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Abstract

The aim of this research work was to study the surface properties and sorption characteristics of differently treated regenerated cellulose fabrics. Surface modifications of viscose, modal and lyocell samples caused by using standard chemical pre-treatment procedures were compared to an alternative activation procedure by applying low pressure oxygen plasma treatment. The elemental chemical composition of the modified fabric surfaces was investigated using X-ray photoelectron spectroscopy (XPS), while hydrophilic/hydrophobic properties were evaluated by determining the water contact angles, as well as thoroughly analysed using Owens–Wendt surface energy (SFE) and surface polarity investigations.

Standard chemical and also plasma treatments changed the surface chemistry of cellulose. Bleaching and alkaline treatments increased the surface carboxylic acid content by approximately 4.8% while plasma treatment increased it by approximately 9.7%. As a consequence, higher hydrophilicity arises as proved by water contact angle decrease; i.e. 24% (61°) after standard chemical treatments and 70% (20°) after plasma treatment. Both chemical treatments increase the SFE and polar components, while the reduction of dispersive components was less pronounced. The oxygen activation treatment has the greatest influence on the SFEs of the samples as well as on polarity of the samples.

Keywords

Regenerated cellulose fabric, chemical pre-treatment, oxygen plasma, surface chemical composition, hydrophilicity, contact angle, Owens–Wendt surface energy, polarity

Introduction

In comparison to standard chemical pre-treatment processes such as bleaching and alkaline treatment, gas plasma treatments are more ecologically acceptable alternatives, and are also well-known as harmless surface modifications regarding mechanical and other important application properties of textiles.^{1,2} Plasma treatments are already widely used for surface modification of different polymer materials and nowadays their application is also found for modification of natural- and synthetic-based textile fabrics. Plasma treatment can effectively change the surface characteristics, such as wettability, soaking capacity, surface energy and adhesive properties of the material. Actually, plasma treatment can induce different effects depending on the experimental conditions: cleaning (removal of contaminants from the surface), etching (changes in surface roughness and morphology) and

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Treatment procedure	Cleaning	Bleaching	Alkaline treatment	
	0.1 w/v Na ₂ CO ₃	0.6 w/v H ₂ O ₂ (35%)	4 w/v NaOH	
	0.1 w/v Sandoclean PC	0.2 w/v Tanatex Geo	0.7 w/v Tanawet BC	
manufacturer	Sybron/Tanatex	TanatexChemicals	Sybron/Tanatex	
	(wetting agent, non-ionic)	(mineral stabiliser for H_2O_2)	(wetting agent, anionic)	
liquor ratio	1:40	1:30	1.40	
рН	10.9	10.7	12.8	
t (min)	30	30	I	
T (°C)	60	98	10	
Samples notations	CV, CMD, CLY	CV _b , CMD _b , CLY _b	CV _a , CMD _a , CLY _a	

Table 1. Conditions for chemical pre-treatment procedures and corresponding sample notation

functionalisation (formation of new functional groups at the surface). Significant changes of the reactivity and the surface properties of cellulose materials that occur during plasma treatment thus give the potential for advantageous applications.³ Therefore, plasma treatment can be an alternative technique towards standard chemical pre-treatment processes that are normally used in textile practice for improving the sorption ability of cellulose fibres⁴ since plasma treatment can drastically improve textile hydrophilic/hydrophobic characteristics.^{5–11}

The distinction between hydrophilic/hydrophobic behaviour is, of course very important for the understanding of surface behaviour. Up to a decade ago, it was assumed that there was a single scale for evaluating the hydrophilicity using contact angle measurements. Dispersive and acid-base (i.e. polar) forces are present in all materials and contribute to the work of adhesion. Acid-base components have the potential for enhancement via surface modification, to increase interfacial interaction, thus producing adhesive bonds. Atomic force microscopy (AFM) is a tool not only to image the topography, but also provides valuable information regarding adhesion and surface density using force curves.^{12–14} SFE is considered to be a measure of interactive intermolecular forces between the surface and liquid phase. In order to quantitatively determine dispersive and polar components, several mathematical approaches are known.^{15–29}

The aim of this research work was to evaluate the effects of the oxygen plasma treatment as an alternative activation procedure vis-à-vis to standard chemical pretreatment procedures regarding surface properties. The surface modifications in respect of surface chemical composition were estimated by X-ray photoelectron spectroscopy (XPS), while hydrophilic/hydrophobic characterisation was evaluated through water contact angle measurements. Using the two-component mathematical model, the overall surface energy, as well as its polar and disperse components, were obtained.

Experimental

Materials

Three different types of regenerated cellulose fabric were studied i.e. viscose (CV), modal (CMD), and lyocell (CLY), as produced by Lenzing Ag, Austria. The surface mass of the fabrics was 165 g/m^2 , yarn count of $22 \times 22 \text{ Ne}$, count of 375 warp threads/10 cm and 320 weft threads/10 cm.

Treatment procedures

Chemical pre-treatment procedures. The fabric samples were cleaned using non-ionic washing agent in order to obtain a well-defined reference substance (these samples are referred to, later in the text, as non-treated). Samples were then bleached or alkaline treated according to the data presented in Table 1. The cleaning and bleaching procedure were performed using an Ahiba–Turbomat apparatus, while performing an alkaline treatment the samples were immersed into cold sodium hydroxide solution. The alkaline treatment conditions as used were experimentally chosen as the most optimal ones and considering the fact that hot treatment, at even lower concentrations, would worsen the mechanical properties.

After alkaline treatment the samples were washed in hot water (60–70°C) first, and then in cold water (20°C), in order to remove the unreacted chemicals and/or their excess. Then the rinsing in dilute (37%) hydrochloric acid (2 g/L) was performed. After all pre-treatments, the fabric samples were rinsed with distilled water until the conductivity of the rinsing water was less than 3μ S/cm.

Oxygen plasma treatment. Vacuum dried (vacuum oven type VS-50SC Kambič; $T = 20^{\circ}C$, p = 100 mbar, t = 24 h) reference samples (CV, CMD and CLY)



Figure 1. Plasma system for treatment of fabric samples. I – oxygen, 2 – high-pressure valve, 3 – leak valve, 4 – vacuum gauge, 5 – RF coil, 6 – plasma chamber, 7 – air inlet valve, 8 – rotary pump, 9 – RF generator.

were treated in oxygen plasma according to the experimental system shown in Figure 1. The plasma chamber is an integral part of the vacuum system pumped with a two-stage oil rotary pump with a pumping speed of $40 \text{ m}^3/\text{h}$. The discharge chamber is a spherical cylinder with an inner diameter of 36 cm and a height of 30 cm. Plasma was created with an inductively coupled RF (radio frequency) generator, operating at a frequency of 27.12 MHz and output power of about 500 W. A water cooled copper coil was coupled with the RF generator via a matching network optimised for electrodeless coupling so the coil basically worked as an antenna. Due to the very large volume of the discharge chamber a high power was applied in order to assure the sustenance of uniform plasma in the entire volume. This high frequency allowed for good acceleration of free electrons in the oscillating electric field induced within the coil and thus excitation of gaseous particles by an electron impact. The frequency is large enough to practically prevent any acceleration of heavy charged particles and thus unwanted heating of gaseous molecules at elastic collisions with positively charged ions. Commercially available oxygen was leaked into the discharge chamber. The pressure was measured using an absolute vacuum gauge and was adjusted, during continuous pumping, by using a precise leak valve. During all experiments, the pressure was fixed at 75 Pa. Using these discharge parameters, a plasma with an ion density of the order of $1015 \,\mathrm{m}^{-3}$, an electron temperature of about 3 eV, and a density of neutral atoms of the order of 1021 m^{-3} was obtained. The samples were treated in oxygen plasma for 30 s, and denoted as CV_p, CMD_p and CLY_p. After plasma treatment the samples were exposed to air for a short time and then immediately mounted into XPS and tensiometer device for evaluating the modification effects.

Methods

Determination of elemental surface chemical composition and O/C ratio

High-resolution XPS was applied for the elemental surface chemical composition and determination of O/C ratios, which were calculated from the survey spectra. The relative amounts of carbons with different number of bonds to oxygen were determined from high-resolution carbon (C) 1 s spectra. The relative concentrations of carbon and oxygen as well as concentration of different carbon-oxygen functional groups respectively, were measured for each treatment, and then compared to the elemental surface chemical composition of the non-treated material.

The samples were analysed by a TFA XPS instrument from Physical Electronics. The base pressure in the XPS analysis chamber was about 6×10^{-10} mbar and the samples were excited with X-rays over a specific 400 µm area using monochromatic Al K $\alpha_{1,2}$ radiation at 1486.6 eV. The photoelectrons were detected by a hemispherical analyser, positioned at an angle of 45° with respect to the surface normal. Energy resolution was about 0.6 eV. Survey-scan spectra were measured at a pass energy of 187.85 eV, while for C 1 s individual high-resolution spectra were taken at a pass energy of 23.5 eV and a 0.1-eV energy step. An electron gun for surface neutralisation was used during the measurements, because the samples were insulators.

The measured spectra were analysed using MultiPak v7.3.1 software from Physical Electronics, which was supplied with the spectrometer. The high-resolution C 1s peaks were fitted with four symmetrical Gauss-Lorentz functions. A Shirley-type background subtraction was used. Both the relative peak positions and the relative peak widths (FWHM) were fixed in the curve fitting process.

Surface energy evaluation

The effect of chemical changes on the adhesive properties of the solid surface can be determined by SFE evaluation. The determination of the solid SFE is a complex procedure, and it cannot be measured directly. As such, the evaluation technique consisted of three stages i) characterisation of test liquids using Wilhelmy plate (platinum and PTFE) and Du-Nuoy ring methods, and ii) contact angle determination by bringing various standard liquids in contact with the solid surface, and iii) evaluating the SFE by using a mathematical model (e.g. Zisman, geometric mean, acid-base, etc.).

Characterisation of test liquids. Prior to contact angles determination, standard liquids were investigated in

order to determine their surface tensions (SFTs) and their disperse and polar components. Seven test liquids with different SFTs and different polar and disperse components were chosen: n-heptane, ethylene glycol, ethanol, chloroform, tetrahydrofuran, diodomethane, and water. The SFTs of the first six standard liquids were determined using the Wilhelmy plate method according to DIN 53 914 (application of the standard platinum plate: contact angle $\theta = 0^{\circ}$ for the majority of liquids), while the Du-Nuoy ring method according to DIN 53 993 was applied for water.

The disperse component of used test liquid was determined by measuring the contact angle between a standard poly(tetrafluoroethylene) (PTFE) plate and liquid. According to Good et al.,³⁰ PTFE is assumed to be capable only of dispersive interactions ($\gamma_{\rm S} = \gamma_{\rm S}^{\rm D} = 18.0 \text{ mJ/m}^2$ and $\gamma_{\rm S}^{\rm P} = 0 \text{ mJ/m}^2$). The polar component of the liquid can be then calculated by the difference as:

$$\gamma_1^p = \gamma_1 - \gamma_1^d \tag{1}$$

where γ_1 is the surface tension of the wetting liquid, γ_1^d is the dispersive surface tension component of the wetting liquid, γ_1^p is the polar surface tension component of the wetting liquid.

Contact angle determination. Contact angles between regenerated cellulose fabric samples and different liquids were determined using a capillary rise technique,³¹ applicable for porous materials. Application of the modified Washburn equation allows determining the $\cos\phi$ by measuring the wetting rate of test liquids. N-heptane was used as a liquid (for which the $\cos\phi = 1$), in order to determine the material constant.

The fabric samples were cut into rectangular pieces $(2 \times 5 \text{ cm})$ and hung up onto a sample holder in the Tensiometer Krüss K12 apparatus. The samples' weight was measured as a function of time during the adsorption of the liquid phase. The instrument gathered and displayed graphically the wetting rise curves (m^2/t) , as used to determine the contact angle using the modified Washburn equation. A more detailed description of the experimental procedure is given in previous work.¹⁷

Surface energy evaluation. Hydrophilic/hydrophobic properties of solid surfaces are described by contact angle measurement results (i.e. the hydrophilic $(\varphi < 90^{\circ})$ or hydrophobic $(\varphi > 90^{\circ})$) using water, while using various standard liquids, the samples' surface energy can be determined using one among several common models for evaluating. The commonly used and relatively simple mathematical model, i.e. the Owens–Wendt–Rabel and Kaeble (OW) approach,

 Table 2. Elemental surface chemical composition of differently treated viscose samples (CV) as deduced from XPS survey spectra

	Surface composition (atomic %)			
Sample treatment	С	0	O/C ratio	
Non-treated	57.2	42.2	0.73	
Bleached	60.9	37	0.60	
Alkaline treated	62.5	36.2	0.57	
Oxygen plasma treated	52.I	47.9	0.91	
Theoretical cellulose ³⁴	54.5	45.5	0.83	

was used to evaluate the surface energy of regenerated cellulose samples depending on the treatment used. The polar and dispersive components of surface energy were determined graphically by means of the linear function. The theoretical basis^{26,30–32} and more detailed experimental procedure is written elsewhere.^{17,33}

Evaluation of surface morphology

Scanning electron microscopy was used to see possible changes in the surface roughness and morphology of cellulose fabrics after plasma treatment. Scanning electron micrographs were obtained using a field emission microscope Karl Zeiss Supra 35 VP. A 1 kV accelerating voltage was used and a micrograph was taken at magnification of $20,000 \times$.

Results and discussion

Elemental surface chemical composition and O/C ratio

From the XPS survey spectra the elemental surface chemical composition and O/C ratios for viscose fabric samples (CV) were calculated and are presented in Table 2. The theoretical O/C ratio for pure cellulose is 5:6 or 0.83, while the relative amount of C–C type carbons for pure cellulose should be 0%.^{7,34} Here we should note that in practice small amounts of C–C carbons are always found,⁷ so the amount of C–C type carbons is never zero. In our case, the surface layer of the non-treated CV sample consists of 42.2 atomic % of oxygen and 57.2 atomic % of carbon, which gives an O/C ratio of 0.73. The measured value differs slightly from the theoretical one, due to the surface contamination with adventitious carbon as explained above.

Bleaching and alkaline treatment. The results in Table 2 show that the chemical procedures caused additional surface contamination, as after the bleaching, the carbon concentration increased by about 3.7 atomic

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Sample treatment	Carbon composition (atomic %)				
	C I (C–C) 284.8 eV	C2 (C–O) 286.3 eV	C3 (O-C-O, C = O) 287.5 eV	C4 (O = C-O) 288.9 eV	
Non-treated	16.8	66.9	16.3	0.0	
Bleached	28.7	56.0	10.5	4.8	
Alkaline treated	29.5	54.3	11.5	4.7	
Oxygen plasma treated	12.5	58.5	19.3	9.7	
Theoretical cellulose ³⁴	0	83	17	0	

Table 3. Relative amounts of different carbon-oxygen functional groups determined from high-resolution C I s XPS spectra for viscose (CV) samples as a function of applied treatment procedure

Table 4. Contact angles on the PTFE and surface tensions of test liquids measured at 20°C

		Su	Surface tension (mN/m)		
Test liquid	$arphi_{PTFE}$ (°)	γι	γ^d_1	γ^p_1	
Non-polar					
Chloroform (99%; Kemika Croatia)	53.0 ± 0.0	27.0 ± 0.0	25.9 ± 0.0	1.1 ± 0.0	
Literature data ²⁰		27.1	23.3	3.8	
Diodomethane (99%; Sigma-Aldrich, Germany)	$\textbf{79.0} \pm \textbf{0.0}$	50.8 ± 0.0	50.8 ± 0.0	0.0 ± 0.0	
Literature data ³⁶		50.8	50.8	0	
Polar					
Ethylene glycol (99,5%; Sigma-Aldrich, Germany)	94.9 ± 0.0	47.7 ± 0.0	26.4 ± 0.0	21.3 ± 0.0	
Literature data ³⁷		48.0	31.4	16.4	
Ethanol (99.8%; Merck KgaA, Germany)	45.3 ± 0.0	22.0 ± 0.0	19.7 ± 0.0	2.4 ± 0.0	
Literature data ³⁸		22.1	17.5	4.6	
Tetrahydrofuran (99.9%; Sigma-Aldrich, Germany)	85.0 ± 0.0	27.4 ± 0.0	12.3 ± 0.0	15.1 ± 0.0	
Literature data ³⁷		27.3	12.4	15.0	
Water (mili Q; 0.6–0.1 μScm ⁻¹)	112.1 ± 0.1	71.8 ± 0.3	27.8 ± 0.1	44.0 ± 0.1	
Literature data ³⁹		72.8	26.0	46.8	

% and after alkaline treatment by an additional 5.3 atomic %, which caused a decrease of the O/C ratios to 0.60 and 0.57, respectively. The increased amount of carbon may occur during drying of the samples in the air performed after chemical treatments, which could have introduced some carbon containing substances.

Oxygen plasma treatment. In the oxygen plasma treated sample, a decrease by about 5.1 atomic % of the carbon concentration occurred. The decrease of carbon concentration is related to surface cleaning (i.e. removal of adventitious carbon) that occurred during oxygen plasma treatment and to further oxidation of viscose fabrics due to interaction with an oxygen plasma. Owing to oxygen introduction, the O/C ratio of plasma treated samples increased to 0.91.

In order to analyse surface chemical changes in more detail, high-resolution spectra of C 1s peaks were recorded. From the curve fitting of high-resolution C 1s peaks the relative amounts of C-C and different carbon-oxygen species were determined and are presented in Table 3. The C1 s peak for the non-treated viscose sample consists of three sub-peaks C1, C2 and C3. The highest concentration is evident for the C2 peak (C-O bond) followed by the C3 peak (O-C-O, C = O bond), which is expected as all the carbon atoms in the cellulose unit are bound to at least one oxygen atom. The clearly pronounced C1 peak (C-C bond) is probably due to surface contaminants. This peak is remarkably decreased after oxygen plasma treatment due to the cleaning effects of oxygen plasma.



Figure 2. Wetting rise curves for differently treated viscose samples (CV) monitored during water uptake. CV, non-treated; CV_b , bleached; CV_a , alkaline treated; CV_p , oxygen plasma treated.

Bleaching and alkaline treatment. Both chemical treatments caused a significant increase (by 70%) of the concentration of functional groups associated with the C1 peak (C–C bond) and a significant decrease (by 16%) of the functional groups associated to the C2 and C3 peaks. The increase associated with the C1 peak may be due to several reasons: i) the non-treated sample contains some impurities (16.8 atomic % of C1) and both chemical treatments did not remove them, but rather exposed them more, ii) not sufficient rinsing with water after both chemical treatments were performed, and iii) the drying of the samples in the air could have introduced some C1 containing impurities. Since the samples were washed in warm and cold water, acetified, and rinsed with fresh distillate water (until the conductivity was less than $3 \mu S/cm$; the latter seems to be more likely.

The decrease of the C2 peak (C–O bond) and the C3 peak (O–C–O, C=O bonds) may be due to degradation (in the case of bleaching), or loss of the structure (in the case of alkaline treatment) ³⁵. The process of cellulose oxidation may occur as well during bleaching, which is evident from the appearance of the C4 peak (carboxylic group) in the amount of 4.8 atomic %. Similar surface chemical composition by C4 peak can also be observed after alkaline treatment.

Oxygen plasma treatment. After plasma treatment the C1 peak is decreased by about 26% in comparison to the non-treated samples. As already mentioned, the reason could be the removal of impurities from the sample surface. As expected, a decrease of the C2 peak is evident as well. The latter is associated with the formation

of free radicals. Since all carbon atoms in the cellulose are bound to at least one oxygen atom, the incorporation of new oxygen atoms from the plasma to the material can lead to ring opening and formation of free radicals. Reaction of the radicals with oxygen in plasma or in post-plasma reactions with atmospheric oxygen could explain the formation of oxygen containing functional groups other than those present in the non-treated sample. Such groups are, for example, carbonyls, ethers, esters, carboxyl and peroxides. Their existence could be deduced from the changes in the C3 and the C4 peak.

Plasma treatment had a much stronger influence on the surface chemical composition in comparison with both chemical processes, thus the amounts of the carbonyl groups (C3 peak) and the amounts of the carboxyl groups (C4 peak) were higher by about 70% and by as much as 100% respectively.

Surface tension of liquids

The standard test liquids for evaluating the SFE using the OW model were used. The measured SFT and calculated polar and dispersive components are presented in Table 4. The results were statistically processed and are in good accordance with the literature data for all the test liquids used.

Wetting rise curves

The results of wetting rise, monitored during water sorption, are presented in Figures 2–4. In Figure 2,



Figure 3. Wetting rise curves for differently treated modal samples (CMD) monitored during water uptake. CMD, non-treated; CMD_b, bleached; CMD_a, alkaline treated; CMD_o, oxygen plasma treated.



Figure 4. Wetting rise curves for differently treated lyocell samples (CLY) monitored during water uptake. CLY, non-treated; CLY_b, bleached; CLY_a, alkaline treated; CLY_p, oxygen plasma treated.

the wetting rise curves for viscose (CV), in Figure 3 for modal (CMD), and in Figure 4 for lyocell (CLY) samples, depending on treatment used, are shown. Each curve in the diagrams represents the average value of 10 parallel measurements.

As expected, the lowest wetting rise was observed by the non-treated samples. The plateau was observed after 100 s. Among non-treated samples, the highest amount of absorbed water was observed with CV, the lowest with CMD.

Bleaching. Bleaching increased the wetting rise, mostly with the CMD_b and CLY_b . The lyocell sample was able to absorb the same amount of water as viscose, while CMD_b absorbed the lowest. The mass of absorbed water did not change significantly after 30 s.

Alkaline treatment. Alkaline treated samples were able to absorb the final amount of water within 20 s. Within 30 s the CLY_a sample was able to absorb the highest amount, while with CV_a and CMD_a the amount was the same as for the bleached samples.

Oxygen plasma treatment. Among treatments, plasma had the biggest influence on all the used samples. The highest wetting rise resulted with CMD_p , while CV_p and CLY_p sorbed the water with the same speed. Comparing all three plasma activated samples, no significant difference in water uptake amount could be observed after 30 s.

In Table 5, the amount of water uptake in equilibrium is presented for all used samples depending on the treatment used.

Among chemical treatments, the alkaline process had a bigger influence. The wetting rise increased by

Table 5. Absorbed amount of water in equilibrium for differently treated regenerated cellulose samples. CV, viscose; CMD, modal; CLY, lyocell

		Amount of water uptake (g/g)					
Sample	Non- treated	Bleached	Alkaline treated	Oxygen plasma treated			
CV	0.7 ± 0.0	0.6 ± 0.0	0.7 ± 0.0	0.9 ± 0.0			
CMD	0.5 ± 0.1	0.6 ± 0.0	$\textbf{0.6}\pm\textbf{0.0}$	0.9 ± 0.0			
CLY	0.6 ± 0.0	0.7 ± 0.0	0.8 ± 0.0	0.9 ± 0.0			

up to 40%, while a smaller effect was evident with absorbed water amount (only up to 20%). More than 100% increase in water uptake rise resulted with plasma treated samples. Also, plasma treated samples absorbed from 45–70% more water compared to non-treated.

Applying chemical treatments, the differences among samples are more pronounced. Alkaline treated lyocell CLY_a samples absorbed the highest water amount (0.8 g). All other non-treated or chemically treated samples adsorbed in equilibriums between 0.5 g and 0.7 g of water. The differences among the analysed samples are a consequence of their different structural parameters (i.e. average molecular mass, crystallinity index, degree of polymerisation, etc.). The structure parameters were those obviously more affected by chemical procedures; this was investigated in detail in previous work.^{35,40} Plasma treatment is known to be a surface modification technique, resulting in changes up to a few nanometres.

Water contact angles

On the basis of the wetting rise curves $(m^2 = f(t))$, monitored during water uptake, the water contact angles were calculated and are presented in Figure 5. The results present an average value. 10–20 measurements were performed for each sample to obtain appropriate statistical significance (less than $\pm 2^\circ$). More detailed the results of the water contact angle and standard deviation are given in Table A1 (see Appendix).



Figure 5. Water contact angles of differently treated regenerated cellulose fabric samples. CV, viscose; CMD, modal; CLY, lyocell.

The highest water contact angle is observed with non-treated samples. Both chemical treatments performed resulted in increased hydrophilicity, most significantly with the alkaline treated samples, as contact

Table 6. Overall, polar and dispersive components of the surface energies of differently treated regenerated cellulose fabricsamples. CV, viscose; CMD, modal; CLY, lyocell

Sample	SFE (mJ/m ²)	Polar components (mJ/m ²)	Dispersive components (mJ/m ²)
Non-treated			
CV	32 ± 5	19 ± 4	13 ± 4
CMD	25 ± 5	14±4	12 ± 3
CLY	30 ± 5	16 ± 4	14 ± 4
Bleached			
CVb	32 ± 5	18 ± 4	14 ± 4
CMD₅	28 ± 5	17 ± 4	11 ± 3
CLY _b	31 ± 5	19 ± 4	12 ± 3
Alkaline treat	ed		
CV_a	35 ± 6	26 ± 5	12 ± 3
CMD _a	34 ± 6	23 ± 5	11 ± 3
CLY _a	37 ± 6	26 ± 5	11 ± 3
Oxygen plasm	a treated		
CVp	$\textbf{46} \pm \textbf{7}$	$\textbf{29}\pm\textbf{5}$	17 ± 4
CMD _P	45 ± 6	33 ± 6	12 ± 3
CLYp	50 ± 7	37 ± 6	13 ± 3

angles decreased by 6 to 24%. The significant effect on the hydrophilicity of samples, however, had plasma treatment, as the water contact angles for all the samples were lowered by up to 76%.

Surface energies

Using the contact angle results, as obtained with different test liquids, the samples' SFE and their polar and disperse components were calculated according to the Owens-Wendt mathematical approach. The results were statistically processed and are presented in Table 6.

Non-treated samples have the lowest SFE and polar components, while possessing the highest part of the dispersive components.

Bleaching. Bleaching showed little effect, as slightly increased the SFE and polar components, while a decrease was observed in dispersive components. The oxidation process introduced new carboxylic groups, as evident by appearance of C4 peak (see Table 3). The latter resulted as an increase in sample polarity followed by water contact angle decrease (see Figure 5).

Alkaline treatment. Alkaline treatment showed a more pronounced effect. The SFE increased from 9–36%, while an even larger increase could be observed with polar components. Dispersive components decreased, but the reduction was less noticeable. Treatment using NaOH solution caused an increased 'reactivity'.



Figure 6. Regenerated cellulose sample polarity and water contact angle as a function of different treatments. CV, viscose; CMD, modal; CLY, lyocell.



Figure 7. Typical SEM images of a) non-treated and b) plasma treated viscose samples.

The reason could be explained by loosening the intrafibrilar amorphous region. The hydroxyl groups located in amorphous regions became more accessible (i.e. capable of intermolecular interactions with the probe liquid). The latter is supported by new peak appearance (i.e. C4 see Table 3) and a significant increase in polar components (see Table 6).

Oxygen plasma treatment. Plasma treated samples possess the highest SFE. A significant increase is observed with polar as well as with dispersive components, but the ratio of dispersive components contributing to the SFE decreased (i.e. 10-40%). An increase can be explained by two somewhat different phenomena: plasma treatment usually causes two parallel effects on the polymer surface. First, the changes in surface chemical composition that occur due to the formation of new functional groups (see Table 3) as well as due to activation of remaining hydroxyl groups occurring after breaking the hydrogen bond.³ Second, an increase of the surface area of the samples, caused by the etching process⁴¹ also has an influence on the hydrophilic character. The most pronounced effect of plasma treatment was, however, the huge increase in the polar components of SFE for all the samples.

The CMD sample, regardless of the treatments used, possesses the lowest values for SFE as well as for

both components. The cellulose molecules in modal fibres are densely packed and highly oriented. Besides that, as a result of the production process, they possess a different void system. The diameter and the volume of voids are smaller, but the area is larger and the voids are more densely distributed compared to CV and CLY. The voids for CMD were those that were the most affected by the chemical treatments, resulting in improved hydrophilicity.⁴²

Samples polarities

Polarities for all the three types of regenerated cellulose samples and respective water contact angles, as a function of different treatments, are presented in Figure 6.

The polarity by non-treated samples varied from 53 to 59%. After bleaching a slight increase in polarity was obtained. A bigger increase in polarity resulted after alkaline treatment, while the biggest influence had plasma treatment. The results from SFE polarity follow the tendency of the water contact angle values; i.e. after all used treatments the sample polarity increased while the water contact angle decreased. This is in agreement with Good's theory,³⁰ where the closer the solid polarity matches the liquid polarity, the more favourable the wetting will be (i.e. the lower the energy of wetting the solid with liquid).

Surface morphology

Finally, it is worth mentioning that etching of textiles and other polymers is often inhomogeneous, which causes increased surface roughness after prolonged treatment. In order to check any influence of plasma treatment on the samples, scanning electron microscopy was applied. Figure 7a represents a typical SEM image of non-treated textile fabrics while a treated textile fabric is shown in Figure 7b.

Although the magnification is rather large, no important change in surface morphology is observed. This observation is somehow paradox since many authors^{41,43} reported increased surface roughness. In order to explain the discrepancy we have to stress that not all authors use plasma created with the same (or similar) discharges. Many authors use capacitively coupled RF discharges and place a sample on the RF plate. Capacitively coupled RF discharges are famous for the high voltage sheath that appears next to RF plates. Positively charged ions cannot follow oscillations in sheath voltage but they feel the effective averaged value. They enter the sheath and accelerate in the strong effective field so they bombard the surface of textiles with a large kinetic energy which is often of the order of 100 eV. Such energetic ions often cause damage on the textile surface which is observed as an increased roughness. Other authors including us use electrodeless discharges for sustaining gaseous plasma. In such a case the samples are kept at a floating potential. The difference between plasma potential (often called space potential) and floating potential in such plasma is only about 10 V. The ions thus do not accelerate much before reaching the sample surface so the surface modifications due to ion bombardment are much less important in electrodeless discharges than in capacitively coupled discharges.

Conclusions

The aim of the presented research was to characterise the surface properties of regenerated cellulose fabrics after modification by standard chemical processes that are often used in textile practice and by oxygen plasma treatments. The surface modifications were evaluated by studying elemental surface chemical composition with XPS, while hydrophilic improvements were investigated through water contact angle measurements as well as comprehensively determined by means of Owens–Wendt surface energy and polarity.

All applied treatments altered the surface chemical composition of all samples. Although the results obtained from chemically treated samples indicated an increase in carbon concentration and a decrease in O/C ratio, the samples became more hydrophilic. Plasma treatment had the most pronounced change as a result of two effects: it eliminated impurities from the sample surface and it additionally caused formation of new functional groups (carboxyl) by incorporation of oxygen atoms to the surface. Plasma treatment was therefore proved to be a very promising technique for surface modification of regenerated cellulose fabrics. The acquired knowledge about plasma treatment efficiency could therefore be foreseen as the future substitution for conventional pre-treatment processes. It is also known to be a fast and extremely gentle technique, and can significantly reduce the amount of chemicals required by the standard chemical processes, and thus the concentration of pollutants released into the environment. Additionally, it can be applied to the production of those innovative textile materials with properties that cannot be achieved via wet processing.

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Appendix

Water contact angles of differently treated regenerated cellulose fabric samples

Table AI.	Water co	ntact a	angles	of	differently	treated
regenerated	cellulose	fabric	sampl	es		

	Water contact angle (°)				
Sample	Non-treated	Bleached	Alkaline treated	Oxygen plasma treated	
CV	66 ± 1.8	070 ± 1.6	59 ± 1.3	16 ± 2.0	
CMD	83 ± 0.3	77 ± 1.54	63 ± 1.2	25 ± 2.0	
CLY	74 ± 1.0	73 ± 2.0	59 ± 1.8	18 ± 1.0	

CV, viscose; CMD, modal; CLY, lyocell.