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Rentgenska fotoelektronska spektroskopija za določanje kemijskih sprememb na površini bombaža po obdelavi s korona in nizkotlačno plazmo

Izvirni znanstveni članek

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Izvleček

Surovo, beljeno in beljeno/merceriziranо bombažno tkanino smo obdelali v zračni korona plazmi in nizkotlačni plazmi vodne pare. Pred obdelavo s plazmo in po njej smo površine bombažnih tkanin preiskali z rentgensko fotoelektronsko spektroskopijo (XPS). Rezultati raziskave kažejo, da plazemska obdelava bombaža selektivno čisti necelulozne komponente, na površini bombaža se povečata koncentracija kisika in število funkcionalnih skupin, temelječih na kisiku. Oksidacija površin bombažne tkanine je močnejša pri uporabi korona plazme kot pri uporabi nizkotlačne plazme.

Ključne besede: bombaž, celuloza, korona, nizkotlačna plazma, XPS, rentgenska fotoelektronska spektroskopija

1 Uvod

Bombaž je sestavljen pretežno iz celuloze, vsebuje pa tudi nekaj necelulozних sestavin, kot so voski, pektin in proteini. Da bi bombažna vlakna lahko barvali oz. plemenitili, jih moramo primerno pripraviti. [1, 2] Za ta namen je znanih kar nekaj metod, pri katerih pa je problem velika poraba vode in kemikalij. Okolju prijaznejša je plazemska tehnologija. [3, 4] Ta je primerna zlasti za obdelavo tekstilij zaradi vpliva na tanek sloj površine in zaradi inertnosti do poškodb notranjih delov vlaken. Plazmo generiramo s pomočjo elektromagnetnega polja, v katero uvajamo organske ali anorganske snovi, večinoma pline. Večina načinov obdelave bombaža s plazmo različnih plinov in mešanic je bila izvedena laboratorijsko. Namen obdelave je bil doseči večjo hidrofilnost, hi-

X-Ray Photoelectron Spectroscopy for Determination of Chemical Changes on the Cotton Surface After Corona and Low-Pressure Plasma Treatment

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Abstract

Raw, bleached and bleached/mercerized cotton fabrics were treated in air corona and in low-pressure water vapor plasma. The surfaces of untreated and plasma treated cotton fabrics were investigated with X-ray photoelectron spectroscopy (XPS). Research results show that plasma selectively cleans non-cellulosic substances of cotton, oxygen concentration on the surface and binding of oxygen containing functional groups to the surface is noticeable. The oxidation of cotton surfaces is stronger when using corona plasma than when using low-pressure plasma.

Keywords: cotton, cellulose, corona, low-pressure plasma, XPS, X-ray photoelectron spectroscopy

1 Introduction

Cotton is mainly composed of cellulose with some non-cellulosic components such as waxes, pectin and proteins. The purpose of modification of cotton fibers is to change their reactivity, i.e. to make them suitable for dyeing or finishing. (1, 2) Several techniques have ap-

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peared to reach this goal but the main problem is a large consumption of water and chemicals. More environmentally friendlier is plasma technology. (3, 4) It is especially effective technique for modifying the surface properties of textiles without altering the interior part of the fiber. Plasma is generated by introduction of organic or inorganic substance, usually gas into electromagnetic field. Most of the plasma treatments of cotton using various gases were performed in laboratories in effort to increase hydrophilicity, hydrophobicity, flame retardancy, nanosilver adhesion, UV protection and bleaching of a raw material. (5-16) The introduction of hydrophilic groups to the cotton can be made with plasma using oxygen, ambient air, ozone, argon and some other gases. (17, 18) A suitable method for determination of the functional groups on a material is X-ray Photoelectron spectroscopy (XPS), often called Electron spectroscopy for Chemical Analysis (ESCA). (19-21) In the photoelectron spectrum, which represents the distribution of emitted photoelectrons 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. In literature one can find quotations of XPS analysis of plasma modified cotton substrates which were pre-prepared with various procedures prior to plasma modification (i.e. alkaline boiling, scouring, laundering). But to study plasma modification of cotton it is important to know about chemical changes of cotton samples that were not cleaned or otherwise pre-prepared. The purpose of our study was to evaluate the surface changes of raw, bleached and bleached/mercerized cotton fabrics before and after plasma treatment. For a treatment of cotton samples air atmospheric corona plasma and low-pressure RF water vapor plasma were used. The results of this research can help us to determine if a use of plasma treatment can replace some of pretreatments and in that way reduce a use of water and chemicals.

2 Experimental

2.1 Material

Raw, bleached and bleached/mercerized 100% cotton fabrics, supplied by Tekstina, Ajdovščina

drofobnost, ognjevarnost, adhezijo nanosrebra, zvišati UV-zaščito in belino bombaža. [5–16] S kisikovo, zračno, ozonsko, argonsko in drugimi plazmami so v tanek sloj površine bombaža vgrajevali hidrofilne skupine. [17, 18] Ena primernih metod za določanje funkcionalnih skupin na materialu je spektroskopija fotoelektronov, vzbujenih z rentgenskimi žarki (XPS ali ESCA, *ang.* XPS = X-ray Photoelectron Spectroscopy, ESCA = Electron Spectroscopy for Chemical Analysis). [19–21] V spektru fotoelektronov, ki pomeni porazdelitev izsevanih fotoelektronov po njihovi vezavni energiji, so prisotni vrhovi, značilni za elemente, ki se nahajajo na površini vzorca do globine okoli 6 nm. Literatura pretežno navaja analize XPS plazemsko spremenjenih bombažnih substratov, ki so bile pred obdelavo s plazmo pripravljene z različnimi postopki (npr. izkuhavanje, razškrobljenje, pranje). Za študije obdelave bombažnih substratov na plazemskih sistemih je pomembno znanje o kemijskih spremembah na bombažnih substratih, ki niso bili predpripravljeni oz. očiščeni. Namen naše raziskave je bil določiti površinske kemijske spremembe na surovi, beljeni in beljeni/merceriziran bombažni tkanini pred uporabo plazme in po njej. Plazmi, ki smo ju v ta namen uporabili, sta bili atmosferska zračna korona plazma in nizkotlačna RF-plazma z vodno paro. Z dobljenimi rezultati poskušamo prikazati, da se z direktno plazemsko obdelavo lahko izognemo nekaterim postopkom predpriprave substrata, kar bi pri nadaljnjih tehnoloških procesih zmanjšalo porabo vode in kemikalij.

2 Eksperimentalni del

2.1 Material

Za raziskavo smo uporabili surovo, beljeno in beljeno/merceriziran 100-odstotno bombažno tkanino v vezavi platna, ki jo izdeluje Tekstina, Ajdovščina. Lastnosti uporabljenih tkanin so opisane v preglednici 1.

Table 1: Properties of cotton fabrics

Cotton fabric	Mass (g/m^2)	No. of warp threads (threads/cm)	No. of weft threads (threads/cm)
S	136,8	53	29
B	119,4	54	28
M	119,2	52	26

S – raw, B...bleached, M – bleached/mercerized

2.2 Obdelava tkanin s plazmo

Bombažne tkanine smo obdelali v atmosferski korona plazmi, kjer je bil kot delovni plin uporabljen zrak, in nizkotlačni RF-plazmi, kjer je bila kot delovni plin uporabljena vodna para. Načini ob-

were used. Properties of fabrics are described in Table 1.

2.2 Plasma treatment of fabrics

Cotton fabrics were treated in two different plasma, i.e. atmospheric corona plasma with ambient air as a working gas, and low-pressure RF plasma using water vapor as a working gas. The methods of plasma treatments are described in detail in literature (12, 14, 22). The samples investigated by XPS are marked according to the treatments (Table 2).

2.3 X-ray photoelectron spectroscopy

Information on the chemical composition and chemical bonds of surface atoms of cotton fabrics was obtained with XPS analysis. 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 analyzed. In the photoelectron spectrum, which represents the distribution of emitted photoelectrons 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 (23). The aluminium monochromatized source of X-ray light with a power of 200 W was used. The energy of an X-ray beam was 1486.6 eV, while the energy resolution during the analysis was 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 (24). The attained results were normalized to 100%. The relative error at the calculation of surface composition is approximately

delave z obema plazmama so podrobno opisani v literaturi. [12, 14, 22] V preglednici 2 so predstavljene oznake vzorcev, ki smo jih preiskali z metodo XPS.

Table 2: Identification of samples

Sample	Description of cotton sample
S	Raw untreated
S_C	Raw corona plasma treated
S_P	Raw low-pressure plasma treated
B	Bleached untreated
B_C	Bleached corona plasma treated
B_P	Bleached low-pressure plasma treated
M	Bleached/mercerized untreated
M_C	Bleached/mercerized corona plasma treated
M_P	Bleached/mercerized low-pressure plasma treated

2.3 Spektroskopija fotoelektronov, vzbujenih z rentgensko svetlobo

Informacije o kemijski sestavi in o kemijskih vezeh elementov na površini bombažnih tkanin smo pridobili z analizo XPS. Pri tej metodi v spektrometru XPS obsevamo vzorec z monokromatsko rentgensko svetlobo in analiziramo energijo izsevanih fotoelektronov. V spektru fotoelektronov, ki pomeni porazdelitev izsevanih fotoelektronov glede na njihove vezavne energije, so prisotni vrhovi, značilni za elemente, ki so na površini vzorca do globine okrog 6 nm. Analiza je potekala v ultravisokem vakuumu, ki je bil med analizo okoli 10^{-7} Pa. Analizo smo izvedli na spektrometru XPS izdelovalca Physical Electronics Inc., model TFA XPS na Odseku za tehnologijo površin in optoelektroniko na Institutu „Jožef Stefan". [23] Pri analizi smo uporabili aluminijev monokromatizirani vir rentgenske svetlobe z močjo 200 W. Energija rentgenskega žarka je bila 1486,6 eV, energijska ločljivost med analizo pa okrog 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 območja. 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. [24] Dobljene rezultate smo normalizirali na 100 odstotkov. Relativna napaka pri izračunu sestave površine je približno 20-odstotna, tako, da je občutljivost metode približno 0,5 at. %. Pri analizi sestave površine smo vsak vzorec analizirali na dveh različnih mestih in izračuna-

20%, while the XPS method sensitivity is about 0.5 at.%. Each sample was analyzed at two different places and the average composition was calculated. The XPS method does not enable the analysis of hydrogen and helium. In addition to 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 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 software MultiPak, version 8.1. Prior to the spectra processing, 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

3.1 Surface composition

From the wide energy range XPS spectra the surface composition was calculated and the results are presented in Table 3. The O/C concentration ratio of XPS analysis is very sensitive to surface changes so it was calculated and is presented in Figure 1. The surface composition of cellulose which is the main component of a cotton is 54.4 at% carbon and 45.5 at.% oxygen, and the O/C ratio 0.83. (25, 26)

3.2 Chemical bonding of surface elements

From the high-resolution XPS carbon C 1s spectra, the existence of chemical bonds among the surface atoms can be inferred. Spectra C 1s (Fig. 2) are presented for a case of raw cotton fabric, namely for untreated, corona plasma and low-pressure plasma treated sample. With curve fitting procedure, the carbon spectrum C 1s was decomposed into the peaks C1, C2, C3 and C4. From the binding energies of these peaks, the chemical bonds of atoms can be inferred with a help of data from the literature (3, 27, 28). 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

li 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 območja. 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 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.

3 Rezultati

3.1 Sestava površine

Iz velikosti vrhov XPS preglednih spektrov smo izračunali sestavo vzorcev, ki je podana v preglednici 3. Pri analizi XPS se je pokazalo, da je razmerje koncentracij O/C zelo občutljivo na spremembe na površini, zato smo ga izračunali in predstavili na sliki 1. Sestava čiste celuloze kot ene glavnih komponent bombaža (ob tem, da se upoštevata samo kisik in ogljik, ker metoda XPS ni občutljiva na vodik) znaša 54,5 at. % ogljika in 45,5 at. % kisika in s tem povezano razmerje O/C enako 0,83. [25, 26]

Table 3: The chemical composition (C, O), O/C ratio concentrations and percentage of C1, C2, C3 and C4 in C 1s peaks presenting different chemical bonds of carbon atoms

Sample	C (at.%)	O (at.%)	O/C (at.%)	C1	C2	C3	C4
S	88.4	11.6	0.13	79.8	15.9	4.3	0
S_C	57.5	39.9	0.69	38.9	41	16.4	3.7
S_P	79.8	20.2	0.25	62.6	23.9	8.2	5.3
B	65.7	34.3	0.52	31.6	56.7	11.8	0
B_C	55.5	44.5	0.80	20.8	54	19.5	5.7
B_P	63.2	36.8	0.58	26.1	55.5	15.9	2.6
M	69.6	30.4	0.44	40.0	47.6	12.4	0
M_C	54.7	45.3	0.83	11.3	69.3	15.5	3.9
M_P	62.5	37.5	0.60	24.8	47.8	20.7	6.8

3.2 Kemijska vezava elementov na površini

Iz visokoločljivih XPS spektrov C 1s preiskanih vzorcev lahko sklepamo na kemijske vezi elementov na njihovi površini. Spek-

286.6 eV is assigned to the bond C–O. The C3 component at the energy 288.0 eV is assigned to the bonds C=O in O–C–O, while the component C4 at the binding energy 289.5 eV is assigned to the bonds O–C=O (carboxyl group). The same procedure was done for XPS spectra C 1s of bleached and bleached/mercerized cotton fabric samples. Relative concentrations of C1 – C4 are presented in Table 3 and Figure 3.

4 Discussion

4.1 Raw cotton fabric

The XPS spectra of raw cotton fabric are not similar to the XPS spectra of cellulose. (25, 26) The surface of raw untreated cotton fabric contains a high concentration of carbon and a low concentration of oxygen. This is not characteristic for cellulose. XPS spectrum C 1s of cellulose also does not include C–C/C–H bonds (C1 peak in Figure 1). The surface of raw cotton is rich in C atoms (C–C/C–H bonds), what could indicate the presence of C–C/C–H bond rich substances, such as waxes, pectin and proteins. The samples after plasma treatment have a higher concentration of O/C ratio (the samples contain more of the oxygen and less of the carbon atoms). The change of O/C ratio is higher on samples treated in corona plasma than on samples treated in low-pressure plasma (Table 3). The increase of O/C concentration ratio is expected since plasma interaction with cotton causes the surface oxidation. Changes of C-atom bonds after corona and low-pressure plasma treatment are visible from Fig. 2 and Fig. 3: increase of C–O and C=O bonds (C2 and C3 peak). Increase of C–O bonds is distinctive after corona plasma treatment (41 %) than af-

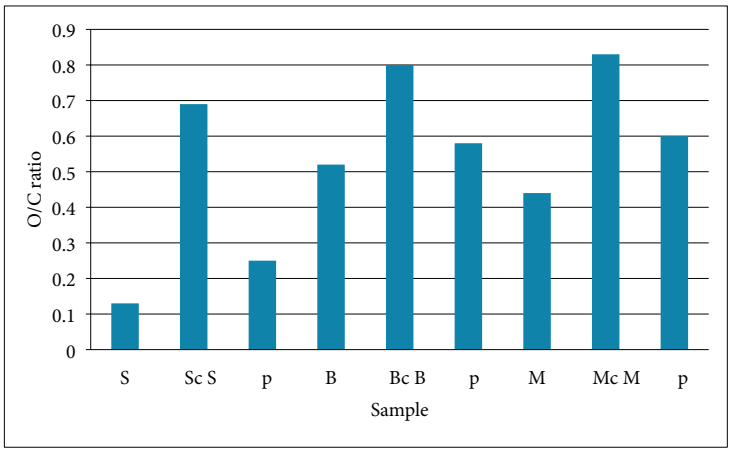

Figure 1: The concentration ratio between O and C on the surfaces of cotton samples

tri C 1s (slika 2) so prikazani za primer surove bombažne tkanine, in sicer za neobdelan, s korona plazmo in z nizkotlačno plazmo obdelan vzorec. Z metodo prilagajanja krivulj (*ang.* curve fitting) smo razstavili ogljikov spekter C 1s na vrhove C1, C2, C3 in C4. Iz vezavnih energij teh vrhov je mogoče pri uporabi podatkov iz literature [3, 27, 28] sklepati na kemijske vezi atomov. Komponento C1 pri vezavni energiji 285,0 eV pripisujemo vezem C–C/

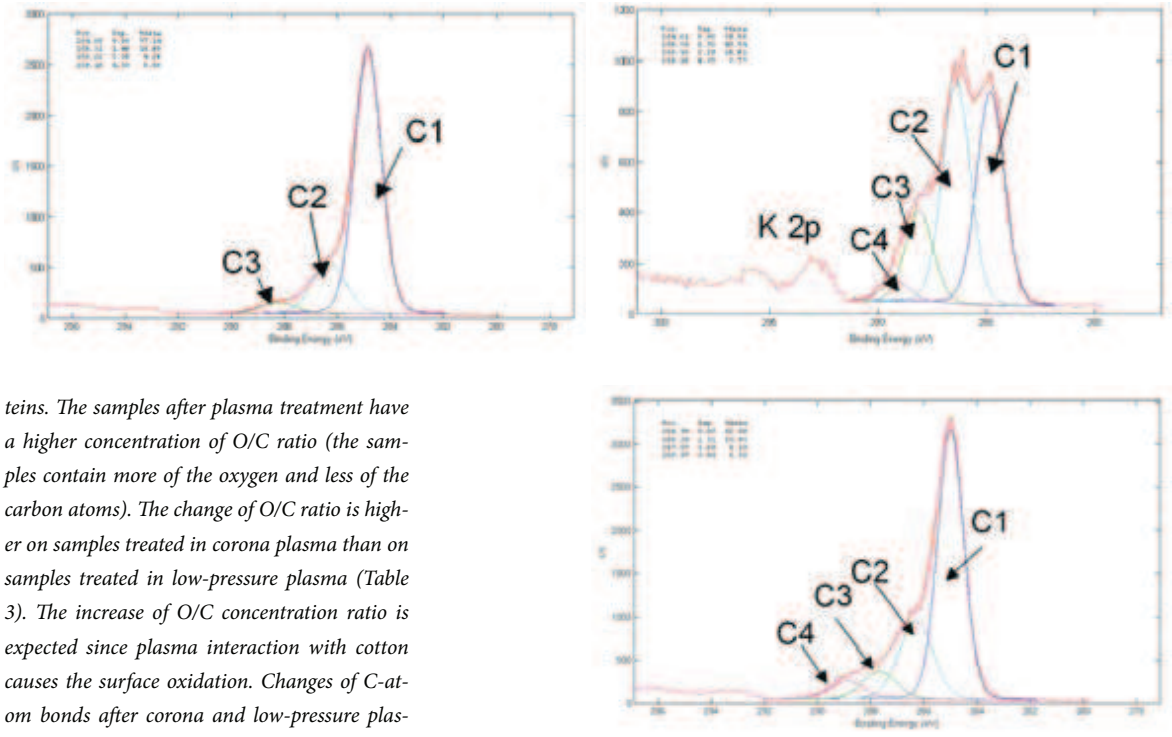

Figure 2: High energy-resolution XPS spectrum C 1s obtained from the surface of raw cotton: (a) untreated, (b) corona plasma treated, (c) low-pressure plasma treated

ter low-pressure plasma treatment (23.9 %). It is similar for C=O bonds. After corona plasma treatment the bonds increase to 16.6 %, while they increase to 8.2 % after low-pressure plasma treatments. With both plasma treatments formation of O–C=O bonds (C4 peak) is noticeable. C 1s specter of plasma treated samples resembles to the spectra of cellulose, which could indicate that plasma selectively cleaned the non-cellulosic parts present on a surface of a raw untreated cotton fabric.

4.2 Bleached cotton fabric

The surface composition of bleached cotton fabric is very different from the surface composition of raw cotton. The surface of bleached cotton fabric is pre-oxidized. The C 1s specter of bleached cotton is similar to C 1s specter of cellulose. Prior to plasma treatment (corona or low-pressure) bleached sample contains a large amount of oxygen (34.3 at%, Table 3). Besides a smaller portion of C–C/C–H bonds (31.6 %) and C=O bonds (11.8 %), it contains mostly of C–O bonds (C2 peak, 56.7 %). After a treatment with corona plasma the content of oxygen increases from 34.3 at% to 44.5 at%, while the treatment in low-pressure plasma increases oxygen to 36.8 at%. After both plasma treatments the content of C–O (C2 peak) remains the same (~55 %) and some changes are present also: content of C=O bonds increases (C3 peak) and appearance of O–C=O bonds is noticeable (C4 peak). Increase of bonds is distinctive after corona plasma treatment than after low-pressure plasma treatment. Content of C–C/C–H bonds decreases (C1 peak) after both plasma treatments.

4.3 Bleached/mercerized cotton fabric

The surface of bleached/mercerized cotton fabric is very different than the surface of raw cotton fabric, but is similar to the surface of bleached cotton fabric. From Fig. 3 and Table 3 it is evident that the surface of untreated sample contains mostly C–O and C=O bonds, and smaller amount of C–C/C–H bonds. After plasma treatment the oxygen content on surface increases (increase of O/C ratio, Fig. 1). Increase of O/C ratio is distinctive after corona plasma treatment, where the oxygen concentration in-

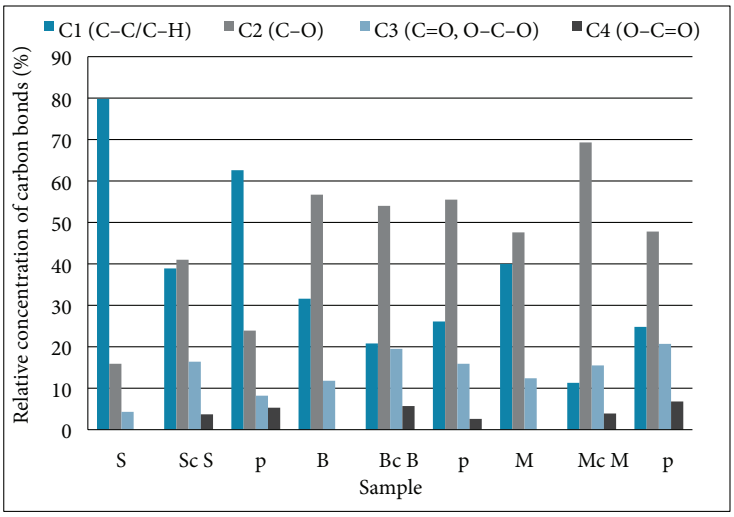

Figure 3: Relative concentration of carbon bonds on the surface of cotton samples

C–H. Komponento C2 pri vezavni energiji 286,6 eV pripisujemo vezi C–O. Komponento C3 pri vezavni energiji 288,3 eV pripisujemo vezi C=O ali O–C–O. Komponento C4 pri vezavni energiji 289,5 eV pripisujemo vezem O–C=O (karboksilna skupina). Mogoči so tudi drugi tipi vezi, kot smo jih navedli. Enako smo obdelali spektre XPS C 1s za vzorce beljene in beljene/merceriziranе bombažne tkanine, relativne deleže komponent C1 – C4 pa podali v preglednici 3 in prikazali na sliki 3.

4 Razprava

4.1 Surova bombažna tkanina

Spektri surove bombažne tkanine XPS niso podobni spektrom XPS čiste celuloze. [25, 26] Od teh se razlikujejo po tem, da kaže surov bombaž pred obdelavo v plazmi visoko koncentracijo ogljika in nizko koncentracijo kisika na površini, kar naj ne bi bilo značilno za celulozo. Spekter XPS C 1s iz čiste celuloze tudi naj ne bi vseboval vezi C–C/C–H oziroma komponente C1 v spektru (slika 2 (a)). Dobljeni rezultati kažejo, da so atomi C večinoma na površini v vezi C–C/C–H, kar ni značilno za čisto celulozo. To lahko pomeni, da so na površini druge snovi bogate z vezmi C–C/C–H, kot so voski, pektin in proteini. Vzorci po obdelavi s plazmo vsebujejo več kisika in manj ogljika kot pred plazemsko obdelavo, kar se kaže v povečanem razmerju koncentracij O/C. Sprememba v razmerju O/C je pri vzorcih, obdelanih v korona plazmi, večja kot pri vzorcih, obdelanih v nizkotlačni plazmi (slika 1). Povečanje razmerja O/C je v našem primeru pričakovano, saj prihaja v plazmi do oksidacije površine vzorcev oz. se poveča vezava kisikovih funkcionalnih skupin. Iz slik 2 in 3 je razvidno, da se na površini surove bombažne tkanine po korona in nizkotlačni plazemski ob-

creases to 45.3 at%, while increases to 37.5 at% after low-pressure plasma treatment. Due to oxidation process in plasma, the content of C–C/C–H bonds (C1 peak) deceases and the change is more noticeable for bleached/mercerized cotton than for a bleached cotton fabric. Concentration of C–O bonds is increased in the case of corona plasma treatment, from 47.6 % to 69.3 %, while it remains almost equal for low-pressure plasma treatment (47.8 %). After both plasma treatments the content of C=O bonds (C3 peak) increases and appearance of O–C=O bonds is noticeable. These changes are more distinct after low-pressure plasma treatment than after corona plasma treatment.

5 Conclusion

The samples of raw, bleached and bleached/mercerized fabrics were treated in atmospheric air corona plasma and low-pressure water vapor plasma. XPS method was used to evaluate the surface chemical changes of samples. Comparing to cellulose, it is clear that the surface of raw untreated cotton (S) has higher concentration of C and C–C/H–H bonds and a lower concentration of O, which can be contributed to the presence of non-cellulosic substances such as waxes, proteins and pectin. The surfaces of bleached (B) and bleached/mercerized (M) cotton fabrics are alike but very different from S. B and M are pre-oxidized and therefore more similar to cellulose. The surfaces of corona and low-pressure plasma treated cotton fabrics are oxygen reach, which can be contributed to oxidation process in plasma. Increase of oxygen atoms is more noticeable on corona plasma treated samples (Sc, Bc and Mc), which can be contributed to longer treatment time than in low-pressure plasma. The concentration of oxygen on Sc and Sp is higher than on B or M. This means that by using plasma technology some of the technological processes of pretreatment of cotton fabrics before dyeing can be avoided. Plasma treated raw cotton fabric absorbs the same or more of dyestuff as untreated bleached or bleached/mercerized cotton fabric, which was demonstrated in previous researches. (11, 13, 14) The surfaces of plasma treated bleached and bleached/mercerized cotton fabrics (Bc, Bp, Mc and Mp) are richer in oxygen content,

delavi spremeni tudi število vezi: naraste število C–O in vezi C=O (vrhova C2 in C3). Prirastek vezi C–O je izrazito večji po obdelavi v korona plazmi (41-odstoten) kot po obdelavi v nizkotlačni plazmi (23,9-odstoten) in podobno velja tudi za prirastek vezi C=O, ki se po obdelavi v korona plazmi zvišajo na 16,4 odstotka in po obdelavi v nizkotlačni plazmi na 8,2 odstotka. Na obeh plazemsko obdelanih vzorcih nastanejo vezi O–C=O vezi (vrh C4) na račun vezi C–C/C–H. Spekter C 1s plazemsko obdelanih vzorcev postane bolj podoben spektru čiste celuloze, kar pomeni, da plazma selektivno očisti necelulozne komponente, ki so prisotne na površini surovega neobdelanega bombaža.

4.2 Beljena bombažna tkanina

Površina beljene bombažne tkanine se bistveno razlikuje od površine surove bombažne tkanine, saj je pred tem oksidirana. Spekter C 1s vzorca beljenega bombaža je podoben spektru C 1s čiste celuloze. Na vzorcu beljene bombažne tkanine je veliko kisika (34,3 at.%, preglednica 3). Večinoma so na površini C–O vezi (C2 vrh, 56,7 %), poleg manjšega deleža vezi C–C/C–H (31,6 %) in vezi C=O (11,8 %). Po obdelavi s korona plazmo se na površini vzorca poveča vsebnost kisika s 34,3 at.% na 44,5 at.%, medtem ko po obdelavi z nizkotlačno plazmo kisik naraste nekoliko manj, na 36,8 at.%. Delež vezi C–O (C2 vrh), ki je največji, ~ 55 %, ostane po plazemski obdelavi enak. Vendar pa po plazemski obdelavi naraste število vezi C=O (C3 vrh) in nastanejo vezi O–C=O vezi (C4 vrh). Prirastek obeh omenjenih vrst vezi je večji po obdelavi s korona plazmo kot po obdelavi z nizkotlačno plazmo. Delež C–C/C–H vezi (C1 vrh) se zmanjša po obeh načinih plazemske obdelave.

4.3 Beljena/mercerizirana bombažna tkanina

Površina beljene/mercerizirane bombažne tkanine se bistveno razlikuje od površine surove bombažne tkanine, vendar je podobna površini beljenega vzorca. Iz slike 3 in preglednice 3 je razvidno, da so na površini plazemsko neobdelane beljene/mercerizirane bombažne tkanine večinoma prisotne vezi C–O in C=O, poleg manjšega deleža vezi C–C/C–H. Vzorcem, ki so bili izpostavljeni plazmi, naraste delež kisika, kar prepoznamo kot prirastek razmerja O/C, ki je prikazan na sliki 1. Ta prirastek je večji po obdelavi v korona plazmi, kjer koncentracija kisika naraste na 45,3 at.%, medtem ko po obdelavi v nizkotlačni plazmi naraste vsebnost kisika na 37,5 at.%. Zaradi oksidacije v plazmi se delež vezi C–C/C–H (vrh C1) zmanjša, vendar je ta sprememba večja kot pri beljeni bombažni tkanini. Delež vezi C–O se pri koronski obdelavi najbolj poveča, in sicer s 47,6 % na 69,3 %, medtem ko pri obdelavi z nizkotlačno plazmo ostane približno enak (47,8 %). Po obeh plazemskih obdelavah naraste število vezi C=O (C3 vrh) in nastanejo vezi O–C=O (vrh C4). Te spremembe so izrazitejše po obdelavi z nizkotlačno plazmo kot s korona plazmo.

where the oxidation is weaker in low-pressure plasma then in corona plasma. Appearance of new O–C=O bonds is noticeable on the surfaces of all plasma treated samples, where low-pressure plasma has a greater influence.
Both plasma systems used for this research are different; one operates at atmospheric and other at low pressure. That is why it is impossible to achieve the same treatment conditions. So it is logical to consider there will be different chemical changes for all three cotton fabrics. The selection of plasma system and its parameters depend on the next technological process which will be performed on the treated material.

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5 Sklep

Vzorce surove, beljene in beljene/merceriziranе tkanine smo obdelali z atmosfersko zračno korona plazmo in nizkotlačno plazmo vodne pare. Z metodo XPS smo preiskali površine vzorcev in tako določili njihove kemijske spremembe. Če primerjamo vzorce s čisto celulozo, opazimo, da je na površini surovega neobdelanega bombaža (S) večja koncentracija vezi C in C–C/H–H in manjša koncentracija O, kar pripisujemo prisotnosti necelulozних snovi, kot so voski, proteini in pektin. Površini beljenega (B) in beljenega/merceriziranega (M) neobdelanega bombaža sta med seboj podobni in se od površine S bistveno razlikujeta v tem, da je površina teh vzorcev bolj oksidirana in s tem že bolj podobna čisti celulozi. Na vzorcih, ki so bili obdelani v obeh vrstah plazme, opazimo rast števila kisikovih atomov na površini vzorcev, kar je posledica oksidacije površine v plazmi. Prirastek števila kisikovih atomov je bolj opazen na korona obdelanih vzorcih (Sc, Bc in Mc), kar je lahko tudi posledica daljšega obdelovanja vzorcev v korona kot v nizkotlačni plazmi. Opazimo tudi, da je koncentracija kisika na Sc in Sp višja kot pri vzorcu B ali M. To pomeni, da se z uporabo plazemske tehnologije lahko izognemo določenemu tehnološkemu procesu predpriprave materiala za barvanje, saj plazemsko obdelan material navzema enako ali več barvila, kar smo v prejšnjih raziskavah s poskusi barvanja tudi dokazali.[11, 13, 14] Tudi površine beljenih in beljenih/merceriziranih bombažnih tkanin, obdelanih v korona in nizkotlačni plazmi (Bc, Bp, Mc, Mp), so bogatejše s kisikom in je oksidacija manjša v nizkotlačni plazmi kot pri uporabi korona plazme. Na površinah vzorcev, ki so bili obdelani v obeh vrstah plazme, nastanejo nove vezi O–C=O, ki pa jih je več po obdelavi z nizkotlačno plazmo kot s korona plazmo.
Ker sta bila uporabljena plazemska sistema za raziskavo popolnoma različna, prvi se izvaja pri atmosferskem, drugi pa pri nizkem tlaku, je nemogoče pri obeh sistemih ustvariti enake razmere za obdelavo. Logično je, da glede na to dosledno upoštevamo, da so kemijske spremembe na površinah vseh treh bombažev nastale v popolnoma različnih razmerah. Izbira plazme in njenih parametrov je navadno odvisno od nadaljnjega tehnološkega procesa, ki ga moramo na materialu še izvesti.

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7 Literatura

1. KRÄSSIG, H. A. *Cellulose: structure, accessibility and reactivity*, Gordon and Breach Publishers, Yverdon, 1993.
2. *Cellulosics dyeing*. Ed.: J. Shore. Alden Press, Oxford : Society of dyers and colourists, 1995.
3. VESEL, A., MOZETIČ, M. Surface functionalization of organic materials by weakly ionized highly dissociated oxygen plasma. *Journal of Physics: conference series*, 2009, vol. 162 (012015).
4. VESEL, A., MOZETIČ, M., STRNAD, S., STANA-KLEINSCHEK, K., HAUPTMAN, N., PERŠIN, Z. Plasma modification of viscose textile. *Vacuum*, 2010, vol. 87 (1), p. 79–82.
5. NAVANEETHA PANDIYARAJ, K., SELVARAJAN, V. Non-thermal plasma treatment for hydrophilicity improvement of gray cotton fabrics. *Journal of Materials Processing Technology*, 2008, vol. 199 (1–3), p. 130–139.
6. McCORD, M. G., HWANG, Y. J., QIU, Y., HUGHES, L. K., BOURHAM, M. A. Surface analysis of cotton fabrics fluorinated in RF plasma. *Journal of Applied Polymer Science*, 2003, vol. 88 (8), p. 2038–2047.
7. TSAFACK, M. J., LEVALOIS-GRÜTZMACHER, J. Towards multifunctional surfaces using the plasma-induced graft-polymerization (PIGP) process: Flame and waterproof cotton textiles. *Surface and Coatings Technology,* 2007, vol. 201 (12), p. 5789–5795.
8. NAVARRO, A., BAUTISTA, L. Surface modification and characterization in cotton fabric bleaching. *Proceedings of 5th World Textile conference AUTEX 2005, Portorož, Slovenija,* 2005, p. 188–194.
9. TSAFACK, M. J., LEVALOIS-GRÜTZMACHER, J. Flame retardancy of cotton textiles by plasma-induced graft-polymerization (PIGP). *Surface and coatings technology*, 2006, vol. 201, (6), p. 2599–2610.
10. GORJANC, M., MOZETIČ, M., GORENŠEK, M. Priprava bombažne tkanine z nizkotlačno plazmo za boljšo adhezijo nanosrebra = Low-pressure plasma for pretreatment of cotton fabric for better adhesion of nanosilver. *Tekstilec*, 2009, vol. 52 (10–12), p. 263–269.
11. GORJANC, M., MOZETIČ, M., BUKOŠEK, V., GORENŠEK, M. Impact of low-pressure plasma on dyeability of cotton. V *4th International Textile, Clothing & Design Conference Magic world of textiles : book of proceedings*. Ed.: Dragčević, Z. Zagreb : Faculty of Textile Technology, University of Zagreb, 2008, p. 359–363.
12. GORJANC, M., JOVANČIĆ, P., BUKOŠEK, V., GORENŠEK, M. Study of adsorption of nano silver on cotton pretreated with plasma. V *Proceedings of the 9th Autex Conference*. Izmir : Ege University, Engineering Faculty, Department of Textile Engineering, 2009, p. 1029–1032.

13. GORJANC, M., MOZETIČ, M., JAZBEC, K., GORENŠEK, M. Influence of ICRF water vapour plasma on dyeability and UPF of cotton fabrics. V *41st International Symposium on Novelties in Textiles and 5th International Symposium on Novelties in Graphics and 45th International Congress IFKT,* Ljubljana, Slovenia, *Symposium proceedings*. Ljubljana : Faculty of Natural Sciences and Engineering, Department of Textiles, 2010, p. 351–356.
14. GORJANC, M., BUKOŠEK, V., GORENŠEK, M., VESEL, A. The influence of water vapor plasma treatment on specific properties of bleached and mercerized cotton fabric. *Textile research journal*, 2010, vol. 80 (6), p. 557–567.
15. TEMMERMAN, E., LEYS, C. Surface modification of cotton yarn with a DC glow discharge in ambient air. *Surface and coatings technology*, 2005, vol. 200 (1–4), 686–689.
16. SHAHIDI, S., GHORANNEVISS, M., MOAZZENCHI, B., ANVARI, A., RASHIDI, A. Aluminum coatings on cotton fabrics with low temperature plasma of argon and oxygen. *Surface and Coatings Technology*, 2007, vol. 201 (9–11), p. 5646–5650.
17. VANDER WIELEN, L. C., OSTENSON, M., GATENHOLM, P., RAGAUSKAS, A. J. Surface modification of cellulosic fibers using dielectric-barrier discharge. *Carbohydrate polymers*, 2006, vol. 65 (2), p. 179–184.
18. SUN, D., STYLIOS, G. K. Fabric surface properties affected by low temperature plasma treatment. *Journal of materials processing technology*, 2006, vol. 173 (2), p. 172–177.
19. BRIGGS, D., GRANT, J. T. *Surface analysis by Auger and X-ray Photoelectron Spectroscopy*. IMP & Surface spectra, Trowbridge, 2003.
20. BRIGGS, D. *Surface analysis of polymers by XPS and static SIMS*, Cambridge University Press, Cambridge, 2005.
21. VESEL, A. XPS study of surface modification of different polymer materials by oxygen plasma treatment = XPS preiskave modifikacije površine različnih polimerov s kisikovo plazmo. *Inf. MIDEM*, 2009, vol. 38 (4), p. 257–265.
22. GORENŠEK, M., GORJANC, M., BUKOŠEK, V., KOVAČ, J., JOVANČIĆ, P., MIHAILOVIĆ, D. Functionalization of PET fabrics by corona and nano silver. *Textile Research Journal*, 2010, vol. 80 (3), p. 253–262.
23. KOVAČ, J., ZALAR, A. Zmogljivosti rentgenskega fotoelektronskega spektrometra (XPS) na Institutu Jožef Stefan. *Vakuumis*t, 2005, vol. 25 (3), p. 19–24.
24. MOULDER, J. F., STICKLE, W. F., SOBOL, P. E., BOMBEN, K. D. *Handbook of X-Ray Photoelectron Spectroscopy*. Eden Prairie, Minnesota, USA : Physical Electronics Inc., 1995.
25. JOHANSSON, L.S. Monitoring fibre surfaces with XPS in papermaking processes. *Microchimica Acta*, 2002, vol. 138 (3–4), p. 217–223.
26. JOHANSSON, L. S., CAMPBELL, J. M., STENIUS, P., PERE, J., BUCHERT, T. Surface characterization of cellulosic materi-

als with XPS. *Abstracts of papers of the American Chemical Society*, 2001, vol. 221 (1), p. U180–U180.

27. FRAS, L., JOHANSSON, L. S., STENIUS, P., LAINE, J., STANA-KLEINSCHEK, K., RIBITSCH, V. Analysis of the oxidation of cellulose fibres by titration and XPS. *Colloids and Surfaces A: Physiocochem. Eng. Aspects*, 2005, vol. 206 (1–3), p. 101–108.
28. FREIRE, C. S. R., SILVESTRE, A. J. D., NETO, C. P., GANDINI, A., FARDIM, P., HOLMBOM, B. Surface characterization by XPS, contact angle measurements and ToF-SIMS of cellulose fibers partially esterified with fatty acids, *Journal of Colloid and Interface Science,* 2006, vol. 301 (1), p. 205–209.