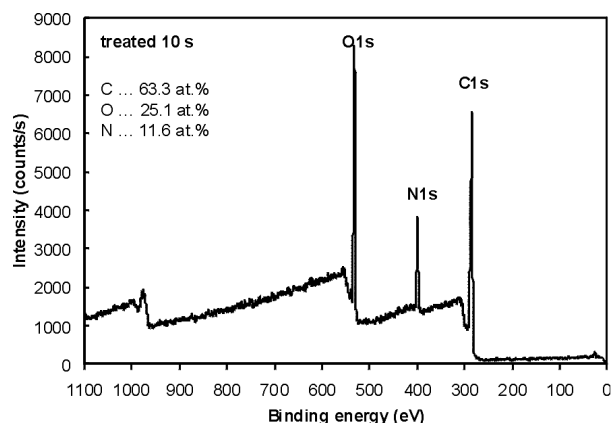

Figure 6: XPS spectrum of the sample treated with nitrogen plasma for 10 s
Slika 6: XPS-spekter vzorca, ki je bil obdelan z dušikovo plazmo 10 s

nitrogen. The list of candidates is pretty long. **Figure 2** reveals the candidates. The most reactive particles are usually those with the highest potential energy – positively charged molecules. The density of ions in plasma, however, is pretty low (the order of magnitude is solely 10^{15} m^{-3}) so they cannot cause such rapid functionalization. The list of neutral particles with potential energy abound 10 eV, which are chemically very reactive, too, include a variety of molecular excited states as shown in **Figure 2**. Finally, there are also neutral atoms in the ground as well as excited states. In plasma of some other two-atom molecules such as hydrogen, the concentration of excited molecules is pretty low because the radiative life time of those states is short, and their contribution to chemical reactivity is easily neglected. Nitrogen molecules, on the other hand, have most excited states metastable meaning that the radiative decay due to electrical dipole interactions is not allowed. The concentration of such highly excited molecules is thus pretty large, definitely larger than the concentration of ions. Namely, in plasma with a rather low electron temperature the positive ions are created by step-like process and not directly by electron impact ionization of a molecule in the ground state. Since a variety of excited states is available, the interaction of nitrogen plasma with polymer materials is far from being well understood. In addition, nitrogen plasma is also rich in high vibrationally excited molecules. **Figure 4** reveals some. Unlike oxygen plasma, where the vibrational population is usually limited to few lowest excited states, molecules nitrogen plasma are found in energetic excited states with potential energy up to about 10 eV. Such molecules are chemically reactive, too, so they can also contribute to functionalization of polymer materials.

Figures 5, 6 and 7 reveal that the concentration of nitrogen does not depend on treatment time, as long as it is at least 3 s. This effect is explained by saturation of the surface layer nitrogen functional groups. As mentioned earlier, the molecules and atoms capable of chemical interaction with a polymer abound in nitrogen plasma so saturation is obtained quickly.

More surprising is enrichment of the surface film with oxygen. This effect cannot be explained by poor purity of nitrogen, since the original gas in the flask contains over 99.99% of nitrogen and since the tube connecting the flask with the needle valve is made from copper that does not represent a significant source of oxygen. Also, the vacuum system is hermetically tight as no nitrogen is detected in the residual atmosphere. The enrichment is rather explained by interaction of water molecules with the surface film. As already mentioned, the ultimate pressure is several Pa and the residual atmosphere contains practically only water vapor. The dissociation energy of water molecules is below the excitation energy of nitrogen metastables, so a collision with a nitrogen molecule found in a metastable excited state is likely to cause dissociation of water molecule to

OH and O radicals. These radicals are chemically very reactive and interact with organic materials causing formation of oxygen functional groups. In fact, a competition between oxygen and nitrogen probably appears: both functional groups can be created on a polymer surface and the exact functionalization depends on the fluxes of nitrogen and oxygen reactive particles onto the polymer surface. A study of the reaction probabilities is definitely beyond the scope of current paper but should be addressed in order to understand the functionalization of polymers with nitrogen rich functional groups in industrial environments. Finally, it is worth mentioning that many polymers absorb substantial amounts of water which is slowly released under vacuum conditions so avoiding of oxygen radicals is a hard task in real environment.

5 CONCLUSION

The functionalization of polymer surface with nitrogen was addressed. XPS results clearly showed that simple nitrogen plasma was a suitable medium for modification of FET surface with nitrogen groups. The exact mechanisms that lead to functionalization are, however, far from being well understood. This is predominantly due to the fact that numerous highly excited molecules are found in nitrogen plasma. Optical emission spectroscopy revealed that not only electronically excited, but also vibrationally excited molecules abound in our plasma. The enrichment of the surface layer with oxygen observed at current experiments reveals that functionalization with nitrogen functional groups only may be a pretty difficult task in industrial environments. The oxygen containing radicals are formed in nitrogen plasma by dissociation of water molecules. The concentration of water in a vacuum system can be minimized by intensive and/or prolonged pumping, using high vacuum compatible systems and drying of the polymer before entering the system, but all these procedures are difficult to apply in real industrial environments.

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