HYDROPHOBIZATION OF POLYMER POLYSTYRENE IN FLUORINE PLASMA

HIDROFOBIZACIJA POLIMERA POLISTIREN S FLUOROVO PLAZMO

Alenka Vesel

Center of Excellence for Polymer Materials and Technologies, Tehnološki park 24, 1000 Ljubljana, Slovenia
alenka.vesel@ijs.si

Modification of surface properties of polymers by plasma fluorination was studied by X–ray Photoelectron Spectroscopy (XPS). Samples of polystyrene (PS) were exposed to weakly ionized reactive gaseous plasma created in tetrafluormethane (CF_4) gas. Reactive plasma particles rapidly interacted with the samples forming a surface film rich with CF_x functional groups. The appearance of these groups was monitored by high-resolution XPS, while the resultant modification of surface properties was monitored by water drop contact angle technique. Survey XPS spectra showed a substantial concentration of over mole fraction 50 % of fluorine, while high resolution C1s spectra revealed the appearance of different functional groups. The CF_2 group was predominant as approximately a third of carbon atoms was found in this group. The contact angle measurement revealed simultaneous modification of the surface free energy from moderately hydrophobic original material to highly hydrophobic state, as the water contact angle increased from original 85° to 111°. Plasma fluorination is therefore a suitable method for improving of surface properties of polymers for biomedical applications.

Keywords: CF_4 plasma, fluorination, PS polymer, polystyrene, surface functionalization, hydrophobization, XPS

Z metodo rentgenske fotoelektronske spektroskopije (XPS) smo preiskovali spremembe v površinski sestavi polimerov pri plazemski fluorinaciji. Vzorce polistirena (PS) smo izpostavili šibko ionizirani reaktivni plinski plazmi, ustvarjeni v fluorometanu (CF_4). Reaktivni delci iz plazme so izredno hitro reagirali s površino vzorca, zaradi česar je nastala tanka površinska plast, bogata s CF_x-skupinami, kar je povzročilo spremembo omočljivosti vzorca. Nastanek teh skupin smo dokazali z metodo XPS, medtem ko smo spremembo omočljivosti določali s kontaktnim kotom vodne kapljice. Iz preglednih XPS spektrov je razvidna znatna koncentracija fluora na površini vzorca z molskim deležem večjim od 50 %. Iz visoko ločljivih spektrov ogljika smo določili različne fluorove funkcionalne skupine, med katerimi je največji delež, skoraj eno tretjino, zavzemala skupina CF_2. Z merjenjem kontaktnega kota smo ugotovili porast hidrofobnosti površine, saj je kontaktni kot narasel iz začetnih 85° na 111°. Rezultati so pokazali, da je plazemska fluorinacija primerna metoda za izboljšanje površinskih lastnosti polimerov za biomedicinske aplikacije, kjer želimo imeti čim bolj inertno površino.

Ključne besede: CF_4-plazma, fluorinacija, PS-polimer, polistiren, površinska funkcionalizacija, hidrofobizacija, XPS

1 INTRODUCTION

Polymer materials are nowadays widely used in industry and medicine. The type of polymer suitable for particular application is chosen according to chemical, mechanical and thermal properties, as well as the production cost. The surface properties of selected polymers are often not optimal for particular application. In such cases they should be modified prior to application. Improved hydrophilicity is usually obtained by surface functionalization with polar functional groups, and better hydrophobicity is assured by incorporation of highly non-polar groups. Numerous techniques have been invented for modification of surface properties but it seems that nowadays one technique predominates. The technique is mild treatment by non-equilibrium gaseous plasma[1–11]. Namely, this technique is extremely fast, ecologically benign and rather inexpensive. Increased hydrophilicity is obtained by treatment with oxygen (and sometimes nitrogen) plasma. Numerous authors reported excellent results for several types of polymers including polyethylene terephthalate[12–14], polyethersulphone[15–16], polyphenylene sulphide[17], polystyrene[18,19], polyvinyl-chloride[20–22], polyethylene naphthalate[23], polymethyl methacrylate[24], cellulose[25–29] etc. The opposite effect, i.e. increased hydrophobisation, is achieved by treatment with gases rich in fluorine such as CF_4 or C_2F_6.[30–34]

Hydrophobisation of polymers is required in cases where adhesion of liquids should be minimized. A classical example is medicine. The wounds are protected by plasters. Both for the medical reasons as well as patient comfort it is important that the plaster does not stick to the wounded place too strongly. Although the major part of the plaster made from cellulose to soak the liquids[35–39] the uppermost layer is made from a hydrophobic polymer, typically in the form of perforated membrane, which allows for a good transport of liquids and simultaneously for poor adhesion onto the wounded place. Typical examples of currently applied membrane include PET, PES and PP. In some cases the surface properties of these materials assure a good functionality, but in many cases they fail and the plaster stick on to a wound. Obviously, a material with better properties should be applied or, alternatively, the surface of such materials should be made more hydrophobic.

As mentioned earlier, a suitable method for hydrophobization of polymer materials is application of gaseous plasma. In the present paper we address the hydrophobization of polystyrene by treatment with mild plasma created in tetraflour methane.

2 EXPERIMENTAL

2.1 Plasma treatment of polymer

Experiments were performed with a polystyrene (PS) 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. Commercially available CF_4 gas was leaked into the discharge chamber. The pressure was measured by an absolute vacuum gauge. At our experiments, the pressure was fixed at 75 Pa. The samples of PS foil were treated in CF_4 plasma for 3 s and 10 s.

Since it is known that polymer surface which was treated in plasma is not stable with time, we have performed also ageing studies. After plasma treatment one of the samples which was treated for 3 s was stored in a dry plastic box and left ageing for 4 d.

2.2 X-ray photoelectron spectroscopy (XPS) characterization

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 $K_{\alpha 1,2}$ 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.

2.3 Water-contact angle measurements

Wettability was examined immediately after the plasma treatment by measuring the water contact angle with a demineralised water droplet of a volume of 3 μL.

A home made apparatus equipped with a CCD camera and a PC computer was used for taking high resolution pictures of a water drop on the sample surface. Each determination was obtained by averaging results of 5 measurements. The relative humidity (45 %) and temperature (25 °C) were monitored continuously and were found not to vary significantly during the contact angle measurements. The contact angles were measured by our own software which enables fitting of the water drop on the surface in order to allow a relatively precise determination of the contact angle.

3 RESULTS AND DISCUSSION

Immediately after the plasma treatment the surface wettability of the samples was measured by water drop. The measurements showed a decrease of surface wettability since the contact angle has increased from 85° for untreated PS sample to about 110° for plasma treated sample. Such contact angle is often found on polymers treated in CF_4 plasma and was found also for PET polymer. A well pronounced increase of the contact angle is a good sign for surface hydrophobization which is due to formation of unpolar fluorine functional groups at the surface. This was proved by XPS measurements.

Figure 1 shows the XPS survey spectrum of untreated and treated PS sample. Since PS is hydrocarbon polymer we can observe only one peak due to carbon on untreated sample (hydrogen can not be detected by
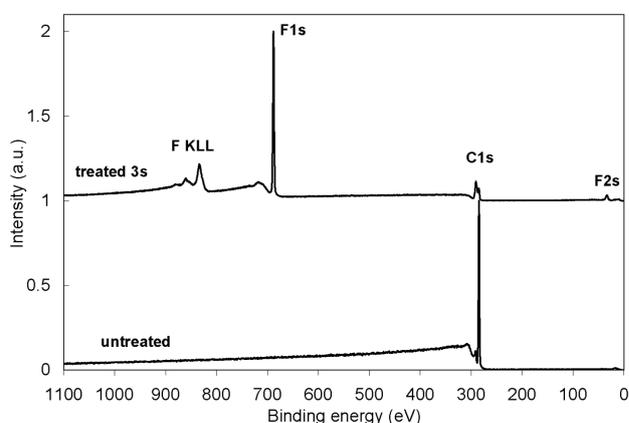

Figure 1: XPS survey spectra of untreated and plasma-treated PS showing attachment of fluorine to the surface
Slika 1: Pregledni XPS-spekter neobdelanega in plazemsko obdelanega vzorca PS

Table 1: Surface composition of the plasma treated PS samples (atom fractions, x/%)
**Tabela 1:** Površinska sestava plazemsko obdelanih vzorcev PS (atomski deleži, x/%)

Sample	C	F	O	F/C	O/C
Untreated PS	100				
Treated in CF$_4$ plasma for 3 s	43.0	56.5	0.5	1.31	0.012
Treated in CF$_4$ plasma for 10 s	43.4	56.1	0.5	1.29	0.012
Treated 3 s and aged 1 d	43.0	56.3	0.7	1.31	0.016
Treated 3 s and aged 4 d	42.6	56.0	1.4	1.31	0.033
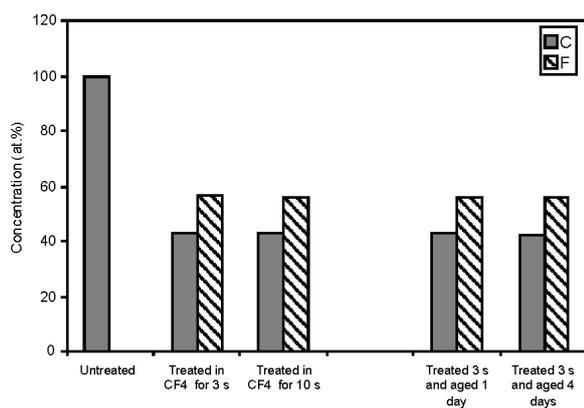
Figure 2: Comparison of surface composition of the PS samples (see also **Table 1**)
**Slika 2:** Primerjava površinske sestave vzorcev PS (glej tudi **tabelo 1**)

XPS). After plasma treatment a new huge peak is observed which corresponds to fluorine. Corresponding surface composition is shown in **Table 1** and **Figure 2**. The concentration of fluorine at the surface is rather high more than 50 atomic %. The surface is well saturated with fluorine atoms since there is no difference between 3 s and 10 s of treatment. Small amount of oxygen which is also detected on plasma treated surface is due to the presence of water vapour in the vacuum system. Incorporation of fluorine to the polymer surface caused formation of different functional groups, which can be deduced from high resolution spectrum of carbon. In **Figure 3** is shown a comparison of carbon peaks before and after plasma treatment. Untreated sample has only one big peak due to C-C (from aliphatic chain) and –C=C bonds (from phenyl ring). Another small peak can be observed at high binding energies at about 291 eV which is a satellite peak that is typical for aromatic polymers. A huge difference is observed in the shape of the carbon peak of the treated samples indicating formation of different functional groups at the surface. Functional groups can be determined by decomposition of the measured peak into subpeaks which are shown in
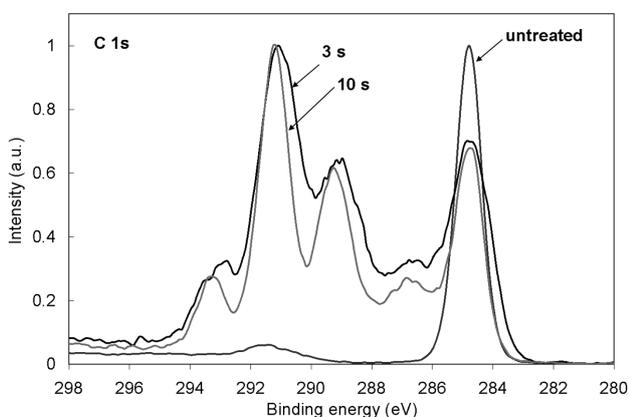
Figure 3: Comparison of carbon C1s spectra of untreated and plasma-treated PS samples
Slika 3: Primerjava spektrov ogljika C1s neobdelanega in plazemsko obdelanega vzorca PS
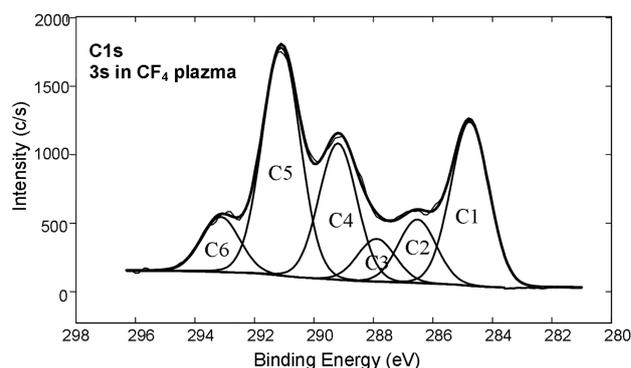
Figure 4: Example of curve fitting of C1s peak of a PS sample treated for 3 s showing formation of new peaks due to formation of different carbon-fluorine functional groups, which are presented in **Table 2**
Slika 4: Primer spektra ogljika C1s vzorca PS obdelanega 3 s, v katerem smo z metodo prilagajanja krivulj določili podvrhove, ki pripadajo različnim fluorovim funkcionalnim skupinam, nastalih med obdelavo (glej tudi **tabelo 2**)

Table 2: Chemical binding of carbon atoms of plasma treated PS samples.
Tabela 2: Vezava atomov ogljika na plazemsko obdelanih vzorcih PS

Peak assignment	C1	C2	C3	C4	C5	C6
Binding energy (eV)	284.8	286.5	287.8	289.2	291.2	293.2
Chemical binding	C-C	CH_2-CHF	CHF	CF	CF_2	CF_3
Untreated	100 %					
Treated 3 s	23.8	9.2	6.2	19.8	33.0	8.0
Treated 10 s	22.7	9.0	5.6	21.9	33.4	7.4
Treated 3 s and aged 1 d	22.9	7.6	5.7	21.6	34.3	8.0
Treated 3 s and aged 4 d	24.8	7.6	6.1	20.5	32.8	8.1

Figure 4. **Figure 4** shows that incorporation of fluorine resulted in formation of different functional groups at the surface which can be attributed to CF_3, CF_2, CF and CHF groups[30]. The concentration of these groups is presented in **Table 2**. The majority of fluorine is found in CF_2 groups.

Here we should also mention, the fluorine-containing polymers may be sensitive to x–ray degradation during recording of spectra. In our case we did not observe any degradation (modification of the shape of carbon spectra) with time, since exposure times were low.

The ageing of the samples was studied as well. The surface composition was measured for samples aged one day and four days. As shown in **Table 1** it was not possible to observe any trend of ageing during first four days since the concentration of fluorine is stable. Normally the plasma treated samples are ageing very fast[18], especially the first day because we can observe remarkable changes in water contact angle on samples treated in oxygen plasma. Here the contact angle was stable within these four days. An explanation for this is the following: polymers treated in oxygen plasma which is used to make surface hydrophilic have high surface energy, which is energetically unfavourable. Therefore such surface tends to decrease an excess of surface energy which leads to surface rearrangement and ageing.

During hydrophobization with CF_4 plasma treatment the surface energy is lowered. Surfaces having low surface energy are more stable than the one with high surface energy.

During treatment of samples in plasma we may either have substitution of fluorine atoms to the surface or deposition of C_xF_y radicals. Therefore the formation of fluorine functional groups needs further discussion. CF_4 molecules are dissociated in plasma into CF_3, CF_2, CF molecules and F atoms. In our case we have only substitution of fluorine atoms to the surface, because deposition is normally observed when using gas with higher carbon content and bigger molecular mass (e.g. C_2F_6, C_3F_8). It was observed for PET (polyethylene terephthalate) polymer which was treated at the same conditions, that the mass of the sample was little lower after the treatment. This was due to etching and definitely not due to deposition.

4 CONCLUSION

The results presented in this paper clearly indicate that treatment of PS with CF_4 plasma improves the hydrophobic character of this polymer. Even a brief exposure allowed for functionalization of the surface film with fluorine rich functional groups. High resolution XPS C1s spectra revealed formation of different fluorine groups including CHF, CF, CF_2, CF_3. The majority of carbon atoms are bounded in the CF_2 group as in polytetraflourethylene (PTFE), but the XPS results also revealed about 8 percent of fluorine richest CF_3 groups. All this groups allow for a stable hydrophobization of the PS polymer, since the concentration did not decrease even after prolonged ageing. The technology is therefore suitable for application in medicine for improving of the medical plaster quality.

ACKNOWLEDGEMENT

5 REFERENCES

[1] M. Mozetič, A. Zalar, P. Panjan, M. Bele, S. Pejovnik, R. Grmek, Thin Solid Films, 376 (**2000**), 5–8

[2] M. Klanjšek - Gunde, M. Kunaver, M. Mozetič, P. Pelicon, J. Simčič, M. Budnar, M. Bele, Surf. Coat. Int. B, 85 (**2002**), 115–121

[3] M. Kunaver, M. Klanjšek - Gunde, M. Mozetič, A. Hrovat, Dyes Pigm., 57 (**2003**), 235–243

[4] M. Mozetič, Vacuum, 71 (**2003**), 237–240

[5] M. Kunaver, M. Mozetič, M. Klanjšek - Gunde, Thin Solid Films, 459 (**2004**), 115–117

[6] A. Drenik, A. Vesel, M. Mozetič, J. Nucl. Mater., 386–388 (**2009**), 893–895

[7] A. Vesel, M. Mozetič, Inf. Midem, 40 (**2010**) 1, 67–73

[8] M. Mozetič, Mater. Tehnol., 44 (**2010**) 4, 165–171

[9] Drenik, U. Cvelbar, K. Ostrikov, M. Mozetic, J. Phys. D: Appl. Phys., 41 (**2008**) 11, 115201-1–115201-7

[10] A. Ricard, M. Gaillard, V. Monna, A. Vesel, M. Mozetic, Surf. Coat. Tech., 142–144 (**2001**), 333–336

[11] D. Babič, I. Poberaj, M. Mozetič, Rev. Sci. Instrum., 72, (**2001**), 4110–4114

[12] I. Junkar, U. Cvelbar, A. Vesel, N. Hauptman, M. Mozetic, Plasma Processes Polym., 6 (**2009**) 10, 667–675

[13] A. Vesel, M. Mozetic, A. Zalar, Vacuum, 82 (**2008**) 2, 248–251

[14] A. Vesel, I. Junkar, U. Cvelbar, J. Kovac, M. Mozetic, Surf. Interface Anal., 40 (**2008**) 11, 1444–1453

[15] T. Vrlinic, A. Vesel, U. Cvelbar, M. Krajnc, M. Mozetic, Surf. Interface Anal., 39 (**2007**) 6, 476–481

[16] J. Feng, G. Wen, W. Huang, E. Kang, K. G. Neoh, Polym. Degrad. Stabil., 91 (**2005**) 1, 12–20

[17] U. Cvelbar, M. Mozetic, I. Junkar, A. Vesel, J. Kovac, A. Drenik, T. Vrlinic, N. Hauptman, M. Klanjsek - Gunde, B. Markoli, N. Krstulovic, S. Milosevic, F. Gaboriau, T. Belmonte, Appl. Surf. Sci., 253 (**2007**) 21, 8669–8673

[18] A. Vesel, Surf. Coat. Technol., 205 (**2010**) 2, 490–497

[19] M. J. Wang, Y. I. Chang, F. Poncin - Epaillard, Surf. Interface Anal., 37 (**2005**), 348

[20] M. Sowe, I. Novak, A. Vesel, I. Junkar, M. Lehocky, P. Saha, I. Chodak, Int. J. Polym. Anal. Ch., 14 (**2009**) 7, 641–651

[21] A. Asadinezhad, I. Novak, M. Lehocky, F. Bilek, A. Vesel, I. Junkar, P. Saha, A. Popelka, Molecules, 15 (**2010**) 2, 1007–1027

[22] A. Asadinezhad, I. Novak, M. Lehocky, V. Sedlarik, A. Vesel, I. Junkar, P. Saha, I. Chodak, Plasma Processes Polym., 7 (**2010**) 6, 504–514

[23] A. Vesel, K. Elersic, I. Junkar, B. Malic, Mater. Tehnol., 43 (**2009**) 6, 323–326

[24] B. Tomcik, D. R. Popovic, I. V. Jovanovic, Z. L. J. Petrovic, J. Polym. Res. – Taiwan, 8 (**2001**) 4, 259–266

[25] A. Vesel, M. Mozetic, A. Hladnik, J. Dolenc, J. Zule, S. Milosevic, N. Krstulovic, M. Klanjsek - Gunde, N. Hauptman, J. Phys. D: Appl. Phys., 40 (**2007**) 12, 3689–3696

[26] M. Gorjanc, V. Bukosek, M. Gorensek, A. Vesel, Tex. Res. J., 80 (**2010**) 6, 557–567

[27] N. Puač, Z. Lj. Petrović, M. Radetić, A. Djordjević, Mat. Sci. Forum, 494 (**2005**), 291–296

[28] P. Jovancic, D. Jocic, M. Radetic, T. Topalovic, Z. L. Petrovic, Curr. Res. Adv. Mater. Process, 494 (**2005**), 283–290

[29] A. Vesel, M. Mozetic, S. Strnad, K. Stana–Kleinschek, N. Hauptman, Z. Persin, Vacuum, 84 (**2010**) 1, 79–82

[30] N. Vandencasteele, H. Fairbrother, F. Reniers. Plasma Process. Polym., 2 (**2005**), 493

[31] M. Gorjanc, V. Bukosek, M. Gorensek, M. Mozetic, Tex. Res. J., 80 (**2010**) 20, 2204–2213

[32] R. di Mundo, F. Palumbo, R. d'Agostino, Langmuir, 24 (**2008**), 5044–5051

[33] S. Marais, Y. Hirata, C. Cabot, S. Morin - Grognet, M. R. Garda, H. Atmani, F. Poncin - Epaillard, Surf. Coat. Technol. 201 (**2006**) 3–4, 868–879

[34] F. Poncin–Epaillard, D. Debarnot, Inform. Midem, 38 (**2008**), 252

[35] K. Stana - Kleinschek, T. Kreže, L. Fras Zemljič, V. Ribitsch, Mater. Res. Innov., 6 (**2001**) 1, 13–18

[36] Z. Peršin, K. Stana - Kleinschek, M. Sfiligoj - Smole, T. Kreže, Tex. Res. J., 74 (**2004**), 55–62

[37] T. Kreže, K. Stana - Kleinschek, V. Ribitsch, Z. Peršin, M. Sfiligoj - Smole, Mater. Res. Innov., 9 (**2005**) 1, 108–129

[38] L. Fras Zemljič, L. Johansson, P. Stenius, J. Laine, K. Stana - Kleinschek, V. Ribitsch, Colloids Surf. A, 260 (**2005**), 101–108

[39] Z. Peršin, K. Stana - Kleinschek, T. Kreže, Croat. Chem. Acta, 75 (**2002**), 271–280