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# WATER-VAPOUR PLASMA TREATMENT OF COTTON AND POLYESTER FIBRES

## OBDELAVA BOMBAŽNIH IN POLIESTRSKIH VLAKEN S PLAZMO VODNE PARE

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This study deals with the treatment of cotton and polyester fibres with a low-pressure, inductively coupled RF plasma, in which the water vapour from the fibres was used as a plasma-forming gas. Cotton, which is a hydrophilic, natural, cellulose fibre and polyester, which is a hydrophobic, synthetic, polyethylene terephthalate fibre, were used. Plasma characteristics during the treatment were investigated using optical emission spectroscopy (OES). The morphological and chemical changes in the fibre surfaces induced by plasma treatment were analysed using atomic force microscopy (AFM), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The optical emission spectra showed the presence of OH and H radicals at the beginning of the plasma treatment, whereas a CO Angstrom band appeared in the spectra recorded during the plasma treatment of both fibres. The cotton fibre roughness showed a three-fold increase after the plasma treatment that increased the surface area by approximately 8 %. The changes in the polyester fibre roughness were much less distinct and the surface area increased by approximately 3 %. The plasma treatment induced an increase in the O/C atomic ratio by approximately 43 % for cotton and 56 % for polyester fibres. The etching action of the water-vapour plasma was thus found to be more effective on the surface of cotton fibres than on polyester fibres. However, the water content of polyester fibres was sufficiently high to cause an oxidation of the fibre surface that was even higher than the oxidation of cotton.

Keywords: water-vapour plasma, effectiveness of treatment, cotton, polyester, water content, morphological and chemical changes

Raziskava vključuje obdelavo bombažnih in poliestrskih vlaken z nizkotlačno induktivno sklopljeno RF-plazmo vodne pare. Izvir vodne pare kot delovnega plina so bila vlakna bombaža, predstavnika hidrofilnih naravnih celuloznih vlaken, in vlakna poliestra, predstavnika hidrofobnih sintetičnih polietilenteraftalnih vlaken. Lastnosti plazme med obdelavo tekstilnih vzorcev so bile preiskane z optično emisijsko spektroskopijo (OES). Morfološke in kemijske spremembe površin plazemsko obdelanih vlaken so bile analizirane z mikroskopijo na atomsko silo (AFM), z vrstično elektronsko mikroskopijo (SEM) in rentgensko fotoelektronsko spektroskopijo (XPS). Optični emisijski spektri so na začetku obdelave s plazmo pokazali prisotnost OH in H radikalov. Med plazemsko obdelavo obeh vrst vlaken so bili v optičnih emisijskih spektrih opazni tudi trakovi, ki izvirajo iz prehodov radikalov CO. Po obdelavi s plazmo se je hrapavost površine bombažnega vlakna trikrat povečala, kar je vplivalo na povečanje specifične površine za približno 8 %. Spremembe v hrapavosti so bile pri poliestrskem vlaknu manj izrazite, specifična površina vlaken se je povečala za približno 3 %. Po obdelavi s plazmo se je na površini obeh vrst vlaken povečalo razmerje O/C, in sicer za 43 % pri bombažu in za 56 % pri poliestru. Glede na vsebnost vode v tekstilnih vzorcih je imela obdelava s plazmo vodne pare večji učinek jedkanja na bombažnih kot na poliestrskih vlaknih. Kljub temu je poliester vseboval dovolj vodne pare, da se je površina vlaken v plazmi oksidirala. Oksidacija na poliestru je bila celo večja kot na bombažu.

Ključne besede: plazma vodne pare, učinkovitost obdelave, bombaž, poliester, vsebnost vode, morfološke in kemijske spremembe

## 1 INTRODUCTION

Non-equilibrium gaseous plasma is a unique technology for treating the surfaces of fibrous polymers without affecting their bulk properties.[1–9] Accordingly, plasma systems using different power sources, pressures, electrode configurations and gasses have been used to generate plasma discharges and treat polymers.[10–20] Oxygen-containing plasma increases the specific surface area and surface energy of polymers, which results in an incorporation of oxygen-containing groups, such as C–O, O–C=O and C=O.[21–26] Plasma discharges in water vapour can potentially be used in a wide range of applications.[27–32] Water-vapour plasma is superior to the other plasma-forming gasses because of its unique properties, i.e., an extremely high enthalpy, environmentally safe conditions, a relatively low cost and an endless amount of plasma-forming gas.[33] Water-vapour plasma generates a high concentration of OH radicals that can further dissociate to H and O radicals,[34–36] although the probability of a dissociation of OH radicals is lower than that of a dissociation of water molecules (some of the OH radicals remain undissociated).[36] The first effect of a plasma treatment is the functionalization of the polymer surface, which is followed by etching reactions. These reactions are initiated by an H-atom abstraction and formation of a free radical.[35,37–40]

Cotton and polyester are the two most important and widely used polymers in the textile industry. They differ from each other in their chemical and morphological structures, and the amounts of water content. There are several publications dealing with the influence of diffe-

rent plasma discharges on the surface properties of cotton or polyester, but these two polymers were rarely investigated together under the same plasma parameters. The aim of this study was to investigate the surface changes of cotton and polyester after a treatment with water-vapour plasma under the same plasma parameters. The water vapour from the fibres was used as a plasma-forming gas. The low-pressure plasma was chosen as an environmentally friendly (pre)treatment of the textiles, water vapour was chosen as an environmentally safe and cheap plasma-forming gas that is already present in the fibres, and the same plasma parameters were chosen to investigate the surface changes occurring on the two different yet most commonly used polymers. Additionally, plasma treatment was observed using OES, where the optical spectra were recorded during the treatment of textiles. The changes to the fibre surfaces were investigated using SEM, AFM and XPS analyses.

## 2 EXPERIMENTAL WORK

### *2.1 Materials and methods*

Scoured, bleached and mercerised cotton woven fabric (119 g/m$^2$) made by Tekstina, d. d., Ajdovščina, and washed polyester woven fabric (67 g/m$^2$) made by Velana, d. d., Ljubljana, were used in the study.

Low-pressure, inductively coupled, radiofrequency (RF) plasma was used for the treatment. Our RF reactor scheme was previously presented in detail.[27] The plasma was created using a fixed frequency of 27.12 MHz, an output power of approximately 5 kW, a pressure of 20 Pa and a current of 0.4 A. Water vapour was used as a working gas. The fabric was the source of the water vapour. The fabric samples were treated for 30 s.

### *2.2 Analyses and measurements*

The water content of the fabric samples was determined according to the standard SIST ISO 6741-1:1996.

The plasma treatments were observed using optical emission spectrometry. An Avantes AvaSpec-3648 optical spectrometer with a 3648-pixel CCD detector array and a 75 cm focal length was used. This spectrometer records the optical emission spectra in the wavelength range of 200–1100 nm with a resolution of 0.5 nm.

The sample morphology was evaluated using a JEOL JSM 6060 LV scanning electron microscope. The samples were coated with a thin layer of gold before observation.

The sample surface topography was evaluated using an atomic force microscope (AFM/MFM – Veeco Dimension 3100) in the contact mode. Surface scans of 1 μm$^2$ square areas were performed at 22 °C in atmosphere for different sample positions using a scanning rate of 1.51 Hz. Images with a resolution of 256 × 256 lines were obtained using the Nanoscope software with a Flatten filter. From the AFM analyses, the mean roughness ($R_a$; the arithmetic average of the deviation from the centre plane), root-mean-square roughness ($R_{ms}$; the standard deviation of the *Z*-value within a given area) and surface area (*SA*; a three-dimensional given region) were calculated as the mean values of 10 AFM scans of different sample regions. The standard error of the mean was calculated to perform statistical analyses.

The sample-surface chemical compositions were analysed with X-ray photoelectron spectroscopy using a PHI-TFA XPS spectrometer (Physical Electronics Inc). The analysed areas had a diameter of 0.4 mm and a depth of approximately 3–5 nm. The sample surfaces were excited with the X-ray radiation from a monochromatic Al $K_\alpha$ source at a photon energy of 1486.7 eV. The sample-surface chemical compositions were quantified on the basis of the XPS peak intensities measured for two different spots on the sample using the MultiPak v7.3.1 software from Physical Electronics that was supplied with the spectrophotometer.

## 3 RESULTS AND DISCUSSION

Inductively coupled RF plasma excited at the ultimate pressure emitted the spectra shown in **Figure 1**. As water remained in the samples, the residual atmosphere was mostly water vapour. Therefore, hydrogen emission lines were the main lines that were visible in the optical emission spectra recorded at the beginning of the treatment (**Figure 1**).

Hydrogen is a good emitter of radiation, which is why the intensities of the Balmer series emission lines are so high. Water molecules dissociate into the hydrogen and oxygen atoms, but in the OES spectra of the inductively coupled plasma at the ultimate pressure, the oxygen lines are not present, whereas the excitation energy of oxygen atoms is much higher than the excitation energy of hydrogen atoms. Nitrogen emission bands are

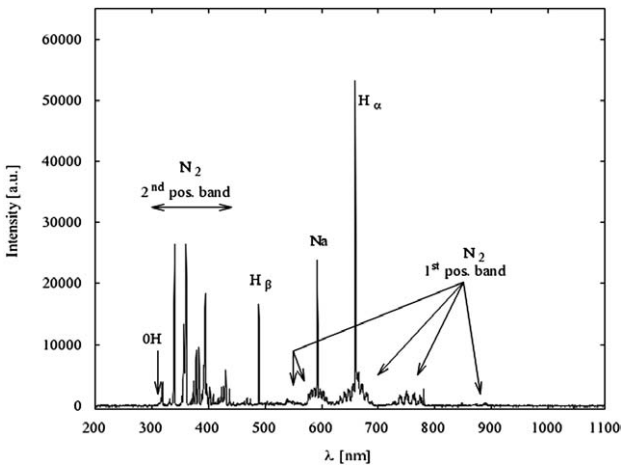


**Figure 1:** OES spectra of the plasma, generated at the ultimate pressure before etching

**Slika 1:** OES-spektri plazme, ustvarjene pri končnem tlaku pred jedkanjem

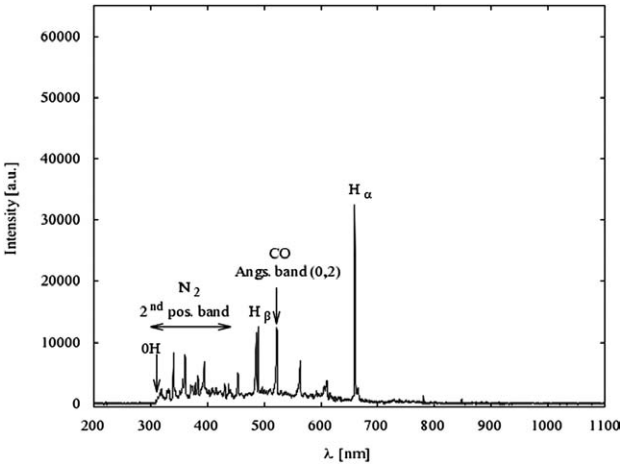


**Figure 2:** OES spectra of the plasma during the etching of cotton
**Slika 2:** OES-spektri plazme med jedkanjem bombažnega vzorca

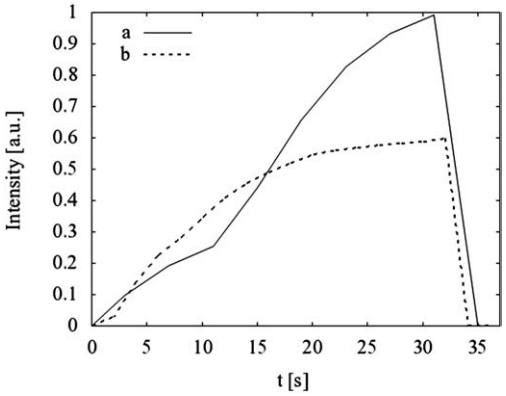


**Figure 4:** Time evolution of the CO emission peak (519 nm), normalised with the $H_\beta$ line during the treatment of: a) cotton and b) polyester
**Slika 4:** Časovni razvoj emisije vrha CO (519 nm), normaliziranega s $H_\beta$-črto, med obdelavo vzorca: a) bombaž, b) poliester

present in the spectra because of the small leakages in the system.

The optical spectra recorded during the treatment of the samples (**Figures 2** and **3**) revealed several CO Angstrom-band emission lines as well as a broad continuum between 400 nm and 700 nm that most likely resulted from a partial overlapping of the radiative transitions within CO molecules. The CO emission lines are attributed to the etching of the cotton and polyester samples. OES is a qualitative technique and, therefore, the density of particles cannot be determined from these measurements. However, CO is a poor emitter and from the high CO emission lines, we can conclude that the etching was efficient.

The time evolution of the etching was recorded after the CO Angstrom band (0, 2) emission peak was observed. To eliminate the effects of different spectrometer optical-fibre positions, the CO emission line (519 nm) was normalised with the $H_\beta$ line. The time evolution of the normalised CO emission line during the sample treatment is presented in **Figure 4**.

Better etching was achieved for the cotton samples when compared with the polyester samples. The etching rate for both samples increased monotonically with time. This etching increase was attributed to the thermal effects: the samples underwent heating during the treatment that increased the etching rate.

The etching effects of the water-vapour plasma treatment were further examined using SEM and AFM analyses. The SEM images of cotton and polyester fibres before and after the plasma treatment are presented in **Figure 5**. Under the used plasma parameters, the impurities on the cotton surface were cleaned and removed (**Figures 5a** and **c**). The same plasma parameters did not induce such changes to the polyester surface (**Figures 6a** and **c**). The plasma treatment did not cause any visible

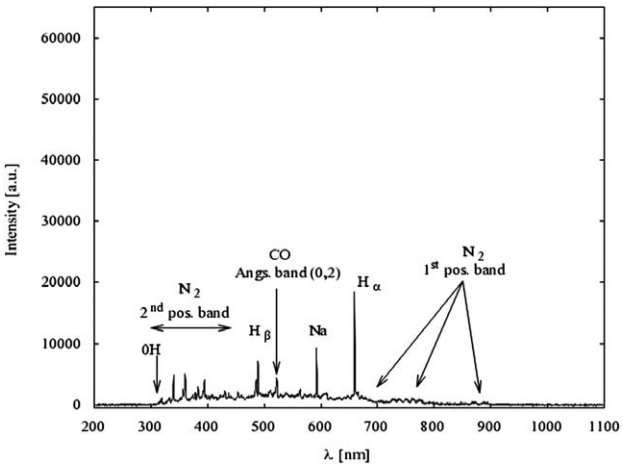


**Figure 3:** OES spectra of the plasma during the etching of polyester
**Slika 3:** OES-spektri plazme med jedkanjem poliestrskega vzorca

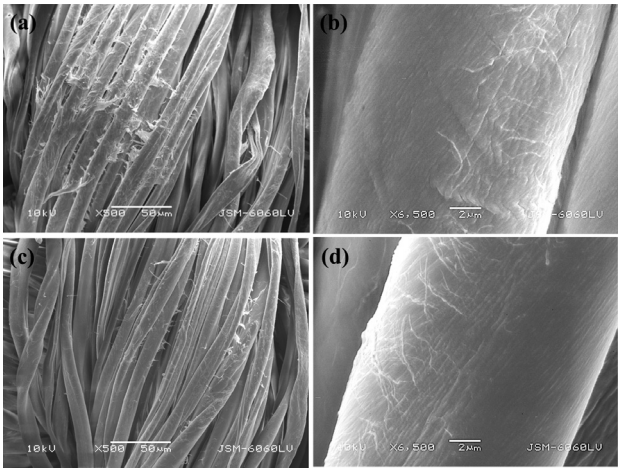


**Figure 5:** SEM images of: a), b) untreated cotton and c), d) plasma-treated cotton fibres; 500-times magnification was used for a) and c), 6500-times magnification for b) and d)
**Slika 5:** SEM-posnetki vlaken: a), b) neobdelanega bombaža ter c), d) s plazmo obdelanega bombaža; a) in c) 500-kratna povečava in b) in d) 6500-kratna povečava

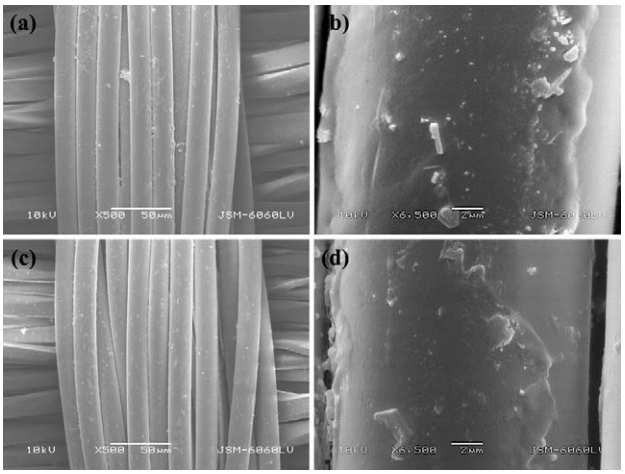


**Figure 6:** SEM images of: a), b) untreated polyester and c), d) plasma-treated polyester fibres; 500-times magnification was used for a) and c), 6500-times magnification for b) and d)
**Slika 6:** SEM-posnetki vlaken: a), b) neobdelanega poliestra ter c), d) s plazmo obdelanega poliestra; a) in c) 500-kratna povečava in b) in d) 6500-kratna povečava

morphological surface changes on cotton (**Figures 5b** and **d**) or on polyester fibres (**Figures 6b** and **d**), indicating that the bulk properties of both types of fibres remained unchanged.

AFM analyses showed the changes in the nanotopography that were induced by the water-vapour plasma treatment of both samples (**Figure 7**).

The quantitative evaluation of the nanotopography changes is presented in **Figure 8** in terms of $R_a$ and *SA*. As the calculated $R_{ms}$ values had the same trend as the $R_a$ values, they are not presented in the paper. The plasma treatment produced a three-fold $R_a$ increase in the cotton fibres, but did not cause significant changes in the polyester fibres (**Figure 8a**). The calculated *SA* values obtained after the plasma treatment were also higher for cotton than for polyester fibres (**Figure 8b**). For cotton and polyester, the *SA* values increased by approximately 8 % and 3 %, respectively. These results are in agreement with the obtained OES results. A higher etching effectiveness of the water-vapour plasma during the cotton treatment was caused by a different water content of the sample, i.e., 6.9 % for cotton and 0.5 % for polyester. A higher fibre water content leads to a higher level of reactive plasma species in the discharge, which contributes to an enhanced etching effect.

The XPS analyses (**Table 1**) suggest that the oxidation of plasma-treated cotton and polyester is not dependant on their water contents. After a plasma treatment, the atomic concentration of carbon (C1s, 285 eV) decreased and the atomic concentration of oxygen (O1s, 533 eV) increased in both cases. The calculated

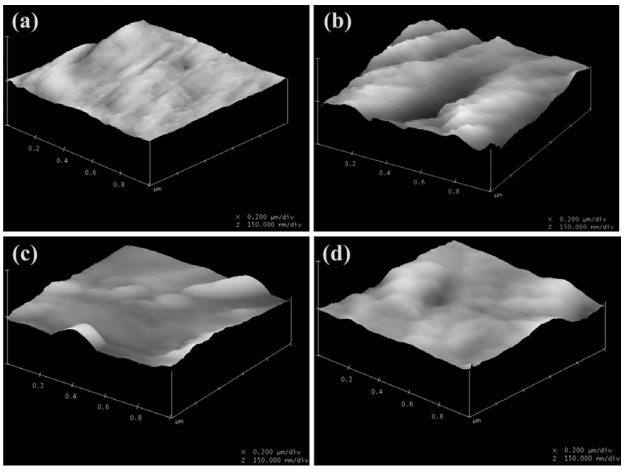


**Figure 7:** AFM scans of: a) untreated cotton, b) plasma-treated cotton, c) untreated polyester and d) plasma-treated polyester fibres
**Slika 7:** AFM-posnetki vlaken: a) neobdelanega bombaža, b) s plazmo obdelanega bombaža, c) neobdelanega poliestra in d) s plazmo obdelanega poliestra

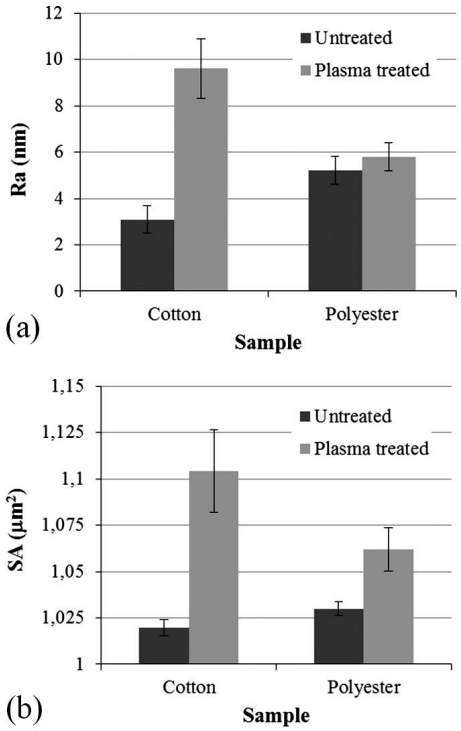


**Figure 8:** a) Mean roughness, $R_a$, and b) surface area, *SA*, of cotton and polyester samples
**Slika 8:** a) Srednja vrednost hrapavosti, $R_a$, in b) specifična površina, *SA*, bombažnih in poliestrskih vzorcev

**Table 1:** Elemental compositions of the fabric-sample surfaces determined with a XPS analysis
**Tabela 1:** Elementarna sestava površine vzorcev tkanin, dobljena z XPS-analizo

| Sample | Elemental composition in mole fractions (%) | | Atomic ratio O/C |
|---|---|---|---|
| | *x*(C) | *x*(O) | |
| Untreated cotton | 69.4 | 30.6 | 0.44 |
| Plasma treated cotton | 61.3 | 38.7 | 0.63 |
| Untreated polyester | 72.0 | 28.0 | 0.39 |
| Plasma treated polyester | 62.2 | 37.8 | 0.61 |

increases of the O/C atomic ratios were 43 % for cotton and 56 % for polyester. Despite a low water content of the polyester sample, the fibre oxidation during the plasma treatment was successful.

## 4 CONCLUSIONS

A low-pressure water-vapour plasma was used for treating cotton and polyester fabrics. The source of the water vapour was the fabric itself. The basis of this research was to investigate the surface changes in the two chemically and morphologically different textiles when the same plasma parameters were used. Before and after the plasma treatment the surface properties of cotton and polyester fibres were evaluated and compared using the XPS, SEM and AFM analyses. The plasma treatment of the textiles was observed using an OES analysis. The results showed that the etching rate increases with the treatment time for both types of polymers due to the sample heating during the plasma treatment. The etching effect of the low-pressure water-vapour plasma was more pronounced for the hydrophilic cotton fibres than for hydrophobic polyester fibres. The cleaning effect on the surface of the cotton fabric was observed, when the surface impurities were removed. Under the used plasma parameters, surface morphology of the fibres remained unchanged for both types of polymers, indicating that the bulk properties of the fibres remained undamaged. The water content of both types of polymers was sufficiently high to achieve a good oxidation of the fibre surfaces.

This preliminary research is very important for understanding what is happening during plasma treatment of cotton and polyester and how the same plasma parameters influence the surface changes made to these two most important and widely used polymers. Since cotton and polyester are also used together as a cotton/polyester blend, the results will help us with our further research focusing on the water-vapour plasma (pre)treatment of blends.

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