

The Influence of Surface Modification on Related Functional Properties of Wool and Hemp

P. Jovančić^{1,a}, D. Jocić¹, M. Radetić¹, T. Topalović², Z. Lj. Petrović³

¹Textile Engineering Department, Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia and Montenegro

²Textile Technology Group, Faculty of Science and Technology, University of Twente, P.O. Box 217, Enschede – 7500 AE, The Netherlands

³Institute of Physics, Pregrevica 118, 11080 Zemun, Serbia and Montenegro

^apera@tmf.bg.ac.yu

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Abstract. The new concept of the combined treatment consisting of specific fibre surface tailoring and activation prior to biopolymer or enzyme post-application is introduced. Low-temperature plasma treatment is considered as very useful for superficial treatment of wool and hemp. Some interesting combinations of low-temperature plasma and enzymatic treatments are presented in this paper. These treatments result in an increase in wettability, dimensional stability, polymer adhesion and dyeability of both, wool and hemp fabrics.

Introduction

The surface properties of textiles are important determinants of their usefulness and many conventional chemical treatments are applied to modify these properties. Important properties of textiles such as wetting, swelling, penetrability, dyeability and polymer adhesion, are strongly influenced by their surfaces. Also, it is well known that there is a specific structure-property relationship in wool as well as in hemp fibres. In general, structure and morphology of the upper surface layer (several nanometers thick) of wool differ from hemp fibres. The hydrophobic nature of the wool surface is attributed to the presence of 18-methyleicosanoic acid (18-MEA), which is covalently bound to the fibre as thioester to cysteine residues of the wool protein. Fatty acid chains of 18-MEA are oriented away from the fibre to produce a “polyethylene-like” layer at the fibre surface, thus making the epicuticle hydrophobic and resistant to attack of different agents [1-3]. Therefore, by removing the covalently bound fatty acid monolayer, an increase in hydrophilicity of the fibre surface occurs, which could enhance dye uptake and polymer adhesion. On the other hand, the demand for apparel usage of hemp has increased owing to the fibre quality of comfort, hygiene and elegance. However, the hemp fibre has a high crystallinity that contributes to higher bending stiffness and processing difficulty [4]. Accordingly, in the last decade the most investigated treatments for the surface modification of wool and hemp fibres were low-temperature plasma (LTP) and enzymatic treatments, which could be combined with biopolymer after-treatment.

LTP treatment is the most commonly used method for a specific fibre surface modification, as it exclusively affects the surface, both physically and chemically, without altering the material bulk properties. Specific modification of the surface layer can be achieved by surface bombardment with ions, electrons, free radicals, metastables and UV photons, which directly or indirectly participate in plasma-chemical reactions. LTP treatments seemed to be an effective mean for modification of wool, cotton and flax surface properties [4, 5-6].

Nowadays, the use of protease enzymes to achieve wool shrink-resistance, better whiteness and improved handle is of considerable interest [7-10]. Shrink resistant wool is the major priority but, if enzymes are applied at levels that provide the required shrink resistance, wool fibres will

often be unacceptably damaged owing to irregular treatment [11-13]. Enzymes alone or in combination with peroxide are also successfully employed in wool bleaching [14], as auxiliary agents in wool dyeing [15-16], and for wool handle modification by reducing wool fibre stiffness and prickle [17-18]. Cellulase enzymes have found an application in cotton finishing [19] and recently they have been involved in hemp processing [20].

Much attention has also been focused on natural polymers as a possible substitute for synthetic polymers. Polysaccharide chitosan (CHT) has a promising future as its positive charge provides unique chemical and biological properties and makes it attractive for a wide range of textile applications. CHT solubility in acidic solutions makes it particularly suitable for industrial purposes. The chemistry of CHT is similar to that of cellulose, but it reflects also the fact that the 2-hydroxy group of cellulose has been replaced with an acetamide group, which through N-deacetylation becomes a primary aliphatic amino group. In wool finishing, CHT has been used as a shrink-resist agent [21-22] and as an agent for improving the dyeability of wool [23-25].

During last decade, we mainly investigated the novel treatment techniques complying with the purpose to obtain wool shrink resistance. Accordingly, we successfully combined dry technique (LTP plasma) and different liquid systems (peroxide, enzyme) with a liquid system (CHT). The new established concept was to use LTP plasma (both microwave and radio-frequency, using different plasma gases) and enzymatic treatment combined with peroxide treatment as the pre-treatment, followed by CHT treatment. In this paper, we present some results of the enzymatic treatment, applied after previous specific surface "tailoring" of wool and hemp fibres by LTP plasma treatment. Apart from the assessment of shrink resistance effect obtained (Woolmark TM31), we measured the wettability, swelling and contact angle [26]. XPS analysis has been used to provide evidence about the chemical changes on the surface of the fibre [27-28]. SEM observation [13] and AFM analysis [29] have been used for routine examination and gaining of information about fibre topography.

LTP wool treatment

Both microwave (2.45 GHz) (MW) and radio-frequency (13.56 MHz) (RF) plasma treatments have been investigated in order to assess the influence of different types of plasma reactors on wool properties. The experience with two types of plasma reactors confirmed that they both give good results of the surface modification, but we were able to control plasma parameters much better when using RF plasma [30-31].

The results of area shrinkage for RF plasma treated knitted wool fabric (Table 1) showed that very short N₂ plasma treatment times (10 s) give uncertain results. However, the air plasma treated as well as H₂O plasma treated samples provide similar area shrinkage value regardless of the treatment time. The plasma treatment times over 40 s do not induce further improvement, suggesting that treatment time of 40 s is sufficient to increase the wettability, shrink-resist properties and enhance polymer adhesion to wool fibre. These findings have been confirmed by advancing contact angle measurements using water as wetting liquid. Sharp decrease in contact angle at short treatment time (10 s) suggest that species present in plasma react very fast with fatty acid chains on wool fibre surface. The amount of hydrophilic groups formed on the outermost epicuticle layer increases with prolongation of treatment time up to 40 s [32].

This improvement of wetting properties of plasma treated wool is due to existence of new hydrophilic groups on the fibre surface and modification or even partial removal of the fatty layer, which has been confirmed by XPS analysis [28, 33]. Air, N₂ and H₂O plasma treatments result in a decrease in relative atomic concentration of C and an increase in relative atomic concentration of O (Table 2), suggesting that oxidation of the fatty layer present on the outermost part of the epicuticle occurred. Furthermore, the C/N atomic ratio decreases from 12.0 for untreated to 8.2, 8.7 and 8.6 for air, N₂ and H₂O plasma treated wool, respectively. It could be a result of the partial removal of hydrocarbon chains of fatty layer.

Table 1 Area shrinkage percentage (Woolmark TM31) of LTP plasma (RF) treated wool knitted fabrics.

Sample	Area shrinkage after two 5A cycles
Untreated	/
N ₂ , 100W, 1mbar, 10s	49.2 %
N ₂ , 100W, 1mbar, 40s	12.3 %
N ₂ , 100W, 1 mbar, 120s	5.8 %
Air, 100W, 1mbar, 10s	11.4 %
Air, 100W, 1mbar, 40s	11.4 %
Air, 100W, 1mbar, 120s	10.7 %
H ₂ O, 100W, 1mbar, 10s	16.0 %
H ₂ O, 100W, 1mbar, 40s	12.0 %
H ₂ O, 100W, 1mbar, 120s	11.6 %

Table 2 Elemental concentration (at. %) for untreated, air (40s), N₂ (40s) and H₂O (40s) plasma treated wool. The error associated with each measurement is <5% of the reported.

	Elemental concentration (%)						
	C	O	N	S	Si	C/N	O/C
Untreated	76.7	13.5	6.4	2.7	0.7	12.0	0.18
Air (40s)	62.9	27.0	7.7	1.3	1.1	8.2	0.43
N ₂ (40s)	64.9	26.1	7.4	1.2	0.4	8.7	0.40
H ₂ O (40s)	68.0	22.9	7.9	1.2	<0.1	8.6	0.34

The deconvolution of the C_{1s} photoelectron peak corresponding to air, N₂ and H₂O plasma treated wool fabrics (Table 3) reveals a decrease in adventitious (C_{adv}) and aliphatic carbon (C-C, C-H), and an increase in C-O, C-N, carbonyl (C=O) and carboxylate groups (COO⁻) compared to untreated wool. The carbonyl group present at the wool surface has been attributed to amide group of the protein material located below the fatty layer. This could indicate that the protein material is more “detectable” by XPS after plasma treatment, due to material removal from the fatty layer present on the wool surface.

Table 3 Relative intensity data of the deconvoluted C_{1s} spectra of untreated, air (40s), N₂ (40s) and H₂O (40s) plasma treated wool.

	Elemental concentration (%)				
	C _{adv} (%)	C-C, C-H (%)	C-O, C-N (%)	C=O (%)	COO ⁻ (%)
Untreated	15.2	57.4	18.0	8.4	1.0
Air (40s)	5.7	51.3	21.7	17.0	4.3
N ₂ (40s)	8.8	47.3	22.7	17.0	4.2
H ₂ O (40s)	2.7	56.3	22.0	14.3	4.7

The splitting of some cystine disulphide linkages occurs due to an oxidative effect of air, N₂ and H₂O plasma resulting in formation of sulphonic groups that could be easily detected by XPS S(2p) spectra [27, 28, 33].

We observed that wettability, shrink resistance and polymer adhesion properties tended to decay with time after RF plasma treatment, mainly for wool treated at short times [34]. Regardless of the plasma gas used, the advancing contact angle increases as a function of time elapsed after the treatment. The wettability decay rate was similar in the case of wool treated for 40 s and 120 s, whereas it was faster for the fibres treated for 10 s. The results show that after 30 days of ageing the

advancing contact angle achieves a value that is practically independent of the plasma exposure time, suggesting that the new groups on the fibre surface have been totally reorganized [27].

LTP-chitosan wool treatment

The wettability decay was another reason why we insisted on immediate after-treatment with chitosan in order to stabilize the effects obtained by plasma treatment and attain the maximum efficiency of the treatment [35-36]. In order to qualitatively evaluate chitosan adsorption on wool, CHT treated wool was subjected to the staining process [35] that clearly showed considerably higher chitosan adsorption on plasma pretreated wool compared to untreated wool. This has been additionally confirmed with contact angle measurements. The advancing contact angle tends to decrease with LTP treatment and hydrophobic untreated fibre surface ($\theta_{ADV} > 90^\circ$) becomes hydrophilic ($\theta_{ADV} < 90^\circ$). Table 4 shows [37] that CHT treatment does not influence the contact angle in comparison with untreated fibre, but in the case of fibre treated with LTP+CHT the contact angle (78°) considerably increases in respect to the value of LTP treated fibre. This confirms the presence of chitosan on the fibre surface which remains more hydrophilic compared to untreated fibre, but more hydrophobic than the surface of the fibre treated with LTP alone.

Table 4 Advancing contact angle (θ_{ADV}) values for untreated, CHT, LTP and LTP+CHT treated keratin fibres measured by the Whilhelmy balance method.

Sample	Untreated	CHT	LTP	LTP+CHT
θ_{ADV}	$102^\circ \pm 4$	$100^\circ \pm 2$	$55^\circ \pm 4$	$78^\circ \pm 4$

SEM observation did not show visible chitosan on the fibre surface even when high chitosan amounts had been applied (up to 1%), but the evidence of some interfibre chitosan bonding could be seen [35]. This implies that chitosan forms a very thin film on wool fibres, which is sufficient to provide additional shrink-resist effect.

LTP-enzyme wool treatment

The area shrinkage (two 5A wash cycles) of H₂O LTP treated wool noticeably decreases compared to untreated wool (see Table 1 and Fig. 1). This effect could be attributed to superficial changes such as roughening of the fibre surface after LTP treatment, modification or partial removal of highly hydrophobic F-layer present on the wool surface, and oxidation of the wool surface that increases the content of oxidized sulphur species [27, 38].

The application of enzymes after LTP pretreatment easily imparts machine washability to wool regardless of the enzyme used. Low weight loss after LTP treatment confirmed that only fibre surface is affected chemically and physically without altering the bulk properties of wool [38]. After subsequent enzymatic treatment, the weight loss tends to increase and thus, a higher enzyme concentration and prolonged treatment time should be avoided despite excellent shrink-resist effect achieved. The damage of wool could be easily controlled by correct choice of enzyme, enzyme dosage and treatment time.

XPS analysis monitored the superficial chemical changes after LTP and LTP+Enzyme treatments. Plasma treatment results in a decrease in relative atomic concentration of C and an increase in relative atomic concentration of O, suggesting oxidation of the fatty layer present on the outermost part of the epicuticle. LTP+Enzyme treatment leads to a further decrease in C/N atomic ratio (Table 5).

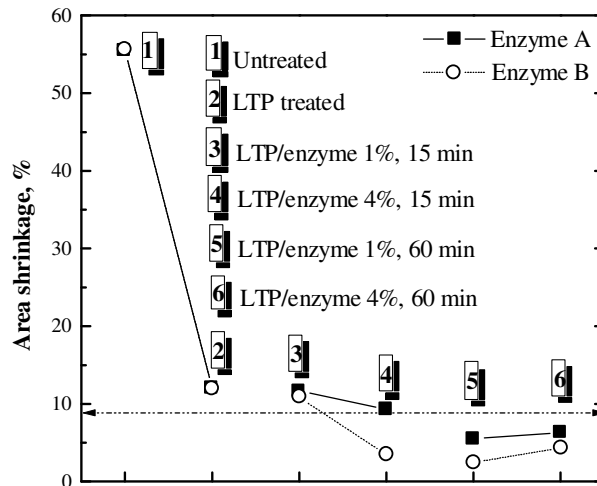


Fig. 1 Area shrinkage after 2x5A Wascator shrinkage test cycles for different treatments.

The values of the C/N ratio of 4.1 for LTP+Enzyme A treatment and 4.3 for plasma-enzyme B treatment are similar to the reported C/N atomic ratio of 3.4 for the amino acid analysis of epicuticle [39] and to the C/N atomic ratio of 5.1 found for wool treated with potassium t-butoxide in t-butanol [40]. This could be attributed to complete F-layer removal by enzymatic treatment applied after LTP treatment.

Table 5 Elemental concentration (atom %) and atomic ratios for untreated, LTP, LTP+Enzyme A (1%, 60 min) and LTP+Enzyme B (1%, 60 min) treated wool. The error associated with each measurement is <5% of the reported.

Elemental concentration (atom %)	Atomic ratio						
	C _{1s}	O _{1s}	N _{1s}	S _{2p}	Si _{2p}	C/N	O/C
Sample							
Untreated	76.7	13.5	6.4	2.7	0.7	12.0	0.18
LTP	68.0	22.9	7.9	1.2	<0.1	8.6	0.34
LTP+Enzyme A	58.6	23.1	14.2	2.9	1.2	4.1	0.39
LTP+Enzyme B	59.4	22.6	13.8	3.2	0.9	4.3	0.38

The deconvolution of the C(1s) photoelectron peak corresponding to plasma treated wool reveals a decrease in the adventitious (C_{adv}) and aliphatic carbon (C-C, C-H), and an increase in C-O, C-N, carbonyl (C=O) and carboxylate groups (COO⁻) compared to untreated wool (Table 3). This could indicate that the protein material is more “detectable” by XPS after plasma treatment, suggesting that material from the fatty layer present on the wool surface was removed. The carbonyl group present on the wool surface has been attributed to amide group of the protein material located below the F-layer [27]. An increase in carboxylic acid after LTP treatment is a result of the oxidation of hydrocarbon chains located at the wool surface, which is in accordance with the decrease of the amount of covalently bound surface lipids present in wool.

LTP+Enzyme treatment decreases additionally the relative content of aliphatic carbon (C-C, C-H), and carboxylate groups (COO⁻) and increases the relative content of adventitious carbon (C_{adv}) and an unidentified peak carbon (C_{unknown}) on the wool surface compared to plasma treated wool alone [38]. This implies that important changes have occurred on the wool surface as a consequence of enzyme treatment applied after plasma treatment. The epicuticle or even exocuticle layer could be affected by plasma-enzyme treatment after complete removal of F-layer. The presence of amide peptide bonds is more visible although some of them could be hydrolysed as a result of subsequent enzymatic treatment.

From relative intensity data of deconvoluted XPS S(2p) spectra we learned that LTP treated wool produced an increase in signal intensity at 168 eV, indicating oxidation of disulfide bonds to the S⁶⁺ form as a result of the formation of cysteic acid and probable presence of more than one sulphur oxidation species [38]. After subsequent enzymatic treatment, the intensity of the signal corresponding to oxidized sulphur species decreases significantly, in a similar way as H₂O₂ treatment [41].

LTP-enzyme hemp treatment

The influence of LTP and CHT treatment on wool dyeability has already been examined [25, 27]. Various factors influencing dyeing behaviour of superficially modified wool, particularly pH and temperature, were considered [42-43]. LTP treatment of wool could increase the apparent dyeing rate by reduction of the surface barrier effect without any change in diffusion rate within the bulk phase. The present chitosan layer on the surface of the fibre always acts as a predominant dyeing site in very short dyeing times, thus accumulating dye and in later stages “desorbing” the dye to the wool fibre. This effect is obvious independently on dyeing temperature, but its duration diminishes with increasing temperature [32].

LTP treatment affects the hemp dyeability in a very similar way. An increase in dyeing rate, final dye exhaustion and Kubelka-Munk values of dyed hemp fabric was obtained. The hemp fibre surface is more hydrophilic (an increase in water retention values), which can be attributed to plasma etching of the fibre surface and macroscopic porosity changes in hemp fibre [4, 20]. It seems that plasma etching increased fibre porosity and induced topographical changes, making hemp fibre more susceptible to dye and water molecules. The positive effect of plasma treatment is more prominent in the case of dyeing with C.I. Acid Blue 113 than with C.I. Direct Red 81 (Fig. 2). Enzymatic treatment alone as well as LTP+Enzyme treatment impaired the hemp dyeability with C.I. Acid Blue 113 due to a possible removal of the surface amorphous region of the fibre, the main site of dye penetration [4]. Untreated, LTP, Enzyme and LTP+Enzyme treated samples show similar and low colour fastness values, which were considered satisfactory taking into account that cold dyeing procedure was applied [44].

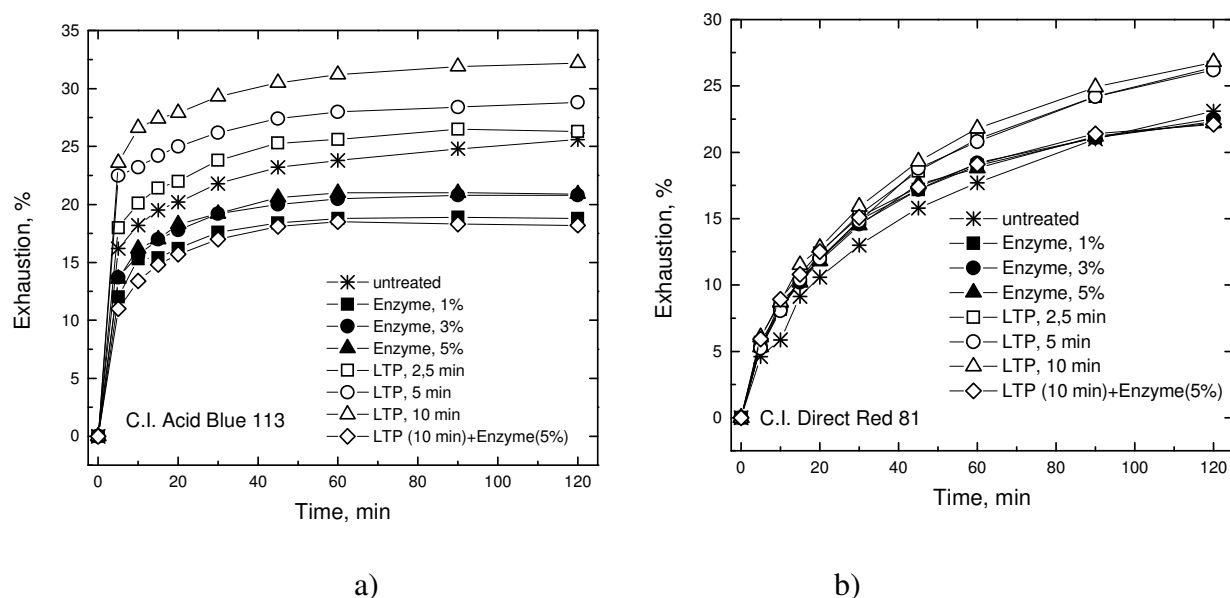


Fig. 2 Dyeability of untreated, LTP, enzyme and LTP+Enzyme treated hemp fabrics.

Conclusion

The treatments of wool and hemp fibres by low-temperature plasma and enzymes cause significant changes in their surface chemical composition and topography. These changes provide improved functionality and apart from the main benefit of obtaining dimensional stability, there are other benefits as enhanced wettability, polymer adhesion and dye affinity of wool and hemp. Additional research on application of combined LTP plasma-enzyme treatments in wool and hemp finishing are in progress.

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