Influence of Corona Discharge and Chitosan Surface Treatment on Dyeing Properties of Wool

Nebojša Ristić,[1] Petar Jovančić,[2] Cristina Canal,[3] Dragan Jocić[4]

[1]*High Professional School of Textile, Leskovac 16000, Serbia*
[2]*Textile Engineering, Faculty of Technology and Metallurgy, University of Belgrade, Belgrade 11120, Serbia*
[3]*Department Farmàcia i Tecnologia Farmacèutica, Facultat de Farmàcia, Universitat de Barcelona, Barcelona 08028, Spain*
[4]*Engineering of Fibrous Smart Materials (EFSM), Faculty of Engineering Technology (CTW), University of Twente, Enschede 7500AE, The Netherlands*

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ABSTRACT: In this work, the effects of single and combined corona discharge (CD) and biopolymer chitosan treatment (CS) on the sorption properties and dyeability of woolen fabric were studied. Physical and chemical changes on the fiber surface were assessed by using different methods. It has been confirmed that wettability and dyeability of wool were improved after single and combined treatments. The changes in elemental composition of wool fiber surface were followed by means of X-ray photoelectron spectroscopy. The relationship between chemical changes and both wettability and dyeability after CS is discussed. On chitosan treated samples, the color intensity increased uniformly with increasing chitosan concentration. The samples treated with combined treatment (corona/chitosan) had the highest color intensity, due to synergistic effect of the treatments. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 2487–2496, 2010

Key words: biopolymer; corona; dyeing; wool; ESCA/XPS

INTRODUCTION

The wool surface morphology plays an important role in wool processing and maintenance. To modify wool surface properties, for the purpose of improving sorption characteristics and reducing shrinking tendency due to felting, traditionally, a chemical process of chlorination is used, which has the consequence of producing absorbable organic halogen (AOX) compounds. Currently, rigorous environmental legislation imposes the limits to the commercial use of chlorination, thus pushing the industry to develop alternative, environmentally friendly methods for wool surface modification such as enzyme treatment,[1] low temperature plasma treatment,[2] and chitosan biopolymer treatment.[3,4]

Wool dyeing rate, except by dye characteristics and process parameters, is determined by fiber morphology and by the state of adsorbed water in fiber. Wool fibers consist of central structure – cortex, made of lengthy cortical cells surrounded by cuticle cells overlapping each other. Each cuticle cell is made of the internal region with low sulfur content (endocuticle), the central part rich in sulfur (exocuticle A and B), and a thin (only 5–7 nm thick) outer layer known as epicuticle.[5,6] It is believed that epicuticle consists of an outer lipid layer (F-layer) bound via ester and thioester bonds to the below laying cysteine rich protein layer. Lipid layer is a methyl-branched 21-carbon fatty acid, identified as 18-methyl eicosanoic acid (18-MEA) oriented away from fibers.[7] The presence of hydrophobic F-layer on the wool fiber surface and the high amount of disulfide links in exocuticle A form a diffusion barrier to dye molecules. It was found that, when more than 20% of covalent bonded fatty acid is removed by an efficient treatment, the wetting and dyeing times with an acid dye are significantly reduced.[8] Between cuticle cells and cortex, there is a cell membrane complex (CMC-layer), with an intercellular binder or cement in its bulk, which is being very important for acid dye sorption in wool fiber.[9] Analyzing the influence of fiber morphology and water penetration on dye diffusion in wool, Hori and Zollinger[10] have determined that dyes penetrate through narrow gaps between the scales, and not frontally through epicuticle, because of F-layer on the outer side of epicuticle. They have also determined that a larger part of the penetrating water exists in the form of non-freezing water, causing a glass transition temperature decrease, whereby they explained the domination of free volume mechanism in wool dyeing over the expected pore mechanism.

Correspondence to: N. Ristić (bojana1998@ptt.rs).

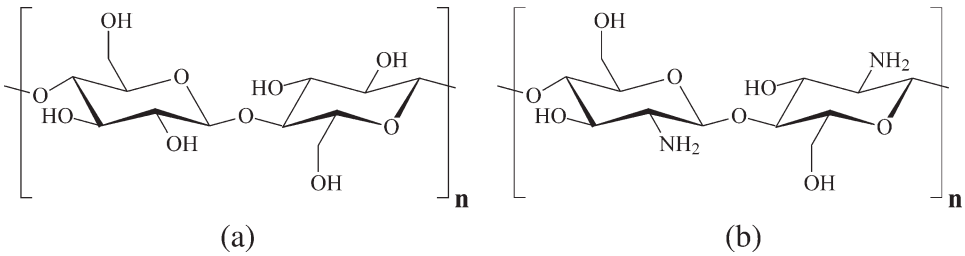

Figure 1 Chemical structure of cellulose (a) and chitosan (b).

A number of comprehensive studies on low temperature plasma treatment of wool fiber, show that the treatment can enhance the processing and performance of wool fiber such as lower felting tendency,[11] improvement of dyeability and washing[12,13] and obtaining a more reactive surface.[14] The effect of low temperature oxygen plasma on wool dyeability with acid, chrome and reactive dyes was studied.[15] In all the systems tested, the treated samples had lower halftime of dyeing and higher equilibrium exhaustion compared to the untreated ones. Also, with all dyes, substantivity to treated wool was increased, especially with reactive dyes (4.95 times).

Extent of scale damage was identified on plasma treated wool fabrics by using SEM.[16] By using FTIR analysis, changes of several wave numbers were identified indicating polar functional group incorporation in the fiber structure, which induced fast wettability determined by measuring water droplet adsorption time.

Corona discharge (CD), as a type of low temperature plasma treatment, represents an economical and environmentally acceptable process appropriate for industrial purposes, since it occurs at (or near) atmospheric pressure. It has been reported that the effect of CD treatment on woolen fabrics was the increase of positive charge and zeta potential as a result of chemical changes on the fiber surface.[17] In a recently published review article, it was demonstrated that CD and other low temperature plasmas modify physically and chemically the natural and chemical fibers, inducing improvements in hydrophilic, antistatic, dyeing and printing properties.[18] Ryu et al.[19] studied the effects of corona and plasma pretreatments of wool on color intensity of printed samples. They concluded that corona discharge incorporates oxygen atoms into the fiber and enhances wettability, resulting in increased acid dyes intensity of printed fabrics. Moreover, it has been recently reported that CD increases exhaustion and dyeing rate of natural dye *Rhizoma coptidis* on woolen fabric.[20]

Ever increasing consumers' requirements for "green" and "eco" textiles resulted in application of natural polymers in textile processing. Chitosan biopolymer can be considered a cellulose derivative, wherein C2 hydroxyl group is replaced by primary aliphatic amino group (Fig. 1).

Because of biocompatibility, biodegradability, water binding capacity and reactivity of amino and hydroxyl groups, chitosan can be regarded as an environmentally friendly substitute for synthetic agents in wool finishing since it enhances wool dyeability and provides shrink-resistant properties.[21] Numerous investigations indicate multiple applicability of chitosan in wool dyeing and finishing, as a single agent or in combination with other agents, e.g., enzymes (for enhancing wool dyeability[22]) or H_2O_2 and enzymes (for reducing shrinkage and enhancing wettability[23,24]). Furthermore, chitosan was used in combined treatments with H_2O_2 and a nonionic surfactant to improve wool shrink-resistance and dyeability.[25,26]

The aim of this work is to investigate the chemical changes on wool fiber surface after CD treatment, correlate the wool surface properties with wettability, and to determine the positive effect of CD treatment on chitosan adsorption and treated wool material dyeability with acid dyes.

EXPERIMENTAL

Materials and chemicals

Wool 2/2 twill woven fabric of 206 g/m^2 weight per unit area, made of multi folded yarn (600Z × 2S540, 21 tex), was used in all experiments. Before any further treatment the fabric was washed with nonionic surfactant solution, then thoroughly rinsed with distilled water and dried at room temperature.

Chitosan was obtained as commercial product (Chitoclear) from Primex (Norway) and had following characteristics: deacetilation degree 96%; viscosity 102 mPa s (1% solution); solubility 99.9%; dry matter content 85%; and ash content 0.1%. Chitosan was used as received, without further purification.

The commercial grade dye Supramin Red GG (CI Acid Orange 19; C.I. 14690), supplied by DyStar (Germany), was used for dyeing of wool samples (untreated and corona/chitosan pretreated). This is a simple monoazo dye (M_R 519 g/mole) containing

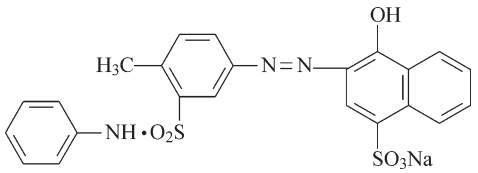

Figure 2 Chemical structure of CI Acid Orange 19.

one sulfonic acid group and markedly hydrophilic in character (Fig. 2).

All other chemicals (acetic acid; sodium sulfate; potassium dichromate) were of analytical grade and they were used without further purification.

Wool fabric treatment

Corona discharge

For CD treatment, fabric samples of dimensions 55 × 35 cm were treated in CD equipment Corona – Plus TYP TF-415 (Vetaphone, Denmark). The treatment power was kept constant (800 W) as well as the gap between electrode and roll (4 mm). The sample was passing twice through the discharge area in each cycle. Treatments were done with 3 and 5 cycles, with the roller rotation speed maintained at 4 and 10 min^{-1}, so the corresponding resident times were 40, 60, 80, and 130 s (samples CD_{40}, CD_{60}, CD_{80}, and CD_{130}, respectively).

Chitosan treatment (CS)

For chitosan treatment (CS), the solutions were freshly prepared by dissolving specified quantity of chitosan in distilled water containing acetic acid (3 g/L). Chitosan solutions of concentrations of 1, 5, and 10 g/L were used. The fabric samples were treated in these solutions for 20 min at 25°C with constant stirring. After treatment, the samples were squeezed (laboratory padder), dried at room temperature, rinsed with distilled water and dried again. To assess the possibilities of combined treatment (CDCS), sample pretreated with corona discharge (CD_{40}) was subsequently treated with chitosan under the same conditions as nonpretreated samples. Table I shows sample labeling and corresponding treatment parameters for the samples that have been used for dyeing experiment.

Characterization methods

X-ray photoelectron spectroscopy (XPS) analysis

X-ray photoelectron spectroscopy (XPS) was used to investigate surface chemical changes after CD treatment of the wool fabric. The samples were analyzed using ESCA-LAB MKII spectrometer (VG Scientific) with Mg, Kα monochromatic radiation source (1253.6 eV) and using 300 W power. Spectra were obtained with monochromator and take-off angle of 0°, working with residual vacuum of 10^{-6} Pa. The survey spectra, to determine elemental concentrations of the surface layer (C, O, N, and S in Table II) were taken in the range 0–1100 eV (with 0.3 eV increments). Carbon spectra (C1s) of high resolution were taken in the range of 280–300 eV (with 0.1 eV increments) from which the chemical state of carbon was determined (C1 to C4). The curve fitting was made using Spectrum NT software. All binding energies were calculated with respect to the reference value of carbon (C1s) photoelectron signal at 285 eV.[27,28] The curve peak positions on C1s deconvoluted spectra were fixed at 284.6 eV for C1 (C—H or C—C), 286.4 eV for C2 (C—O), 288.1 eV for C3 (C=O or O—C—O) and 288.9 eV for C4 (COOH).[29–32] The chemical shifts of peaks were from 1.60 to 4.68 eV.

TABLE I
Sample Labeling and Treatment Parameters for Wool Samples

Sample label	Treatment
UT	Untreated
CD_{40}	Treated with CD (40 s exposure time)
CS1	Treated with 1 g/L chitosan
CS5	Treated with 5 g/L chitosan
CS10	Treated with 10 g/L chitosan
CDCS1	CD_{40} + 1 g/L chitosan
CDCS5	CD_{40} + 5 g/L chitosan
CDCS10	CD_{40} + 10 g/L chitosan

Scanning electron microscope analysis

Scanning electron microscope (SEM) JSM 5300 (JEOL, Japan) was used to characterize surface morphology of wool fibers after CD treatment. The samples for were prepared by standard preparative technique applying gold layer to produce a conductive surface, using a JFC 1100E ION SPUTTER (JEOL, Japan) apparatus for cathode gold vaporization for 5 min.

Wetting measurements

For the evaluation of improved water sorption after CD treatment, both AATCC 39-1980 Test Method and capillary method[33] were used to assess the wetting rate and the level of capillary action, respectively.

According to AATCC test, the wetting time is measured by placing one droplet of water from a burette onto a stretched sample from a distance of 1 cm. The wetting time is measured as the time required for the water mirror to disappear from the surface. The results presented are an average of five measurements.

The capillary method was used to evaluate water sorption (i.e., level of capillary action) after the treatments and the results were processed on the basis of general relations for wetting process [eqs. (4) and (5)]. According to this method, fabric strips of dimensions 30 × 3 cm were positioned with their lower edge in contact with wetting liquid, which in our case was diluted (1 g/L) potassium dichromate aqueous solution (for more obvious reading of capillary wicking). The height (h) reached by liquid in time (t) is measured. The results obtained are the average of three measurements in warp direction and three measurements in weft direction.

According to Poiseuille's law, the rate of capillary wicking in a porous medium is given by:

$$\frac{dh}{dt} = \frac{{R_D}^2}{8\eta}\frac{\Delta P}{h} \tag{1}$$

where h is the height reached by the liquid front in time t; R_D is the mean hydrodynamic pore radius, η is the viscosity of liquid and ΔP is the pressure difference, i.e.

$$\Delta P = \frac{2\gamma\cos\theta}{R_S} - \rho g h \tag{2}$$

where γ and ρ are the surface tension and density of the liquid, θ is the contact angle of the liquid with solid matter, R_S is the mean static pore radius and g is gravity acceleration. Static pore radius R_S is equal to the geometric pore radius, and hydrodynamic radius depends on pore tortuosity.[34]

In equilibrium state ($\Delta P = 0$), maximum height h_{eq} reached by liquid is given as:

$$h_{eq} = \frac{2\gamma\cos\theta_{eq}}{\rho g R_S} \tag{3}$$

where θ_{eq} is the equilibrium (static) contact angle, usually lower than the dynamic one.

In early process stages, hydrostatic pressure in eq. (1) can be neglected, so integration of eq. (1) gives Washburn equation:

$$h^2 = \frac{r\gamma\cos\theta}{2\eta}t \tag{4}$$

with $r = {R_D}^2/R_S$; this term represents equivalent radius of capillary porous structure.[35]

Hence, values of h^2 must be linearly dependent on time:

$$h^2 = Dt \tag{5}$$

where slope D is the capillary diffusion coefficient dependent on capillary size r and physical and chemical characteristics of the liquid.[36] Therefore, textile fabric surface treatment that changes r and contact angle θ consequently induces changes of capillary diffusion coefficient D.

Dyeing of wool samples

Dyeing of samples (3 g) was performed in dyeing apparatus TYP G7B (Ahiba, Switzerland) with vertical material movement, in 180 mL dyeing solution (liquor-to-goods ratio 60:1), containing dye (1.5% owf), sodium sulfate (5% owf) and acetic acid to adjust pH 4.5. After reaching boiling temperature (30 min), the dyeing was continued for 50 min. Dyed samples were washed with warm and cold distilled water and dried at room temperature.

Reflectance values (R), CIELAB color coordinates (L^*, a^*, b^*) and ΔE values were measured using the reflectance spectrophotometer Spectraflash SF600X (Datacolor) with the standard procedure (D65/10). Color intensity (K/S) was determined at maximum absorption wavelength (500 nm) from Kubelka-Munk equation:

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \tag{6}$$

Washing and rubbing fastnesses were determined on dyed samples according to ISO 105-C06:1994 and ISO 105-X12:2001 standard, respectively.

RESULTS AND DISCUSSION

Surface chemical analysis

Surface chemical analysis of wool fiber was performed on untreated (UT) and CD treated sample (CD_{40}) by the use of XPS method. Results obtained for untreated wool (Table II) are compatible with literature data[30,35,37] showing that wool fiber surface consists of 75–80% carbon, 10–12% oxygen, 6–9% nitrogen, and 2–3% sulfur. Identified sulfur originates from thio-ester bonds between fatty acids and protein matrix of epicuticle and from disulfide bonds in the protein layer of epicuticle. Nitrogen originates from epicuticle protein material, positioned under fatty acid mono layer. Oxygen arises from amide and other hydrophilic groups existing in

TABLE II
Elemental Surface Composition From XPS Survey Spectra

	Elemental composition (%)				Atomic ratio	
Sample	C	O	N	S	O/C	C/N
UT	79.3	10.7	7.3	2.7	0.13	10.86
CD_{40}	71.5	20.1	7.4	0.9	0.28	9.66

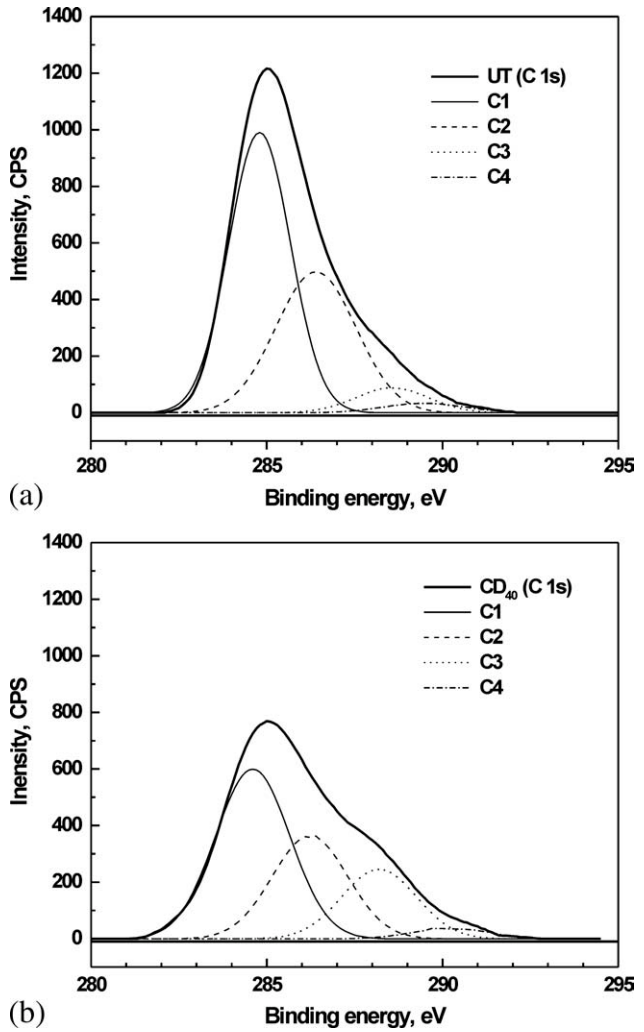

Figure 3 Deconvoluted high-resolution C1s XPS spectra of untreated (UT) (a) and CD treated (b) wool.

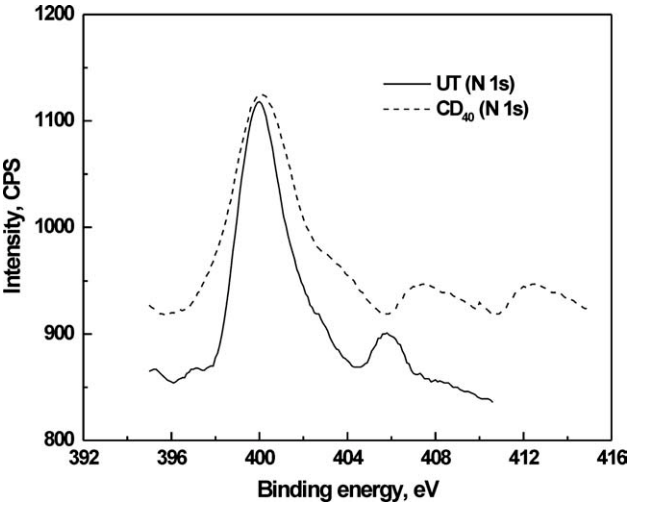

Figure 5 High-resolution N1s XPS spectra of untreated (UT) and CD treated wool.

untreated fibers, whereas carbon originates from wool protein and surface fatty layer.

CD treatment modifies chemically the wool surface. Results obtained from survey spectra for elemental surface composition show that both C and S amount decrease, while amounts of O and N are increased on CD treated sample (CD_{40}, Table II. Furthermore, Figures 3–6 present high-resolution spectra for carbon, sulfur, nitrogen, and oxygen (untreated and CD treated sample).

The total carbon content was reduced by about 10% after CD treatment (Table II), due to the etching effect of wool fiber surface, which results in modification and partial removal of surface lipids. As the consequence of surface etching, outer wool layer was exposed to corona discharge action resulting in chemical changes on lateral amino acid groups and terminal polypeptide chains in wool, increasing

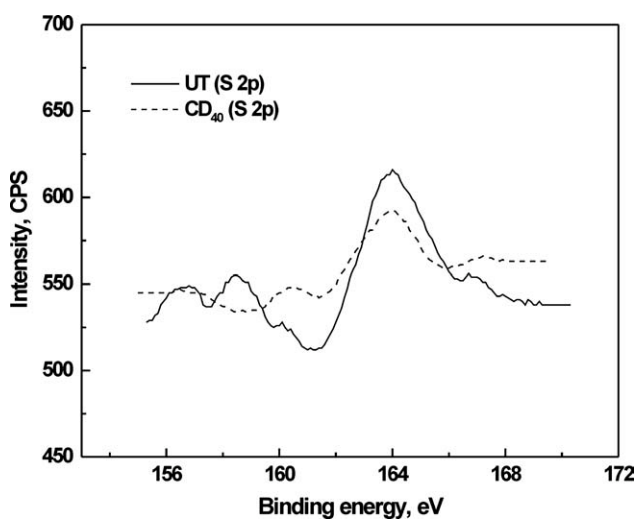

Figure 4 High-resolution S2p XPS spectra of untreated (UT) and CD treated wool.

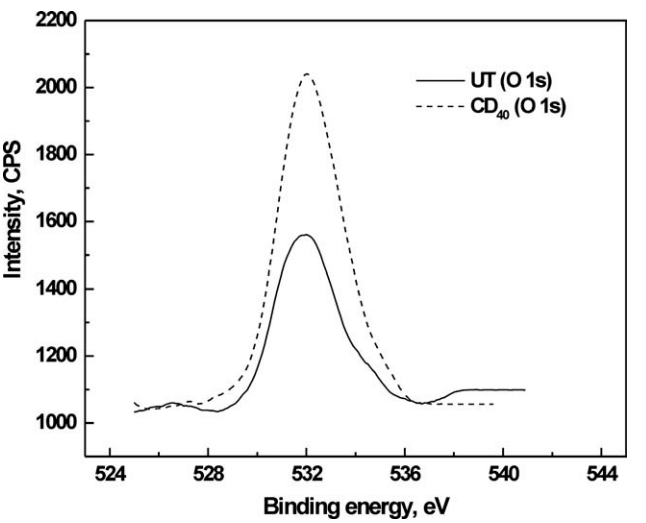

Figure 6 High-resolution O1s XPS spectra of untreated (UT) and CD treated wool.

amounts of N and O atoms but reducing the amount of S atoms. The significantly increased oxygen content on CD treated sample (↑88%) and O/C atomic ratio (↑115%), indicates an increase of oxygen functional groups as a result of intensive oxidation of hydrocarbon chains of F-layer.[38] At the same time, atomic ratio C/N is reduced (↓11%) as a specific indicator of partial removal of hydrophobic wool surface layer and increase of fiber hydrophilicity.[25,26] Small increase of nitrogen signal intensity (Fig. 5) is related to the removal of the top wool fiber layers, thus making accessible the protein epicuticle layer under the F-layer. Increasing of nitrogen atom portion in wool can enhance positive charge of wool due to the protonation of amino and imino groups on lateral amino acid chains producing new adsorption sites for negatively charged ions.

Sulfur content is significantly decreased after CD treatment, because a treated sample contains only one third part of sulfur atoms present at the original sample. In Figure 4, peak of S_{2p} at 164 eV, corresponding to S—S and S—C groups, has lower intensity at CD treated sample, and at the same time signal intensity at 168 eV is increased. Significant decrease of S content indicates that, in addition to the partial removal of lipid layer hydrocarbon chains on the surface, there also occurs a modification of epicuticle protein matrix with fatty acid monolayer linked to it. This is very possible because plasma action ranges to about 10 nm in depth below the fiber surface, whereas epicuticle has a thickness of 5–7 nm.

The signal increase at higher bond energy for S_{2p} is an indicator of increasing of sulfur atom oxidation state on the wool fiber surface and it suggests a conversion of cystine residues to cysteic acid residues, according to the following relation:[39]

$$W - S(II) - S - W \rightarrow W - S(IV)O_3H$$

where W is the wool.

Since the peak at 168 eV is broad and the signal is not proportionally increased with S atom decrease (at 164 eV), it is assumed that complete conversion of cystine to cysteic acid did not happen, i.e., a part of sulfur present in the CD treated wool sample is the consequence of intermediate oxidation products of cystine (cystine monoxide and cystine dioxide). Cystine monoxide and cystine dioxide are more reactive than the initial disulfide, therefore the wool fiber becomes a more reactive substrate for compounds containing nucleophilic groups, such as anionic dyes.

Deconvolution of high-resolution C1s XPS spectra (Fig. 3) enabled the evaluation of functionalization of wool surface by incorporating oxygen containing groups. The relative amounts of carbon with various oxygen bonds are shown in Table III.

TABLE III
Relative Amounts of Differently Bound Carbon From High-Resolution C1s XPS Spectra

	Carbon components (%)			
Sample	C1	C2	C3	C4
UT	55.57	36.28	5.76	2.40
CD_{40}	47.87	29.49	19.65	2.99

CD treatment produces a decrease of aliphatic carbon C1 (C—C, C—H) as a proof of oxidation of surface lipids and increase of oxygen containing functional groups. Furthermore, CD treatment induces a curve shift from an area corresponding to hydroxyl-like groups C—O (C2) towards C=O (C3) group area with small portion of COOH (C4) groups, which is in accordance with recently issued layout of plasma oxidation of wool fibers:[38]

$$C—C \rightarrow C—O \rightarrow C=O \rightarrow O—C=O$$

Polar C=O group content on CD treated sample (Table III) is about 3.5 times higher and COO^- group content is about a quarter higher compared to the untreated (UT) sample. Therefore, it can be concluded that C=O group is a prevailing oxidation component in wool after CD treatment. Since the detected C=O groups correspond to the protein material located beneath F-layer, they can be considered as an indicator of progressive oxidation and removal of F-layer from wool fiber surface. The detected chemical changes on the wool fiber surface treated with CD are expected to increase the free surface energy, wettability, dye affinity, and other hydrophilic properties.[40]

Surface morphology

SEM images (Fig. 7) show a distinguishable physical modification of wool fiber surface after CD treatment (130 s). The surface of untreated wool fiber [Fig. 7(a)] is smooth between the scales which show sharp edges without any damage. After CD treatment the wool surface generally becomes rough [Fig. 7(b)], probably due to the etching effect induced by the bombardment of wool fabric surface with electrons avalanche and other species in CD atmosphere.[41] Moreover, the shape of scale edges is changed, as they become rounded and less sharp, and—in some cases—they are even ripped off [Fig. 7(c)]. This change is not uniform, because unmodified scales can be observed, too.

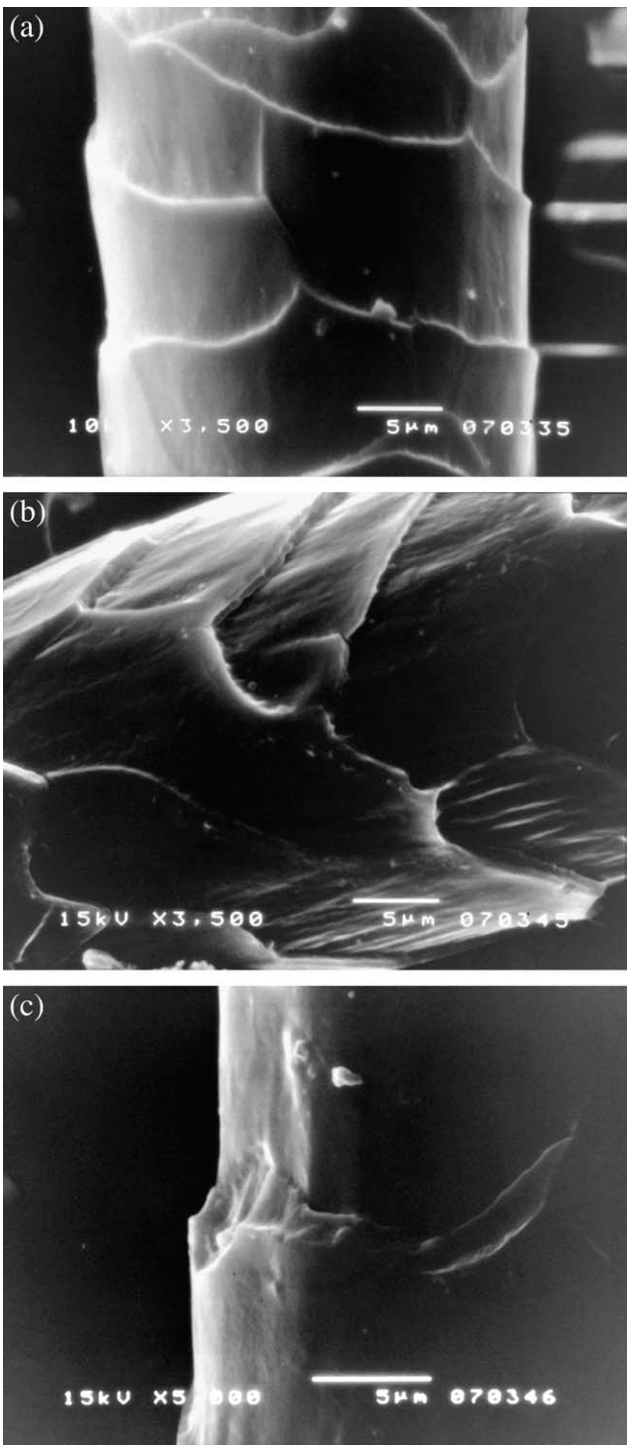

Figure 7 SEM micrographs of untreated (a) and CD treated (b, c) wool at different magnifications.

Wettability properties

Wettability of textile material is extremely important for the kinetics of chemical treatments, wearing comfort and maintenance. Wettability of fiber surfaces can be modified by changing chemical constitution of polymers or by applying hydrophilic finishing agents. Even though wool fiber originally contains a large amount of various polar groups, resulting in high moisture sorption and regular swelling in water, the hydrophobic nature of the fiber surface reduces the expected wettability and adversely affects the dyeing and printing processes of wool fabrics. Nevertheless, CD treatment is expected to significantly improve wetting properties of the wool fabric, which have been assessed by water droplet absorption (AATCC test) and capillary wicking tests. A significant change from hydrophobic surface of untreated fiber to hydrophilic surface of CD treated wool fiber was observed (Table IV).

The results of AATCC test show that untreated wool is highly hydrophobic and has no capability to either absorb water droplets or to capillary transport the liquids. However, even after the shortest CD treatment (40 s), the wool sample shows a significant improvement of wettability which is progressively enhanced with prolonged CD treatment time (Table IV). The increased wettability can be attributed to the oxidation of F-layer and to newly formed oxygen polar groups.[42] Changes of chemical composition of CD treated samples (incorporating oxygen containing functional groups to the fiber surface, Table III), induce the increase of surface free energy and fiber-water interaction, resulting in relatively quick water absorption and capability to transport liquids through pore system, this being a prerequisite for effective dyeing of textile. To diffuse into the fibrous medium, liquid must initially wet the fiber surface before being able to move trough the networked pore system by capillary forces. Moreover, interfiber pores must be of suitable diameter to produce sufficient capillary pressure for the liquid transport. However, the liquid retaining capacity of the fibrous material is determined not only by pore size but also by the total porosity.

As seen from Figure 8, CD treated wool samples have the capability of capillary liquid transport. At constant CD power, capillary action gradually increases with increased treatment time. After 100 s of capillary wicking test, liquid reached 20 mm capillary wicking height with CD_{40} sample, while with CD_{130} sample wicking height reached 50 mm. In the initial stage of the capillary wicking (first 60 s), h^2 vs. time plots (Fig. 9) agree well with the straight

TABLE IV
Wettability and Capillary Diffusion Coefficient D

Sample	Wettability (s)	D (cm^2/s)
UT	$\propto$	–
CD_{40}	164.5	3.38
CD_{60}	105.4	4.75
CD_{80}	43.6	6.63
CD_{130}	12.8	31.06

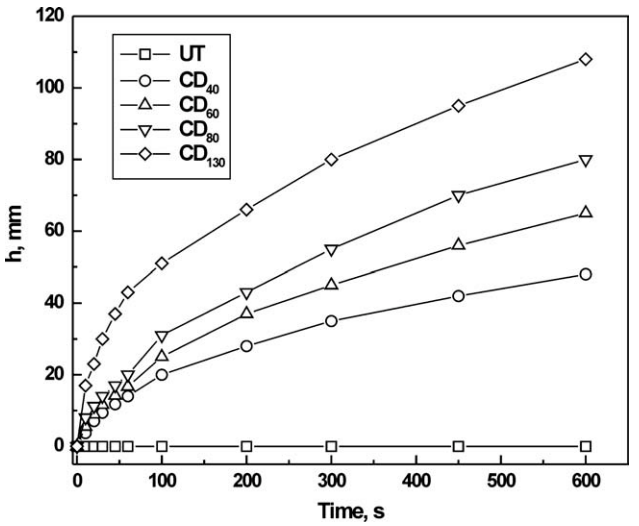

Figure 8 Capillary wicking of untreated (UT) and CD treated wool at different exposure times.

lines that can be obtained using Washburn equation [eq. (5)]. These results are in compliance with improved wettability (AATCC test), previously observed in all samples after CD treatment. Modification of chemical constitution of fiber surface produced by the bombardment with CD species is primarily responsible for the enhanced wettability and liquid transport capability, though there are reports that pore sizes in CD treated fabric structure could be enlarged and consequently affect the capillary pressure, thus increasing the capillary wicking.[43]

According to the data shown in Table IV it is obvious that less wetting time the higher capillary diffusion coefficient D, indicating that wetting and capillary wicking are two closely related processes in the sense that the liquid that does not wet the fibers could not penetrate the fabric, i.e. wettability is a prerequisite for capillary wicking.[44,45]

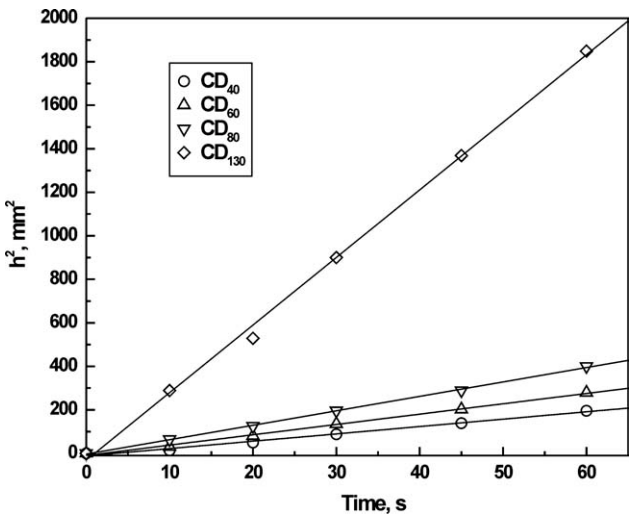

Figure 9 Capillary wicking (h^2 vs. time plots) of CD treated wool at different exposure times.

TABLE V
Color Coordinates and Color Difference ΔE of Wool Fabric Samples Dyed with CI Acid Orange 19

Sample	L^*	a^*	b^*	ΔE^*
UT	52.1	54.0	49.1	–
CD_{40}	51.8	53.6	48.7	0.36
CS1	51.7	53.9	48.9	0.38
CS5	51.5	53.8	48.8	0.61
CS10	51.2	54.2	48.7	0.76
CDCS1	50.7	53.7	48.5	0.95
CDCS5	51.1	54.2	48.9	1.23
CDCS10	51.1	54.5	49.2	1.84

Dyeing properties

The effect of pretreatment (CD, CS, and CDCS) on dyeability of wool was evaluated by measuring color coordinates and calculating color intensity from reflectance values.

Even though the values of CIELAB coordinates a^* and b^* (Table V) indicate that most of the treated samples are slightly less red (except CS1, CDCS5, and CDCS10) and slightly less yellow (except CDCS10) than the UT sample, it could generally be concluded that the treatment type had not significantly affected hue, because overall hue differences are very small. However, all treated samples show noticeably deeper coloration, confirmed by the decrease of lightness L^*, which depends on the pretreatment applied. The most intensively colored samples are obtained after combined (CDCS) treatment. Furthermore, the color intensity values (K/S) obtained on wool fabric samples treated with CD and/or CS are higher compared to the UT sample (Fig. 10).

The negligible increase of color intensity (↑2.08%) on CD treated sample can be explained by the fact

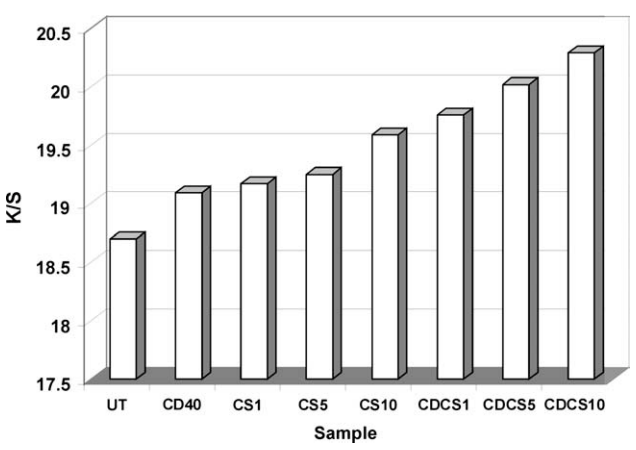

Figure 10 Color intensity (K/S) of wool fabric (UT, CD, CS, and CDCS) dyed with CI Acid Orange 19.

TABLE VI
Color Fastness of Wool Fabric Samples Dyed with CI Acid Orange 19

Sample	Washing	Rubbing	
		Dry	Wet
UT CD_{40}	4	5	5
CD_{40}	4	5	5
CS1	4	5	5
CS5	4	5	5
CS10	3–4	4–5	4–5
CDCS1	4	5	5
CDCS5	4	5	5
CDCS10	3–4	4–5	4–5

that identified chemical changes are limited to a thin surface layer of few tenths of nanometer, so the number of active groups, capable for interaction with dye, remains almost the same. Therefore, a significant increase of equilibrium dye exhaustion does not happen, despite the improvements in wettability and capillary transport of dye through the fabric structure.

Chitosan (CS) treated wool samples had higher color intensity (↑2.5–4.8%) and it increased monotonously with chitosan concentration. When wool is being treated with chitosan solution, adsorption of chitosan on wool takes place owing to: ionic interactions between negatively charged functional groups of wool and positively charged amino group of chitosan; low-energy bonds between hydroxyl groups of chitosan and hydroxyl and amide groups of wool. During dyeing in acidic medium, chitosan – as a polyelectrolyte with high positive charge density – creates additional sites for adsorption of negative ions of acid dye. This assumption is based on the fact that there is an interaction between protonated chitosan amino groups and sulfonic groups of acid dye with limited stoichiometrics of 1 : 1.[46] Therefore, the deposited highly de-acetylated chitosan created a higher positive charge on wool surface and enabled additional quantity of mono-sulfonated ions of acid dye (CI Acid Orange 19) to be bound to the fiber.

Considering the assumption that acid dye anions will be absorbed rather on cationic chitosan amino group than on wool fibers,[46] it can be supposed that chitosan layer on the wool represents a dominant site for dye adsorption in early stages of dyeing with further diffusion of dye to interior zones of the wool fiber.

Combined (CDCS) treated samples of wool fabric showed the highest bonding capacity for acid dye (↑5.7–8.5%), and color intensity was higher compared to samples treated only with CD or chitosan. Even though increased dye sorption can be considered as an effect of treatments applied, it seems very likely that on wool surface, previously enriched with anionic groups by CD treatment, a higher quantity of chitosan is deposited resulting in higher dye exhaustion, even when the treatment is performed with diluted chitosan solution to maintain the required touch of the treated material. Continuous chitosan layer deposited on wool surface wherefrom most of F-layer is previously removed enables frontal (trans-cellular) diffusion of acid dyes so that higher dye uptake is achieved in shorter time.

Washing fastness values (Table VI) of pretreated samples (CD, CS, and CDCS) were almost the same as the values obtained for the UT sample. This implies that the dye-substrate bonding mechanism in principle remained the same. However, rubbing fastness was reduced by half of unit at the highest chitosan concentration used, which could be attributed to higher dye concentration (dye accumulation) in the fiber surface layer as the consequence o partial dye distribution to chitosan layer too.

CONCLUSIONS

CD treatment modifies the surface of wool fibers, improving to a large extent the hydrophilic properties and, partly, the dyeability. Intensive chemical changes are manifested as a progressive oxidation of F-layer and modification of protein matrix of epicuticle. Oxygen functional groups are incorporated in fiber structure with C=O group as the dominant oxidation component. With increasing CD treatment time, wettability and capability of capillary liquid transport are enhanced. Anyhow, color intensity after dyeing of CD treated wool is only slightly increased because the chemical modifications are limited to the layer with a thickness of a few tenths of nanometer. Applying chitosan to CD treated wool fabric increases the color intensity proportionally with the chitosan concentration, as the consequence of the creation of additional sites for acid dye adsorption. Hence, combined CD and CS enrich wool with suitable functional groups, thus improving the dyeability.

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