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Preiskava kemijskih sprememb na površini PET pletiva z rentgensko fotoelektronsko spektroskopijo po obdelavi s korona plazmo in po staranju pletiva

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X-Ray Photoelectron Spectroscopy Characterisation of Chemical Changes on PET Knitted Goods Surface after Corona Treatment and Ageing

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Abstract

Polyester knitted goods treated with atmospheric corona plasma were investigated with X-ray photoelectron spectroscopy. The surface composition and chemical bonding of surface atoms were analysed after the plasma treatment and subsequent ageing of samples. The PET knitted goods were one-side treated in a corona air atmospheric plasma apparatus operating at 900 W power of the generator, regulated with the number of passages set to 30 and 60. The results of the study show that the oxygen concentration and the content of carbon-oxygen bonds on the sample surfaces after the corona plasma treatment substantially increase (ratio O/C increases from 0.31 to 0.53–0.61). This demonstrates that the air corona plasma treatment induces a high concentration of oxygen containing functional groups on the treated surface. The one-day ageing in Xenotest does not cause any significant changes in the composition, while the one-month ageing of samples in Xenotest leads to considerable surface changes. The oxygen concentration decreases dramatically, the ratio O/C namely falls from 0.54–0.61 to 0.13–0.16 for the plasma-treated samples.

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Izvleček

Z rentgensko fotoelektronsko spektroskopijo (XPS) smo preiskali poliestrno (PET) pletivo pred obdelavo in po njej v atmosferski korona plazmi. Izvedli smo tudi preiskavo kemijskih sprememb plazemsko obdelanih vzorcev po staranju. PET pletivo je bilo enostransko obdelovano v korona zračnem atmosferskem plazemskem aparatu pri moči generatorja 900 W v 30 in 60 ciklih. Rezultati študije kažejo, da na površini vzorcev koncentracija kisika in delež vezi med atomi C in O po obdelavi v korona plazmi vidno narasteta (razmerje O/C se zviša z 0,31 na 0,53–0,61). To kaže, da korona plazma povzroči na površini visoko koncentracijo funkcionalnih skupin, ki vsebujejo kisik. Enodnevno staranje vzorcev v Xenotestu ne kaže posebnih sprememb v sestavi površin, enomesečno staranje vzorcev v Xenotestu pa pripelje do znatnih sprememb na površini. Koncentracija kisika se močno zniža, razmerje O/C na plazemsko obdelanih vzorcih pa pade z 0,54–0,61 na 0,13–0,16.

Ključne besede: PET pletivo, atmosferska korona zračna plazma, XPS, kemijska sestava površine

1 Uvod

Namen raziskave je bil z rentgensko fotoelektronsko spektroskopijo proučiti kemične spremembe na površini poliestrnega (PET) pletiva po obdelavi z atmosfersko korona plazmo in ugotoviti tudi vpliv staranja vzorcev na obstojnost sprememb, ki nastanejo na površini zaradi vpliva plazme.

Polietilentereftalat (PET) je linearni poliester, ki ga sestavljajo or-

Keywords: PET knitted goods, atmospheric corona air plasma, XPS, surface chemical composition

1 Introduction

The purpose of the research was to investigate the chemical changes on the surface of polyester (PET) knitted goods with the X-ray photoelectron spectroscopy (XPS) after the treatment with an atmospheric corona plasma. A further goal was to establish how the ageing of samples influences the stability of surface changes induced with a plasma.

Polyethylene terephthalate (PET) is a linear polyester comprised of organic substances with recurring ester groups (–COO–). Its characteristics, such as excellent dimension stability, high crease resistance, good elasticity recovery, warm hand, quick drying, excellent resistance to light and heat, acids, alkali, some solvents, oil and fats, as well as its good strength and breaking elongation, have led into the massive polyester production, which has superseded the production of other synthetic fibres [1]. PET has high UV-absorption capabilities for rays with λ = 313 nm. Due to its compact structure and high crystallinity, PET is dyed with disperse dyes at high temperature at pressure. Dyeing is a phase within the production of PET products, which substantially increases its final price. Therefore, scientists have been working on the simplification of PET dyeing for some time now. So far, the additives (i.e. carriers) are known which lower the glass transition temperature of fibres and hence enable PET dyeing with disperse dyes at boiling temperature and CO_2 dyeing at 31.3 °C when the movement of molecules increases dramatically at supercritical conditions of CO_2.

Currently, research on various functionalizations of PET surfaces is being conducted in order to increase the number of hydrophilic groups in PET and consequently, improve dyeability. The literature includes quite a few investigations on the influence of different plasmas on the PET surface, which cause PET hydrophilation and substantially influence the dye absorption during PET dyeing [2–8]. The X-ray photoelectron spectroscopy (XPS or ESCA) is the

ganske snovi s ponavljajočimi se estrnimi skupinami (–COO–). Njegove lastnosti, kot so odlična dimenzijska stabilnost, visoka odpornost proti mečkanju, dobra povratna elastičnost, topel otip, hitro sušenje, visoka odpornost na svetlobi in na toploto, proti kislinam, alkalijam, nekaterim topilom, oljem in maščobam, kot tudi dobra trdnost in raztezek pri pretrgu, so privedle do masovne proizvodnje poliestra, ki prekaša proizvodnjo ostalih sintetičnih vlaken [1]. PET ima visoke UV absorpcijske sposobnosti za žarke z λ = 313 nm. Zaradi kompaktne strukture in visoke kristaliničnosti se PET barva z disperzijskimi barvili pri visokih temperaturah pod pritiskom. Barvanje je faza v predelavi PET izdelka, ki njegovo končno vrednost precej poveča. Zato znanstveniki že dolgo razmišljajo, kako barvanje PET poenostaviti. Znani so dodatki (carrierji), ki znižajo temperaturo steklastega prehoda vlaken in s tem omogočajo barvanje PET z disperzijskimi barvili pri vrenju, pa tudi barvanje v CO_2 pri 31,3 °C, ko pri superkritičnih pogojih CO_2 gibanje molekul barvil drastično naraste.

Danes potekajo raziskave različnih načinov funkcionalizacije PET površin za povečanje števila hidrofilnih skupin v PET in s tem obarvljivosti. Literatura navaja precej poskusov vpliva različnih plazem na površino PET, ki povzročijo hidrofiliranje PET in drastično vplivajo na sprejemanje barvil pri barvanju PET [2–8]. Metoda, s katero na površini tekstilije lahko določimo vsebnost različnih elementov in razmerja med njimi, je rentgenska fotoelektronska spektroskopija (XPS ali ESCA). V tej raziskavi predstavljamo vpliv korona plazme na PET pletivo, kot tudi vpliv staranja s plazmo obdelanega PET na spremembe na površini pletiva. Znano je, da je prisotnost različnih funkcionalnih skupin na površini materiala tista, ki bistveno vpliva tudi na obarvljivost PET. Zato smo PET pletivo obdelovali v korona plazmi in s pomočjo analize XPS ugotavljali spremembe v vsebnosti hidrofilnih in hidrofobnih funkcionalnih skupin v površinski plasti neobdelanega in v plazmi obdelanega PET pletiva.

2 Eksperimentalni del

2.1 Material

Po pletenju v podjetju Zvezda, d. d., so PET pletivo obdelali v vodi sobne temperature in ga s hitrostjo 25 m/min toplozračno stabilizirali pri temperaturi 170 °C. Za raziskavo je bilo uporabljeno termostabilizirano snutkovno 100-odstotno PET pletivo (v nadaljevanju tp) v vezavi prestavljena resa (Zvezda, d. d., Kranj) z naslednjimi lastnostmi:

osnova: 10 niti/cm, 50 dtex PET,
votek: 16 niti/cm, 167 dtex teksturiran PET filament
masa: 42,6 g/m^2.

Preglednica 1 prikazuje način priprave vzorcev. V preglednici 1 so zbrani vzorci, ki smo jih preiskali z metodo XPS.

Table 1: Samples marked according to treatment they underwent

	Sample	
1	T1	initially thermostabilized PET knitted goods (tp)
2	T1-1d	tp, aged for 1 day with illumination in Xenotest
3	T1-1m	tp, aged for 1 month with illumination in Xenotest
4	T1C	tp treated in corona plasma, 30 cycles
5	T1C-1d	tp treated in corona plasma, 30 cycles and aged for 1 day with illumination in Xenotest
6	T1C-1m	tp treated in corona plasma, 30 cycles and aged for 1 month with illumination in Xenotest
7	T2C	tp treated in corona plasma, 60 cycles
8	T2C-1d	tp treated in corona plasma, 60 cycles and aged for 1 day with illumination in Xenotest
9	T2C-1m	tp treated in corona plasma, 60 cycles and aged for 1 month with illumination in Xenotest

method employed to determine the contents of different elements on the textile surface and ratios among them. This research presents how a corona plasma influences PET knitted goods, as well as the ageing influence on the changes on the plasma-treated PET knitted goods surface. Originating from the fact that the presence of various functional groups within the material surface considerably influences PET dyeability, the PET knitted goods were treated in a corona plasma and by means of the XPS analysis, the changes in the content of hydrophilic and hydrophobic functional groups in the surface layer of untreated and plasma-treated PET knitted goods were established.

2 Experimental

2.1 Material

After the PET knitted goods were knitted at the company Zvezda Plc (Kranj), they were treated in water at room temperature and stabilized with warm air at speed 25 m/min and temperature 170 °C. For the purpose of the research, thermostabilized warp-knit 100% PET knitted goods (below tp) were used with the following characteristics:

warp: 10 threads/cm, 50 dtex PET,

weft: 16 threads/cm, 167 dtex textured PET filament,

weight: 42.6 g/m².

Table 1 shows how samples were prepared and includes the samples investigated with XPS.

2. 2 Obdelava PET pletiva s korona plazmo

PET pletivo smo enostransko obdelali v korona zračni atmosferski plazmi v Corona-Plus CP-Lab MKII (Vetaphone, Denmark) plazemskem aparatu [9]. 270 × 500 mm velike vzorce pletiva smo vstavili na valj (valj je v bistvu elektroda, pokrita s silikonskim plaščem), ki se je vrtel z najmanjšo hitrostjo 4 m/min. Razdaljo med elektrodami je predstavljala 2 mm zračna odprtina. Korona plazma se je generirala v zračno odprtino med elektrodo in valjem. Moč generatorja je znašala 900 W, uravnali pa smo število prehodov valja s pletivom na 30 in 60.

Obdelave s korona plazmo so bile izvedene na Oddelku za tekstilno inženirstvo, Fakultete za tehnologijo in metalurgijo, Univerze v Beogradu. Reaktor s korona plazmo je prikazan na sliki 1.

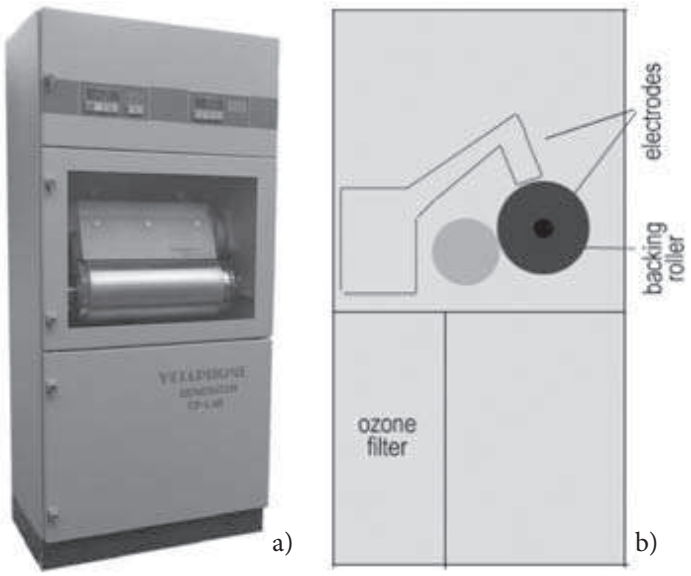

Figure 1: a) laboratory corona plasma apparatus, b) apparatus scheme

2.2 Corona plasma treatment of PET knitted goods

The PET knitted goods were one-side treated in a corona air atmospheric plasma in the Corona-Plus CP-Lab MKII (Vetaphone, Denmark) plasma apparatus [9]. The knitted goods samples, 270 × 500 mm in size, were placed onto the roll (i.e. an electrode roll covered with a silicon coating), rotating at the minimum speed, i.e. 4 m/min. The distance between the electrodes was a 2-mm air gap. The corona plasma was generated within the air gap between the electrode and the roller. The power of the generator, which was 900 W, was regulated with the number of passages set to 30 and 60.

The corona plasma treatment was performed at the Department of Textile Engineering, Faculty of Technology and Metallurgy, University of Belgrade. The reactor with the corona plasma is illustrated in Figure 1.

2.3 PET knitted goods ageing in Xenotest

The photo-ageing of thermostabilized PET knitted goods was conducted in the Xenotest Alpha (Atlas) apparatus with a xenon arc lamp. The samples were illuminated according to the SIST EN ISO 105-B02: 1999/A1:2002 standard [10]. The illumination took place at the constant power 42 W/m² for 1 day and for 30 days corresponding to a 10- or 300-day, respectively, exposure to natural daylight. The chemical changes on the PET knitted goods surface were determined with an XPS analysis.

2.4 X-ray photoelectron spectroscopy

The PET knitted goods were investigated with the XPS method. With this method, the information on the surface chemical composition and chemical bonds of surface atoms can be obtained from the XPS spectra. The results on the application of the XPS method for investigating the PET samples treated with a plasma have been published in the literature [5, 11–14].

During the XPS analysis, a sample is illuminated with the monochromatic X-ray light in an XPS spectrometer and the energy of emitted photoelectrons from the sample surface is analysed. In the photoelectron spectrum, which represents the distribution of emitted photo-

2.3 Staranje PET pletiva v Xenotestu

Fotostaranje termostabiliziranega PET pletiva smo izvedli v aparatu Xenotest Alpha (Atlas), opremljenem z izvorom ksenonske svetlobe. Vzorci so bili osvetljevani skladno z navodili SIST EN ISO 105-B02: 1999/A1:2002 standarda [10]. Osvetljevanje je potekalo pri konstantni moči 42 W/m², in sicer en dan in 30 dni, kar ustreza 10-dnevnemu oz. 300-dnevnemu osvetljevanju na dnevni svetlobi. Kemijske spremembe na površini PET so bile določene z analizo XPS.

2.4 Rentgenska fotoelektronska spektroskopija

Vzorce PET pletiva smo preiskali z rentgensko fotoelektronsko spektroskopijo (ang. *X-ray photoelectron spectroscopy* – XPS ali ESCA). S to metodo smo posneli spektre XPS na površini vzorcev in dobili informacije o kemijski sestavi in o kemijskih vezeh elementov na površini. O uporabi metode XPS za preiskavo vzorcev PET, obdelanih s plazmo, so znani rezultati iz literature [5, 11–14]. Pri tej metodi v spektrometru XPS obsevamo vzorec z monokromatsko rentgensko svetlobo in analiziramo energijo izsevanim fotoelektronom. V spektru fotoelektronov, ki pomeni porazdelitev izsevanih fotoelektronov po njihovi vezavni energiji, so prisotni vrhovi, značilni za elemente, ki so na površini polimernega vzorca do globine okoli 6 nm. Analiza je potekala v ultravisokem vakuumu, ki je bil med analizo okoli 10^{-7} Pa. Analizo smo izvedli na spektrometru XPS proizvajalca Physical Electronics Inc., model TFA XPS na Odseku za tehnologijo površin in optoelektroniko na Institutu Jožef Stefan [15]. Pri analizi smo uporabili aluminijev monokromatizirani izvir rentgenske svetlobe z močjo 200 W. Energija rentgenskega žarka je bila 1486,6 eV, energijska ločljivost med analizo je bila okoli 0,7 eV. Analizna površina je imela premer 0,4 mm, signal med analizo XPS pa je prihajal iz plasti, debele do 6 nm. Med analizo smo posneli dve vrsti spektrov XPS. Najprej smo posneli pregledni spekter prek širokega energijskega področja. V tem spektru smo identificirali prisotne elemente in izračunali njihove koncentracije tako, da smo ugotovljene intenzitete delili z relativnimi faktorji občutljivosti, kot jih navaja izdelovalec spektrometra XPS [16]. Dobljene rezultate smo normalizirali na 100 odstotkov. Relativna napaka pri izračunu sestave površine je okoli 20-odstotna in občutljivost metode je približno 0,5 at. %. Pri analizi sestave površine smo vsak vzorec analizirali na dveh različnih mestih in izračunali povprečno sestavo. Z metodo XPS ni mogoče analizirati vodika in helija.

Na dveh mestih vsakega vzorca smo posneli visokoenergijsko ločljive spektre značilnih vrhov elementov C 1s in O 1s prek ozkega energijskega področja. Iz oblike in energije vrhov v teh spektrih smo s pomočjo podatkov iz literature sklepali na kemijsko vezavo elementov na površini. Med analizo so se vzorci električno nabijali, zato smo jih obstreljevali z nizkoenergijskimi elektroni iz nevtralizacijske puške. Spektre XPS smo obdelali s programskim orodjem Multipak, verzija 8.1. Pred obdelavo spektrov smo spektre zamaknili tako, da je bil v spektru ogljika C 1s, vrh, ki je značilen za kemijsko vez C–C/C–H, pri vezavni energiji 285.0 eV.

electrons as a function of their binding energy, peaks can be observed which are typical of elements from the sample surface up to 6 nm in depth. The analysis took place in an ultra-high vacuum, which was during the analysis approximately 10^{-7} Pa. The analysis was performed in the XPS spectrometer produced by Physical Electronics Inc., model TFA XPS at the Department of Surface Engineering and Optoelectronics at the "Jožef Stefan" Institute [15]. The Al monochromatized source of X-ray light with the power of 200 W was used. The energy of an X-ray beam was 1486.6 eV, while the energy resolution was during the analysis approximately 0.7 eV. The analysis area was 0.4 mm in diameter and the signal during the XPS analysis came from the surface layer up to 6 nm in thickness. During the analysis, two types of XPS spectra were recorded. Firstly, a spectrum through a wide energy range was recorded. In this spectrum, the present elements were identified and their concentrations were calculated by dividing the peak intensities with the relative sensitivity factors provided by the XPS spectrometer manufacturer [16]. The attained results were normalized to 100%. The relative error at the calculation of surface composition is approximately 20%, while the XPS method sensitivity is about 0.5 at.%. Each sample was analysed at two different places and the average composition was

3 Rezultati preiskav

3.1 Sestava površine

Slika 2 prikazuje pregledne spektre XPS, dobljene na preiskanih vzorcih pred obdelavo in po njej v plazmi.

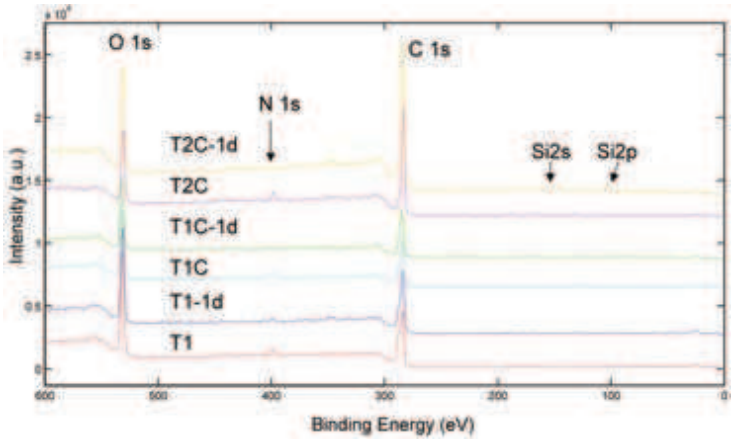

Figure 2: XPS spectra of PET knitted goods

V spektrih so prisotni vrhovi C 1s, O 1s, N 1s, Si 2p in Si 2s. Iz velikosti teh vrhov smo izračunali sestavo vzorcev, ki je podana v preglednici 2.

Table 2: The chemical composition (C, O, N, Si) in at %, ratio of concentrations of O/C, N/C and percentage of C1, C2, C3 and C4 in C 1s peaks presenting different chemical bonds of carbon atoms

Sample	C (at.%)	O (at.%)	N (at.%)	Si (at.%)	O/C	N/C	C1 (%)	C2 (%)	C3 (%)	C4 (%)
T1	74.0	22.9	3.1	0	0.309	0.042	73.1	18.1	0	8.8
T1-1d	74.8	24.5	0.7	0	0.328	0.009	49.1	25.1	18.3	7.5
T1-1m	86.2	11.7	0.0	2.1	0.136	0.000	83.7	9.3	3.9	3.6
T1C	60.5	37.0	2.5	0	0.612	0.041	46.9	27.8	0	25.3
T1C-1d	63.4	35.5	1.1	0	0.560	0.018	42.2	30	12.9	14.8
T1C-1m	86.8	11.5	0.0	1.9	0.132	0.000	83.1	8.5	3.9	4.4
T2C	62.6	33.6	3.9	0	0.536	0.063	56.8	24.5	0	18.7
T2C-1d	65.5	34.0	0.5	0	0.519	0.007	57.1	28.3	9.6	5.1
T2C-1m	84.9	13.8	0	1.3	0.163	0.000	83.3	9.4	3.7	3.6

Razmerje koncentracij O/C in N/C ter delež komponent C1, C2, C3 in C4 v ogljikovem spektru C 1s smo izračunali in predstavili v preglednici 2. Omenimo naj, da znaša teoretična sestava PET polimera (ob upoštevanju samo kisika in ogljika, ker metoda XPS ni občutljiva na vodik) 71,4 at. % ogljika in 28,6 at. % kisika in s tem povezano razmerje O/C = 0,40.

calculated. The XPS method does not enable the analysis of hydrogen and helium. In addition to the wide energy range spectra, high-energy resolution spectra of characteristic peaks of the elements C 1s and O 1s were recorded through a narrow energy range. From the shape and binding energy of the peaks within these XPS spectra, the chemical bonding of surface elements

3.2 Kemijska vezava elementov na površini

Slika 3 prikazuje visokoločljive spektre XPS C 1s iz preiskanih vzorcev pred staranjem, po obdelavi v korona plazmi in po enodnevnem staranju v Xenotestu.

Na sliki 4 so prikazani spektri C 1s vzorcev po enomesečnem staranju v Xenotestu.

Iz visokoločljivih spektrov lahko sklepamo na kemijske vezi elementov na površini vzorcev. Z metodo prilagajanja krivulj smo

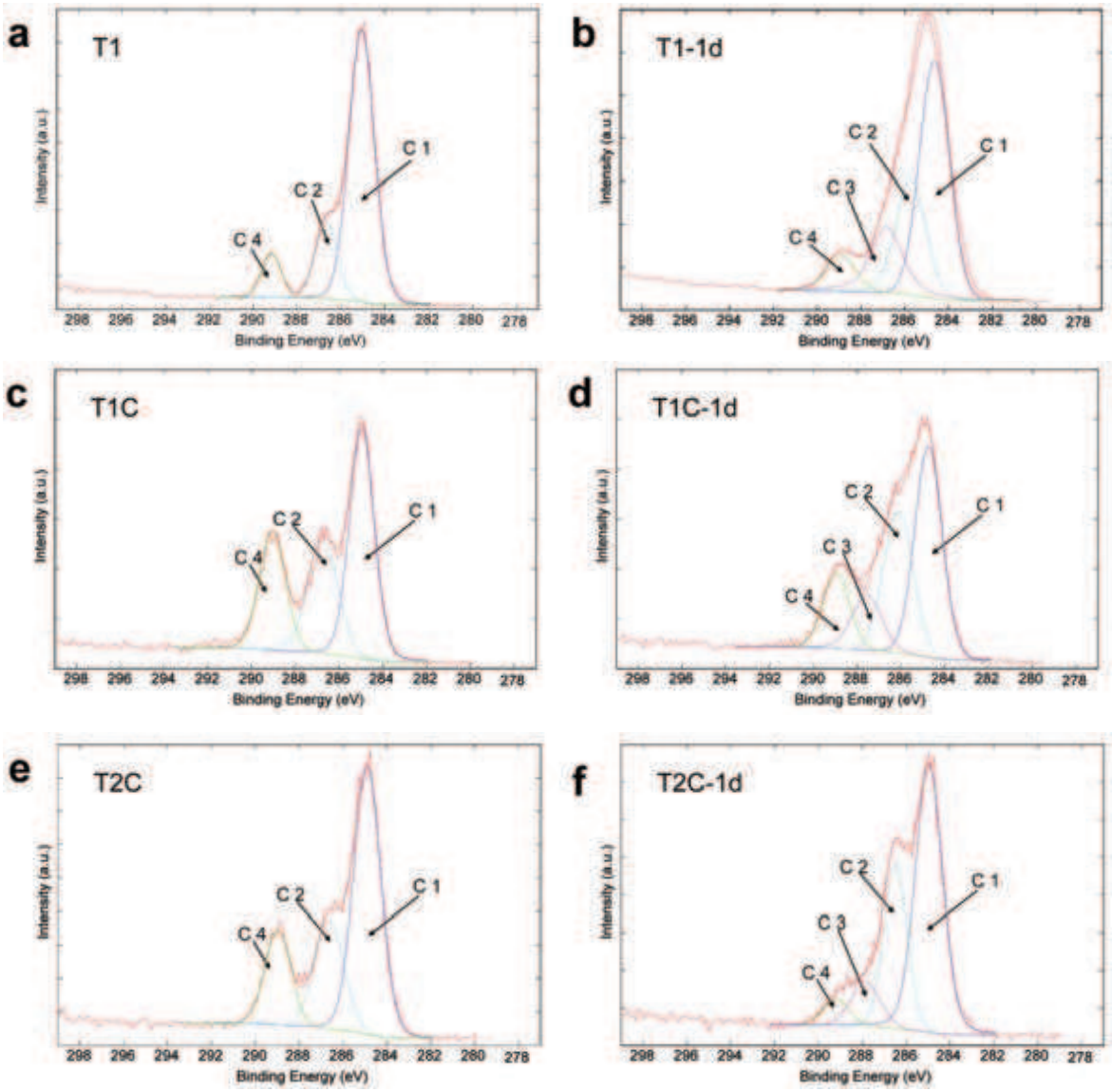

Figure 3: High-resolution XPS spectra C 1s obtained with surface analyses of:
a) initially thermostabilized PET knitted goods (tp),
b) initially thermostabilized PET knitted goods aged for 1 day with illumination in Xenotest,
c) tp treated in corona plasma, 30 cycles,
d) tp treated in corona plasma, 30 cycles and aged for 1 day with illumination in Xenotest,
e) tp treated in corona plasma, 60 cycles,
f) tp treated in corona plasma, 60 cycles and aged for 1 day with illumination in Xenotest

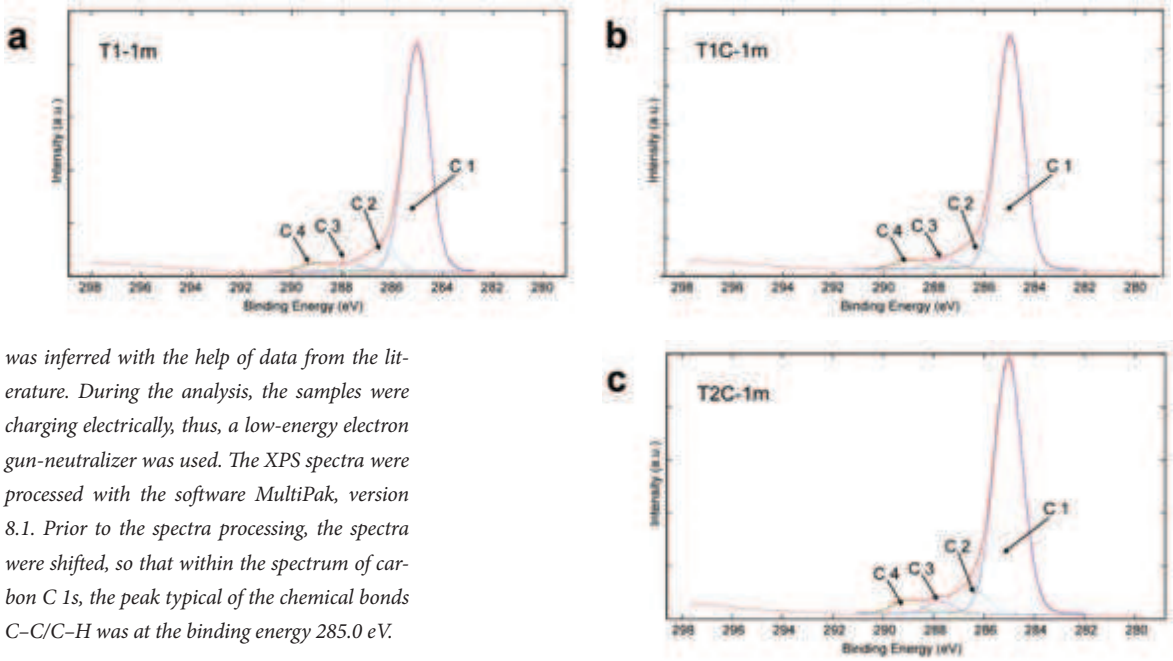

Figure 4: High energy-resolution XPS spectra C 1s obtained with surface analyses of:
a) initially thermostabilized PET knitted goods (tp) aged for 1 month with illumination in Xenotest,
b) tp treated in corona plasma, 30 cycles and aged for 1 month with illumination in Xenotest,
c) tp treated in corona plasma, 60 cycles and aged for 1 month with illumination in Xenotest

was inferred with the help of data from the literature. During the analysis, the samples were charging electrically, thus, a low-energy electron gun-neutralizer was used. The XPS spectra were processed with the software MultiPak, version 8.1. Prior to the spectra processing, the spectra were shifted, so that within the spectrum of carbon C 1s, the peak typical of the chemical bonds C–C/C–H was at the binding energy 285.0 eV.

3 Results and discussion

3.1 Surface composition

Figure 2 shows the wide energy range XPS spectra, obtained on some of the analysed samples before and after the plasma treatment.

The peaks C 1s, O 1s, N 1s, Si 2p and Si 2s are present in the spectra. From the intensity of these peaks, the surface compositions of PET knitted goods before the plasma treatment, after the plasma treatment and after the ageing of samples in Xenotest are shown in Table 2. The ratio of concentrations of O/C and N/C, and the percentage of C1, C2, C3 and C4 components in the C 1s spectrum are present as well.

The concentration ratio O/C and N/C was calculated and demonstrated in Table 2.

At this point, it should be mentioned that the theoretical composition of PET polymer (considering only oxygen and carbon, since the XPS method is not sensitive to hydrogen) contains 71.4 at.% of carbon and 28.6 at.% of oxygen, thus the expected ratio of O/C is 0.40.

3.2 Chemical bonding of surface elements

Figure 3 shows high-resolution XPS carbon spectra C 1s from the analysed samples prior to the ageing, after the corona plasma treatment and after a one-day ageing in Xenotest.

razstavili ogljikov spekter C 1s na vrhove C1, C2, C3 in C4 (sliki 3 in 4). Iz vezavnih energij teh vrhov je mogoče ob uporabi podatkov iz literature [10–14, 15] sklepati na kemijske vezi atomov. Komponento C1 pri vezavni energiji 285,0 eV pripisujemo vezem C–C/C–H. Komponento C2 pri vezavni energiji 286,6 eV pripisujemo vezi C–O oziroma N. Komponento C3 pri energiji 288,0 eV pripisujemo vezem C=O in O–C–O. Komponento C3 pri vezavni energiji 289,5 eV pripisujemo vezem O–C=O (karboksilna skupina). Preglednica 2 prikazuje relativne deleže komponent C1, C2, C3 in C4, ki smo jih ugotovili v spektrih C 1s.

4 Sklepi

Z metodo XPS smo preiskali površine devetih vzorcev PET pletiv. Ugotovili smo:

a) Sestava in kemijska vezava elementov na površini izhodnega termostabiliziranega pletiva T1 sta deloma podobni čistemu PET polimeru. Od čistega PET polimera se razlikujeta po tem, da vzorec T1 vsebuje večji delež C–C/C–H vezi, kar pripisujemo tanki plasti na površini pletiva. Izvor te plasti je verjetno pove-

Figure 4 demonstrates the C 1s spectra of samples after a month of ageing in Xenotest.

From the high-resolution carbon C 1s spectra, the existence of chemical bonds among the surface atoms can be inferred. With a curve fitting procedure, the carbon spectrum C 1s was decomposed into the peaks C1, C2, C3 and C4 (cf. Figures 3 and 4). From the binding energies of these peaks, the chemical bonds of atoms can be inferred with the help of data from the literature [10–15]. The C1 component at the binding energy 285.0 eV can be assigned to the bonds C–C/C–H. The C2 component at the binding energy 286.6 eV is assigned to the bond C–O or C–N, respectively. The C3 component at the energy 288.0 eV is assigned to the bonds C=O in O–C–O, while the component C3 at the binding energy 289.5 eV is assigned to the bonds O-C=O (carboxyl group). Table 2 shows the relative concentration of components C1, C2, C3 and C4, established in the spectra C 1s.

4 Conclusion

The surface investigation of nine PET knitted goods samples with the XPS method leads to the conclusion that:

a. the composition and chemical bonding of surface elements of the initially thermostabilized knitted goods T1 are partly similar to the pure PET polymer. The difference lies in sample T1 containing a larger content of C–C/C–H bonds as expected for pure PET polymer, which is attributed to the thin surface layer on the knitted goods surface. The origin of this layer is probably related to the thermostabilisation process. The ratio O/C is 0.31 and is due to the increased content of bonds C–C/C–H lower than the theoretical ratio O/C for the PET polymer, which is 0.40.

b. the one-day ageing of the initially thermostabilized knitted goods T1-1d in Xenotest does not cause any significant changes in the composition (ratio O/C slightly increases to 0.33).

c. on both samples after the corona plasma treatment (T1C for 30 and T2C for 60 cycles), the oxygen concentration substantially increases (ratio O/C increases from 0.31 to 0.53–0.61) and the content of C–C/C–H bonds decreas-

zan s termostabilizacijskim procesom. Razmerje O/C znaša 0,31 in je zaradi povečanega deleža vezi C–C/C–H manjše kot teoretično razmerje za PET polimer, ki je 0,40.

b) Staranje izhodnega termostabiliziranega pletiva T1-1d v Xenotestu za en dan ne prinese bistvene spremembe sestave (razmerje O/C se nekoliko poveča, na 0,33).

c) Na obeh vzorcih se po obdelavi v korona plazmi (T1C za 30 in T2C za 60 ciklov) močno poveča koncentracija kisika (razmerje O/C naraste z 0,31 na 0,53–0,61) in zmanjša delež C–C/C–H vezi. To kaže, da obdelava v korona plazmi povzroči aktivacijo in funkcionalizacijo površin. Vzorca po obdelavi v korona plazmi T1C (30 ciklov) in T2C (60 ciklov) sta med seboj precej podobna po deležu kemijskih vezi. Razlikujeta se v nekoliko večji koncentraciji kisika in manjšem relativnem deležu C–C/C–H vezi na vzorcu T1C, obdelanem v 30 ciklih glede na vzorec T2C. Oba vzorca po obdelavi v korona plazmi vsebujeta dušik (3–4 at.%).

d) Staranje v plazmi obdelanih vzorcev za en dan povzroči zmanjšanje površinske koncentracije kisika (razmerje O/C pade z 0,61 na 0,56 za T1C-1d oziroma z 0,54 na 0,52 za T2C-1d) in dušika, kar kaže na rahlo deaktivacijo površine. Staranje za en dan po obdelavi v plazmi poveča najbolj relativni delež C–O vezi glede na preostale vezi ogljikovih atomov.

e) Enomesečno staranje vseh vzorcev v Xenotestu vodi do velikih sprememb na površini. Sestava površin postane podobna na vseh vzorcih; to je tako na vzorcu, ki ni bil obdelan v plazmi (T1-1m), kot na obeh v plazmi obdelanih vzorcih (T1C-1m in T2C-1m). Močno se zmanjša koncentracija kisika, razmerje O/C pade z 0,54–0,61 na 0,13–0,16 za vzorce, obdelane v plazmi. To kaže, da povzroči obdelava v Xenotestu deaktivacijo površin in izgubo funkcionalnih skupin s kisikovimi atomi, iz česar sklepamo, da so površine obogatene z ogljikom (močno naraste tudi delež C–C/C–H vezi na račun C-kisikovih vezi) in tudi precej inertne. To kaže, da med obdelavo PET pletiv v Xenotestu verjetno zaradi absorpcije svetlobe zadostne energije iz UV-spektra pride do rekombinacije prostih radikalov na površini (cross-linking) pletiv in do karbonizacije površin. Zanimivo je, da podoben rezultat dobimo tudi na termostabiliziranem vzorcu, ki ni bil obdelan v plazmi.

5 Zahvala

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es. This is a consequence of the corona plasma interaction causing the surface activation and functionalization. The samples are after the corona plasma treatment T1C (30 cycles) and T2C (60 cycles) rather similar to each other according to the content of chemical bonds. The difference is in a slightly higher oxygen concentration and lower relative content of C–C/C–H bonds on sample T1C treated for 30 cycles than on sample T2C. Both samples contain nitrogen (3–4 at.%) after the corona plasma treatment.

d. *the one-day ageing of plasma-treated samples causes the surface concentration of oxygen to lower (ratio O/C drops from 0.61 to 0.56 for T1C-1d, and from 0.54 to 0.52 for T2C-1d) as well as of nitrogen, which points to a slight surface deactivation. The one-day ageing after the plasma treatment increases mostly the relative content of C–O bonds with respect to other carbon atom bonds.*

e. *the one-month ageing of all samples in Xenotest leads to considerable surface changes. The surface composition becomes similar on all samples, i.e. on the sample which was not plasma-treated (T1-1m), as well as on both plasma-treated samples (T1C-1m and T2C-1m). Furthermore, the oxygen concentration decreases dramatically, the ratio O/C falls from 0.54–0.61 to 0.13–0.16 for the plasma-treated samples. This shows that the treatment in Xenotest causes surface deactivation and loss of oxygen-based functional groups, from which it can be concluded that the surfaces are rich in carbon (the content of C–C/C–H bonds increases substantially at the expense of C-oxygen bonds) and are expected to be rather inert. During the treatment of PET knitted goods in Xenotest, it comes to the cross-linking of free radicals on the knitted goods surface and to the surface carbonisation, which is due to the light absorption of the UV-spectrum energy. It is interesting that a similar result is obtained on the plasma-untreated thermostabilized sample as well.*

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6 Literatura

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