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Chitosan contribution on wool treatments with enzyme

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Abstract

In a previous research work, it was observed that the application of biopolymer chitosan (CHT) on wool fabrics before the enzymatic treatment promotes an increase of the weight loss. In order to deep on the role played by CHT, several experimental conditions have been selected according to a hybrid experimental design and different parameters, such as weight loss and shrink-resist properties, have been controlled. To enhance the CHT sorption on the wool fibre surface, wool was submitted previously to a water-vapour low-temperature plasma treatment. The weight loss results reveal that the enzyme effect increases by increasing the CHT concentration applied to untreated wool. However, CHT concentration does not have any influence when wool has been previously treated with plasma. It is deduced that the surface free energy of wool fibres plays an important role on the enzyme activity. Therefore, the results obtained reveal that the main contribution of CHT on hydrophobic surface of untreated wool fibres is to confer hydrophilicity to wool. Furthermore, CHT tends to coat the wool fibres by film formation reducing apparently the fibre damage promoted by enzyme treatment and also reducing the wool shrinkage.

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1. Introduction

Wool fibres can be considered as a natural composite material, being keratinous the main basic constituent. The most important histological components are cortical and cuticular cells. Another minor component is the cell membrane complex (CMC), which forms a continuous phase in the fibre and links cuticular and cortical cells. The cuticular cells are located on the outermost part of the fibre surrounding the cortical cells. The surface of these cells is hydrophobic nature due to the presence of a fatty acid monolayer (F-layer) covalently bounded to the epicuticle protein layer (Negri, Cornell, & Rivett, 1993). This F-layer exerts a considerable influence on the shrinkage properties of wool fabrics during an aqueous washing

process (Molina, Jovančić, Comelles, Bertran, & Erra, 2002) and it is a barrier for different hydrophilic chemical products such as dyes.

Nowadays, the interest for enzymes in textile processes has been increasing with the aim to substitute chemical products or processes that produce effluent contamination, such as the toxic adsorbable organic halogen (AOX) compounds (Doshi & Shelke, 2001). Enzymes have several advantages, because they can react on specific bonds of the substrate under mild experimental conditions, can be easily deactivated and are biodegradable. Different enzymes groups (protease, lipase and lipoprotein lipase) have been investigated to confer wool shrink resistance, better whiteness and improved handle, being protease the most used (Cegarra, 1996; Fornelli, 1994; Haefely, 1989; Heine & Höcker, 1995). However, if enzyme is applied at levels that produce machine washability, wool fibres are frequently damaged (Jovančić, Jocić, & Dumic, 1998; Jovančić, Jocić, Erra, Molina, & Julià, 1998; Riva,

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Cegarra, & Prieto, 1993). In order to reduce wool damage, CHT application before protease treatment with Esperase 8.0L has been investigated (Vílchez, Jovančić, Manich, Julià, & Erra, 2005). The results showed that CHT pretreatment improved considerably the shrink-resist properties of wool fabrics, even when wool was treated with low enzyme concentration. At 0.025% o.w.f. (over weight fibre) Esperase 8.0L concentration, the shrink resistance was attained at the machine washable level with enhanced whiteness degree, and similar mechanical properties that untreated sample. It was also detected that the enzyme effect was increased, in terms of weight loss, due to the CHT pre-treatment.

The polysaccharide-based cationic biopolymer chitosan is poly(1,4)-2-amino-2-deoxy-β-D-glucan (CHT) (Fig. 1), usually obtained by deacetylation of chitin that is widely present in the nature as a component of some fungi, exoskeleton of insects and marine invertebrates (crabs and shrimp). The chemistry of chitosan is similar to that of cellulose, but it reflects also the fact that the 2-hydroxyl group of the cellulose has been replaced with a primary aliphatic amino group. This polysaccharide has several useful properties, such as non-toxicity, biocompatibility, biodegradability, antimicrobial activity (Mathur & Narang, 1990), chemical reactivity (Jeong, Cha, Yu, & Park, 2002) and film forming ability, which makes it an acceptable substitute for synthetic polymers in textile finishing. Among many other uses, it has been shown that chitosan improves the dye coverage of immature fibres in cotton dyeing (Mehta & Combs, 1997) and that it could be successfully used as a thickener and binder in pigment printing of cotton (Bahmani, East, & Holme, 2000).

In wool finishing, chitosan has been used as a shrink-resist agent (Julià, Pascual, & Erra, 2000; Masri, Randall, & Pitman, 1978) as an agent for improving the dyeability of wool (Davidson & Xue, 1994; Filipowska, Walaske, & Ribicki, 2000; Jocić, Julià, & Erra, 1997; Yen, 2001). Fibres treated with chitosan show a different dyeing behaviour which has been investigated (Jocić et al., 2000; Vílchez, Navarro, Jocić, & Erra, 2001). It has also investigated the interaction between chitosan and dye in the solution (Jocić et al., 2001, 2002).

In this work, knitted wool fabric was treated with CHT at different concentrations before enzymatic treatment in an attempt to deep on the role played by this biopolymer. Because of scarce CHT deposition on untreated wool, the fabric was previously treated with low temperature plasma (LTP) to improve the polymer deposition on wool surface

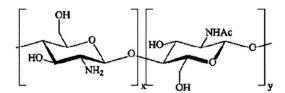


Fig. 1. Chemical structure of chitosan.

(Erra et al., 1999). Accordingly, an experimental hybrid design on untreated and LTP treated wool has been carried out. The variables selected were enzyme concentration, enzymatic treatment time and CHT concentration. Different parameters have been evaluated (weight loss and area shrinkage), which have revealed information about the role of the biopolymer CHT on the enzyme effect. Furthermore, the contact angle on single fibres with or without CHT has been determined, to confirm the contribution of CHT.

2. Experimental

2.1. Materials

Knitted wool with a cover factor 1.22 tex^{1/2}/mm kindly supplied by Pulligan S.A. Spain. Before treatments, it was cleaned by Soxhlet extraction with dichloromethane, rinsed with ethanol and deionized water. Chitosan of known viscosity (369 cps) and degree of deacetylation (84.9%), kindly supplied by Vanson, USA, was used without further purification. The enzymatic product known as Esperase 8.0L was supplied by Novozymes, Denmark. Dark brown European human hair without previous bleaching or dyeing treatments was used as a model for wool fibres for the contact-angle measurements. All other chemical and auxiliaries were laboratory reagent grade.

2.2. Low temperature plasma (LTP) treatments

A radio-frequency (RF) reactor operating at 13.56 MHz was employed. Water vapour was used as plasma gas being the treatment time, the pressure and the incident RF power, 120 s, 100 Pa and 100 W, respectively. Wool fabrics were placed in the vacuum chamber, which was evacuated to a pressure of about 10 Pa before introducing the plasma gas. The distance between the electrodes was 8.5 cm, and the samples were placed in the central position between the electrodes.

2.3. Chitosan treatments

CHT treatments were done in a thermostatically controlled laboratory shaker by the exhaustion method at a liquor-to-wool ratio of 20:1 at 25 °C for 20 min. CHT solutions were freshly prepared by dissolving the different amount of CHT in distilled water containing 0.4% w/v of acetic acid. After treatment, the samples were run (3 m/min, 3 bar) through laboratory padder HVF (Mathis, Switzerland) to remove the excess solution and finally dried at room temperature.

2.4. Enzyme treatments

Enzyme treatments were carried out by the exhaustion method at a liquor-to-wool ratio of 15:1, using a Labomat BFA-12 dyeing machine (Mathis, Switzerland) at 55 °C and pH 9 using 0.2 M Na₂CO₃/NaHCO₃ buffer. After

the treatment, the wool samples were hand-squeezed, rinsed in a pH 4 solution at 70 °C for 5 min and then in cold distilled water, and finally dried at room temperature.

2.5. Experimental design

The experimental levels of applied Esperase 8.0L concentration, 0–0.5% o.w.f., enzymatic treatment time (15–75 min) and CHT concentration (0–1% o.w.f.) were calculated in accordance with the hybrid design for three variables (Roquemore, 1976). The experimental levels of independent variables (Esperase 8.0L concentration, enzymatic treatment time and CHT concentration) are given in Table 1. Analysis of the measured responses, *y*, was performed by the regression equation, i.e. a quadratic polynomial of the type given in the following equation:

$$y = b_0 + \sum_{i=1}^{3} b_i x_i + \sum_{j=1}^{3} b_{ij} x_i x_j$$
 (1)

where y is the measured response and b are regression coefficient values.

The multiple regression analysis and analysis of variance (ANOVA) were employed with the aid of the Statgraphics® Plus program to obtain the regression coefficients and adjusted polynomial equations containing only the variables with a significance above 95%. From the adjusted polynomial equations, graphics of contour were drawn.

2.6. Methods

Weight loss was determined on samples conditioned for at least 48 h at 20 °C and 65% RH. The results are expressed as the percentage of the weight loss of the treated samples compared with an untreated sample.

Area shrinkage was determined according to Woolmark TM 31 by the Wascator model FOM 71 washing machine using ISO 6330 5A wash cycle program three times.

Contact angles were calculated from the dynamic wetting force $(F_{\rm w})$ measurements carried out in an electrobalance KSV Sigma 70 tensiometer electrobalance (KSV Instruments Ltd., Helsinki, Finland) by means the Whilhelmy balance method (Hayes, Robinson, & Ralston, 1994). A single hair fibre was mounted overhanging 2–3 mm from an aluminium support in order to keep the fibre straight and rigid, thereby avoiding the buoyant effect and obtaining constant fibre perimeter during wetting measurements (Molina et al., 2002). The fibre was scanned

for 1 mm at a velocity of 0.5 mm/min for both the advancing (Adv) and receding (Rec) modes. All measurements were made at room temperature (20 °C) for both scale cuticular directions of immersion: against-scale (AS) and with-scale (WS).

The solid–liquid contact angle was measured from Eq. (2):

$$F_{\rm w} = \gamma_1 p \cos \theta \tag{2}$$

where $F_{\rm w}$ is the wetting force, p the fibre perimeter, γ_1 the liquid surface tension and θ the fibre–liquid contact angle. Perimeters of the scanned fibres were estimated from the wetting force measured in a total wetting liquid (decane), where $\cos\theta$ is assumed to be unity.

3. Results and discussion

The complete experimental design, the weight loss and area shrinkage parameter responses of the untreated (UT) and water-vapour LTP-treated wool are given in Table 2. The corresponding adjusted polynomial equations for these parameters are presented in Table 3.

In relation with the weight loss response for UT wool submitted to different CHT and Esperase 8.0L treatments (see Table 2), it can be deduced from the adjusted polynomial equation (Table 3) that the increase of the weight loss is due to the three variables, enzyme concentration, chitosan concentration and enzymatic treatment time. However, there is not any interaction between the variables. The weight loss curves (expressed in %) as a function of Esperase 8.0L concentration and enzymatic treatment time at 0%, 0.5% and 1.0% CHT levels are plotted in Fig. 2. The weight loss tends to increase until a maximum value by increasing the variables. CHT promotes higher weight loss being the maximum values 4% and 5% for 0.5 and 1% of CHT, respectively. This effect could be explained having into account that CHT increases the hydrophilicity of the wool surface (Julià, Cot, Erra, Jocić, & Canal, 1998; Jovančić, Jocić, Molina, Julià, & Erra, 2001). In order to confirm it, the contact angle of human hair fibres surface treated with CHT was determined according to Whilhelmy balance method. Human hair fibres were used for this purpose as a model of the wool fibre surface. Both fibres have similar chemical composition and epicuticle morphology, (Feughelman, 1997), but hair fibres are more rigid than wool fibres. For this reason, hair fibres can be introduced vertically into the wetting liquid, such as water, resulting in reproducible wetting force measurements.

Table 1 Variables and experimental levels

Variables	Codified levels							
	-2	-1.414	-1	0	1	1.414	2	
x_1 = Esperase 8.0L concentration (% o.w.f.)	0.000	0.073	_	0.250	_	0.427	0.500	
$x_2 = \text{Enzymatic treatment time (min)}$	15.00	23.79	_	45.00	-	66.21	75.00	
x_3 = Chitosan concentration (% o.w.f.)	0.000	_	0.250	0.500	0.750	_	1.000	

Table 2
Experimental treatment conditions and weight loss, and area shrinkage responses for untreated and LTP-treated wool

Exp. No.	Coded			Experimental			Weight loss %	Area shrinkage %
	x_1	x_2	<i>x</i> ₃	<i>x</i> ₁ Enz, %	x ₂ , min	<i>x</i> ₃ CHT, %		
(a) Untreate	ed .							
1	0	0	2	0.250	45.00	1.00	4.65	12.96
2	0	0	-2	0.250	45.00	0.00	4.13	33.05
3	-1.414	-1.414	1	0.073	23.79	0.75	1.01	24.02
4	1.414	-1.414	1	0.427	23.79	0.75	2.80	17.08
5	-1.414	1.414	1	0.073	66.21	0.75	1.70	21.53
6	1.414	1.414	1	0.427	66.21	0.75	4.78	19.48
7	2	0	-1	0.500	45.00	0.25	2.30	31.36
8	-2	0	-1	0.000	75.00	0.25	0.00	47.45
9	0	2	-1	0.250	75.00	0.25	2.18	36.30
10	0	-2	-1	0.250	15.00	0.25	0.64	39.29
11	0	0	0	0.250	45.00	0.50	4.47	28.45
12	0	0	0	0.250	45.00	0.50	4.71	29.82
13	0	0	0	0.250	45.00	0.50	4.49	28.41
(b) LTP tree	ated							
1	0	0	2	0.250	45.00	1.00	2.92	2.8
2	0	0	-2	0.250	45.00	0.00	3.25	7.7
3	-1.414	-1.414	1	0.073	23.79	0.75	0.57	4.9
4	1.414	-1.414	1	0.427	23.79	0.75	2.79	5.3
5	-1.414	1.414	1	0.073	66.21	0.75	1.29	7.3
6	1.414	1.414	1	0.427	66.21	0.75	4.62	0.2
7	2	0	-1	0.500	45.00	0.25	4.45	3.5
8	-2	0	-1	0.000	75.00	0.25	0.00	3.0
9	0	2	-1	0.250	75.00	0.25	3.46	5.5
10	0	-2	-1	0.250	15.00	0.25	1.66	4.9
11	0	0	0	0.250	45.00	0.50	3.17	3.3
12	0	0	0	0.250	45.00	0.50	3.65	3.6
13	0	0	0	0.250	45.00	0.50	3.32	3.8

Area shrinkage of UT wool = 57.8%. Area shrinkage of LTP-treated wool = 10.0%.

Table 3
The adjusted polynomial equations for the parameters investigated

(a) Untreated	
Response	
Weight loss	$4.49 + 0.72x_1 + 0.43x_2 + 0.39x_3 - 0.67x_1^2 - 0.61x_2^2$
-	$R^2 = 94.67\%$
Area shrinkage	$28.4 - 2.81x_1 - 7.03x_3$
-	$R^2 = 84.2\%$
(b) LTP treated	
Response	
Weight loss	$3.26 + 1.05x_1 + 0.45x_2 - 0.27x_1^2 + 0.14x_1x_2 - 0.18x_2$
•	$R^2 = 98.5\%$
Area shrinkage	$3.32 - 0.54x_1 - 0.57x_3 - 0.93x_1x_2 - 0.66x_1x_3 +$
	$0.34x_2^2 + 0.45x_3^2$
	$R^2 = 700\%$

Fig. 3 shows the adhesion tension (F/L) hysteresis for the UT- and CHT- treated fibres versus water wetting liquid. In the Table 4 are indicated the corresponding values of the contact angle calculated from the dynamic mean wetting force values (F) obtained for the advancing and receding mode. The adhesion tension hysteresis for UT- and CHT-treated clearly show that the scale direction of fibre immersion does not exert any influence on the advancing (Adv) adhesion tension values. However, for UT fibres the receding (Rec) adhesion tension values are very depen-

dent on the scale direction of fibre immersion, against scale (AS) and with scale (WS), as has been mentioned by Kamath (Kamath, Dansizer, & Weigmann, 1978). But, the WS receding adhesion tension values for CHT-treated fibres tend to increase by increasing the CHT concentration raising the same value as AS receding adhesion tensions values. This means that the dorsal face of the scales is becoming hydrophilic. It is known that (Kamath et al., 1978) advancing contact angles are associated with regions of low wettability (low-energy regions) and receding contact angles with regions of high wettability (high-energy regions).

The advancing contact angles of CHT-treated fibres are lower than UT fibres, being the differences more important in the second hysteresis cycle (Table 4). They reveal that CHT confers hydrophilicity to fibre surface. As a consequence of these results, in the Fig. 4 it is proposed the deposition mechanism of CHT on fibre surface. At low CHT concentration, the adsorption of the biopolymer occurs preferably on the frontal face of the scale because it is more hydrophilic than dorsal face. However, by increasing the polymer concentration the dorsal face of the scale is also coated by the biopolymer conferring wettability. Therefore, the wool surface energy decreases and then, the enzyme interaction on wool surface is improved. For this reason, the higher CHT concentration, the higher weight loss.

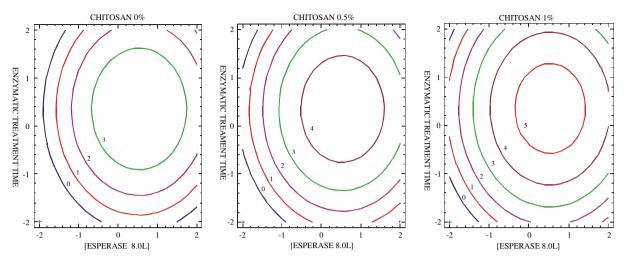


Fig. 2. Weight loss for untreated wool submitted to at different levels of CHT (0.0%, 0.5% and 1.0%) and Esperase 8.0L concentration at several enzymatic treatment times.

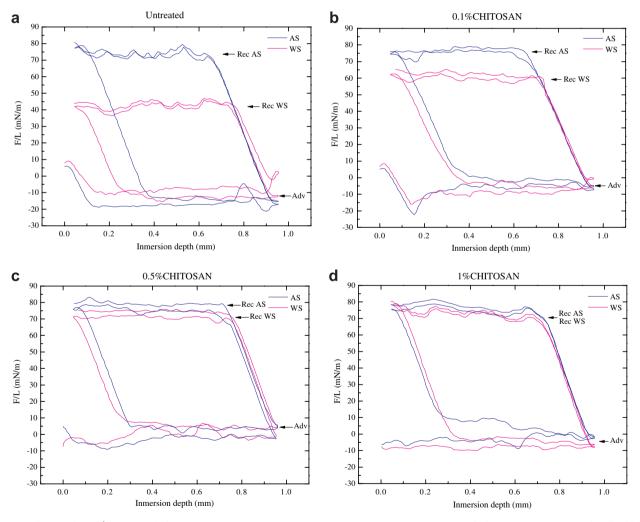


Fig. 3. Adhesion tension (*F/L*) hysteresis for (a) untreated, (b) 0.1%, (c) 0.5%, (d) 1% CHT-treated human hair fibres versus water wetting liquid for the WS and AS cuticular directions of immersion. *Abbreviations:* Adv, advancing; Rec, receding; AS, against scale; WS, with scale.

When wool has been treated previously with LTP and then submitted to CHT and Esperase 8.0L treatments at different experimental conditions (see Table 2), the adjusted polynomial equation (Table 3) reveals that the CHT concentration has no influence on weight loss. For this reason, the weight loss contour graphics are almost the same for

Table 4 Average values of advancing (θ_{Adv}) and receding (θ_{Rec}) contact angles (degrees) of untreated (UT) and fibres treated with different chitosan concentration

Samples	$ heta_{ ext{Adv}}$				$ heta_{ m Rec}$			
	1st cycle		2nd cycle		1st cycle		2nd cycle	
	AS	WS	AS	WS	AS	WS	AS	WS
UT	102.5 ± 2.1	97.7 ± 8.7	100.2 ± 10.3	99. ± 1.7	14.3 ± 54.2	51.2 ± 16.1	13.16	50.3 ± 17.5
0.1% CHT	91.8 ± 8.5	94.0 ± 7.6	88.9 ± 14.1	90.3 ± 6.9	0	31.8 ± 14.7	0	27.2 ± 19.8
0.5% CHT	89.5 ± 8.8	91.5 ± 6.9	81.8 ± 7.3	87.3 ± 3.5	0	14.5 ± 3.5	0	8.8 ± 11.1
1% CHT	92.6 ± 14.5	93.7 ± 15.2	$86. \pm 5.5$	86.5 ± 29.9	9.7 ^a	31.5 ^a	0	29.9 ^a

^a This is the value for one fibre because the value of the other two fibres was zero.

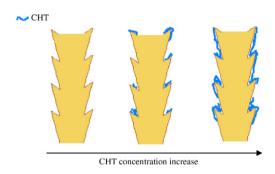


Fig. 4. Mechanism proposed of CHT deposition on wool fibre surface by increasing the biopolymer CHT concentration.

any level of chitosan concentration, being similar to the contour graphic without CHT (Fig. 5). It means that the chitosan application scarcely influenced the weight loss caused by enzyme treatment. The weight loss increases when both Esperase 8.0L concentration and enzymatic treatment time increase. It is not reached a maximum weight loss, just as it was observed in UT wool. It could be attributed to the fact that water-vapour LTP treatment increases dramatically the hydrophilicity of the wool surface by oxidation and removal of the natural hydrophobic barrier of wool (Molina, Jovančić, Jocić, Bertran, & Erra, 2003). Consequently, the low surface energy of the wool

fibres improves the enzyme interaction with the wool surface. Since, the fatty layer of wool fibres has been disappeared the enzyme diffusion into the fibre bulk could be higher than in UT wool.

The area shrinkage of UT wool submitted to enzymatic treatment depends on enzyme and CHT concentration, but not on the enzymatic treatment time, as it can be deduced from the adjusted polynomial equation (Table 3). It means that for the same conditions of Esperase 8.0L and CHT concentration the area shrinkage will be the same whatever the enzymatic treatment time. For this reason, the area shrinkage of treated wool at 45 min is exclusively shown in the Fig. 6. It reflects that the contribution of CHT to the reduction in the area shrinkage is more important than the effect of enzyme concentration. The area shrinkage changes from 45%, at low levels of CHT, to 20%, at high levels of CHT. Whereas, Esperase 8.0L only produces slight changes of the area shrinkage, as it ranges from 45%, at low Esperase 8.0L concentration, to 35% at high concentration levels.

When wool has been pre-treated with water-vapour LTP during 120 s the area shrinkage diminishes considerably (from 58% to10% after the second 5A wash cycle) due to the increase of surface hydrophilicity. A plasma exposure time of 10 s is enough to decrease the advancing contact

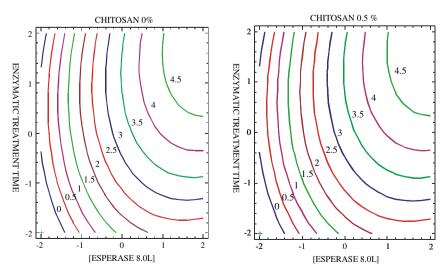


Fig. 5. Weight loss for LTP-treated wool submitted to at 0.0% and 0.5% level of CHT and Esperase 8.0L concentration at several enzymatic treatment times.

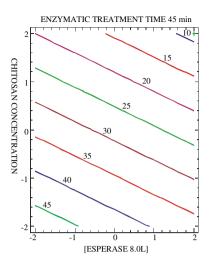


Fig. 6. Area shrinkage after the second 5A wash cycle for untreated wool treated with different concentration of CHT and Esperase 8.0L being the enzymatic treatment time 45 min.

angle from 103° to 60°, providing evidence of new hydrophilic groups in the fibre surface (Molina et al., 2003). From the adjusted polynomial equation (Table 3), it can be deduced that there is an interaction between Esperase 8.0L concentration and enzymatic treatment time and Esperase 8.0L and CHT concentration. Fig. 7a reveals that at low enzyme concentrations (0–0.125%, levels –2 and –1), the area shrinkage tends to increase when the enzymatic treatment time is higher than 45 min. However, the area shrinkage decreases by increasing the enzymatic treatment time when the enzyme concentration is higher than 0.25%. The area shrinkage contour graphic at an enzymatic treatment time of 45 min (Fig. 7b) shows that the effect of CHT on shrinkage reduction is higher when the Esperase 8.0L concentration is higher.

In order to optimize both responses the weight loss and area shrinkage the desirability function was used (Montgomery, 2001). The general approach is to first convert

each response y_i into an individual desirability function d_i that varies over the range $0 \le d_i \le 1$ where if the response v_i is at its goal, then $d_i = 1$, and if the response is outside an acceptable region, $d_i = 0$. Then the design variables are chosen to maximize the overall desirability from the geometric average of individual desirability. In both cases, for UT- and LTP-treated wool, the optimum value is placed at low enzyme concentration and enzymatic treatment time (Fig. 8, green point). In Table 5 the optimum conditions to obtain simultaneously low values of area shrinkage and weight loss are shown. In the case of UT fabric the enzyme and CHT concentration should be 0.0925\% and 1\%, respectively, whereas in the case of LTP-treated, the enzyme and CHT concentration 0% and 0.3%, respectively. The LTP treatment reduces considerably the area shrinkage and for these reason the application of Esperase 8.0L is not necessary. However, the enzymatic treatment improves significantly the handle of LTP+CHTtreated fabrics (S. Vilchez, A.M. Manich, P. Erra, IIQAB-CSIC, unpublished data). In the optimum conditions, the weight loss and area shrinkage for UT fabrics treated with CHT+Esperase 8.0L are 0% and 18%, respectively, and for LTP fabrics treated with CHT+Esperase 8.0L 0% and 1.7%, respectively.

4. Conclusions

The systematic study on CHT treatment followed by enzyme treatment of UT and water-vapour LTP treated, by means an experimental hybrid design, has revealed the main contribution of CHT on the treatments of UT wool with enzyme. The results suggest that the main role played by chitosan is to confer hydrophilicity to wool surface such as low temperature plasma, but with minor extent and by means a different mechanism. Whereas, the oxidative LTP confers wettability properties to hydrophobic UT wool fibre surface by oxidation and removal of fatty layer,

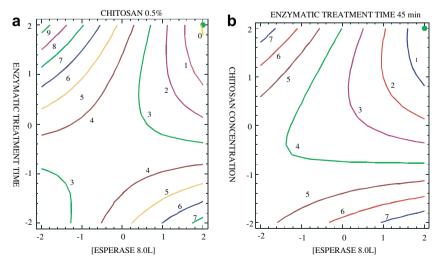


Fig. 7. Area shrinkage after second 5A wash cycle for LTP-treated wool submitted to: (a) Esperase 8.0L treatments at several enzymatic treatment times being CHT level of 0.5% and (b) at different CHT and Esperase 8.0L concentration being the enzymatic treatment time of 45 min.

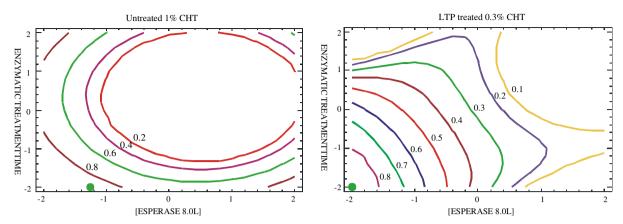


Fig. 8. Desirability of weight loss and area shrinkage for UT and LTP-treated fabrics. • indicates the optimum value.

Table 5
Optimum experimental conditions to obtain the lowest weight loss and area shrinkage percentage for UT and LTP treated wool

	UT		LTP Treated			
	Codified variable	Experimental variable	Codified variable	Experimental variable		
Enz, % o.w.f.	-1.26	0.0925	-2	0		
Time, min	-2	15	-2	15		
CHT, % o.w.f.	2	1	-0.8	0.3		

the biopolymer CHT provide hydrophilicity by coating the hydrophobic dorsal part of scale. Therefore, the enzyme effectiveness is improved causing an increase of the weight loss. Instead, the posterior CHT adsorption on LTP-treated wool fibre the enzyme is being active. It is deduced that by means CHT treatment, the enzyme effect can be modulated by varying the CHT concentration. In the other hand, due to the film formation property of CHT, the movement of some fibres respect to others by an aqueous washing is avoided, with which the natural shrinkage tendency of UT wool fabrics is also reduced.

The progressively weight loss with the enzyme treatment time in the LTP wool; can be attributed to an increase of the interaction between enzyme and wool proteins and the enzyme diffusion into the fibre bulk.

To achieve minimum weight loss and area shrinkage values, on UT wool submitted to Esperase 8.0L, the CHT concentration applied should be high (1% o.w.f.) and the enzyme concentration very low (0.09% o.w.f.) and the enzymatic treatment time not higher than 15 min. When the fabrics has been LTP treated, the Esperase 8.0L concentration and enzymatic treatment time should be maintained at very low level and the CHT concentration not higher than 0.3% o.w.f.

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Unity for the low temperature plasma treatments carried out with a RF plasma reactor.

References

Bahmani, S. A., East, G. C., & Holme, I. (2000). The application of chitosan in pigment printing. *Journal of the Society of Dyers and Colourists*, 116, 94–99.

Cegarra, J. (1996). The state of the art in textile biotechnology. *Journal of the Society of Dyers and Colourists, 112*(11), 326–329.

Davidson, R. S., & Xue, Y. (1994). Improving the dyeability of wool by treatment with chitosan. *Journal of the Society of Dyers and Colourists*, 110, 24–29.

Doshi, R., & Shelke, V. (2001). Enzymes in textile industry – An environment-friendly approach. *Indian Journal of Fibre & Textile Research*, 26, 202–205.

Erra, P., Molina, R., Jocić, D., Julià, M. R., Cuesta, A., & Tascon, J. M. D. (1999). Shrinkage properties of wool treated with low temperature plasma and chitosan biopolymer. *Textile Research Journal*, 69(11), 811–815

Feughelman, M. (1997). Mechanical properties and structure of alphakeratin fibres. In Wool, human and related fibres. Sydney: University of New South Wales Press.

Filipowska, B., Walaske, A., & Ribicki, E. (2000). Teinture et chitosan. L'IndustrieTextile, 1323, 79–81.

Fornelli, S. (1994). Towards an IQ of enzymes – Enzymatic treatments of protein fibres. *Melliand Textilberichte*, 75(2), 120–125.

Haefely, H. R. (1989). Enzymatic treatment of wool. *Textilveredhing*, 24, 271.

Hayes, R. A., Robinson, A. C., & Ralston, J. (1994). Whilhelmy technique for the rapid assessment of solid wetting dynamics. *Langmuir*, 10(8), 2850–2852.

Heine, E., & Höcker, H. (1995). Enzyme treatments for wool and cotton. *Review of Progress in Coloration*, 25, 57-63.

Jeong, Y. J., Cha, S. Y., Yu, W. R., & Park, W. H. (2002). Changes in the mechanical properties of chitosan-treated wool fabric. *Textile Research Journal*, 72(1), 70–76.

Jocić, D., Julià, M. R., & Erra, P. (1997). Application of a chitosan/ nonionic surfactant mixture to wool assessed by dyeing with a reactive dye. *Journal of the Society of Dyers and Colourists*, 113, 25–31.

Jocić, D., Topalovic, T., Vílchez, S., Jovančić, P., Radetic, M., Petrovic, Z. Lj., et al. (2000). Dyeing properties of wool modified by low-temperature plasma and biopolymer. In H. Hoecker & B. Kueppers (Eds.), Proceedings of the 10th international wool textile research conference (pp. 1–11). Germany: Aachen.

Jocić, D., Vílchez, S., Molina, R., Jovančić, P., Navarro, A., Julià, M. R., et al. (2001). The dye sorption properties of the low-temperature plasma and chitosan treated wool. In R. A. A. Muzzarelli & C.

- Muzzarelli (Eds.), *Proceedings of the 4th conference of the European chitin society* (pp. 317–325). Italy: ATEC.
- Jocić, D., Vílchez, S., Topalovic, T., Navarro, A., Julià, M. R., Erra, P. (2002). Biopolymer/dye interaction as the determinant of chitosan treated wool dyeing. In *Proceedings of the IFATCC 19th congress* (pp. 1–6). Paris.
- Jovančić, P., Jocić, D., & Dumic, J. (1998). The efficiency of an enzyme treatment in reducing wool shrinkage. *Journal of the Textile Institute*, 89(2), 390–400.
- Jovančić, P., Jocić, D., Erra, P., Molina, R., & Julià, M. R. (1998). European Microscopy and Analysis, 51, 15.
- Jovančić, P., Jocić, D., Molina, R., Julià, M. R., & Erra, P. (2001). Shrinkage properties of peroxide-enzyme-biopolymer treated wool. Textile Research Journal, 71(11), 948–953.
- Julià, M. R., Cot, M., Erra, P., Jocić, D., & Canal, J. M. (1998). The use of chitosan on hydrogen peroxide pretreated wool. AATCC Review, 30(8), 78–83.
- Julià, M. R., Pascual, E., & Erra, P. (2000). Influence of the molecular mass of chitosan on shrink-resistance and dyeing properties of chitosan treated wool. *Journal of the Society of Dyers and Colourists*, 116(2), 62–67.
- Kamath, Y. K., Dansizer, C. J., & Weigmann, H. D. (1978). Wetting behavior of human hair fibers. *Journal of Applied Polymer Science*, 22, 2295–2306.
- Masri, M. S., Randall, V. G., & Pitman, A. G. (1978). Use of crosslinked chitosan in the finishing treatment of wool fabric for launderingshrinkage control. In R. A. A. Muzzarelli (Ed.), *Proceedings of the 1st* international conference on chitin and chitosan (pp. 306–311). Boston: University of Ancona.

- Mathur, N. K., & Narang, C. K. (1990). Journal of Chemical Education, 67, 938
- Mehta, R. D., & Combs, R. (1997). Coverage of immature cotton neps in dyed fabrics using chitosan after treatment. American Dyestuff Reporter, 86(7), 43–44.
- Molina, R., Jovančić, P., Comelles, F., Bertran, E., & Erra, P. (2002). Shrink-resistance and wetting properties of keratin fibres treated by glow discharge. *Journal of Adhesion Science and Technology*, 16(11), 1469–1485.
- Molina, R., Jovančić, P., Jocić, D., Bertran, E., & Erra, P. (2003). Surface characterization of keratin fibres treated by water vapour plasma. Surface and Interface Analysis, 35(2), 128–135.
- Montgomery, D. C. (2001). *Design and analysis of experiments*. New York: John Wiley.
- Negri, A. P., Cornell, H. J., & Rivett, D. E. (1993). The modification of the surface diffusion barrier of wool. *Journal of the Society of Dyers* and Colourists, 109(5-6), 296–301.
- Riva, A., Cegarra, J., & Prieto, R. (1993). The role of an enzyme in reducing wool shrinkage. *Journal of the Society of Dyers and Colourists*, 109(5-6), 210–213.
- Roquemore, K. G. (1976). Technometrics, 18(4), 419.
- Vílchez, S., Navarro, Jocić, D., Erra, P. (2001). Estudio de procesos de tintura de lana tratada con plasma y/o quitosano. In *Proceedings of* 2001 international textile congress (pp. 522–530) Terrassa.
- Vîlchez, S., Jovančić, P., Manich, A. M., Julià, M. R., & Erra, P. (2005). Chitosan application on wool before enzymatic treatment. *Journal of Applied Polymer Science*, 98(5), 1938–1946.
- Yen, M. S. (2001). Application of chitosan/nonionic surfactant mixture in reactive dyes for dyeing wool fabrics. *Journal of Applied Polymer Science*, 80(14), 2859–2864.