

XPS STUDY OF SURFACE MODIFICATION OF DIFFERENT POLYMER MATERIALS BY OXYGEN PLASMA TREATMENT

Alenka Vesel

Jozef Stefan Institute, Ljubljana, Slovenia

Key words: polymer; PES; PET; PPS; PS; PP; PA6; PTFE; cellulose; oxygen; plasma; functionalization; surface activation; surface modification, XPS

Abstract: A review on surface modification of different polymers by treatment in oxygen plasma is presented. The following polymers were studied: polyethyleneterephthalate (PET), polyethersulphone (PES), polyphenylenesulfide (PPS), Nylon 6 polyamide (PA6), polytetrafluoroethylene (PTFE), polystyrene (PS), polypropylene (PP) and cellulose (ink-jet paper and textile). The polymer samples were treated for 3 s in oxygen plasma (glow region) at a pressure of 75 Pa. Plasma was created by RF generator operating at a frequency of 13.56 MHz and a power of 200 W. The chemical changes of the surface of the samples after the plasma treatment were monitored by using X-ray photoelectron spectroscopy (XPS). The results showed that oxygen plasma treatment is an effective tool for surface modification. On all polymer surfaces increased concentration of oxygen was detected resulting in formation of several new oxygen-containing functional groups. Groups like C-O, C=O and O=C-O were observed. The concentration of the groups which were produced at the same treatment procedure depended on polymer type. The only exception was polymer PTFE where practically no chemical changes were observed.

XPS preiskave modifikacije površine različnih polimerov s kisikovo plazmo

Ključne besede: polimer; PES; PET; PPS; PS; PP; PA6; PTFE; celuloza; kisik; plazma; funkcionalizacija; aktivacija površine; modifikacija površine, XPS

Izveček: Podan je pregled plazemske modifikacije površine različnih polimerov. V raziskavah so bili uporabljeni naslednji polimeri: polietilentereftalat (PET), polietersulfon (PES), polifenilensulfid (PPS), Nylon 6 poliamid (PA6), politetrafluoroetilen (PTFE), polistiren (PS), polipropilen (PP) in celuloza (ink-jet papir in tkanina). Vzorce polimerov smo obdelovali v kisikovi plazmi 3 s pri tlaku 75 Pa. Plazmo smo generirali z radiofrekvenčnim generatorjem pri frekvenci 13.56 MHz in moči 200 W. Spremembe v kemijski sestavi površine po obdelavi v plazmi smo spremljali z metodo XPS. Rezultati so pokazali, da je kisikova plazma učinkovita za modifikacijo površinskih lastnosti polimernih materialov. Ugotovili smo, da se je na površini vzorcev močno povečala koncentracija kisika, kar je imelo za posledico nastanek različnih kisikovih funkcionalnih skupin na površini kot so C-O, C=O in O=C-O. Koncentracija posameznih funkcionalnih skupin pri enakih pogojih obdelave polimerov je bila različna za različne tipe polimerov. Edina izjema je bil polimer PTFE, kjer nismo opazili nobenih sprememb na njegovi površini po obdelavi v plazmi.

1 Introduction

Polymer materials are known for their very poor adhesion properties and wettability. Therefore, they must be modified before printing, painting, coating, for improving biocompatibility etc. One of the most promising methods for modifying the surface properties of polymer materials is plasma treatment. Plasma treatment is ecologically suitable method and it is replacing the traditional wet chemical techniques, which can involve harmful chemicals. By treatment in plasma of different gases we can achieve a wide range of surface wettability, from moderate hydrophilicity to significant hydrophobicity. The hydrophobicity can be achieved by a treatment in plasma created in halogens while for achieving the hydrophilicity of the surface it is the best to use oxygen plasma. In some applications especially biological, when we want to coat the substrate with proteins or DNA for example, nitrogen or ammonia plasma is more desirable than oxygen plasma /1/. It should be noted that plasma treatment does not produce one unique functionality on a polymer surface. Typically, a distribution of several different functional groups is produced. Some of the functional groups may be important and some may actually be detrimental. Thus it is desirable to determine which of the functional group is important for a given application

and to attempt to shift the distribution in favour of a specific functionality by changing the plasma gas or other plasma parameters /2/. In oxygen plasma different functional groups like C-O, C=O, O=C-O or even more exotic groups can be produced on the surface /2/,/3/.

In the literature there are reported different treatment times used for surface modification of polymers ranging from milliseconds /4/,/5/ to several minutes /6/. At milliseconds of treatment it is difficult to talk about surface functionalization, since the first thing that appears at the polymer surface is just removing of contaminants which may also lead to improved wettability. With further treatment time insertion of oxygen/nitrogen atoms at active sites on the polymer surface appears leading to the formation of various functional groups that change the surface wettability. With prolonged treatment time excessive change scission may appear leading to a layer of low-molecular-weight fragments on the surface /3/.

The main drawback of plasma treated surface is ageing. Functional groups formed on the plasma treated surface are not stable with time, as the surface tends to recover to its untreated state. Thus the surface is loosing its hydrophilic character and becoming hydrophobic. There are two processes which are usually responsible for surface ageing:

the first one is the reorientation of the polar groups into the bulk polymer and the second is the mobility of the small polymer chain segments into the matrix, both leading to different free surface energy. It was also reported that the chain mobility mainly occurs in the amorphous region while the mobility in the crystalline region is fairly limited because of an orderly packed structure. Therefore more crystalline polymers are ageing slower. Since plasma treatment can increase the surface crystallinity due to selective etching of the softer amorphous phase, the polymers treated for longer times are usually ageing slower /3/,/4/,/5/,/7/. This is not always true – too long treatment times may again lead to faster ageing due to overtreatment leading to formation of small fragments loosely bound on the surface. Such surface has a greater tendency to ageing because of migration of small fragments to the bulk.

Here it is worth to mention that plasma treatment affects only first few nanometers of material without changing the bulk properties /8/. The quickest method to check the effect of a plasma treatment on the polymer surface is to determine its wettability by contact angle measurements. But this method does not say anything about the chemical modification of the surface. One of the most powerful techniques for determination of various functional groups that can be created on the polymer surface after being exposed to plasma treatment, is X-ray photoelectron spectroscopy (XPS) /8/,/10/. The interpretation of XPS spectra can be quite difficult. A fundamental problem in polymer surface analysis is the occurrence of charging effects due to the insulating nature of polymer materials. With non-monochromatic source this effect is less pronounced than with monochromatic source. To avoid this effect charge neutralization (gun with a low energy electron flux) must be used. A common convention is to shift unfunctionalized C 1s peak (C-C) to 284.8 eV. In some cases all the carbon atoms are chemically shifted – an example is cellulose, where all carbon atoms are bound to at least one oxygen atom. For these materials a peak which is assigned to hydrocarbon contamination can be used as a reference. But this is not always possible since sometimes this peak is not clearly observable.

In general, polymers are quite stable during typical analysis times. However prolonged exposure to X-rays can produce radiation damage of the sample which can cause the spectrum to change with exposure time. A visual evidence of this is a sample discolouration /11/. For example, this can be very easily observed on paper substrates. Especially halogen containing polymers can be sensitive to X-ray induced sample degradation. The result is a loss of halogen atoms with the exposure time /12/.

2 Experimental

2.1 Plasma modification

Experiments were performed with different polymers including PP, PS, PET, PES; PPS; PA6, PTFE and cellulose

materials like ink-jet paper and textile. The samples of these materials were treated in the experimental system shown in Figure 1. The system is pumped with a two-stage oil rotary pump with a pumping speed of 16 m³/h. The discharge chamber is a Pyrex glass cylinder with a length of 200 mm and an inner diameter of 36 mm. A Pyrex glass tube with an inner diameter of 5 mm and a length of 6 cm leads to the afterglow chamber, which is also a Pyrex glass cylinder, with a length of 400 mm and an inner diameter of 36 mm. The plasma is created inside the discharge chamber with an inductively coupled RF generator, operating at a frequency of 27.12 MHz and an output power of about 200 W. The plasma's parameters are measured with a double Langmuir probe and a catalytic probe. The Langmuir probe is placed into the discharge chamber, while the catalytic probe is mounted in the afterglow chamber. Commercially available oxygen is leaked into the discharge chamber, as shown in Figure 2. The pressure is measured with an absolute vacuum gauge. The pressure is adjusted during continuous pumping using a precise leak valve. During our experiments the pressure was fixed at 75 Pa, where the density of the oxygen atoms was the highest. Using these discharge parameters an oxygen plasma with an ion density of 8x10¹⁵ m⁻³, an electron temperature of 5 eV, and a density of neutral oxygen atoms of 4x10²¹ m⁻³ was obtained.

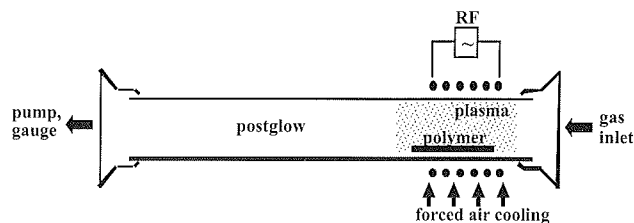


Fig. 1: The plasma chamber.

2.2 XPS characterization

The samples were exposed to air for a few minutes after the plasma treatment and then mounted in the XPS instrument (TFA XPS Physical Electronics) in order to assess the surface of the sample. The base pressure in the XPS analysis chamber was about 6x10⁻¹⁰ mbar. The samples were excited with X-rays over a 400-µm spot area with monochromatic Al K_{α1,2} 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 0.6 eV. Survey-scan spectra were made at a pass energy of 187.85 eV, while for C1s, S2p, N1s, F1s and O1s individual high-resolution spectra were taken at a pass energy of 23.5 eV and a 0.1-eV 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. The peak width (FWHM) was fixed during the fitting process. In this study a C1s (C-C) peak was shifted to 285 eV.

3 Results and discussion

The effect of oxygen plasma treatment of various polymer surfaces was studied. The following polymers were used in the study:

- *only carbon containing polymers*: aliphatic polypropylene PP (Figure 2a) and aromatic polystyrene PS (Figure 2b)
- *oxygen containing polymers*: polyethylene-terephthalate PET (Figure 2c) and cellulose CELL (Figure 2d) like textile and ink-jet paper
- *sulphur containing polymers*: polyphenylenesulfide PPS (Figure 2e) and polyethersulphone PES (Figure 2f)
- *nitrogen containing polymer*: Nylon 6 polyamide PA6 (Figure 2g)
- *halogen containing polymer*: polytetrafluoro-ethylene PTFE (Figure 2h).

3.1 Carbon containing polymers

Carbon containing polymers consist of carbon and hydrogen only. Therefore their XPS spectrum is composed of one peak positioned at a binding energy of 285 eV which corresponds to C-C and C-H bonds. Since there is no oxygen in the original polymer they are very good candidates for studying the effect of oxygen plasma treatment, because it is more easily to observe new peaks due to oxygen incorporation to the surface after plasma treatment. One of such candidates is PP which consists of aliphatic chain containing carbon atoms (Figure 2a). In Figure 3a is shown a comparison of the XPS spectra of the untreated PP surface and PP surface treated for 3 s in oxygen plasma. As already mentioned the C1s spectrum of untreated sample consists of a single peak, while the C1s spectrum after the treatment clearly reveals the new peaks resulting from plasma oxidation. A more detailed understanding of these new species can be obtained using a curve fitting procedure as shown in Figure 3b. Besides the main C1 peak (C-C), there is also a peak C2 which corresponds to C-O bond, peak C3 which corresponds to C=O bond and peak C4 which corresponds to O-C=O bond.

The same is true for the case of plasma treatment of PS (Figure 4a) which is another example of the structurally simple polymer. Here, changes are more pronounced indicating a higher concentration of new functional groups at the surface. In this case not only peaks C2, C3 and C4 are observed, but additional peak C5 appeared as well at a binding energy of 290 eV (Figure 4b) which can correspond to -C(=O)-O-C(=O)- or to -O-C(=O)-O- group at the surface [12]. Also, in Figure 4a is shown a carbon C1s peak of a sample treated for 30 s. We can see that the surface is actually already saturated, since 10-times longer treatment time did not cause any remarkable changes at the surface.

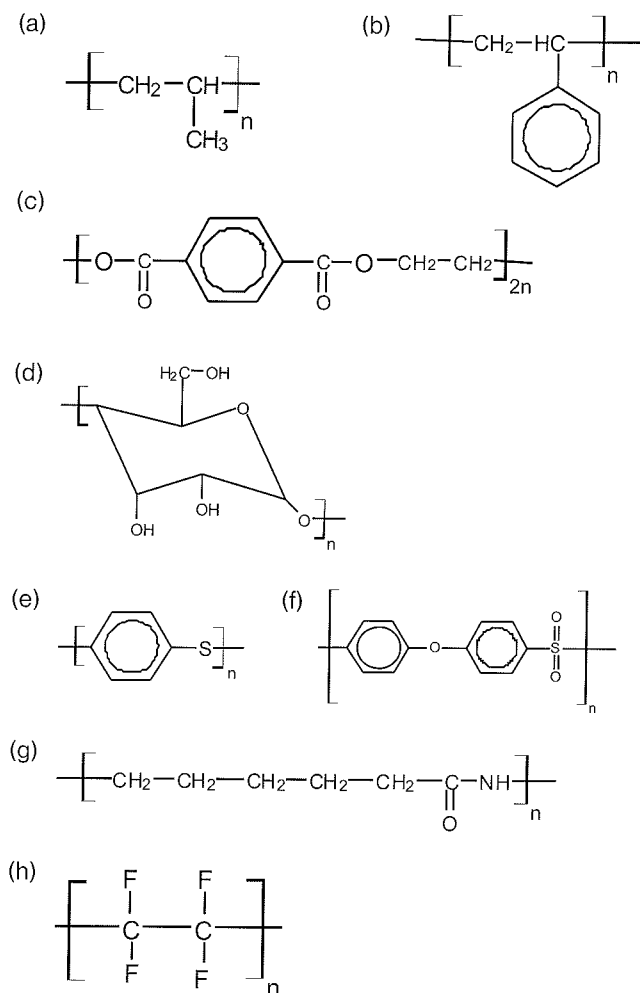


Fig. 2: Structural formulas of polymers used for plasma activation: (a) PP, (b) PS, (c) PET, (d) cellulose, (e) PPS, (f) PES, (g) PA and (h) PTFE.

Another important characteristic of untreated PS in comparison with untreated PP is a small peak at a binding energy of 291 eV - 292 eV (Figure 4a), which is not observed in the case of PP. This peak is due to the $\pi-\pi^*$ shake-up transition and it is characteristic of the aromaticity in the phenyl ring. Therefore this peak is observed only at polymers having phenyl rings [2, 12]. Changes in the intensity of this peak can provide information regarding the extent of ring-opening induced by plasma treatment. In our case, after the plasma treatment the intensity of this peak decreased indicating that plasma caused a destruction of the phenyl ring in PS.

3.2 Oxygen containing polymers

Oxygen containing polymers do not have so simple shape of the XPS spectrum like hydrocarbons. The interpretation of XPS spectra after oxygen plasma treatment of these polymers can be quite complex due to difficulties to distinguish between existing and newly formed oxygen functional groups at the surface. One of the polymers which is very often studied is PET [4, 5, 7, 13, 14, 15]. In Figure 5a is shown a carbon peak for an untreated PET sur-

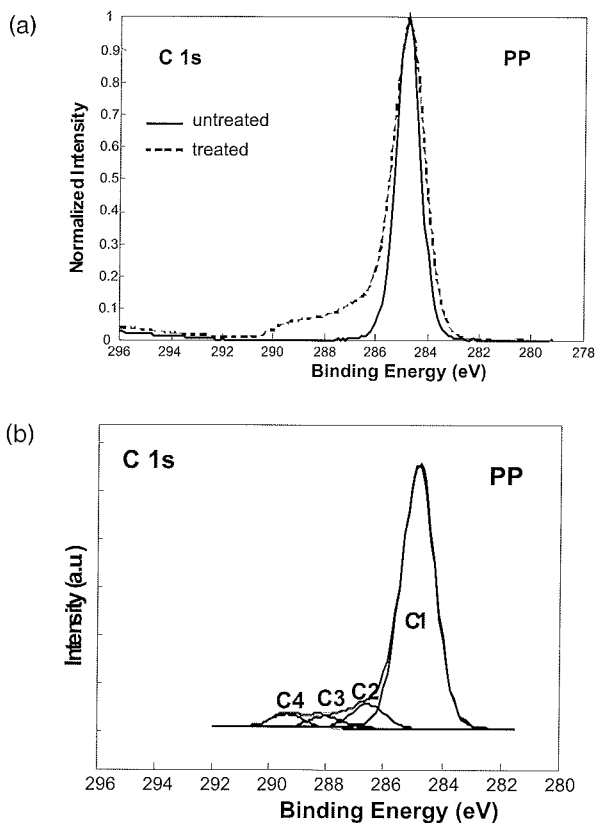


Fig. 3: (a) A comparison of C1s peaks of untreated and treated PP and (b) fitting of C1s peak of treated PP surface.

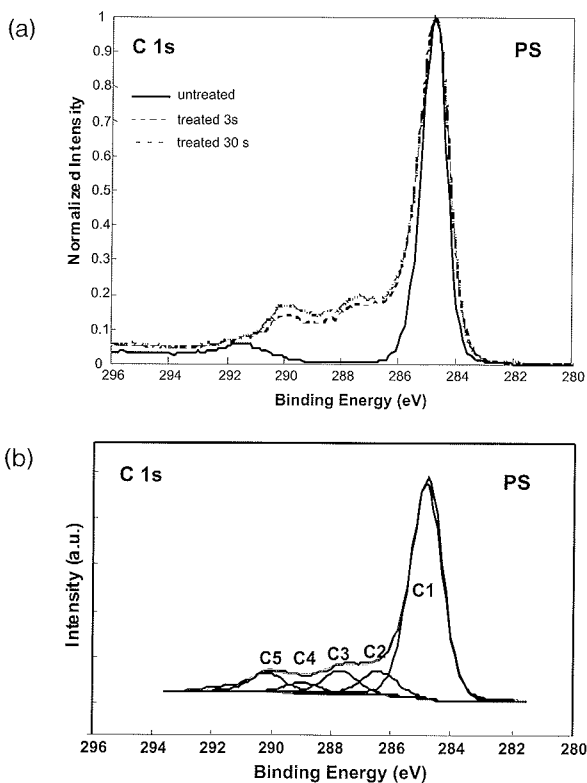


Fig. 4: (a) A comparison of C1s peaks of untreated and treated PS and (b) fitting of C1s peak of treated PS surface.

face. We can observe three peaks: C1 corresponding to C C bonds in phenyl ring, C2 corresponding to C-O bond (eter) and C3 corresponding to O=C-O bond (ester group) (Fig 2c). After the plasma treatment the intensity of the peaks C2 and C3 remarkable increased (Figure 5b) and a new peak C4 is observed due to C=O bond /13/,/14/, /15/,/16/.

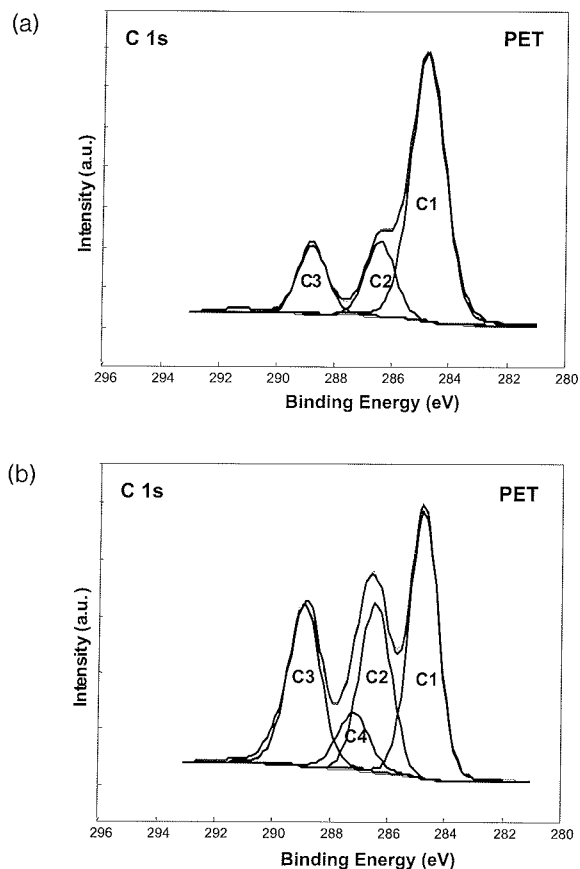


Fig. 5: High-resolution C 1s peak of (a) untreated and (b) treated PET surface.

While in the case of the PET polymer we can still clearly observe changes after oxygen plasma treatment, this is not true for cellulose. In cellulose all carbon atoms are bound to at least one oxygen (Figure 2d): each cellulose unit contains five carbon atoms with a single bond to oxygen C-O (hydroxyl groups) and one carbon atom with two bonds to oxygen O-C-O. Thus, for pure cellulose one would expect just two peaks C2 and C3. In our case for textile (Figure 6a) we observed also the C1 peak, which is often observed on cellulose and is due to the presence of contaminants. After the plasma treatment of textile (Figure 6b), the contribution of C3 peak increased, while the contribution of C2 and C1 peaks decreased. Furthermore, a new peak C4 with a binding energy of 289.2 eV appeared. An increase of the C3 peak is associated with a formation of new functional groups like O-C-O or C=O, while a new peak C4 is attributed to formation of the O=C-O group. Here, it is worth mentioning that, since carbon atoms in the cellulose are bonded to at least one oxygen atom, the

incorporation of new species from plasma can cause the degradation of the molecule. This can be a reason for the decrease of the C2 peak.

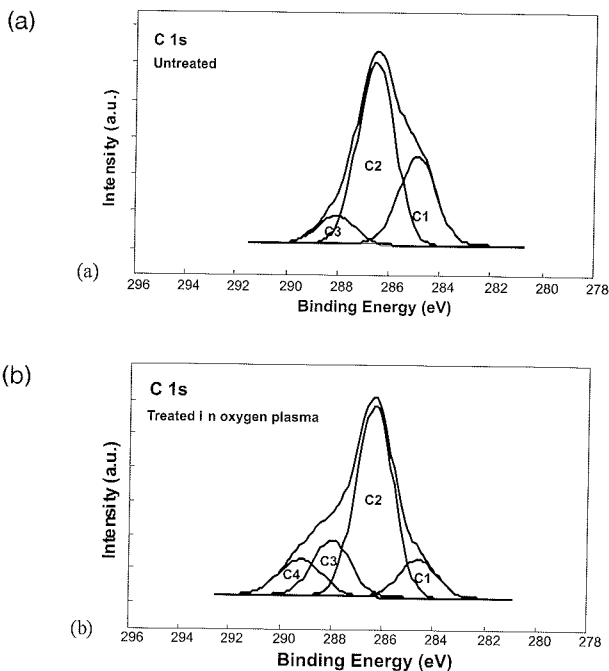


Fig. 6: High-resolution C 1s peak of (a) untreated and (b) treated textile surface.

Interesting is also plasma treatment of paper. At our experiments we used ink-jet paper, which contained about 10 weight % of alkyl ketene dimer (AKD) and few weight % of CaCO_3 , the rest being cellulose. In the untreated sample (Figure 7a) we see typical spectrum of cellulose. We can not observe the peak due to CaCO_3 which is present in the bulk. The situation after 3 s of treatment (Figure 7b) is quite the same as for untreated sample – it is difficult to see any changes, while after 200 s of treatment the situation is much different (Figure 7c). After 200 s of plasma treatment the organic part (cellulose) was burned, while inorganic particles remained. In the XPS spectrum of the ash of this sample we can observe peaks C1, C2, C3 and C4 like in the case of textile and a new peak C5, which is due to carbon atoms in CaCO_3 . Accordingly, XPS survey-scan measurements showed that Ca concentration was increasing with increasing treatment time /17/. This kind of plasma treatment is also known as plasma ashing and it allows as to detect inorganic material which is present in organic samples in so small quantities, that it is below the detection limit of techniques for surface characterization.

3.3 Sulphur containing polymers

With sulphur containing polymers there is a problem with overlapping of peaks due to C-C bond at a BE of 285 eV and C-S bond at a BE of 285.3 eV /18/, /19/ which are not clearly distinguished. In XPS spectrum of the carbon peak of the untreated PES we can see only 2 peaks (Figure 8a): the larger one C1 at 285 eV and the smaller one

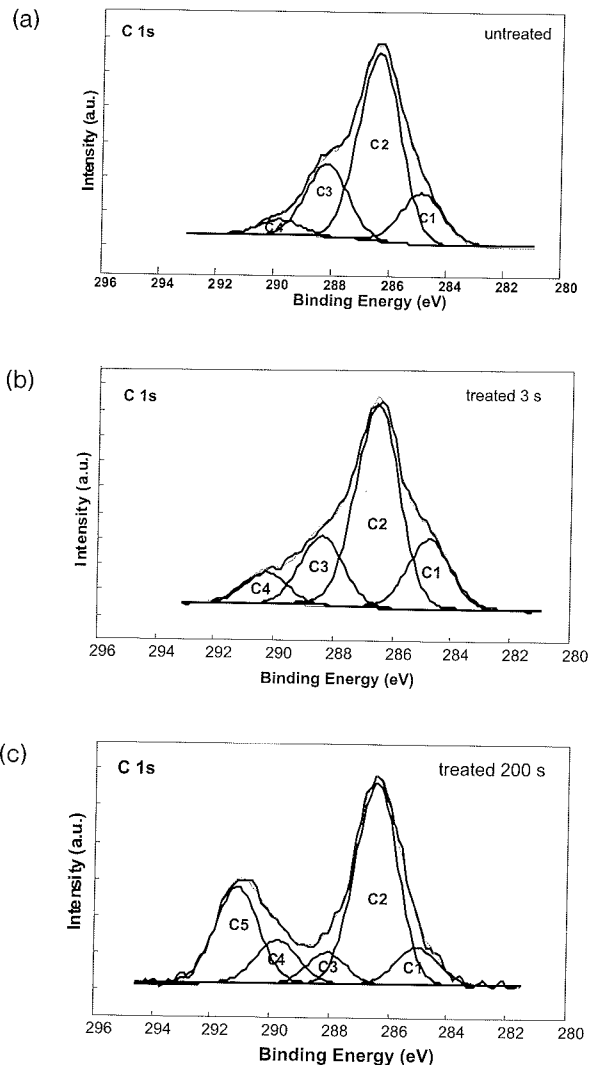


Fig. 7: High-resolution C 1s peak of (a) untreated surface of ink-jet paper, (b) treated for 3s and (c) treated for 200 s.

C2 at 286.5 eV. The larger peak corresponds to a C-C bond, while the smaller peak corresponds to a C-O bond. As already mentioned it is difficult to see the C S peak since it is overlapping with the peak C1. Figure 8b shows XPS spectrum of the carbon C1s peak of the sample treated for 3 s. The carbon peak of the plasma-treated sample is different from the peak of untreated sample. Now, four separate peaks can be observed; namely a new peak C3 due to C=O and a peak C4 due to O=C-O are observed. The peak C2 is enlarged in comparison to the untreated sample /19/.

Of more interest is the plasma activation of polymer PPS. Figure 9a represents the evolution of the C1s peak during oxygen plasma treatment of the PPS polymer. Surprisingly enough, the carbon peak of oxygen plasma treated sample is not much different from the untreated sample. One can therefore conclude that the oxygen-carbon bonds are presented relatively in small concentration. Nevertheless, oxidation of carbon (Figure 9b) resulted in formation of C-O, C=O and O-C=O groups at the surface like in the case

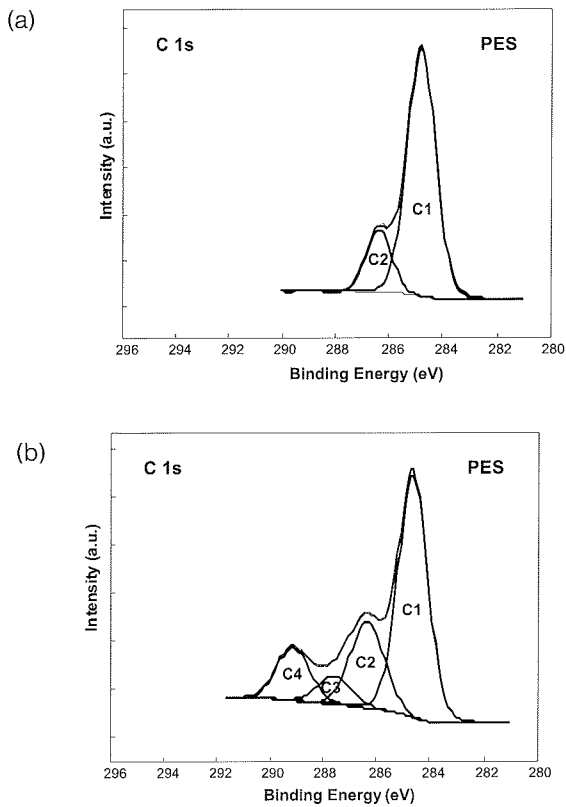


Fig. 8: High-resolution C 1s peak of (a) untreated and (b) treated PES surface.

of PES. But the right mechanism for PPS activation can be deduced from Figure 9c, which represents the high resolution S2p peak. We can see that in this case not only carbon is oxidized but also sulphur /20/. At a beginning sulphur S2p peak (duplet) is positioned at a BE of 163.7 eV corresponding to oxidation state S^{2-} (C-S-C bond). After the oxidation a new broad peak appeared at a BE of about 169 eV. According to the literature, this peak corresponds either to double peaks of S^{4+} or S^{6+} . Namely, the S^{4+} oxidation state is found at 168.2 and 169.4 eV, and S^{6+} at 169.1 and 170.2 eV, respectively. The oxidation state of sulphur therefore changed dramatically after the plasma treatment.

From XPS results of plasma activation of sulphur containing polymers we can conclude that sulphur is more easily oxidized than carbon, like shown in the case of PPS. We can not observe this in the case of polymer PES because sulphur atoms in virgin PES (Figure 2f) are already bounded to oxygen and further binding of oxygen is limited. Prolonged oxygen plasma treatment of PES can cause formation of SO_3^{2-} (leading to polymer degradation) which is desorbed from the surface like shown by Feng et al /18/.

3.4 Nitrogen containing polymers

At plasma treatment of nitrogen-containing polymers we do not observe oxidation of nitrogen like in the case of sulphur-containing polymers. Only carbon atoms are oxidized.

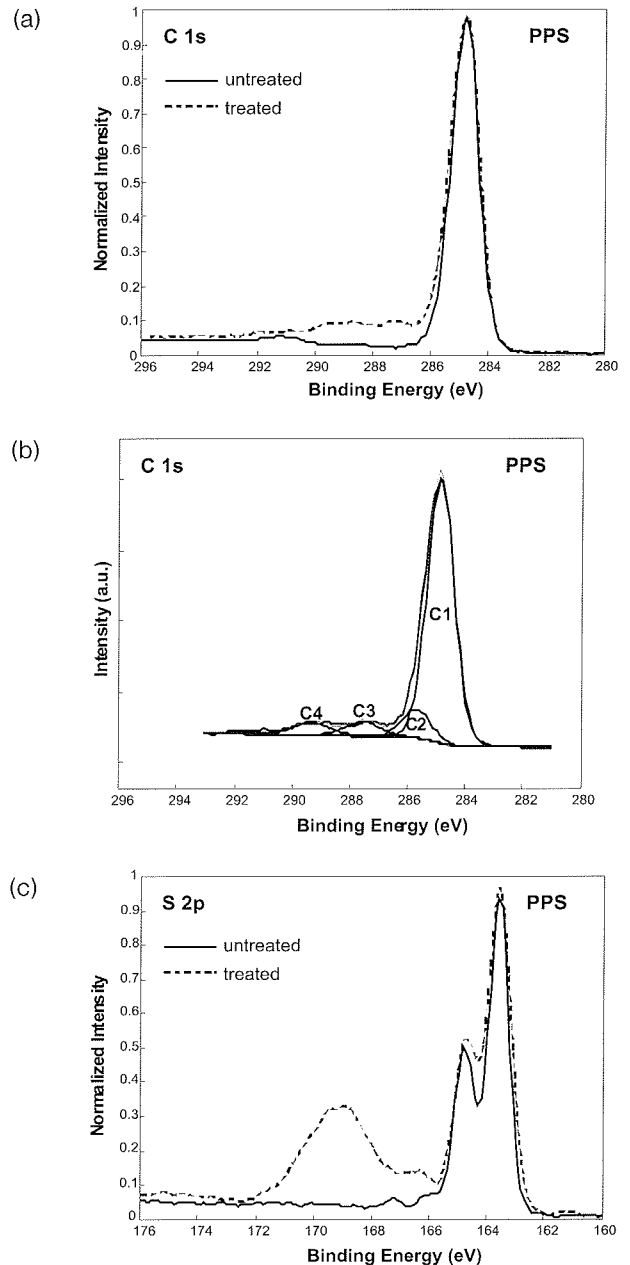


Fig. 9: (a) Comparison of carbon C1s peaks for untreated and treated PPS, (b) fitting of C1s peak of the treated PPS and (c) Comparison of sulphur S 2p peaks for untreated and treated PPS.

One problem associated with nitrogen containing polymers is difficult determination of the exact type and concentration of nitrogen functional groups, since there is a problem with strong overlapping of oxygen- and nitrogen-containing functionalities, because they appear at similar binding energies (Figure10) /12/. Moreover, relevant literature reports different data for binding energies of different nitrogen peaks which are positioned quite close together: C-N (285.5 eV - 286.3 eV), C=N (285.5 eV - 286.6 eV), $C\equiv N$ (286.7 eV - 287.0 eV) /21/, /22/, /23/, /24/, /25/, /26/ and this makes the interpretation of XPS spectra very difficult.

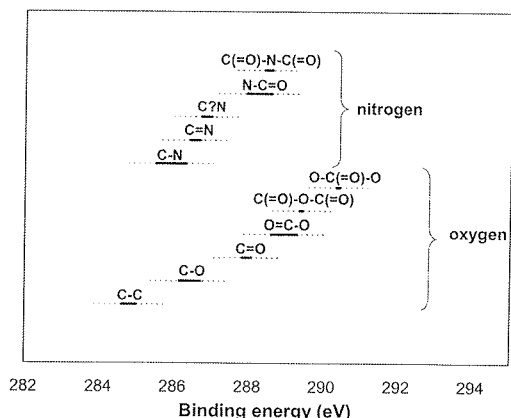


Fig. 10: Expected positions of oxygen and nitrogen functional groups: full line – position of the peak maximum, dotted line – peak width (FWHM).

Also the N1s peak can not give a decisive answer about the nitrogen containing functionalities [27]. The N1s peak is always composed of a single relatively broad symmetric peak that could correspond to different nitrogen states. According to the literature we can find several carbon-nitrogen species (like amines, amides, imides, nitriles, etc.) in the range between 399.1 eV and 400.2 eV [12], [27]. As reported by Morent et al., it is very difficult to incorporate nitrogen at polymer surfaces [27]. Therefore, he assumed that during plasma treatment only nitrogen singly-bonded to carbon are usually formed on the surface. Amide groups (N-C=O) can be also present at the surface, while the presence of the groups where nitrogen is bounded to oxygen (nitro, oxime and nitrate groups) can be definitively excluded, since they should appear at energies 406-408 eV [12], [27] and this is never observed.

An example of plasma treatment of nitrogen-containing polymer PA is shown in Figure 11. Figure 11a shows XPS spectrum of the untreated PA sample. The carbon peak is composed of three peaks; C1 corresponding to C-C bond, C2 at a BE of 286.1 eV corresponding to C-N bond and C3 at a BE of 287.9 eV corresponding to O=C-N bond (amide group). The spectrum of a PA sample treated in plasma (Figure 11b) shows that the peaks C2 and C3 increased, while a new peak C4 appeared as well, corresponding to O=C-O. The increase of C2 component can be explained by formation of C-O groups, which appear at a similar binding energy as C-N group, while the increase of C3 peak can be explained by the formation of C=O group.

3.5 Halogen containing polymers

PTFE is one of the most chemically inert polymers. Therefore it is very difficult to activate its surface by plasma treatment. In Figure 12a is shown a comparison of the carbon peak for untreated and plasma-treated PTFE surface. It can be seen that practically, there is no difference in the shape of XPS spectrum [28]. Also the comparison of the fluorine peaks (Figure 12b) does not show any difference. The

Table 1: Surface composition of the polymer samples before and after plasma treatment for 3s (PTFE 10 min).

Sample	C	O	N	S	F	Ca	Na	K	O/C
Untreated PA6	76.2	13.1	10.7						0.17
Treated PA6	63.0	25.3	11.7						0.40
Untreated PET	73.4	26.6							0.36
Treated PET	60.0	40.0							0.67
Untreated PES	74.6	20.4		5.0					0.27
Treated PES	57.3	37.8		5.0					0.66
Untreated PTFE	33.3	0.6			66.1				0.02
Treated PTFE	31.7	0.5			67.8				0.02
Untreated textile	64.2	35.8							0.56
Treated textile	49.6	50.4							1.02
Untreated paper	75.3	23.0	1.4			0.4			0.31
Treated paper	48.9	45.2	2.3			2.4	1.2		0.92
Treated paper-ash	29.8	47.6				8.5	2.9	11.2	1.60

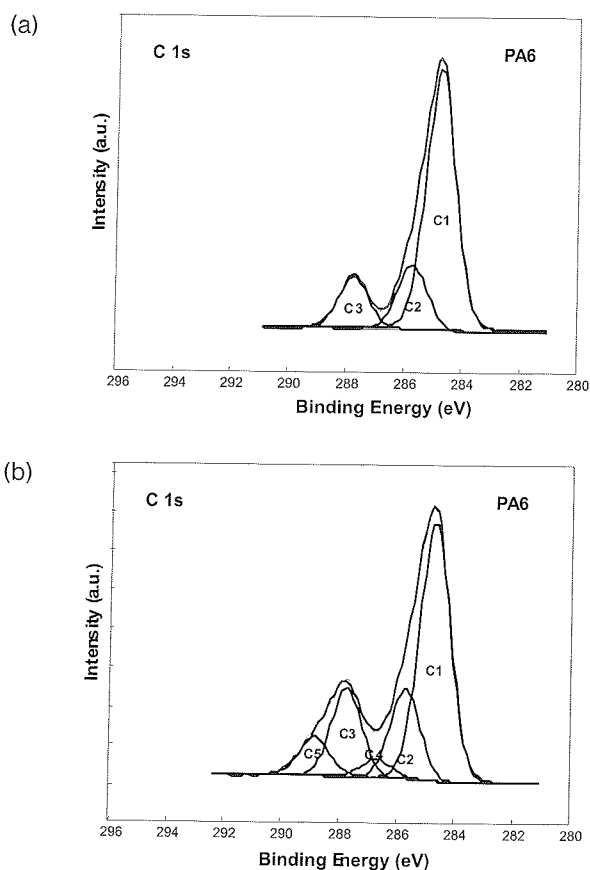


Fig. 11: High-resolution C 1s peak of (a) untreated and (b) treated PA6 surface.

survey-scan measurements showed no changes in oxygen concentration at the surface (Table 1).

Here the treatment time was 1 minute and not 3 s like at all previous polymers. Even after 10 min of treatment the situation was quite the same. So the plasma treatment seems

to be ineffective in this case. Here it is worth to mention that halogen-containing polymers are known to be sensitive to X-ray exposure, resulting in a decrease in the halogen peak intensity and an increase in the C 1s peak intensity /11/,/12/,/29/. In our case we did not observe this effect even after several hours of exposure to X-rays.

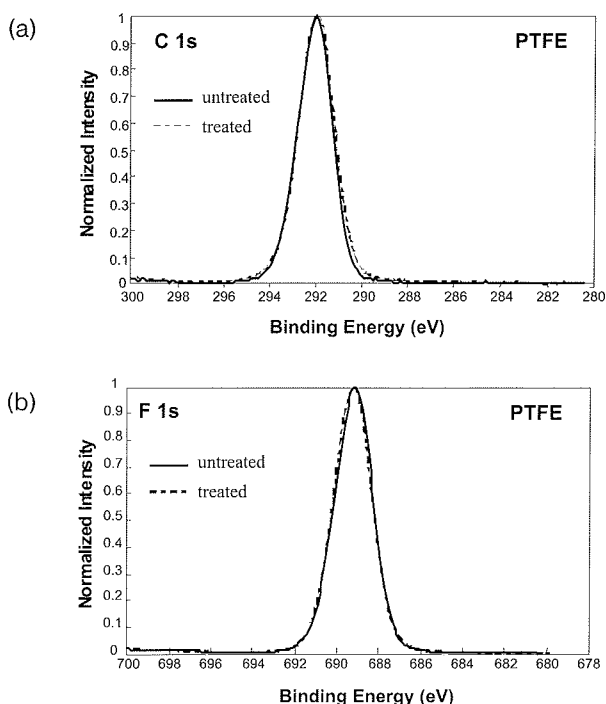


Fig. 12: High-resolution C 1s peak of (a) untreated and (b) treated PTFE surface.

Table 2: Comparison of oxygen uptake for different polymers.

Sample	(O/C) _{before}	(O/C) _{after}	O uptake
PS	0	0.36	
PP	0	0.23	
PPS	0.06	0.41	583%
CELL _{paper}	0.31	0.92	197%
PES	0.27	0.66	144%
PA6	0.17	0.41	141%
PET	0.26	0.61	135%
CELL _{textile} +AKD	0.56	1.02	82%

4 Conclusions

Oxygen plasma was found as an effective method for surface modification of different polymers. The only exception was PTFE, which is known as chemically very inert material and it was not possible to functionalize it even by plasma treatment. On all other samples a higher oxygen concentration was detected on the surface after the plasma treatment (Table 1, Table 2).

Plasma treatment did not produce one unique functionality on a polymer surface but usually a distribution of differ-

Table 3: Comparison of concentration of different functional groups for different polymers.

	C-C ³ C-S	C-O ⁴ C-N	C=O ⁴ O=C-N	O=C-O	¹ -C(=O)-O-C(=O)- ² CO ₃ ²⁻
PP untreated	100%	/	/	/	/
PP treated 3s	78.2%	12.1%	5.3%	4.5%	/
PS untreated	100%	/	/	/	/
PS treated 3s	70.7%	8.9%	8.6%	4.1%	7.8% ¹
PET untreated	75.8%	13.0%	/	11.2%	/
PET treated 3s	34.0%	30.4%	3.9%	31.7%	/
Paper untreated	16.3%	57.0%	22.0%	4.7%	/
Paper treated 3s	19.0%	54.9%	18.0%	8.2%	/
Paper treated 200s	8.9%	48.3%	7.1%	11.1%	24.6% ²
Textile untreated	30.7%	60.0%	9.3%	/	/
Textile treated 3s	12.2%	57.7%	17.7%	12.4%	/
PES ³ untreated	82.1%	17.9%	/	/	/
PES ³ treated 3s	52.4%	22.3%	9.8%	15.6%	/
PPS ³ untreated	100%	/	/	/	/
PPS ³ treated 3s	78.9%	9.0%	6.4%	5.7%	/
PA ⁴ untreated	70.2%	16.5%	13.3%	/	/
PA ⁴ treated 3s	55.8%	17.7%	19.0%	7.5%	/

ent functional groups was produced. On all polymers except PTFE new groups like C-O, C=O and O=C-O were observed; only their concentration was different depending on the polymer type (Table 3). For example, the rate of incorporation of new species after oxygen plasma treatment at identical conditions was found to be greater for PS than for PP. For polymers that do not contain only carbon and hydrogen, the amount of incorporation of new species via plasma treatment is reduced considerably (Table 2). The surface incorporation of new species depends on the number of available carbon atoms that can bond with the reactive species in the plasma. The primary available carbon atoms are those that are only bonded to other carbon atoms or hydrogen. Secondary sites would be carbon atoms with only a single bond to oxygen or nitrogen /2/,/26/. Oxidation of sulphur containing polymers resulted in oxidation of sulphur atoms as well, while this is not the case for oxidation of nitrogen containing polymers, where no groups with nitrogen bounded to oxygen were found.

The surface chemistry of plasma-treated polymers containing carbon-oxygen or carbon-nitrogen functionalities is more complex and is significantly different from polymers containing only carbon-carbon species. Characterization of plasma-induced changes on oxygen- or nitrogen-containing polymers is more difficult due to the more complex chemical structure of the polymer and the number of possible chemical species that can be produced.

Not only oxygen plasma is used for surface modification. Other gasses can be used for plasma modification of polymers surfaces as well like N₂, NH₃, H₂O, CO₂, air and noble gases. The rate and amount of incorporation of new species into a polymer surface via plasma treatment is gas dependent /2/. According to incorporation rate of new species into the surface, the oxygen plasma gives the best results. Noble gas plasma treatments do usually not incorporate new species into the surface. If small amounts of reactive gas (impurities) are present we can still end-up

with incorporation of small amounts of new species at the surface. The real mechanism of surface activation by noble gas plasmas is bond breakage and desorption of various short chain species. Free radicals interact and form crosslinks. Therefore, one of the main effects typical of noble gas plasma treatment is crosslinking of polymer. We must be also aware that if a virgin polymer already contains some functional groups, we can end-up with surface reorganization producing new functionalities without incorporation of new species from plasma.

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*Alenka Vesel
Jozef Stefan Institute, Jamova cesta 39,
Ljubljana, Slovenia*

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