TUNING OF POLY(ETHYLENE TEREPHTALATE) (PET) SURFACE PROPERTIES BY OXYGEN PLASMA TREATMENT

PRILAGODITEV LASTNOSTI POVRŠINE POLIETILEN TEREFTALATA (PET) Z OBELAVO V KISIKOVI PLAZMI

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Modification of surface properties of poly(ethyleneterephtalate) (PET) thin films by treatment with weakly ionized oxygen plasma was studied by contact angles of water and diiodomethane (DIM) drops. Samples were exposed to oxygen plasma with the ion density of $5 \cdot 10^{15}/m^3$ and the neutral oxygen atom density of $3 \cdot 10^{21}/m^3$. Just after the treatment they were characterized by contact angle measurements. Results showed a quick decrease of the water contact angle in the first few seconds of plasma treatment, while prolonged treatment did not cause any substantiated modification. The contact angles of DIM, on the other hand, remained rather constant for the first several seconds of plasma treatment, and increased after prolonged treatment. It was found that the dispersion component of the surface free energy decreased with increasing treatment time, while the polar component increased with treatment time. The results were explained by surface functionalization as well as by roughness effects.

Keywords:poly(ethylene terephtalate), PET, oxygen plasma, contact angle, hydrophilic, functionalization

Površinske lastnosti polimera polietilentereftalata (PET) smo prilagodili specifičnim zahtevam po visoki hidrofilnosti z obdelavo v kisikovi plazmi. Stopnjo hidrofilnosti smo določali iz meritev stičnih kotov dveh kapljevin, in sicer vode in dijodometana. Vzorce smo obdelovali v kisikovi plazmi z gostoto ionov $5 \cdot 10^{15}/m^3$ in gostoto nevtralnih kisikovih atomov $3 \cdot 10^{21}/m^3$. Meritve stičnih kotov kapljic smo opravili takoj po plazemski obdelavi. Rezultati so pokazali hiter padec stičnega kota vodnih kapljic že v prvih sekundah plazemske obdelave. Podaljšan čas obdelave ni prinesel bistvenih sprememb. Stični koti dijodometana so ostali praktično nespremenjeni po prvih nekaj sekundah, z nadaljnjo obdelavo pa so začeli padati. Ugotovili smo, da disperzijska komponenta površinske energije počasi pada s plazemsko obdelavo, medtem ko polarna komponenta raste. Rezultate smo pojasnili s površinsko funkcionalizacijo polimera in povečano hrapavostjo površine.

Ključne besede: polietilentereftalat, PET, kisikova plazma, stični kot, hidrofilnost, funkcionalizacija

1 INTRODUCTION

Polymer materials are nowadays widely used in biology and medicine. They belong to organic materials and often express fairly good biocompatibility. The biocompatibility, however, is never optimal due to the required chemical and mechanical properties of polymers used for specific applications. In order to achieve improved biocompatibility, the surface properties should be modified. The most popular method for modification of surface properties of any material is application of non-equilibrium gaseous plasma treatment. The method is nowadays widely used for the modification of surface properties of bulk materials.[1–18] Plasma of particular interest is created in pure oxygen or oxygen-containing gasses. Non-equilibrium plasma has the great advantage over other techniques and the main one is the ability for the modification of surface properties while leaving the bulk properties intact. This ability is due to the fact that plasma is found at room temperature while chemical reactivity is extremely high. The chemical reactivity of plasma depends on plasma parameters but is typically as reactive as gas inthermal equilibrium would be at the temperature of several 1000 °C. Extremely high chemical reactivity is due to the presence of gaseous particles with a high potential energy.

2 EXPERIMENTAL PROCEDURES

Experiments were performed with model PET films with a thickness of about 50 nm that were prepared as follows. Foils of commercially available PET were Mylar® foil, with a thickness of 175 μm. Mylar® foil was used as a facsimile for PET used in medical devices such as knitted or woven vascular grafts and PET angioplasty balloons. The foil was dissolved in 1,1,2,2-tetrachloroethane. PET films were deposited onto silicon wafers of rectangular shape with dimensions 1.5 cm × 3 cm × 0.20 cm. In order to achieve a uniform coating the crystals were mounted into a spin coater rotating at a maximum of 2000 r/min for 60 s. After this procedure the crystals were dried in an oven at 105 °C for 1 h. The surface free energy (SFE) of the samples was calculated from measured contact angles of water and diiodomethane drops according to OWRK (Owens, Wendt, Rabel, Kaelble) approach. For contact angles

(CA) measurements we used a professional device OCA 35 from Dataphysics (Germany). The device comprises a high speed camera that allows for pretty accurate determination of contact angles for different liquid drops. OWRK approach is one of the most common methods for calculation of the SFE of polymer materials. This model is based on assumption that the interfacial energy can be split to disperse and polar interactions equation (1). If liquid and solid surfaces come into contact there would be an interaction between polar parts as well as disperse parts of both phases at the interphase, but not between polar and disperse parts.[19–23]Therefore, one can determine the polar and disperse part of surface free energy by measuring contact angle between a solid and liquids with different polarity.

$$\gamma_{sl} = \gamma_s + \gamma_l - 2(\sqrt{\gamma_s^d \cdot \gamma_l^d} + \sqrt{\gamma_s^p \cdot \gamma_l^p}) \qquad (1)$$

Where γ_{sl} is solid liquid interface free energy, γ_s is solid free energy and is surface tension of liquid, d and p in superscript correspond to polar and dispersive part of free energies. On the basis of Young equation, the work of adhesion can be calculated from the measured contact angle of a liquid on a solid.[19–23] With rearranging equation (1), the form as shown in equation (2) is obtained and the solid surface free energy is determined from measurement of the contact angle for water and diiodomethane with accurately known polar and dispersive components of their surface tension (**Table 1**). In the work approach, the contact angles of liquids with known values of γ_l, γ_l^d and γ_l^p are measured after which data are fitted to straight line equation (3).

$$\frac{\gamma_l(1+\cos\theta)}{\sqrt{\gamma_l^d}} = \sqrt{\gamma_s^p \left(\frac{\gamma_l^p}{\gamma_l^d}\right)} + \sqrt{\gamma_s^d} \qquad (2)$$

$$y = k \cdot x + b \qquad (3)$$

The equation (2) is the linear function, where the slope of line, k ($k = \sqrt{\gamma_s^p}$) is the polar component and intercept of resulting line, b ($b = \sqrt{\gamma_s^d}$) is dispersive component of the solid's surface free energy (**Figure 5**). The surface free energy calculations were performed using the software SCA 21, supplied with the measuring device (Dataphysics, Germany).
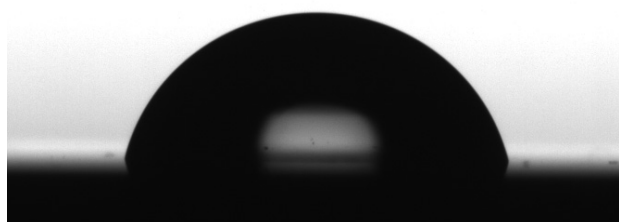
At present experiments thevolume of all drops were fixed to 3 µL. Measurements were performed at room temperature with at least 5 repetitions and with an experimental error within ±2 %.

Table 1: Surface tensions of test liquids for SFE determination
Tabela 1: Površinske napetosti preizkusnih raztopin za določanje površinske proste energije

	γ_l/(mN/m)	γ_l^p/(mN/m)	γ_l^d/(mN/m)
Water	72.8	51.0	21.8
Diiodomethane	50.8	0	50.8

Samples were exposed to oxygen plasma in a plasma reactor which has been described previously.[24–26] The plasma reactor is pumped with a two stage rotary pump and never baked, so the ultimate pressure was 6 Pa. Experiments were performed at the pressure of 50 Pa. The density of charge particles and neutral oxygen atom density were measured with an electrical and a catalytic probe.[26–34] The density of charge particles was $5 \cdot 10^{15}$/m³, while the density of neutral oxygen atoms was $3 \cdot 10^{21}$/m³.

3 RESULTS

The contact angles of water and DIM drops were measured at different treatment times up to 24 s. The photography of a water drop on an untreated sample is presented in **Figure 1**. The contact angle is rather high at 77°, indicating reasonable hydrophobic character of PET. A photo of a DIM drop is presented in **Figure 2**. The contact angle of this liquid is much lower at about 23°. Even a short exposure of a sample to oxygen plasma causes a huge change of the water drop contact angle. **Figure 3** represents a photo of a water drop after exposure to oxygen plasma for 1.5 s. On the other hand, the contact angle of DIM drop remains practically the same. **Figure 4** is a photo of drop after 1.5 s of plasma treatment. The contact angles have been measured at various treatment times and the results are summarized in **Figure 6**.

The contact angle of the water drops quickly decreased from initial 77° to about 17°. This quick drop happened in about 1 second of plasma treatment. With
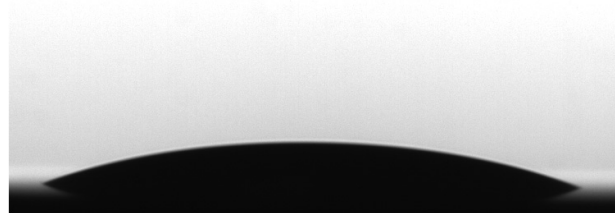

Figure 1: A photography of the water drop on untreated PET sample
Slika 1: Fotografija vodne kapljice na neobdelanem PET-vzorcu

Figure 2: A photography of the diiodomethane drop on untreated PET sample
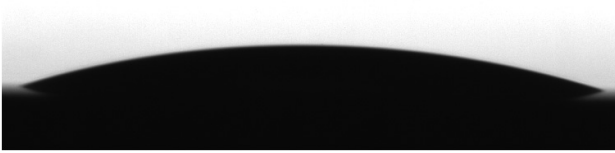**Slika 2:** Fotografija kapljice dijodometana na neobdelanem PET-vzorcu

Figure 3: A photography of the water drop on oxygen plasma treated PET sample for 1.5 s
Slika 3: Fotografija vodne kapljice na PET-vzorcu, ki je bil obdelan s kisikovo plazmo 1,5 s

Figure 5: The OWRK model plot for SFE determination of PET surface
Slika 5: Graf OWRK modela za določitev površinske proste energije PET-površine

further treatment only small, but continuous decrease of water drop contact angle is observed. The behavior the DIM is completely different. The initial contact angle is about 23° and it remains practically unchanged for the first 6 s of plasma treatment. The contact angle increases up to about 33° for prolonged treatments. The results summarized in **Figure 6** allow for calculation of the surface free energy (SFE) according to the procedure described above. The total SFE versus the plasma treatment time is plotted in **Figure 7**. The measurements performed by two different liquids, i.e. water with the surface tension of 72.8 mN/m and DIM with the surface tension of 50.8 mN/m, allow for the determination of the dispersion and polar components of the PET surface energy. The polar and dispersion components of surface tension for both liquids are presented in **Table 1**. The calculated polar and dispersion components of surface free energies versus the plasma treatment time are presented in **Figure 8**.

4 DISCUSSION

The results summarized in **Figures 6 to 8** reveal some interesting features that are worth discussing. A fast drop of the water drop contact angle can be explained by characteristics of oxygen plasma applied at our experiments. As mentioned earlier the density of oxygen atoms in our plasma is $3 \cdot 10^{21}/m^3$. The flux of neutral oxygen atoms on the surface of a sample is calculated using basic equation
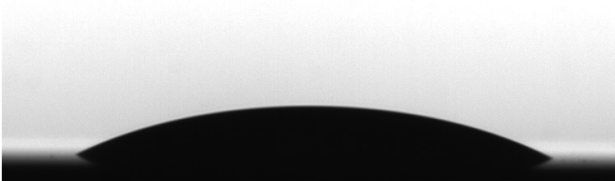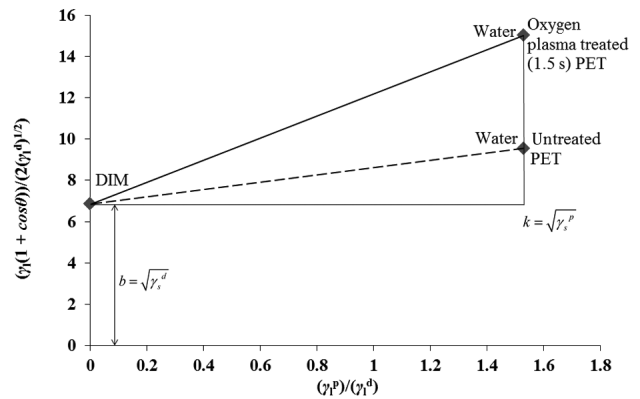
$$j = \frac{1}{4} n v \qquad (4)$$

Where the n is the density of neutral oxygen atoms in the vicinity of our sample and v is the average of the thermal velocity of neutral oxygen atoms which is calculated as

$$v = \sqrt{\frac{8kT}{\pi m}} \qquad (5)$$

Here, k is the Boltzmann constant, T the neutral gas kinetic temperature and m is the mas of one oxygen atom. Taking into account numerical values and assuming the gas is at room temperature the velocity is 630 m/s. The resultant flux of neutral oxygen atoms is about $5 \cdot 10^{23}/(m^2 s)$. This value is really high. The typical surface density of atoms in solid materials is in the order of $10^{19}/m^2$. If all oxygen atoms reaching the surface interacted with solid materials a monolayer of oxygen atoms would form in less than 0.1 ms. The reaction probability is, of course, never equal to 1, but the huge flux of atoms onto the surface of our samples allowed for a rapid saturation of polymer surface with
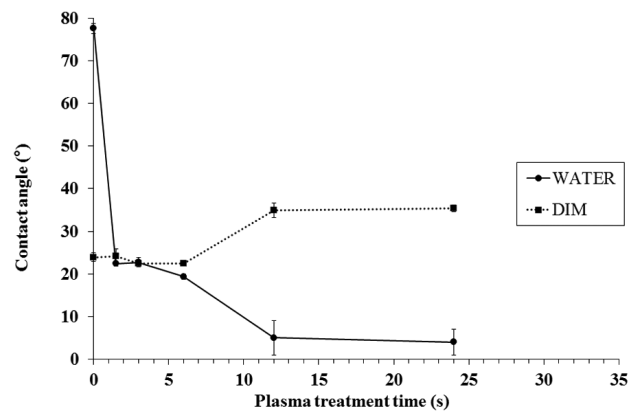

Figure 4: A photography of the diiodomethane drop on oxygen treated PET sample for 1.5 s
Slika 4: Fotografija kapljice dijodometana na PET-vzorcu, ki je bil obdelan s kisikovo plazmo 1,5 s

Figure 6: The contact angles of water and diiodomethane on model PET surface at various oxygen plasma treatment times
Slika 6: Kontaktni koti kapljic vode in dijodometana na modelnih PET- površinah pri različnih časih obdelave s kisikovo plazmo
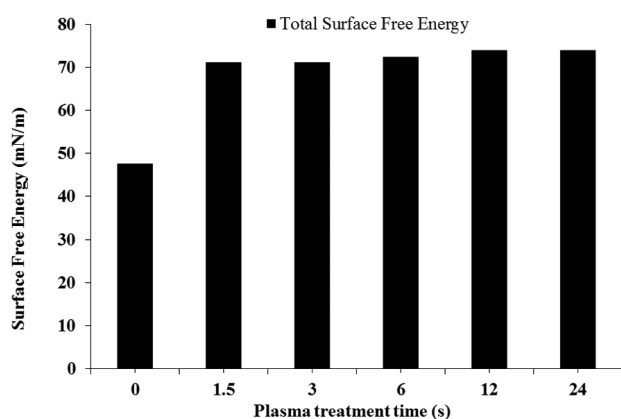
Figure 7: The surface free energies of PET versus the plasma treatment time
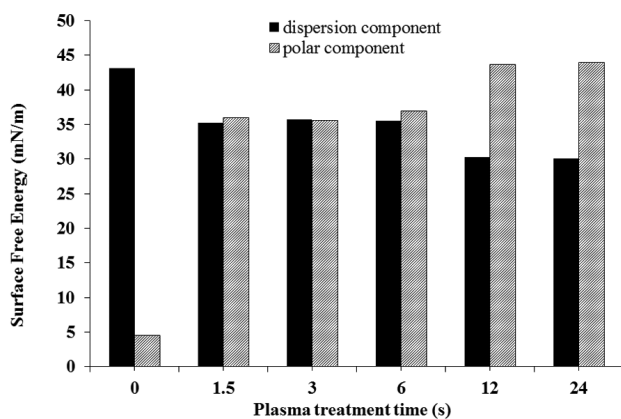**Slika 7:** Površinska energija PET-vzorcev v odvisnosti od časa obdelave s kisikovo plazmo

Figure 8: The calculated polar and dispersion components of surface free energies versus the plasma treatment time
Slika 8: Izračunane vrednosti polarne in disperzne komponente površinske energije v odvisnosti od časa obdelave s kisikovo plazmo

oxygen functional groups. Oxygen functional groups are known to be very polar and this explains a rapid increase of the polar component of SFE just after a brief exposure of the samples to oxygen plasma. **Figure 7** reveals that the SFE keeps increasing slightly with plasma treatment time even though the surface must have been already saturated with functional groups. Such increase can be explained by increased surface roughness. Namely, numerous authors have shown that the treatment of any material by oxygen plasma results in increased surface roughness.[32–34]

The behavior of a DIM drop is completely different as shown in **Figure 6**. The measurements reveal that the contact angle of DIM drops remains practically unchanged for the first several second of plasma treatment and increases only slightly with prolonged treatment time. This behavior is not unexpected taking into account upper considerations. Namely oxygen plasma causes formation of polar functional group that definitely affects the polar component but has little effect on the dispersion component of SFE. Since DIM a non-polar liquid it cannot be affected by formation of polar

functional groups. **Figure 8** even reveals a continuous decrease of dispersion component. This effect can be explained by increased surface roughness. Namely, while the surface roughness increases, real surface area becomes larger and this causes a decrease of the dispersive component.

The total SFE is just a sum of the dispersive and polar components. It is presented in **Figure 7**. As expected, the total SFE increases rapidly when the samples are exposed to oxygen plasma but, since the saturation occurs quickly, the total SFE remains barely unchanged with prolonged treatment. From this point of view it is obvious that the very brief exposure of PET samples to oxygen plasma is efficient for modification of the surface properties of our samples. Such a rapid process allows for negligible modifications of the bulk properties. Neutral oxygen atoms are thermal so they cannot penetrate to any depth due to ballistic effects. They could penetrate into bulk material at elevated temperatures. As mentioned earlier, our plasma is kept at room temperature (in terms of neutral gas kinetic temperature), so the samples cannot be heated by accommodation of neutral oxygen atoms and molecules on the polymer surface. The samples could be heated by other effects. One of them is bombardment of the surface by oxygen ions. The density of ions in our plasma, however, is very low so this heating effect is easily neglected. More important should be heterogeneous surface recombination of neutral oxygen atoms. These atoms may represent a pretty important source of heating as showed by several authors.[38–47] Happily enough, however, the required treatment time is only about 1 s so even this heating channel can neglected. The temperature of our samples therefore remains close to the room temperature so any bulk modifications are absent.

5 CONCLUSION

The surface free energy can be determined rather precisely by measuring contact angles of testing liquids with a known surface tension against polymer surface. Surface free energy of PET surface was modified by treatment with oxygen plasma. The results show an increase of the surface free energy from around 47 mN/m to almost 75 mN/meven after a brief exposure of the polymer to oxygen plasma. The increase is due to increasing of polar component of surface free energy because oxygen plasma causes formation of polar functional group on a polymer. Such a surface is more hydrophilic than untreated one and it is expected that such a surface is by far more biocompatible than original material. The results of our experiments showed that optimal results were achieved even after a second of plasma treatment so the method is suitable for modification of surface properties of delicate organic materials that do not stand heating to elevated temperatures.

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