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Improvement of Chitosan Adsorption onto Cellulosic Fabrics by Plasma Treatment

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Oxygen plasma treatment was applied in order to improve the adsorption of chitosan onto viscose fabric. Modification of the surface and adsorption of chitosan was monitored by determination of XPS spectra, determination of contact angles from rates of water imbibition, and conductometric titration. The plasma treatment resulted in hydrophilization of the surfaces through oxidation. The hydrophilic surfaces were stable for at least 24 h. The treatment also yielded binding sites that resulted in over 20% increase of the amount of chitosan adsorbed over that adsorbed on nontreated fabric. Layers of chitosan adsorbed after plasma treatment were substantially more active as antimicrobial agents than those on nontreated surfaces.

1. Introduction

The development of new fibers for use in healthcare textiles has increased rapidly over the last two or three decades, and is expected to expand even more. The use of natural fibers in medical applications goes back to ancient times and has recently become of great interest due to the fact that natural fibers are readily available and easily produced and because their molecular structure offers excellent potential as a matrix for the design of bioactive, biocompatible, and intelligent materials.[1]

The use of natural cellulose fibers for developing medical materials has recently gained considerable attention, as emphasized by the numerous reviews on the topic.[1−8] Several methods to modify cellulose fibers for medical applications have been described in literature: (i) oxidation procedures, (ii) synthesis of microbial cellulose, (iii) incorporation of metallic nanoparticles, and (iv) various coating strategies at the finishing stages using quaternary ammonium compounds, polyhexamethylene biguanides (PHMB), triclosans, regenerable *N*-halamine and peroxyacid, some synthetic dyes, etc.[1−8]

Among the various polysaccharide products (dextran, hyaluronic acid-derivates, carboxymethyl cellulose-derivates, heparin, carrageenan, and alginate-based products, etc.), chitin and its derivate chitosan are currently the most promising as antimicrobial coatings for cellulose fibers.[7] Chitosan is a natural, renewable resource—a polycationic biopolymer that possesses a well-documented and wide spectrum of biological activity, including antibacterial and antifungal activities.[7,8] Therefore chitosan coatings offer many advantages over traditional treatments of cotton and regenerated cellulose fibers because of their non toxicity, biodegradability, and biocompatibility.

Cellulose fibrous material has to be appropriately activated for efficient irreversible chitosan adsorption; i.e., in addition to using a well-cleaned basic material, it is essential to create appropriate binding sites. For this purpose, different standard chemical processes[9] have been used, which usually modify the fibers both structurally and chemically and, in addition to frequently being ecologically less desirable, are detrimental to the fibers' mechanical properties. With regard to the latter effect, plasma treatments can be used as completely harmless surface activation procedures.

In this paper we describe the utilization of cold plasma treatment to activate cellulose fabric, and the adsorption of chitosan on the plasma-activated fabric. The purpose of the investigation was to evaluate to which extent the antibacterial activity of chitosan-covered fabrics could be improved by the plasma treatment.

Plasma can be described as a (partially) ionized gas and is generated by applying either high temperatures or strong magnetic or electromagnetic fields to a gas. The latter method is used for polymer functionalization. Cold plasma treatment is an extremely versatile technique for modifying polymer surfaces of totally different shapes.[10−17] It has been reported that plasma treatment can improve polymer−polymer adhesion,[10,11] the best results being obtained when using oxygen plasma.[13,18,19] Therefore, in this investigation, which focused on polymer−polymer interaction (cellulose−chitosan) oxygen plasma treatment was applied.

The result of surface activation using oxygen plasma is the formation of different oxygen containing polar functional groups such as C−O, C═O, and O−C═O, which act as nucleophilic centers to which adsorbent atoms can bind.[11,12]

Usually only the outermost layers (2.5−10 nm) of a surface are modified by plasma treatment; therefore, extremely sensitive surface techniques have to be applied to obtain information on surface modifications at a molecular level. In this investigation, the chemical composition of a fabrics surface was determined using X-ray photoelectron spectroscopy (XPS). Furthermore, changes in hydrophilic/hydrophobic fabric characteristics induced by the plasma treatment were evaluated using tensiometry (contact angle method). The influence of low pressure oxygen plasma treatment on the functionalization of cellulose material using chitosan was investigated by conductometric titration and XPS. The results were supported by conventional Kjeldahl analysis. In addition, the effect of plasma treatment on the antimicrobial activity of chitosan-treated fabrics was investigated.

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Table 1. Notation of Samples

sample	treatment of fabric
A	nontreated viscose fabric
B	plasma-treated fabric (24 h after treatment)
C	nontreated fabric impregnated by 0.5% chitosan solution for 24 h
D	nontreated fabric impregnated by 1% chitosan solution for 24 h
E	plasma-treated fabric impregnated by 0.5% chitosan solution for 24 h
F	plasma-treated fabric impregnated by 1% chitosan solution for 24 h

2. Experimental Section

2.1. Material. *Material Preparation.* Regenerated viscose cellulose fabric was obtained from Lenzing AG, Austria. Alkaline washing treatment of the fabric, using 1 g/L Na_2CO_3 and 1 g/L Sandoclean PC (standard washing agent) for 30 min at pH = 10.9 and $T = 60$ C, was applied, in order to obtain a well-defined reference substance.

Following this treatment, the samples were rinsed using distilled water until the conductivity of the rinsing water was less than 3 μS/cm. The processed material was air-dried, climatized and, before plasma treatment, vaccuum-dried ($T = 20$ C, $p = 100$ mbar, $t = 24$ h).

Plasma Treatment. The viscose fabric was treated in oxygen plasma for 30 s. It was found in preliminary experiments (not reported here) that longer treatment times than 30 s tended to result in deterioration of the mechanical properties of the fabric, as also noted by Morales et al.[14] The plasma reactor was a cylindrical Pyrex glass tube with diameter 27 cm and length 30 cm. Plasma was created by an inductively coupled radio frequency (RF) generator with a nominal maximum power of 5 kW at frequency 27.12 MHz. The power used in the experiments was about 800 W. Commercially available oxygen was leaked into the discharge chamber through a leakage valve. The chamber was evacuated using a two-stage oil rotary pump with a nominal pumping speed of 63 m^3/h and an ultimate pressure of about 0.01 Pa. The pressure was fixed at 75 Pa during the experiment. Under these experimental conditions, fairly uniform plasma was created in the entire volume of the discharge chamber. The degree of dissociation was estimated with a catalytic probe and was about 10%, while the degree of ionization was estimated using a simple double electrical probe, and was about 10^{-6}.

Chitosan Treatment. Nontreated and oxygen plasma-treated samples were impregnated with 0.5% and 1% w/w aqueous solutions of chitosan (pH adjusted to 3.6 by adding 1 M hydrochloric acid) for 24 h, respectively. Higher concentrations of chitosan resulted in solutions of too high viscosity for reliable impregnation. pH 3.6 was chosen because the chitosan amino groups will be fully protonated at this pH, and a considerable fraction of the carboxyl groups in the fibers will be dissociated (the pK of glucuronic acids is typically ~3.8). This facilitates electrostatic attraction between chitosan and fibers. The material was passed through an impregnation-wringing machine (foulard W. Mathis) at a pressure of 1.6 bar. After this treatment, the fabrics were dried for 10 min at $T = 40$ C and further air-conditioned for 48 h. Finally, the modified fabrics were washed until constant water conductivity was <1 μS/cm, demineralized, air-dried, and stored under standard atmospheric conditions ($T = 20$ C ± 2 C and relative humidity (RH) = 65% ± 2%). Sample notation is given in Table 1.

Chemicals. The chitosan used for fabric impregnation was commercial-grade low-viscous chitosan from Fluka. It was used without further purification.

2.2. Analytical Methods. *XPS Analysis.* Since we were primarily interested in the modification of surface properties of the fabric and their modification by adsorption of chitosan, we used XPS to analyze effects of the modification procedures. XPS spectra were recorded using the PHI model TFA XPS spectrometer at the Laboratory of Surface and Thin Film Analysis at the Jozef Stefan Institute, Ljubljana, Slovenia. The atomic composition was measured after plasma treatment, and then compared to the elemental chemical composition of the surface of the nontreated material. 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 $K\alpha_{1,2}$ radiations at 1486.6 eV. The photoelectrons were detected by a hemispherical analyzer, positioned at an angle of 45 with respect to the sample's surface normal. Energy resolution was about 0.6 eV. Survey-scan spectra were created at pass energy 187.85 eV. For C1s, individual high-resolution spectra were recorded at pass energy 23.5 and 0.1 eV energy steps. Spectra were recorded from at least three locations on each sample, using an analysis area of 1 mm × 1 mm. The high-resolution spectra were resolved by Gaussian peak fitting of three or four peaks at the energies indicated in Table 3. An additional electron gun for surface neutralization was used during the measurements, in order to compensate for the charging of the nonconducting samples. The differences between the three different spots analyzed on the sample 4 h after plasma treatment were around 3%, and the samples 24 and 96 h after plasma treatment were less than 5%, respectively. The XPS spectra indicated that, during the aging, small changes of surface fabric composition may have occurred.

Table 2. The Elemental Surface Compositions of Nontreated and Oxygen Plasma-Treated Viscose Samples and Their Time Dependencies, from the XPS Survey Spectra

	surface composition		
treatment-time-dependency	C (at. %)	O (at. %)	O/C ratio
nontreated	57.7	42.4	0.90
4 h after plasma treatment	52.1	47.9	0.91
24 h after plasma treatment	51.9	48.2	0.92
96 h after plasma treatment	52.8	47.3	0.89
theoretical cellulose[25,27]	54.5	45.5	0.83

Tensiometry. The samples in fabric form were cut into 2 × 5 cm rectangular pieces and suspended in a special sample holder of a Krüss K12 processor tensiometer. Immediately before measurement, the container with the liquid (*n*-heptane; water) was raised until the sample edge touched the liquid surface. The sample weight-gain during liquid sorption (m) was monitored as a function of time (t). The initial slope of the function $m^2 = f(t)$ is known as the capillary velocity, from which the contact angle can be calculated according to the modified Washburn equation:[20]

$$\cos\theta = \frac{m^2}{t}\cdot\frac{\eta}{\rho^2\cdot\gamma\cdot c} \qquad (1)$$

where θ is the contact angle between the solid and liquid phases, m^2/t is the capillary velocity, η is the liquid viscosity, ρ is the liquid density, γ is the surface tension of the liquid, and c is a material constant.

The constant c was determined for each sample from contact angle measurements using *n*-heptane, for which the contact angle on the fabric was zero and $\eta = 0.4$ mPa s, $\rho = 0.6836$ g/cm^3, and $\gamma = 20.4$ mN/m. Different values of c were obtained for different samples, presumably due to differences in morphology resulting from the different treatments.

The results were statistically processed (a set of parallel measurements until the standard deviation was less than 2) and represent the average value of 10 measurements of the water contact angle.

Conductometric Titration. About 2 g of fabric was cut into thin 30 mm long strips. These were inserted into a glass vessel with 200 mL 1 mM NaCl and 5 mL 100 mM HCl. The suspension was stirred for 30 min, and then titrated in an inert atmosphere (N_2 bubbling) with 0.1 M NaOH added from a 10 mL precision burette. Conductivity was recorded using a Mettler Toledo InLab 730 conductometer. NaOH addition and data collection were controlled by computer. Titrant was added in steps between 0.1 and 0.25 mL, at intervals of 150−7200 s. An equilibrium criterion of 0.1 μS/150 s was set. The amounts of acid were obtained by extrapolation of linear parts of the titration curves to

Table 3. Relative Amounts of Differently Bound Carbons for Nontreated and Oxygen Plasma-Treated Viscose Samples and Their Time Dependencies from High-Resolution Carbon C 1s XPS Spectra

	carbon composition			
treatment-time dependency	C1 (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 (%)
nontreated	17	67	16	0.0
4 h after plasma treatment	12	58	19	10
24 h after plasma treatment	9	54	26	11
96 h after plasma treatment	15	51	24	11
theoretical cellulose[25]	0	83	17	

their points of intersection.[21] A blank titration without fabric was performed in order to calibrate the system and to eliminate the effects of impurities. All reported amounts of weak acids are the mean values of five separate titrations.

Kjeldahl Analysis. About 1.5 g of the sample was digested with H_2S0_4 and a catalyst containing 2.8% TiO_2, 3.0% $CuS0_4$ $5H_2O$, and 94.2% K_2SO_4. The residue was treated with NaOH to liberate NH_3, which was subsequently absorbed in boric acid and titrated with HCl. All samples were analyzed at least in triplicate to ensure reproducibility and to exclude statistical errors.

Antimicrobial Test. The antimicrobial properties of the treated fabrics were evaluated by ASTM E2149-01,[22] which is a quantitative antimicrobial test method performed under dynamic contact conditions. Gram-positive and Gram-negative bacteria as well as fungi were used as test organisms. The incubated test culture in a nutrient broth was diluted using a sterilized 0.3 mM phosphate buffer (KH_2PO_4; pH = 6.8) to give a final concentration of $1.5-3.0 \times 10^5$ colony forming units (CFU)/mL. This solution was used as a working bacterial dilution. Each fabric (0.5−2 g) was cut into small pieces (1 × 1 cm) and transferred to a 250 mL Erlenmeyer flask containing 50 mL of the working bacterial dilution. All flasks were capped loosely, placed on the incubator, and shaken for 1 h at 37 C and 120 rpm using a Wrist Action incubator shaker. After a series of dilutions using the buffer solutions, 1 mL of the diluted solution was plated in nutrient agar. The inoculated plates were incubated at 37 C for 24 h, and the surviving cells were counted. The average values of the duplicates were converted to CFU/mL in the flasks by multiplying with the dilution factor.

The antimicrobial activity was expressed as $R = \%$ reduction of the organism after contact with the test specimen compared to the number of microorganisms cells surviving after contact with the control.[23]

3. Results

3.1. Plasma Treatment of Cellulose. *XPS Analysis.* The elemental surface compositions of nontreated and oxygen plasma-treated viscose samples and their time-dependencies are shown in Table 2. As the analysis depth (escape depth/attenuation length of electrons) in XPS is less than 10 nm,[21,24] the results describe the composition of a limited number of molecular layers on the outermost fabric surfaces.

The analysis of the nontreated sample indicated that the surface consisted of about 42.4 atom % of oxygen and 57.7 atom % of carbon. For pure cellulose, one would expect 45.5 atom % of oxygen and 54.5 atom % of carbon.[21,25] The O/C ratio of the nontreated sample was almost equal to the theoretical cellulose value, indicating that using alkaline washing as a pretreatment process resulted in effective cleaning of the viscose fabric surface, with negligible amounts of impurities.

After 30 s of oxygen plasma activation, the oxygen concentration had increased by 13%. After aging for 24 h, the surface oxygen concentration was still increasing slightly, while 96 h after plasma treatment it remained unchanged. With regard to the elemental surface composition, as deduced from the XPS analysis, no signs of surface aging could be observed as a consequence of applied plasma.

Chemical changes on the surface were analyzed in more detail by recording the high-resolution carbon C 1s spectra of both nontreated and plasma-treated viscose samples.

The C1s spectra of the different samples are shown in Figure 1.

Figure 1 shows that there is a clear difference between the C1s spectrum of the untreated fabric and the three spectra of plasma-treated fabric. The spectrum of the untreated sample could be resolved into three sub peaks, C1−C3. Treatment with plasma resulted in a reduction of the C1 peak and the emergence of a fourth peak, typical of carbon with three bonds to oxygen (i.e., carboxyls). The differences between the three spectra of plasma-treated fabric (as a function of time) were not significant.

The relative amounts of different carbons are given in Table 3.

Because all carbon atoms in cellulose are joined by single or double bonds to either one or two oxygen atoms, for pure cellulose one would expect only C2 and C3 peaks (the amount of carbon bound in terminal carboxyl groups is negligible) with a ratio of 83:17. In practice, a C1 peak (due to C−C bonds) is often observed on cellulose. This most probably results from the presence of contaminants (hydrophobic surface impurities).[26] An example is unbleached kraft pulp, where a typical amount of contaminants is around 6% or even more.[27]

Tensiometry. Figure 2 presents the square of the adsorbed mass versus time for nontreated cellulose fabric and for fabric treated with plasma 4, 24, and 96 h after the treatment. The slopes of these curves characterize the rate of water sorption.

The rise of the curves at the beginning of sorption, e.g. after 10 s, indicates that the imbibition of water was the fastest 4 h after plasma treatment. For all samples, the rate of sorption decreased drastically after a few seconds, while the differences in rate at longer times are not really important. The plasma-treated samples sorbed more water than the nontreated sample. The increase was 137% for the samples measured 4 h after plasma treatment, and somewhat lower at 24 h (100%) and 96 h (92%) after the treatment.

The decrease in sorption is probably due to slow changes in the structure of the fabric, as reflected by the different values of the material constant c in eq 1.

Water contact angles were calculated using eq 1. Average contact angles of water for nontreated and plasma-treated fabrics are presented in Figure 3. The contact angle of the fabric was drastically lowered (from 66 to about 15) by plasma treatment. Aging up to 96 h did not significantly change the contact angle. Increased hydrophilicity after plasma activation is obviously on the one hand due to the formation of new functional groups, but may also be due to minor changes in surface morphology and/or to the cleaning effect of plasma treatment on the surfaces.

3.2. Adsorption of Chitosan onto Plasma-Treated Viscose Fabric. *Conductometric Titration.* Adsorption of chitosan onto cellulose material was investigated using conductometric titra-

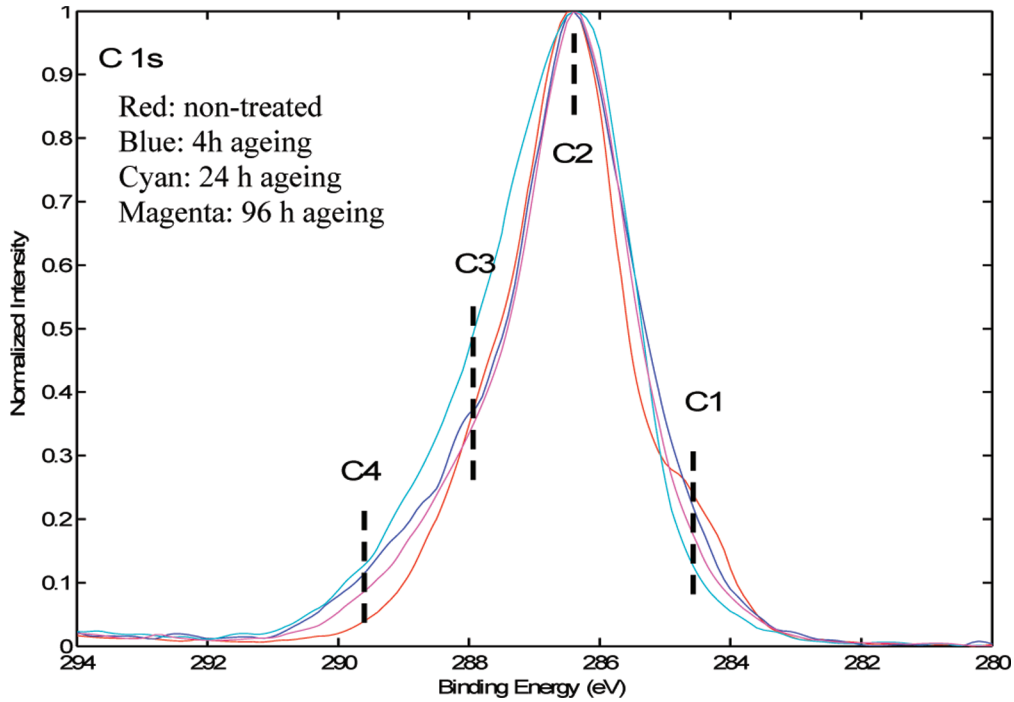

Figure 1. C1 s spectra of nontreated and plasma-treated viscose samples.

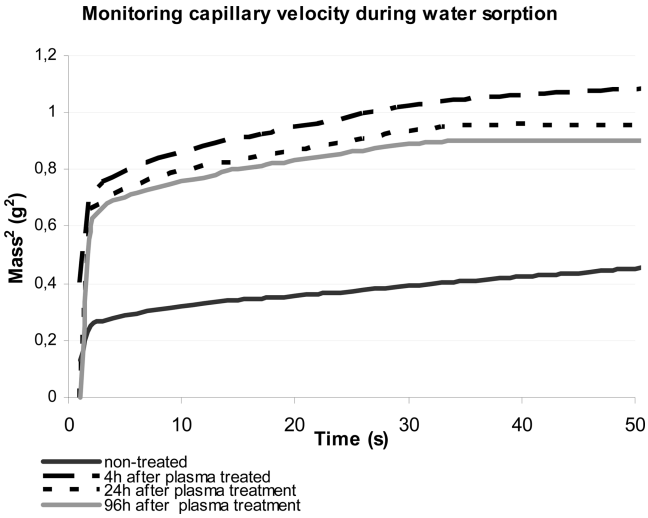

Figure 2. Capillary velocity slope during water sorption monitoring in regard to performed treatment and time dependency.

tion, with special attention given to the plasma activation effect. The amounts of weak acid groups in different samples are shown in Table 4.

Table 4 shows that the amount of acid groups in the surface was increased by plasma treatment (compare samples A and B) and by treatment with chitosan, in particular after immersion in the 1% chitosan solution (samples D and F).

XPS Analysis. Results from XPS analysis of the elemental surface compositions of samples A, B, C, D, E, and F, as well as relative amounts of differently bound carbons based on high-resolution C 1s spectra are given in Table 5. Note that XPS does not detect hydrogen atoms.

Significant amounts of nitrogen were detected only in the samples treated with chitosan (samples C, D, E, and F). Thus, the nitrogen must be due to the amino groups introduced onto the viscose fabric by the adsorption of chitosan, i.e., XPS confirms that chitosan was adsorbed on all surfaces treated with chitosan solutions. The results listed in Table 5 also clearly show that plasma treatment increases the ability of the fabric to absorb chitosan and, hence, are in agreement with conductometric titration results. The increase in the amount of N in samples previously activated by plasma (samples E and F) compared to nontreated samples (samples C and D) was about 14%, irrespective of the chitosan concentration.

Kjeldahl Analysis. Chitosan adsorption was also detected using conventional Kjeldahl analysis.[28] The results indicate the occurrence of nitrogen (%) in the samples impregnated by chitosan solution. Chitosan adsorbed more extensively on the plasma-treated sample: an 18% increase of nitrogen content was observed when using 0.5% chitosan solution compared to the chitosan-treated reference sample (sample C). Immersing the plasma-treated sample in 1% chitosan solution resulted in a 30% increase of nitrogen content.

Antimicrobial Tests. Table 6 presents the antimicrobial properties of samples treated by 1% of chitosan solution. Sample A is a reference, and sample B is oxygen plasma-treated material. When samples A and B are compared, they show an almost similar degree of reduction regarding *Streptococcus agalactiae*, and for both pathogen fungus *Candida albicans* and *Candida glabrata*.

Table 6 shows that the plasma activation for the sample treated by 1% of chitosan solution affected the degree of antimicrobial reduction. *R* for *Staphylococcus aureus* increased from 70% to 91%, and that for *Candida glabrata* increased from 98% to 100%. Even more, the plasma samples treated with 1% chitosan solution (sample F) resulted in a total reduction in *Candida albicans*, for which $R = 0\%$ in the case of the non-plasma-treated sample (sample D).

4. Discussion

Plasma Modification of Cellulose Surfaces. As also reported in earlier investigations,[13,29] the XPS results show that the surface of the cellulose fabric was oxidized by the plasma treatment. The C1 and C2 peaks in the C1s XPS spectrum decreased by 30% and 13%, respectively, while the contribution of C3 carbon increased by 19%, and a new peak (C4) appeared

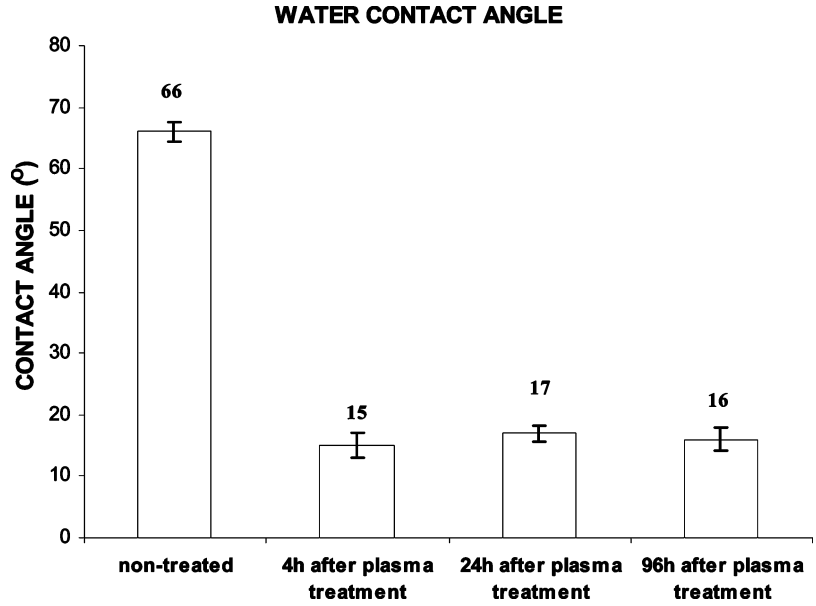

Figure 3. Water contact angles on nontreated and oxygen plasma-treated viscose fabric samples as a function of aging.

Table 4. The Amount of Weak Acid Groups in Viscose Fabric Depending on the Used Treatment[a]

sample treatment	amount of weak acid groups (mmol/kg)
A	50 ± 3
B	56 ± 3
C	50 ± 3
D	60 ± 4
E	55 ± 4
F	73 ± 5

[a] For notation, see Table 1.

with a binding energy of 288.9 eV (Figure 1, Table 3). The same trend was also observed after sample aging, with the one exception: the C1 carbon concentration increased after 96 h sample aging.

The origin of the C1 peak, which should not occur in pure cellulose, is presumably due to remaining impurities containing aliphatic carbon, and it is in accordance with a previous publication.[21] The observed decrease in the C1 peak indicates that plasma treatment resulted in the removal or oxidation of contaminants in the surface, as well as further oxidation, which caused a decrease in C2 carbon concentration. The increases in the C3 and C4 peaks indicate the formation of oxygen−carbon bonds O−C−O or C═O (C3 peak) and O═C−O (C4 peak). This is expected because of cellulose oxidation.

Oxidation of the surfaces can also be inferred from the increased amount of weak acid groups (carboxyls) observed by conductometric titrations (Table 4). Conductometric titration determines the total carboxyls in the fabric, of which those at the surface created by plasma are a very small part. Hence, when nontreated sample A is compared to oxygen plasma-treated sample B, only a slight increase (12%) of weak acidic groups (presumably carboxyls) is observed.

Oxidation of the surface is expected to increase its hydrophilicity. That this was indeed the case is corroborated by the more rapid water absorption and the lowering of water contact angles resulting from plasma treatment (Figure 3).

The oxidized surfaces remained stable for at least 96 h after plasma treatment, as shown both by the detailed C1s spectra (insignificant changes in the C3 and C4 peaks, Table 3) and by the contact angles, which did not change from those measured a short time after the treatment. The strongly increased ability of the fabric to absorb water seen in Figure 2 indicates that plasma oxidation of fiber surfaces is actually not localized to the surface of the outermost fibers in the fabric, but extends also to fiber surfaces deeper down in the pores between fibers. The total amount of water imbibed decreased somewhat after aging for 96 h. A likely explanation is that some hydrophobic contaminations were adsorbed during the storage. This is also indicated by the fact that the relative amount of C1 carbon increased after prolonged fabric storage (Table 3).

Adsorption of Chitosan. Both conductometric titration and XPS indicated that chitosan adsorbed onto the viscose fabric, irrespective of whether it had been treated with plasma or not. The amounts adsorbed on plasma-treated samples were higher than those on nontreated samples, and increased with increasing chitosan concentration in the solution used for treatment. Thus it can be concluded that increasing the number of aldehyde and carboxyl groups due to the plasma activation in the cellulose surface enabled the adsorption of more chitosan.

The amount of C1 carbon (carbon without any bonds to oxygen) in the fabric surface increased after the adsorption of chitosan (samples C, D, E, and F). The reason for this is uncertain, but a likely explanation is that the chitosan may not have been properly deacetylated or may have contained surface-active impurities with hydrocarbon chains (chitosan was not purified before use). However, this does not invalidate the conclusion that increasing amounts of chitosan were adsorbed when the surfaces were treated with plasma and/or the chitosan concentration was increased. Adsorption of chitosan was further confirmed by the Kjeldahl analysis.

The chitosan used in this research contained 5 mmol/kg of weak acidic groups (of $-NH_2$ origin), as determined by conductometric titration. Therefore, the total amount of weak acid groups in the fabric was expected to increase after adsorption of chitosan.

Surprisingly, although XPS and Kjeldahl analysis both indicated the adsorption of chitosan on the fabric surfaces, the amount of dissociating weak acidic groups remained unchanged when the samples were treated with 0.5% chitosan solution for 24 h (sample C). The reason may be the electrostatic attraction (ionic bonds) between carboxylate groups in the nontreated sample A and the protonated amino groups of the chitosan

Table 5. The Elemental Surface Composition from XPS Survey Spectra and Relative Amounts of Differently Bound Carbons Determined from High-Resolution Carbon C 1s XPS Spectra, Using Peak-Fitting into Four Symmetric Gaussian Components[a]

	surface composition (at. %)			carbon composition (at. %)			
sample treatment	C	O	N	C1 (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
A	57.7	42.2	0.3	16.8	66.9	16.3	0.0
B	51.9	48.2	b.d.l.	9.4	54.2	25.7	10.8
C	60.5	37.7	1.4	19.5	55.8	20.9	3.8
D	64.3	34.2	1.5	29.1	56.0	13.0	1.9
E	60.2	38.2	1.6	22.9	59.7	15.7	1.6
F	61.0	36.0	1.7	29.6	49.6	15.9	4.9

[a] In addition to C, O, and N, traces of S and Si were detected on sample F.

Table 6. Antimicrobial Properties of Viscose Nontreated, Oxygen- and Chitosan-Treated Fabrics[a]

	R, %				
	pathogenic bacteria			pathogenic fungi	
sample treatment	*Staphylococcus aureus*	*Escherichia coli*	*Streptococcus agalactiae*	*Candida albicans*	*Candida glabrata*
A	0	0	99	20	34
B	0	0	80	51	21
D	70	0	100	0	98
F	91	0	100	100	100

[a] R = % reduction of the organism.

adsorbed onto the fabric. Simple coverage by chitosan polymer chains that renders the cellulose −COOH groups inaccessible is also possible. Assuming that both mechanisms are of importance, most of the weak acidic groups determined in sample C should belong to chitosan amino groups that did not associate with carboxyls. Using a higher chitosan concentration (1%) for impregnation of the nontreated sample clearly introduced more weak acid (proton-binding amino) groups onto the fabric surface (sample D), i.e., a 13% increase in weak acidic groups compared to sample A and a 20% increase in comparison to sample C.

The results in Table 4 show that plasma treatment increased the ability of the fabric to adsorb chitosan. When the plasma-treated samples were impregnated with the 0.5% chitosan solution (sample E), an 11.2% increase in accessible amino groups was observed in comparison with the nontreated sample C. Plasma activation was even more clearly reflected in a better chitosan adsorption when using the higher chitosan concentration (1%) for fabric impregnation (sample F). A 23.3% increase in the amino groups of sample F was observed in comparison with non-plasma-treated sample D.

Taken together, the XPS and conductometric titration results suggest the following mechanisms for interaction between chitosan and the viscose cellulose fabric as well as the fabric treated with plasma. That there are no carboxyl groups in the surface of sample A (region of 10 nm), and probably also only a few aldehyde groups, which are most likely present as impurities/contaminants,[21] suggests that chitosan adsorption on non-plasma-treated viscose fabric is predominantly driven by physical interactions (van der Waals forces, entropic factors) or hydrogen bonding to OH groups. Plasma treatment introduces aldehyde and carboxyl groups in the surface (as suggested by the conductometric titrations and XPS), which may result in a combination of electrostatic and electrodynamic interactions (ionic and covalent bonds) with additional possibilities for hydrogen bonding. Moreover, the larger amounts of water imbibed into plasma-treated fabric may imply increased accessibility for chitosan to adsorption sites on the fibrous material.

Antimicrobial Properties. The adsorbed chitosan evidently is an active antimicrobial agent. Chitosan adsorbed onto plasma-treated fabric was substantially more active as an antimicrobial agent for the pathogen microorganisms investigated (except *E. coli*). The plasma treatment resulted in a higher degree of chitosan adsorption onto fabric surfaces and consequently higher amount of amino groups, which are responsible for antimicrobial activity.[30−33] Because the number of amino groups in plasma−chitosan-treated samples is higher (conductometric titration, XPS) than that for non-plasma−chitosan-treated samples (C, D), the probability that a protonated amino group meets the bioplasm of bacteria would increase, resulting in a greater reduction capacity.[23]

5. Conclusions

XPS and tensiometry results clearly showed that plasma treatment of viscose fabric led to the formation of appropriate binding sites due to the fabric oxidation raising material hydrophilicity. Adsorption of chitosan onto plasma-activated fabric is more efficient in comparison with non-plasma-treated samples. Moreover by adsorbing chitosan onto a plasma-activated surface, antimicrobial reduction becomes more substantial. Fabric properties as inhibition of Gram-positive pathogen bacteria and both Candida fungus for ∼100% may give to the fabric numerous advanced impacts. They may find its applicability in several fields, e.g., medicine (smart dressing for bandages, surgical gauzes, etc), sanitary goods (napkins, tampons, etc.), textile (advanced fabric), and so forth.

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