INFLUENCE OF CHITOSAN ON WOOL TREATMENTS WITH ENZYME

Vílchez, S.[1]*, Manich, A.M.[2], Jovancic, P.[3], Erra P.[1]

[1]Department of Surfactant Technology, IIQAB-CSIC, c/ Jordi Girona, 18-26, E-08034 Barcelona, Spain

[2] Ecotechnologies Department, IIQAB-CSIC, c/ Jordi Girona, 18-26, E-08034 Barcelona, Spain

[3]Textile Engineering Department, Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, YU-11120 Belgrade, Serbia and Montenegro

Abstract

The application of the biopolymer chitosan (CHT) on wool fibres prior to enzymatic treatment was investigated in order to control the enzymatic action and also to reduce the wool damage. However, it was unclear to know the influence of CHT on wool enzyme treatments from the results obtained. To enhance the CHT sorption on the fibre surface, wool has been previously treated with low-temperature plasma. Several experimental conditions have been selected according to a hybrid experimental design and different parameters have been controlled. The results obtained reveal that CHT confers hydrophilicity to the hydrophobic wool fibre surface promoting the interaction between the enzyme and the wool fibre.

Introduction

The use of proteolytic enzymes to achieve wool shrink-resistance, better whiteness and improved handle [1-4] is interesting in order to replace conventional processes that produce absorbable organic halogen compounds (AOX). However, it is necessary to control enzymatic action to prevent wool damage. For this reason wool fabric was pre-treated with chitosan in an attempt to efficiently control enzymatic action. Chitosan is nowadays considered as a useful textile auxiliary due to their properties such as film formation, water absorption capacity, antimicrobial effects, etc. Because of chitosan is weakly bound to unmodified fibre we have made a pre-treatment with low temperature plasma (LTP) to promote the formation of new anionic groups on the fibre [5, 6] thus enhancing the chitosan binding. Accordingly, an experimental design on untreated and LTP treated wool has been carried out. The variables selected were enzyme concentration, enzymatic treatment time and chitosan concentration. Different parameters have been evaluated such as weight loss and area shrinkage. Contact angles measurements of single human hair fibres were used as a model of wool fibre to study the wetting properties of the fibres treated with different chitosan concentration.

Materials and Methods

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, U.S.A., 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.

Methods

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 seconds, 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.

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

Enzyme treatments: they 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 55º C and pH 9 using 0.2 M Na_2CO_3/ $NaHCO_3$ buffer. After the treatment, the wool samples were hand-squeezed, rinsed in a pH 4 solutions at 70ºC for 5 minutes and then in cold distilled water, and finally dried at room temperature.

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 3 variables [7]. 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 Equation 1:

$$y = b_0 + \sum_{i=1}^{3} b_i x_i + \sum_{j=1}^{3} b_{ij} x_i x_j \qquad \text{Equation 1}$$

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 =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

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 significance above 95%. From the adjusted polynomial equations, graphics of contour were drawn.

Tests

a) Weight loss was determined on samples conditioned for at least 48 h at 20º C and 65% RH. The results are expressed as the percentage of the weight loss of the treated samples compared with an untreated sample; b) Area shrinkage: was determined according to Woolmark TM 31 by the Wascator model FOM 71 washing machine using ISO 6330 5A wash cycle programme 3 times; c) Contact angles: were calculated from the dynamic wetting force (F_w) measurements carried out in an electrobalance KSV Sigma 70 contact angle meter (KSV Instruments Ltd., Helsinki, Finland) by means the Whilhelmy balance method [8].

Results and Discussion

The experimental treatment conditions and the adjusted polynomial equations as well as weight loss and shrinkage area responses for untreated and LTP treated wool, are given in Table 2 and 3 respectively.

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

a) Untreated

Exp. no.	Coded			Experimental			Weight loss %	Area shrinkage %
	x_1	x_2	x_3	x_1 Enz, %	x_2 min	x_3 CHT,%		
1	0	0	2	0.250	45.00	1.00	4.65	13.0
2	0	0	-2	0.250	45.00	0.00	4.13	33.0
3	-1.414	-1.414	1	0.073	23.79	0.75	1.01	24.0
4	1.414	-1.414	1	0.427	23.79	0.75	2.80	17.1
5	-1.414	1.414	1	0.073	66.21	0.75	1.70	21.5
6	1.414	1.414	1	0.427	66.21	0.75	4.78	19.5
7	2	0	-1	0.500	45.00	0.25	2.30	31.4
8	-2	0	-1	0.000	75.00	0.25	0.00	47.4
9	0	2	-1	0.250	75.00	0.25	2.18	36.3
10	0	-2	-1	0.250	15.00	0.25	0.64	39.3
11	0	0	0	0.250	45.00	0.50	4.47	28.4
12	0	0	0	0.250	45.00	0.50	4.71	29.8
13	0	0	0	0.250	45.00	0.50	4.49	28.4

b) LTP treated

Exp. no.	Coded			Experimental			Weight loss %	Area shrinkage %
	x_1	x_2	x_3	x_1 Enz, %	x_2 min	x_3 CHT,%		
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

UT 57.78
LTP 10

Table 3: The adjusted polynomial equations for the parameters investigated.

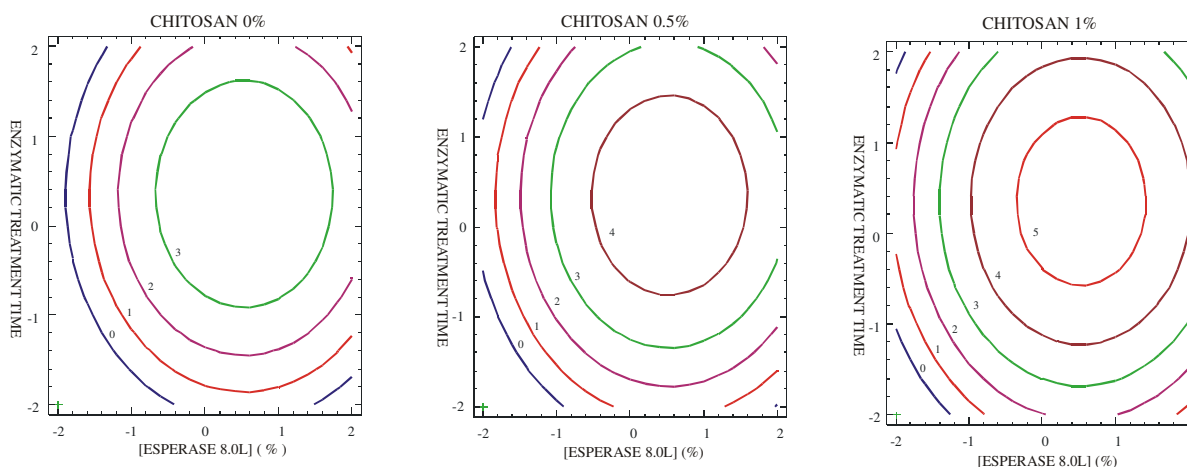a) Untreated

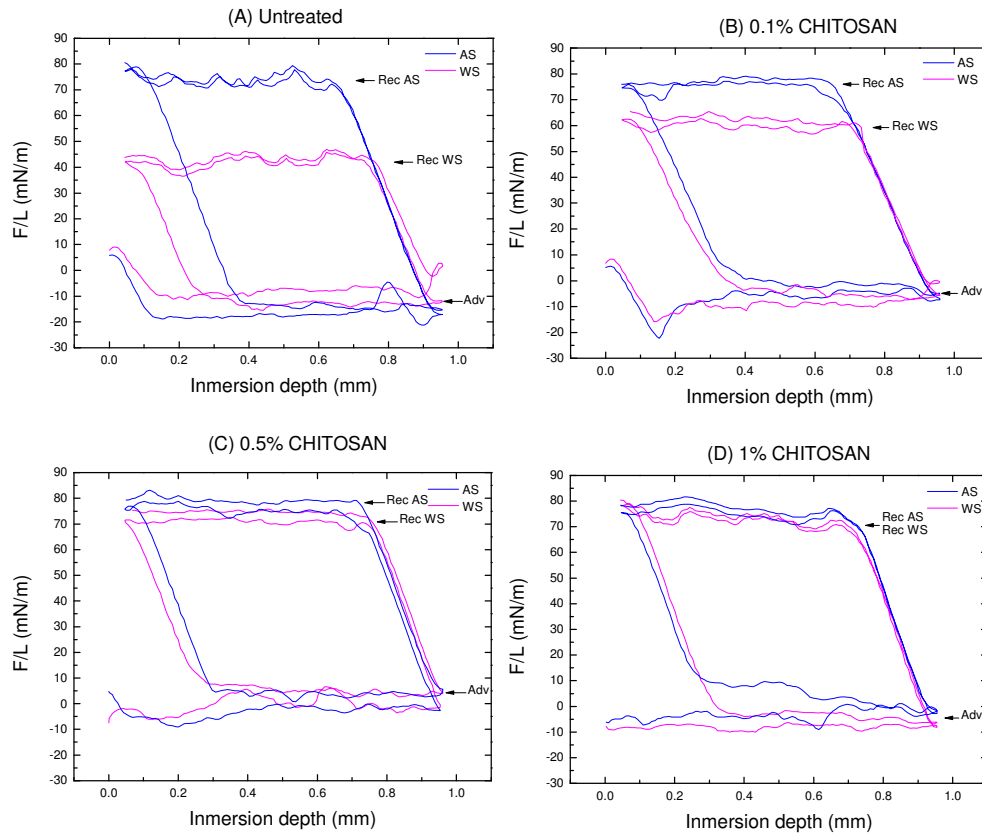| Response	
Weight loss	$4.49+0,78\ x_1+0.43\ x_2+0.39x_3-0.67\ x_1^2-0.61\ x_2^2$ $R^2= 94.67\%$
Area shrinkage	$28.4-2.81\ x_1-7.03\ x_3$ $R^2= 84.2\%$

b) LTP treated

Response	
Weight loss	$3.26 + 1.05\ x_1 + 0.45\ x_2 - 0.27\ x_1^2 + 0.14\ x_1x_3-0.18\ x^2$ $R^2= 98.5\%$
Area shrinkage	$3.32-0.54\ x_1-0.57\ x_3-0.93\ x_1x_2-0.66\ x_1x_3+0.34\ x_2^2+0.45\ x_3^2$ $R^2= 79\%$

The weight loss tends to increase until a maximum value by increasing the variables (Fig.1). 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 fibre surface [5, 9].

Figure 1 : Weight loss for wool submitted to at 0.0% and 0.5% level of CHT and Esperase 8.0L concentration at several enzymatic treatment times.

In order to confirm it, the contact angle of human hair fibres surface treated with different CHT concentration 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 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. The adhesion tension (F/L) hysteresis (Fig. 2) for UT and CHT treated fibres clearly show that the scale direction of fibre immersion into the wetting liquid, water, does not exert any influence on the advancing (Adv) adhesion tension values. However, for UT fibres the receding (Rec) adhesion tension values are very dependent on the scale direction of fibre immersion, against scale (AS) and with scale (WS), as has been mentioned by Kamath [10]. 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. That means that the hydrophobic dorsal face of the scales is becoming hydrophilic.
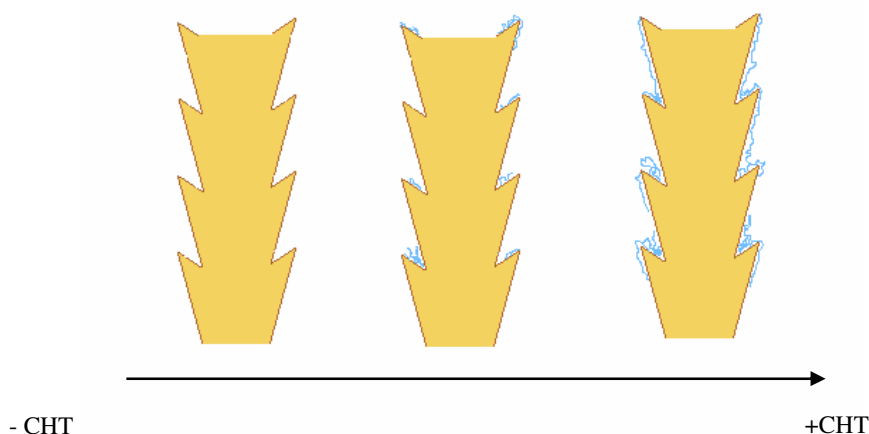
Figure 2 : Adhesion tension (F/L) hysteresis (two cycles) for (a) untreated, (b) 0.1% , (c) 0.5%, (d) 1% CHT treated human hair fibers versus water wetting liquid for the WS and AS cuticular directions of immersion. Abbreviations: Advancing (Adv), receding (Rec), against scale (AS), with scale (WS).

As it can see in Table 4, where are indicated the corresponding values of the contact angles, the scales become hydrophilic since the advancing contact angles values are about 90°. They confirm that CHT confers hydrophilicity to fibre surface.

Table 4: Average values of advancing (θ_{Adv}) and receding (θ_{Rec}) contact angles (degrees) of untreated (UT) and hair treated fibres with different chitosan concentration.
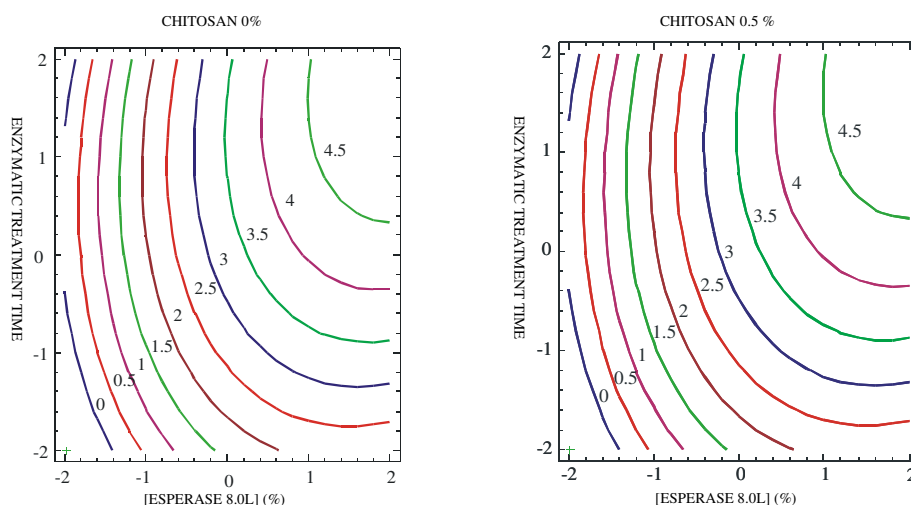
Samples	θ_{Adv}				θ_{Rec}			
	1st cycle		2nd cycle		1st cycle		2nd cycle	
	AS	WS	AS	WS	AS	WS	AS	WS
UT	102.5±2.1	97.7±8.7	100.2±10.3	99.±1.7	14.3±54.2	51.2±16.1	13.16	50.3±17.5
0.1% CHT	91.8±8.5	94.0±7.6	88.9±14.1	90.3±6.9	0	31.8±14.7	0	27.2±19.8
0.5% CHT	89.5±8.8	91.5±6.9	81.8±7.3	87.3±3.5	0	14.5±3.5	0	8.8±11.1
1% CHT	92.6±14.5	93.7±15.2	86.±5.5	86.5±29.9	9.7	31.5	0	29.9

As a consequence of these results, it is proposed a mechanism of CHT deposition on wool fibres surface (Fig 3). At low CHT concentration, the adsorption of the biopolymer occurs preferably on the frontal face of the scale because it is hydrophilic. However, by increasing the polymer concentration the dorsal face of the scale is also covered by the biopolymer conferring wettability. Therefore, the enzyme interaction on wool surface is improved. The higher CHT concentration, the higher weight loss is.

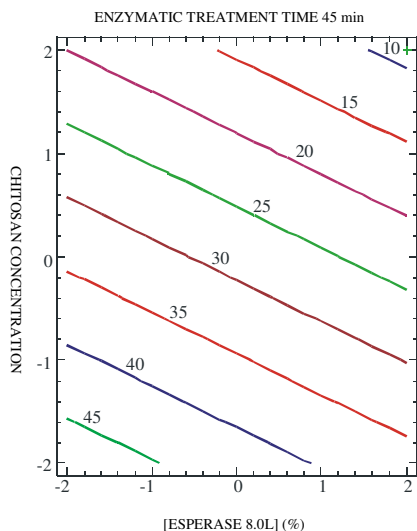**Figure 3 :** CHT deposition on wool fibre surface by increasing the biopolymer CHT concentration.

When wool has been treated previously with LTP and then submitted to CHT and Esperase 8.0L treatments at different experimental conditions (Table 2), the adjusted polynomial equation (Table 3) reveals that the CHT concentration does not have any influence on weight loss. For this reason, the weight loss contour graphics are almost the same for any level of chitosan concentration, being similar to the contour graphic without CHT (Fig. 4). 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 [11]. Consequently, the low surface energy of the wool fibres improves the enzyme interaction with the wool surface and for this reason CHT deposition does not confer additional hydrophilicity to wool surface.
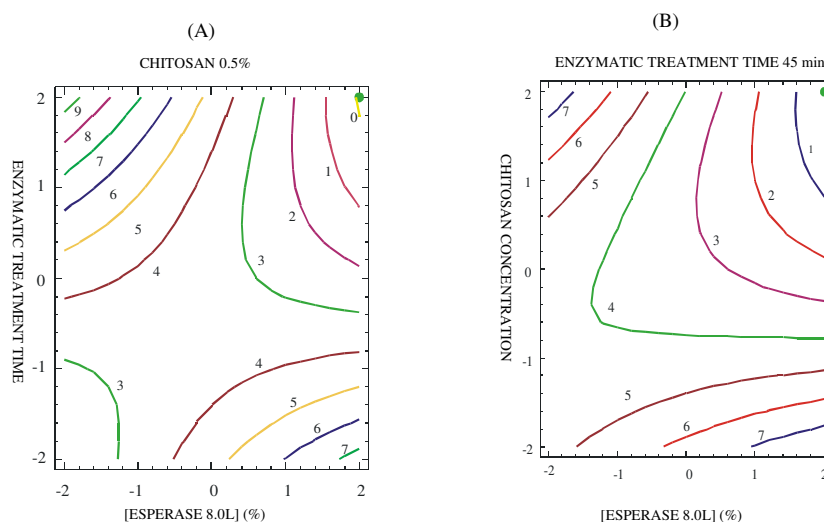

Figure 4 : Weight loss for LTP treated wool submitted to at 0.0% and 0.5% level of CHT and Esperase 8.0L concentration at several enzymatic treatment times.

The area shrinkage of UT wool submitted to enzymatic treatment is dependent on enzyme and CHT concentration, but is independent of the enzymatic treatment time as it can be deduced from the adjusted polynomial equation (Table 3). That 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. 5. 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. We think that the tendency of CHT to film formation on wool surface and its water absorption capacity are the most important factors to produce shrink-resist effect.

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

Figure 6 :　　　Area shrinkage after second 5A 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.

When wool has been pre-treated with water vapour LTP during 120s the area shrinkage diminishes considerably (from 58 to10 after the second 5A cycle of shrinkage test) due to the increase of surface hydrophilicity. Fig. 6A 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 45min. 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. 6B) shows that the effect of CHT on shrinkage reduction is more effective when the Esperase 8.0L concentration is high.

Conclusions

The results suggest that the main role played by chitosan is to confer hydrophilicity to the hydrophobic wool surface such as low temperature plasma 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, the biopolymer CHT provides hydrophilicity by coating the hydrophobic dorsal part of scale. Therefore, enzyme interaction with wool fibres is improved causing an increase of the weight loss. Instead, the posterior CHT adsorption on LTP treated wool fibre has no influence on enzyme activity. It is deduced that by means CHT treatment, the enzyme activity on UT wool fibres can be modulated by varying the CHT concentration. Moreover, due to the film formation and water absorption capacity properties of CHT, the movement of some fibres respect to others is avoided when the wool fabrics are submitted to an aqueous washing process. Therefore the natural shrinkage tendency of UT wool fabrics is also reduced.

Acknowledgements

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