ACTIVATION OF POLYMER POLYETHYLENE TEREPHTHALATE (PET) BY EXPOSURE TO CO_2 AND O_2 PLASMA

AKTIVACIJA POLIMERA POLIETILENTEREFTALATA (PET) S CO_2- ALI O_2-PLAZMO

Alenka Vesel

Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia
Center of Excellence for Polymer Materials and Technologies, Tehnološki park 24, 1000 Ljubljana, Slovenia
alenka.vesel@guest.arnes.si

A comparison of O_2 and CO_2 plasma treatment for the functionalization of PET (polyethylene terephthalate) is presented. The plasma was created in a glass discharge chamber at a pressure of 75 Pa by an electrodeless RF discharge. The RF generator operated at a frequency of 27.12 MHz and a power of about 200 W. The samples were cut into small pieces and exposed to plasma for different periods. Immediately after the treatment the samples were characterized by high-resolution XPS. A comparison of both survey and high-resolution C1s peaks revealed that the amount of the specific functional groups formed on the surface during the plasma treatment was the same for the CO_2 and O_2 plasma. Within the limits of the experimental error the concentration of hydroxyl groups was about 34 % and carboxyl groups was about 29 % for a sample treated in both plasmas for 30 s. The results were explained by the rapid dissociation of both molecules to neutral oxygen atoms that are fairly stable in glass discharge tubes and readily react with the surface of polymer materials. Any effect of CO radicals is neglected since oxygen atoms are chemically more reactive, so possible differences in the surface functionalization might have been observed only for extremely short treatment times and/or orders of magnitude lower pressure.

Keywords: oxygen plasma, carbon dioxide plasma, PET polymer, surface functionalization, surface modification, XPS

Primerjali smo vpliv plazme, generirane v kisiku ali ogljikovem dioksidu, na funkcionalizacijo polimera PET (polietilen-tereftalat). Plazmo smo ustvarili v stekleni razelektritveni cevi z RF-generatorjem s frekvenco 27,12 MHz in močjo 200 W. Tlak plina v cevi je bil 75 Pa. Vzorce polimera smo različno dolgo izpostavili plazemski obdelavi, nato pa smo jih analizirali z visokoločljivostnim XPS-spektrometrom. Iz primerjave preglednih in visoko ločljivih XPS-spektrov smo ugotovili, da je delež novo nastalih funkcionalnih skupin enak za obe plazmi: O_2 in CO_2. V obeh primerih je bila koncentracija hidroksilnih skupin okoli 34-odstotna, koncentracija karboksilnih skupin pa okoli 29-odstotna. Podobnost obeh plazem smo razložili z močno disociacijo obeh molekul O_2 in CO_2 na nevtralne atome kisika, ki so v razelektritveni cevi dokaj stabilni in zaradi svoje reaktivnosti reagirajo s površino polimernega materiala. Vpliv radikala CO, ki nastaja pri disociaciji molekule CO_2 smo zanemarili, ker so kisikovi atomi veliko bolj reaktivni kot CO.

Ključne besede: kisikova plazma, plazma ogljikovega dioksida, polimer PET, funkcionalizacija površine, površinska modifikacija, XPS

1 INTRODUCTION

Low-pressure weakly ionized plasma is a popular tool for the modification of the surface properties of solid materials. It is often regarded as an ecologically benign alternative to wet chemical processing. The major effect of the plasma surface interaction is the potential interaction within the excited plasma particles and the atoms on the surface of the solid material. The result of the interaction is either a reduction or oxidation of the material surface.[1–12] Accordingly, plasmas created in different gases are used to obtain certain effects. For reduction proposes, a hydrogen plasma is often applied. The major technology based on the interaction of a hydrogen plasma with solid materials is discharge cleaning, i.e., the removal of oxidizing impurities from the surface of the materials.[1–5] A more modern technology based on the application of hydrogen plasma is the synthesis and/or modification of nanomaterials.[6–9]

Oxidation, on the other hand, is performed by a plasma created in various gases.[10–12] Oxygen, nitrogen, water vapour and carbon dioxide are gasses suitable for the generation of plasma with oxidizing particles. The technologies based on the application of oxidizing plasma include discharge cleaning (in this case degreasing),[13,14] plasma etching[15–17], plasma sterilization[18–19] and the plasma synthesis of metal oxide or nitride nanoparticles.[20–23] Another technology of particular importance is the surface activation of organic materials.[24–31] Generally speaking, any organic material can be functionalized by required functional groups using a plasma created in an appropriate gas. In practise, however, the type and concentration of specific functional groups created on a surface of specific organic material, is limited. In particular, the functionalization of polymer materials using oxygen plasma often leads to the appearance of at least three different functional groups (like hydroxyl, carbonyl and carboxyl). Although many attempts have been made to control the concentration of each functional group on the surface of organic materials, the results are far from being satisfactory. In

order to avoid the formation of all possible oxygen-rich functional groups on the surface of the polymer, the application of a plasma created in different gases was suggested. For instance, several attempts have been made to functionalize polymer PET (polyethylene tereph-thalate) with carboxylic groups using a plasma created in carbon dioxide instead of oxygen.[32,33] The aim of this paper is a comparison of the plasma created by the same discharge in the same plasma vessel but in two different gases: oxygen and carbon dioxide. The appearance of different functional groups was monitored by high-resolution XPS (X-ray photoelectron spectroscopy).

2 EXPERIMENTAL

2.1 Plasma treatment of polymer

Experiments were performed with a polyethylene terephthalate (PET) foil from DuPont. The samples were treated in the experimental system which was pumped with a two-stage oil rotary pump with a pumping speed of $4.4 \cdot 10^{-3}$ m^3 s^{-1}. The discharge chamber was a Pyrex cylinder with a length of 0.6 m and an inner diameter of 0.036 m. The plasma was created with an inductively coupled RF generator, operating at a frequency of 27.12 MHz and an output power of about 200 W. Commer-cially available oxygen or carbon dioxide was leaked into the discharge chamber. The pressure was measured by an absolute vacuum gauge. During our experiments, the pressure was fixed at 75 Pa. The samples of PET foil were treated in O_2 or CO_2 plasma for 10 s and 30 s.

2.2 X-ray photoelectron spectroscopy (XPS) characte-rization

The surface of the plasma-treated PET samples was analyzed with an XPS (X-ray Photoelectron Spectro-meter) instrument TFA XPS Physical Electronics. The base pressure in the XPS analysis chamber was about $6 \cdot 10^{-8}$ 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 and 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 AND DISCUSSION

Samples were exposed to oxygen or carbon dioxide plasma for 10 s and 30 s. The time of 10 s is a typical treatment time that ensures the saturation of the surface with oxygen-rich functional groups. **Figure 1** represents the XPS survey spectra of an untreated sample and samples treated with O_2 and CO_2 plasma. We can observe qualitatively that the concentration of carbon is decreased in favor of oxygen for both plasma-treated samples. The quantitative results are summarized in **Table 1**. The experiments were repeated several times in order to minimize any statistical errors so the values presented in **Table 1** are averaged over several measure-ments. The statistical error is within 1 %, indicating fairly reproducible results. It is interesting that the concentration of carbon and oxygen is practically the same for samples treated with oxygen and carbon dioxide plasma. Furthermore, the differences between the 10 s and 30 s treatment times are minimal. This is just another confirmation of the well-known fact that saturation of the surface with functional groups occurs before 10 s of treatment time.[34,35]

Table 1: Comparison of the surface composition of the PET polymer treated in oxygen or carbon dioxide plasma.
Tabela 1: Primerjava površinske sestave polimera PET, obdelanega v kisikovi plazmi ali plazmi ogljikovega dioksida

Sample	C	O
untreated sample	73.1	26.9
CO_2 plasma – 10 s	55.9	44.1
O_2 plasma – 10 s	56.5	43.5
CO_2 plasma – 30 s	55.9	44.2
O_2 plasma – 30 s	56.9	43.2

The survey spectra presented in **Figure 1** give us information about the concentration of elements in the
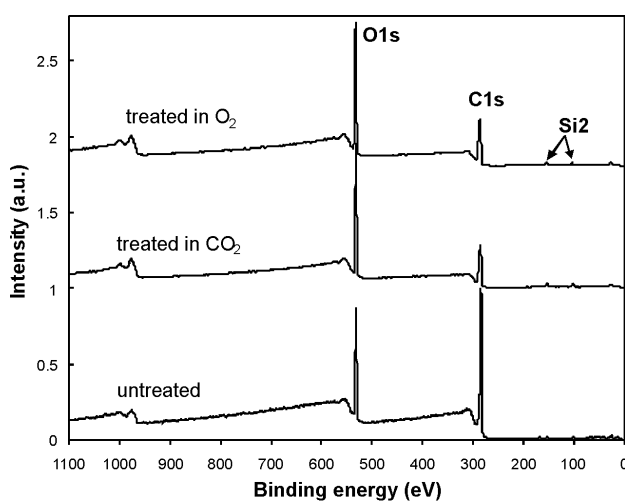

Figure 1: Comparison of XPS survey spectra of untreated PET sample and of PET sample treated in O_2 or CO_2 plasma for 10 s
Slika 1: Primerjava preglednega XPS-spektra neobdelanega vzorca polimera PET ter vzorca polimera PET, obdelanega 10 s v O_2- ali CO_2-plazmi
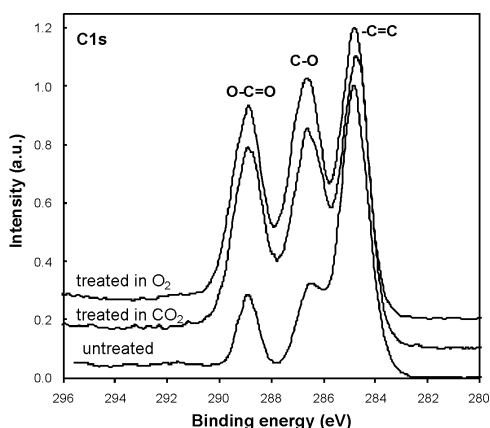
Figure 2: Comparison of high-resolution XPS spectra of carbon C1s of untreated PET sample and of PET sample treated in O_2 or CO_2 plasma for 10 s
Slika 2: Primerjava visoko ločljivega XPS-spektra ogljika C1s neobdelanega vzorca polimera PET ter vzorca polimera PET, obdelanega 10 s v O_2- ali CO_2-plazmi

Table 2: Comparison of the concentration of different functional groups formed on PET polymer during treatment in oxygen or carbon dioxide plasma.
Tabela 2: Primerjava koncentracije različnih funkcionalnih skupin, nastalih na površini polimera PET med obdelavo v kisikovi plazmi in plazmi ogljikovega dioksida

Sample	-C=C	C-O	O=C-O
untreated sample	75.8	13.0	11.2
CO_2 plasma – 10 s	42.4	32.3	25.3
O_2 plasma – 10 s	42.2	31.7	26.1
CO_2 plasma – 30 s	38.7	33.1	28.3
O_2 plasma – 30 s	36.5	34.3	29.2

surface film but do not tell us anything about the concentration and the type of each particular functional group. In order to get an insight into the concentration of the functional groups, we performed high-resolution XPS measurements of the carbon C1s peak. Again, we performed the analysis on several samples, but a typical result is presented in **Figure 2**. The major peak at 285 eV corresponds to the –C=C bond, the peak at 286.3 eV to the C-O(H) bond, while the well-pronounced peak at 288.8 eV corresponds to –COO- (carboxyl and ester group). As expected, from the knowledge gained from **Figure 1** and **Table 1**, the concentration of hydroxyl C-OH and carboxyl functional groups -COOH is increased dramatically. Interesting, however, no difference is observed between the sample treated in O_2 and CO_2 plasma. **Table 2** represents a quantification of the results presented in **Figure 2**. Again, the values presented in **Table 2** are averaged over several samples. It is interesting that the concentration of different functional groups on all the samples is practically the same, or definitely within the limit of the experimental error. From these results we can conclude that both O_2 and CO_2 plasma treatments lead to the formation of practically the same functional groups.

The upper result is explained by taking into account the characteristics of the oxygen and carbon dioxide plasmas. Since the ionization fraction in both plasmas is practically the same, and is of the order 10^{-6}, the charged particles play a minor role in the surface modification of our sample. The dissociation fraction, on the other hand, is at least five orders of magnitude larger than the ionization fraction. Such a huge difference between the ionization and dissociation fraction is explained by the probabilities of neutralization and recombination. The probability for the surface neutralization of charged particles does not depend on the type of the material facing plasma and is very close to 1. The surface recombination probability, on the other hand, is very sensitive to the surface properties and may be anything between 10^{-6} and 1.[36-37] In the case of glass discharge chambers, the probability for surface recombination is fairly low, since oxygen atoms do not chemisorb on the glass surface. In both cases, the result of the dissociation is atomic oxygen. Since the dissociation energies for oxygen molecules and CO_2 molecules are similar, it is expected that the dissociation probability would be practically the same in both plasma. Moreover, the surface recombination probabilities are also similar for both gases. Taking into account these considerations we can explain the observed functionalization of the polymer. In both O_2 and CO_2 plasmas the major reactants are neutral oxygen atoms. There is no reason that the atoms originating from oxygen molecules or carbon dioxide molecules would act differently. Any differences might have appeared at much lower treatment times, i.e., well before the saturation of the surface with functional groups is observed. Such experiments, however, are not possible in our labs since we do not have a pulsed plasma generator.

4 CONCLUSION

Well-defined foils of polymer PET were exposed to plasma created in oxygen and carbon dioxide gases in order to study any possible differences in the surface functional groups created during plasma processing. High-resolution XPS was applied to study the type and concentration of different functional groups. Within the limits of the experimental error, we can clearly conclude that there are no differences in the oxygen functional groups between the treatment with oxygen and the carbon dioxide plasmas. Our results were explained by the formation of a large density of neutral oxygen atoms in both plasmas, since these atoms are the major reactance in low-pressure, weakly ionized, highly reactive plasma.

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