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Plasma effect on the chemical structure of cellulose fabric for modification of some functional properties

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Abstract

The present paper describes efficiency of the low-pressure plasma process for improving of deposition process on chemical-physical activated cellulose fabric surfaces. The surface of cellulose substrates was pre-treated with O_2 plasma followed by acrylic acid (AAc) as monomer in plasma polymerisation process with surface of cotton fabrics in continuous treatment process was used (O_2/AAc). AAc as monomer was applied on the fabric surface using PE-CVD process. Modifications of cellulose fibres were studied in respect to surface effects by means of SEM microscopy while the chemical effects of plasma treatment were studied using X-ray photoelectron spectroscopy. Results indicate that the surface of the cotton fibres was cleaner and smooth with micro-fibrils visible along to fibre axis after treatment with AAc, what is in correlation with results of hydrophilic properties of O_2/AAc treated samples. According to XPS spectra results, oxygen plasma is certainly changed the chemical surface structure of tested cotton fabrics whereby the deposition of the AAc nano-layer on the fibre surface was enabled.

Keywords: cellulose fabric, plasma treatment, surface modification, chemical structure, XPS, SEM

1. Introduction

Low-temperature plasma treatment is one of the most versatile techniques in material surface modification. It has been widely used in many applications of textile area for targeted surface modifications mainly include the improving of dyeability, printability wettability, soil resistance of natural textile materials such as cotton [1-5] and silk [6], flame, water- and oil-repellent [7], antimicrobial efficacy, antibacterial and antifungal properties [8,9], physical properties [10], etc. It should be noted that the multifunctional pronounced effect could be achieved if the plasma treatment combined with a variety of other agents, primarily a variety of organic and inorganic particles of micro- and nano-sizes.

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In recent years, all the more pervasive use of carboxylic acids that serve as precursors for some final processing application such as metal ions in achieving of antibacterial protection [11,12]. Carboxylic acids are polar compounds and in favorable conditions they can form hydrogen and covalent bonds with cellulose, creating active centers, and this is the reason why they are used in this study too. In addition, under certain conditions, plasma can encourage the polymerization of the surface layer and the formation of the polymer film, which can affect on the binding of metal ions as antimicrobial agents, for example [13-15]. Carboxylic acids are well known for their antibacterial properties, and combine it with some other means of achieving multifunctional effects that are of great importance for materials with both economic and environmental aspects. Plasma technology, when developed at a commercially viable level, has strong potential to offer in an attractive way achievement of new functionalities in textiles [16].

Paper present a part of the research related to the treatment of acrylic acid applied to the cotton as polymerizing agent in the low-pressure plasma system in a continuous treatment process whereby the dry sample was pre-treated with O_2 plasma. The focus is on the application of plasma and its possible dual role: on the one hand, it is the surface functionalization of the cellulose substrate, and on the other hand, plasma should serve as a medium for the final deposition of antimicrobial agents.

The effects of plasma treatments were analyzed by SEM microscopy and XPS spectroscopy to determine the fiber surface and chemical changes. For the testing the impact of plasma on hydrophilic properties of fabric surface, simple drops test was used in experiment.

2. Experimental

2.1. Materials, devices and reagents

Plain weave cotton fabric was industrially prepared (desized and scoured). In the Tab. 1, physical characteristics of the pre-treated and raw cotton fabrics are presented. Raw cotton fabrics were additionally pre-treated with sodium hydroxide to partially remove hydrophobic compounds from the fibre surfaces. Single-thread yarn of cotton fibres approximately equally fineness have been used in experiment.

Table 1. Characteristics of raw and pre-treated (scoured) cotton fabrics with NaOH used in experiment.

Sample	Weight of unit area (gm^{-2})	Thickness (mm)	Fabric density (threads. cm^{-1}) warp/weft	Linear yarn density (tex) warp/weft
Raw cotton fabric	119.4	0.32	23/19	29.4/25.0
Cotton fabric scoured with NaOH	130.6	0.35	25/20	29.4/25.0

Treatments were done using Low-pressure Plasma Systems type Tetra 30 PC LF-40kHz. Oxygen (purity 99.99%) as non-polymerizing gas was used for surface activation of the samples. Acrylic acid p.a. as a polymerizing vapour using *Plasma Enhanced Chemical Vapour Deposition process* (PE-CVD) was applied.

2.2. Plasma treatments

Plasma surface activation was made on woven fabrics with low-pressure (LP) - plasma TETRA 30 PC LF laboratory system. Plasma system consist of square vacuum chamber volume of 34 L with four trays arranged symmetrically inside the chamber between five planar electrodes located at a constant distance and capacitively coupled through a matching network to a 40 kHz LF-generator (1.0 kW capacity). The standard part of plasma system is standard rotary vane pump; suction power of approx.16 m^3/hour (from Leybold) with electromagnetic valve to prevent that oil vapor gets back into the vacuum chamber were used. Oxygen gas of high level of purity was applied in the process. All process parameters are fully PC controlled.

Surface Activation by Oxygen (O_2) Non-polymerizing Gas

Dried fabric samples (200 mm x 200 mm) were put on four symmetrically separated trays and subjected to pure oxygen plasma treatment for 5 minutes. During treatment flow rate was kept constant at 40 cm^3/min. Working pressure was fixed at 0.4 mbar. Operating power was kept constant at 300 W.

PE-CVD Process using Acrylic Acid (AAc) as Monomer

Plasma polymerization processes using vapours of acrylic acid as precursor (monomer) were carried out. The vapours of pure acrylic acid monomer were introduced into the vacuum chamber at a working pressure of 0.3 mbar and constant flow rate at 40 cm^3/min. An operating power was kept constant at 100 W. Treatment times of 10 and 30 minutes have been studied. At the end of low-pressure plasma treatments an air-flushing for 10 s followed by venting of the vacuum chamber for 60 s have been done for each experiment.

2.3. Methods

Scanning electron microscopy (SEM)

The morphological changes of untreated and acrylic acid treated cellulosic fabrics surfaces were investigated using JEOL 6060LV Scanning Electron Microscopy (SEM) technique. According to the technical specification of the equipment, the magnification range of the specimen is from 8x to 300 000x, voltage range from 0.5 kV to 30 kV, angle of inclination from -10º to 90º, with rotation 360°, which allows the study of the morphology of fibres in a wide range of possible changes, including a reliable determination of changes caused by plasma, for example. In all samples the surface was steamed using a mixture of 90% Au / Pd 10% to obtain a conductive fibres surface and allow its scanning. Testing of morphological changes for the purposes of this study was done with magnification at 2000x.

X-ray photoelectron spectroscopy (XPS)

The chemical surface composition of the plasma treated cellulose fabrics was investigated by X-ray Photoelectron Spectroscopy (XPS or ESCA, electron spectroscopy for chemical analysis). XPS is quantitative spectroscopic technique for determination of elementary chemical analysis, empirical formula of pure materials, chemical and electronic state of the elements that are found in material. Using this technique the chemical surface composition of the plasma treated cellulose fabrics was investigated. The measurements were performed with an PHI ESCA-5500 spectrometer under ultra high vacuum (UHV).

Results of analysis of samples are presented as a general XPS spectra and C1s high-resolution spectra and allow identification of ratio of O/C content per sample. XPS spectra obtained by irradiation of the cotton sample with X-ray beams, whereby at the same time, kinetic energy and the number of electrons at a distance up to 10 nm from the analyzed material surface are measured. XPS detect all elements with an atomic number (Z) of 3 or more. Hydrogen (Z=1) or helium (Z=2) could not be detected due to the lower atomic number. Typical XPS spectra are the sum of the number of detected electrons (Y-axis) relative to the binding energy of detected electrons (X-axis). Each element gives characteristic peaks at characteristic binding energies, through which directly identifies each element within or on the surface of such materials. With a graphical representation of the XPS spectra, relative ratios of certain chemical groups were presented in Tab. 1.

Hydrophilic properties using simple drop test

Drop test was used to measure the absorption time of water drops into textiles, according to standard AATCC 79-2000. This method is also used to analyse wicking properties of tested samples. If the water drop is absorbed on the textile material surface for less than 3 second, the material surface is very hydrophilic. Automatic pipette to ensure always-equal volume of water drops have been used in our tests. Additionally, the shape of water drop residue on the surface of materials was measured.

3. Results and discussion

3.1. Surface Analysis by SEM technique

Micro-morphological analysis of untreated and treated cotton fibres surface using SEM microscopy is presented in the Fig. 1.

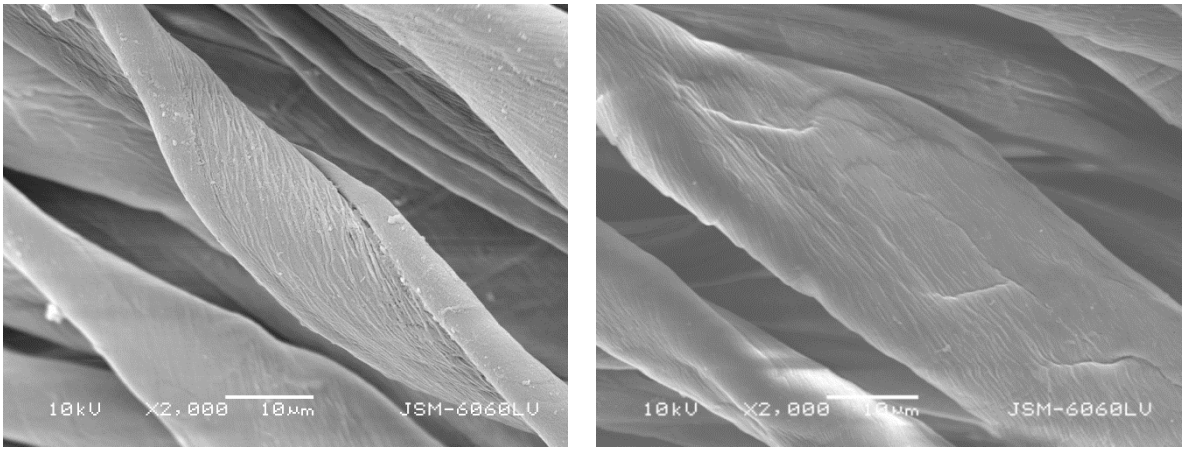

Fig. 1. SEM images of cotton fibres, magnification 2000x: (a) fibres of untreated cotton fabrics; (b) fibres after treatment with oxygen and acrylic acid in plasma process (O_2/AAc process).

In the Fig. 1(a) it is visible a common morphology of cotton fibers with microfibrils mainly oriented along the axis of fibres. In the Fig. 1(b) appearance of the cotton fibres treated with oxygen and acrylic acid (O_2/AAc) plasma process is presented. The fibre retains the microfibrilar structure but the surface was cleaner and smooth compared to the untreated cotton fibres.

Analysis of Surface Chemistry by XPS technique

XPS analysis was used to determinate the chemical composition in the surface layers of the untreated and plasma treated cotton fabrics. Results of XPS study are presented as general XPS spectra (Fig. 2.) and as C1s high-resolution spectra (Fig. 3.). In addition, to the graphical display the percentages of individual chemical elements (from ratio C/O atoms) were detected at the searched area (Tab. 2.).

Table 2. XPS data of general spectra for tested cotton sample

Sample	%C1s	%O1s	%O/C
I- untreated cotton fabric	73.91	26.09	0.35
II- cotton sample pre-treated with oxygen plasma for 5 min.	63.59	35.64	0.56
III- cotton sample treated with O_2/AAc process for 30 min.	76.07	22.76	0.30

According to XPS data it is certain that the oxygen plasma generate more polar groups on the fiber surfaces, which was confirmed with decreased of C1s content while the content of O1s was increased. The O/C ratio on the surface of the oxygen plasma activated fabric was increased 0.21 compared to untreated one. It mean that a large number of oxygen polar functional groups were introduced onto the cotton fabrics surface when treated with oxygen low-pressure plasma. Contrary, the sample treated with acrylic acid after activation using oxygen plasma (sample III) O/C ratio on the surface of the treated cotton sample decreased 0.26 compared to the activated sample with

oxygen plasma. Such results are confirmed the forming the polymer nano-layer of applied acrylic acid in the surface layer of the cotton fabrics using PE-CVD process.

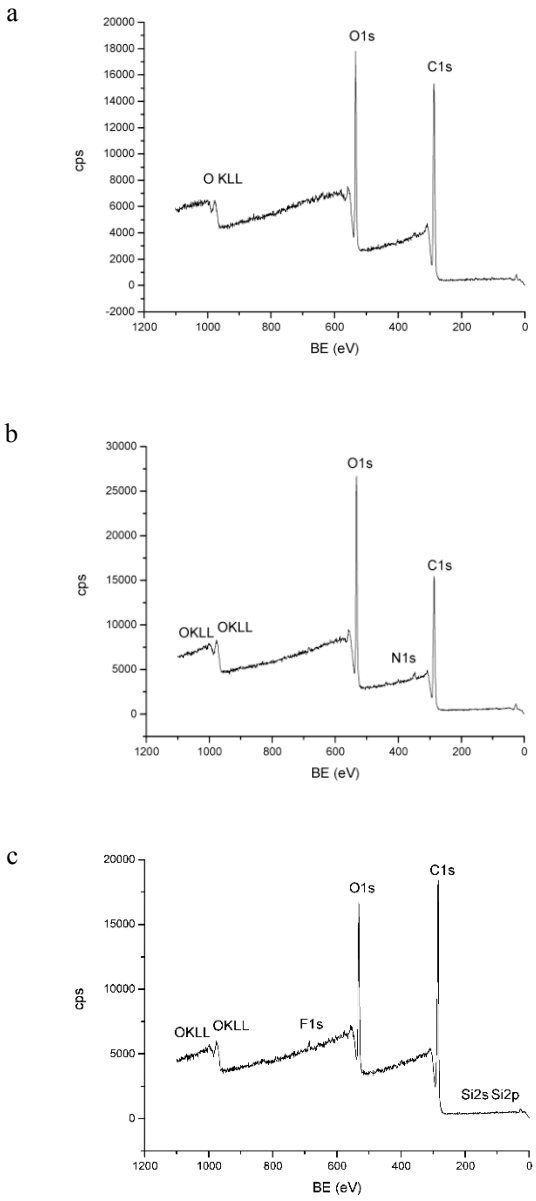

Fig. 2. Graphical display of general spectra: (a) cotton untreated; (b) cotton treated with O_2 plasma, (c) cotton treated with O_2/AAc process

In order to find out which functional groups were generated in the surface layer after plasma treatments, deconvolution analysis of C1s spectrum was performed. In the Fig. 3. the C1s high-resolution spectra of samples treated with oxygen plasma are presented. In relation to the untreated sample with the visible general curve (red curve), four individual curves with its corresponding peaks were shown. Each peak corresponds to the energies of the bonds between carbon atoms and oxygen C-C/C-H bond at 285.0 eV, C-O bond at 286.6 eV, O-C=O, C=O bond

at 288.1 eV and O-C=O bond at 289.5 eV. With a graphical representation of the XPS spectra, the percentages of the chemical bonds, are shown in Tab. 3.

Table 3. XPS data of high resolution C1s spectra for tested cotton sample

Sample	%C-C/C-H	%C-O	%C=O/O-C-O	%O-C=O
I- untreated cotton fabric	40.9	38.4	13.8	6.9
II- cotton sample pre-treated with O_2 plasma for 5 min.	22.6	39.5	26.6	11.3
III- cotton sample pretreated with O_2/AAc process for 30 min.	26.0	58.8	0.3	15.0

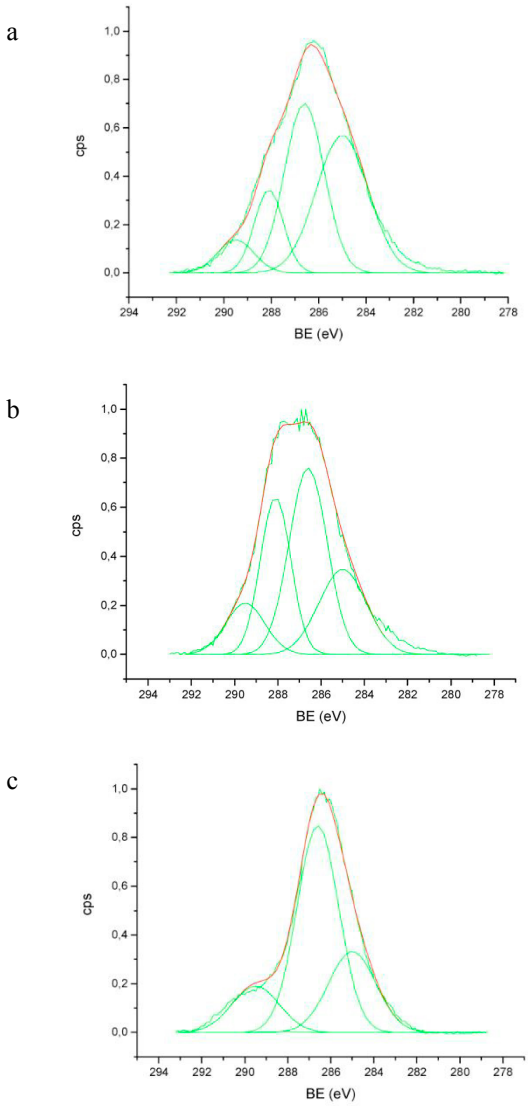

Fig. 3. Graphical display of C1s high - resolution spectra: (a) cotton untreated; (b) cotton treated with O_2 plasma, (c) cotton treated with O_2/AAc process

Compared to the C1peak, the intensity of the C2, C3 and C4 peaks was increased after oxygen plasma treatment. The measurement of oxygen content, with respect to the carbon content, confirmed this assumption (Tab. 3.). From the content variation of each chemical components presented in Tab. 3., the C-C/C-H and C=O/O-C-O components

decreased while the C-O and O-C=O components increased after O_2/AAc treatment. The presented results indicate on some carboxyls and carbonyls groups were generated onto the cotton surface, which play important role of hydrophilic effect decreased.

Hydrophilicity of the samples after acrylic acid treatment

As an indicator of hydrophilicity, time of absorption of water drops measured on the untreated (raw and scoured with NaOH) cotton sample, samples pre-treated with O_2 plasma and treated with O_2/AAc process for 10 and 30 min treatment time was determined. The obtained results are listed in Tab. 4.

Table 4. Results of the water drops absorption time of tested cotton fabrics treated with plasma

Sample - Treatment		*t* (s)
Uuntreated cotton sample (raw)		> 3600
O_2 plasma treated, 5 min		10.0
COTTON (raw)	O_2 + 10 min AAc process	8.2
	O_2 + 30 min AAc process	132
Untreated cotton sample (scoured with NaOH)		5.1
O_2 plasma treated, 5min		0.8
COTTON (scoured with NaOH)	O_2 + 10 min AAc process	5.6
	O_2 + 30 min AAc process	1

The obtained results (in Tab. 4.) indicate that the surface of the raw cotton fibres treated with acrylic acid as monomer in plasma vacuum became more hydrophobic, especially after prolonged treatment time of 30 min. Results of the scoured cotton samples indicate on the same assumptions but with less reliability of obtained results. However, it can be concluded that the results of hydrophilic properties are in correlation with results of SEM analysis where the surface of the tested cotton fibres cleaner and smooth, and XPS results which confirmed the forming of the polymer nano-layer of applied acrylic acid on the cotton fabric surface.

4. Conclusions

According to presented results, it could be concluded that the plasma is certainly acting on the surface of the cotton fabric, creating morphological changes in the form of surface etching. The surface becomes more accessible for better binding of various chemical agents.

Obtained results indicate that the cotton fibres surface becomes cleaner and smooth after treatment with AAc monomer, compared to the untreated cotton fibres. Such results are in correlation with results of the hydrophilic properties of cotton samples after the treatment using O_2/AAc process.

XPS analysis results confirmed such findings. According to XPS spectra, it is certain that the oxygen plasma generate more polar groups on the fibre surfaces, which was confirmed with decreased of C1s content while the content of O1s was increased. Oxygen plasma certainly changed the chemical surface structure of tested cotton whereby the deposition of the AAc nano-layer on the fibre surface was enabled.

Moreover, the presented results indicate on some carboxyl and carbonyl groups were generated on the cotton surface, which play important role of hydrophilic effect decreased.

Acknowledgements

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