APPLICATION OF X-RAY PHOTOELECTRON SPECTROSCOPY FOR CHARACTERIZATION OF PET BIOPOLYMER

UPORABA RENTGENSKE FOTOELEKTRONSKE SPEKTROSKOPIJE ZA KARAKTERIZACIJO PET BIOPOLIMERA

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X-ray photoelectron spectroscopy (XPS) is probably the most popular method for characterization of polymer surfaces. Although this technique is widely used, small details are often very important for proper evaluation of experimental results. Some details are addressed in this paper. First, the influence of surface roughness is examined and the results show substantial differences in high-resolution C1s spectra although the survey spectra remain fairly unaffected by the roughness. Second, the influence of the X-ray brilliance is studied for classical sources such as Mg K_α at 1253 eV, Al K_α at 1486 eV and Al K_α monochromized light. No substantial difference between the classical Mg and Al sources were found, while the high resolution spectra obtained using monochromatized light have a much better resolution. These details are very important in practical applications. Some examples including vascular grafts are shown in this paper.

Keywords: polymer, PET, surface characterization, XPS, roughness, vascular graft

Rentgenska fotoelektronska spektroskopija je bržkone najširše uporabljena metoda za karakterizacijo površin polimerov. Kljub široki uporabi pa se pogosto pripeti, da postanejo podrobnosti izredno pomembne za pravilno interpretacijo rezultatov. Nekatere tovrstne podrobnosti so obravnavane v tem prispevku. Pregledni spektri niso posebej občutljivi na hrapavost vzorcev, kar pa ne velja za visoko ločljive C1s spektre. Slednji so drugačni za gladko polimerno folijo, hrapavo folijo in umetno žilo, izdelano iz identično enakega materiala. Poleg hrapavosti lahko na videz C1s spektra vpliva tudi brilijantnost uporabljene svetlobe. V tem prispevku so bili uporabljeni trije različni izviri rentgenske svetlobe in sicer Mg K_α pri 1253 eV, Al K_α pri 1486 eV in monokromatizirana Al K_α, pri čemer je bil za monokromatizacijo uporabljen silicijev kristal. Meritve so pokazale bistveno boljšo resolucijo visoko ločljivega C1s spektra z uporabo monokromatizirane svetlobe. Rezultati preiskav imajo neposredno praktično uporabnost, saj jasno nakazujejo omejitve Rentgenske fotoelektronske spektroskopije za karakterizacijo površin realnih vzorcev, ki so značilno hrapavi in površinsko funkcionalizirani, posebej še umetnih žil izdelanih iz polietilentereftalata.

Ključne besede: polimer, PET, karakterizacija površin, XPS, hrapavost, umetne žile

1 INTRODUCTION

Polymer materials are nowadays widely used in different branches of industry as well as in biology, pharmacy and medicine.[1–7] Examples of applications in biomedicine include a variety of containers for drugs as well as biological samples, simple instruments such as catheters, and very sophisticated body implants such as artificial blood vessels.[4,7] Polymer materials often express fairly good biocompatibility. In many cases, however, the biological response to polymer materials is not adequate. In such cases the surface properties of polymers should be modified. Modification stands for changing the surface morphology, composition and structure.[8–12] The surface properties depend on many parameters but the most important one is the presence of different surface functional groups. Polymers that are nowadays used for biomedical applications have fairly optimized surface properties – some of them are highly hydrophobic, some moderately hydrophilic, while the majority are in between these two limits. As mentioned earlier, such surface properties may be adequate for some applications, but in many other cases, more extreme surface properties are required. In such cases, the surface of biopolymers should be modified. A variety of methods for modification of the biopolymer surface properties have appeared including wet chemical treatments,[13] ion bombardment, exposure to intensive ultraviolet light sources, and application of gaseous discharges.[14–17] The latter seems to be predominant in the last decade. A reason for this is probably the fact that gaseous discharges combine effects that are achieved by other three groups of techniques mentioned above. Depending on specific requirements one can always choose a right discharge to create gaseous plasma with required characteristics. Most gases transformed to the state of plasma emit radiation in a wide range from infrared to ultraviolet, and some gases also emit in vacuum ultraviolet range.[18–20] On the other hand, the formation of specific functional groups on the surface of polymer materials during plasma treatment depends largely on the type of gas used to create plasma. In general, hydrophobization of polymer materials is achieved by application of fluorine rich gases with minimal admixture of oxidative gases.[21–25] On the other hand, hydrophilization is achieved using gases that form

highly polar functional groups on the surface of polymers.[26–34] Although air, nitrogen and sulphur oxide plasma can be used, best results are usually achieved using pure oxygen or a mixture of oxygen and a noble gas.[8] The newly formed functional groups depend also on the flux of plasma radicals onto the sample surface so it pays to measure basic plasma parameters,[35] especially density of neutral atoms formed from parent molecules by electron impact dissociation.[36–38]

Application of gaseous plasma for functionalization of polymers usually leads to improvement of the surface properties, but extreme results are always obtained only in the case of increased roughness of the material. The so called lotus effect which is well known from nature is actually a very good combination of surface hydrophobicity and microstructured surface.[39] This combination leads to extremely high contact angle of a water drop and thus to the so called self-cleaning effect.[40] Something similar holds for superhydrophilicity: it is a combined effect of a high surface energy and micro- or nano-structured texture that allows for the capillary effect. Such extreme conditions of the surface properties have found some important applications in biomedicine. Obviously, the nano- or microstructured polymer materials are of great importance in advanced biomedicine. Unfortunately, however, experimental techniques for surface characterization have been developed for characterization of perfectly flat materials. The most powerful methods for surface characterization of functionalized organic materials are X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS).[41–43] Application of such techniques to rough polymers represents a task that is not at all trivial. In this paper some practical considerations about characterization of such real materials by X-ray photoelectron spectroscopy (XPS) are addressed.

2 EXPERIMENTAL

Experiments were performed with a biopolymer that is often used for medical applications – polyethylen-etheraphtalate (PET). The material is used for instance for body fluid containers, some types of catheters and some types of vascular grafts (artificial blood vessels). Three types of PET materials were used at our experiments: (*i*) a flat foil, (*ii*) a rough foil and (*iii*) a real vascular graft. The flat foil was purchased from Goodfellow. It was semi-crystalline PET foil with a thickness of 0.25 mm. A piece of the foil was treated with sand paper (grid 320) in order to increase the surface roughness. Both treated and untreated foils were cleaned in ultrasound bath with pure alcohol in order to remove any surface impurities.

X-ray photoelectron spectroscopy characterization was performed with our XPS device TFA XPS Physical Electronics. We used three different sources of X-rays: (i) Mg K_α, (ii) Al K_α, and (iii) Al K_α, monochromatized.

The first source gives fairly monochromatized light at the photon energy of 1253 eV. The FWHM is supposed to be 0.7 eV. The second source peaks at the photon energy of 1486 eV and has the FWHM of 0.85 eV. The second source was also used with a further monochromatization which was realized with a silicon crystal. The monochromatization allows for a better FWHM of 0.25 eV, but the monochromator itself represents a loss for X-rays.

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 obtained at a pass energy of 187.85 eV and 0.4 eV energy step. High-resolution spectra of C1s were made at a pass energy of 23.5 eV and 0.1 eV energy step. An additional electron gun was used for surface charge neutralization since the samples are insulators. The concentration of elements was determined by using MultiPak v7.3.1 software from Physical Electronics, which was supplied with the spectrometer.

3 RESULTS

All three types of PET samples were mounted in the XPS instrument just after the ultrasound cleaning. Survey spectra were taken with Al monochromatized light which we use as a default source of X-rays for polymer characterization. A typical survey spectrum is shown in **Figure 1**. As expected, only peaks corresponding to carbon and oxygen are found in the survey spectrum. Such spectra were found on all three samples and differences between different samples and between different spots on particular samples were hardly detected. The deviation in elemental composition as calculated from the survey spectrum shown in **Figure 1** was only about 1 at.%. It is important that the ratio between carbon and oxygen is very close to the theoretical value for PET material which is 71.4 at.% of carbon and 28.6 at.% of oxygen.
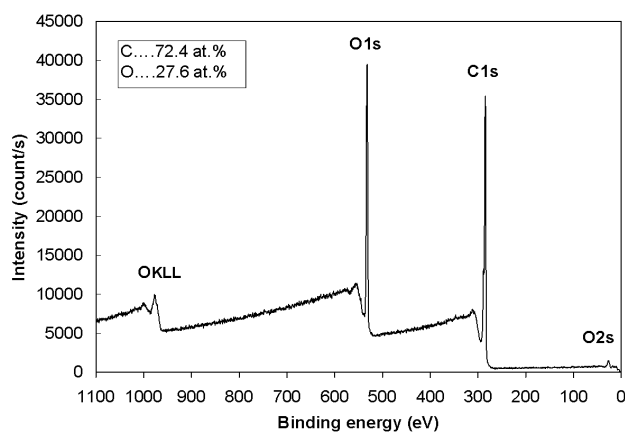

Figure 1: A typical XPS survey spectrum of a rough PET foil obtained by excitation with monochromatized X-rays
Slika 1: Značilni pregledni XPS-spekter hrapave PET folije, posnet z monokromatizirano rentgensko svetlobo
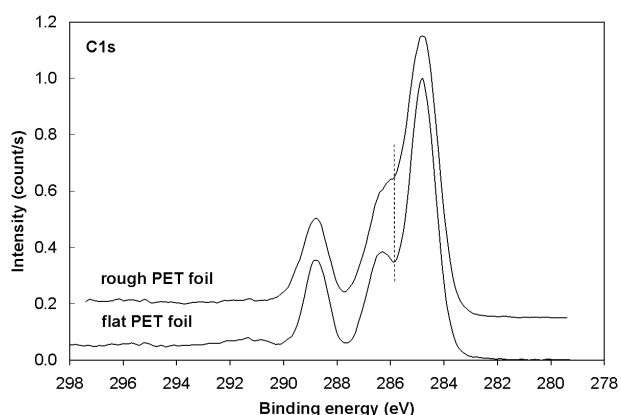
Figure 2: High resolution XPS spectra obtained for a flat PET foil (lower curve) and a rough foil (upper curve). Monochromatized X-rays were used for sample excitation.

Slika 2: Visokoločljivi XPS-spekter gladke folije PET (spodnja krivulja) in hrapave folije (zgornja krivulja), posnet z monokromatizirano rentgensko svetlobo.

Figure 4: High resolution XPS spectra of a flat PET foil obtained using three different X-ray sources: monochromatized (lowest curve), standard Mg (middle) and standard Al (upper)

Slika 4: Visokoločljivi XPS-spektri, posneti na površini gladke folije PET s tremi različnimi rentgenskimi izvori: monokromatiziranim (spodnja krivulja), standardnim Mg (srednja krivulja) in standardnim Al izvorom (zgornja krivulja)

Comparison between high-resolution C1s spectra obtained at a flat and a rough polymer foil is shown in **Figure 2**. It is clearly visible that a knee observed on the rough material at the binding energy of about 286 eV transforms to a well defined peak when the experiment is performed with a flat foil. Furthermore, the shape of the high-resolution C1s peak for the rough sample depends on the particular spot, while for flat samples we always obtain a spectrum as shown in **Figure 2**. In order to demonstrate the site dependence of the C1s spectrum for a rough surface, we performed characterization at different spots and selected results that differ extraordinary. Such a selection is shown in **Figure 3**. It is clearly visible that the knee which is at about 286 eV appears at different intensities. All spectra shown in **Figure 2 and 3** were taken with a monochromatized Al source.

In order to check the influence of the X-ray source on the quality of high-resolution C1s peaks we performed
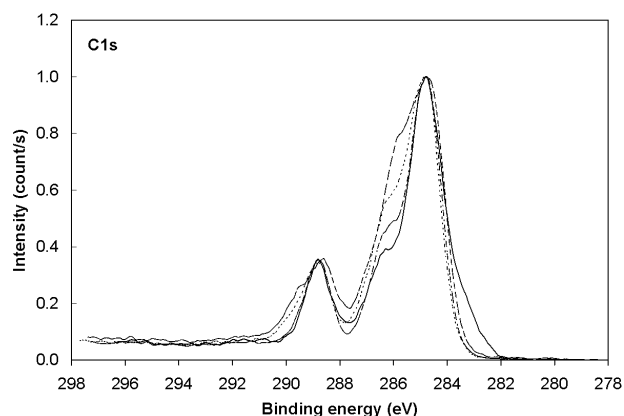
characterization of the same material with all three different sources. Typical results are presented in **Figure 4**.

Finally, an experiment has been performed also using a real vascular graft. A comparison between a typical spectrum measured on a flat Al foil and a vascular graft is shown in **Figure 5**. In this case, as in most others, we used X-rays from a monochromatized source for sample excitation.

4 DISCUSSION

The high-resolution C1s spectra presented in **Figures 2-5** were all taken on exactly the same material (PET polymer) but one can observe rather big differences. Let as first address the influence of the surface roughness. The results obtained with a monochromatized light are shown in **Figures 2 and 3**. All spectra were normalized according to the height of the major peak which

Figure 3: High resolution XPS spectra obtained at four different spots on the surface of a rough PET foil. Monochromatized X-rays were used for sample excitation.

Slika 3: Visokoločljivi XPS-spektri, posneti na štirih različnih področjih na površini hrapave folije PET. Za vzbujanje smo uporabili monokromatizirano rentgensko svetlobo.
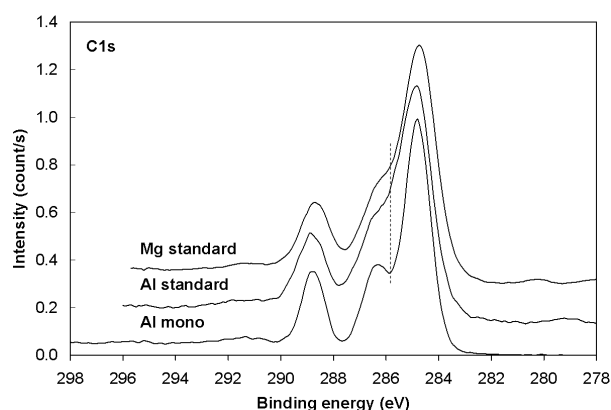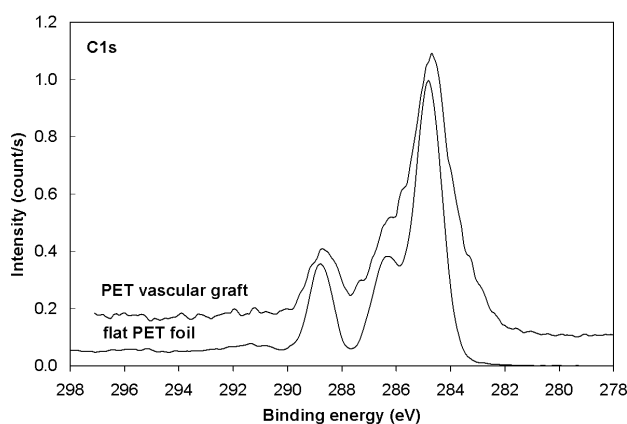

Figure 5: High resolution XPS spectra for a flat PET foil and a vascular graft made from PET polymer

Slika 5: Visokoločljivi XPS-spektri, posneti na površini gladke folije PET in na površini umetne žile iz polimera PET

corresponds to chemical bonds between carbon atoms or between carbon and hydrogen atoms. An important difference between a flat foil and the rough foil is observed in **Figure 2**. The most striking effect is the peak at the energy of about 286 eV which is fairly well seen from the spectrum obtained at the flat foil, while it transforms to a knee for the rough foil. More than obvious, the de-convolution of the spectrum obtained for the flat foils is a much simpler task than for the rough foil. Furthermore, the width of the major peak is larger for the case of the rough foil than for the flat foil. Finally, the minimum observed at the binding energy of about 287.5 eV is much better expressed for the flat foil. All these details are very important in proper explanation of the XPS results. Namely, many functional groups appear as peaks or just knees on the curve between 282 and 290 eV.[8,41] The left-most peak in **Figure 2** corresponds to the ester group. The middle peak (represented by a knee for the rough foil) corresponds to the ether group. In between there could be a carbonyl group. The height of the minimum between the left-most and the middle peak can be merrily due to a poor resolution of the spectrometer, but it can be also due to the presence of a functional group. Since our material is chemically very pure, we can exclude the presence of a functional group, so the behaviour of the curve for the rough foil is due to worsened resolution induced by surface roughness rather than presence of a carbonyl group.

The roughness effect on the high resolution XPS C1s spectrum is even much more pronounced in **Figure 3**. As mentioned earlier this Figure represents four measurements obtained at different spots on the surface of the same sample. De-convolution of the spectra presented in **Figure 3** is rather arbitrary. The middle peak could be attributed to different concentrations of ether group on the surface of the material. Such interpretation is definitely wrong since all spectra were taken for the same material which has been well cleaned prior to the XPS analyses. Similar considerations also apply for the left-most peak which corresponds to the ester group. Broadening of this peak is merely due to roughness and not appearance of new functional groups.

Spectra shown in **Figure 3** were all taken using monochromatized light. The effect of un-chromatized light is not shown in this paper for rough materials because even characterization by the rather brilliant light causes many artefacts. The effect of different light brilliance is therefore shown only for flat materials. **Figure 4** represents high-resolution C1s spectra obtained using all three different sources. The spectra are normalized to the height of the major peak. One can clearly observe that the effect of poor monochromatization of X-rays is similar to the effect of rough material. In both cases we can observe only a knee on the curve at the energy of about 286 eV. Also, the height of the well between the left most and the middle peak is increased in the similar way as in the case of the rough

material characterized by monochromatized light. Namely, comparison of **Figures 3 and 4** show very little difference in the behaviour of the well.

The effect of surface roughness is even more pronounced for the case of vascular graft. The comparison between a spectrum obtained on the flat foil and a spectrum obtained on a vascular graft is presented in **Figure 5**. Here, the dominant peak becomes very broad due to extremely rough surface of knitted artificial blood vessel. It is even difficult to distinguish the knee corresponding to the ether group, although it is definitely present in the material. Also, the shape of the well between the left-most and the middle peak is difficult to interpret. Since we know well that material is pure PET, we can conclude that the peculiar shape is an artefact of the extremely high surface roughness. A person not knowing the exact chemical composition could have easily attributed the shape of the well to an existence of another functional group.

5 CONCLUSIONS

Experimental observations presented in this paper clearly indicate the importance of monochromatized light for characterization of PET biopolymer. While the survey spectrum is practically not influenced by the brilliance of the X-rays, the high resolution peaks are. Poor X-ray brilliance causes broadening of the spectral features and a loss of details that might be crucial for proper reading of high resolution spectra. The effect is particularly important for polymers where peak shifting due to different chemical bonding is relatively weak. The silicon-crystal monocromator obviously performs well although the FWHM is improved only by a factor of 2 as compared to an un-chromatized magnesium source. An even stronger broadening of peaks is observed for rough surfaces. High resolution C1s spectra measured for rough PET foil vary considerably from spot to spot so it pays to perform experiments on several spots and average them for better accuracy. Application of non-chromatized light for characterization of rough polymers is strongly discouraged – the distortion of spectra is often so strong that any result drawn from spectra de-convolution is questionable.

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