Chitosan Application on Wool Before Enzymatic Treatment

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ABSTRACT: The influence of a chitosan application on wool fabric before a treatment with a proteolytic enzyme has been investigated. The enzymatic treatment enhances whiteness and confers shrink resistance to wool, but an increase in the enzyme concentration leads to a detrimental effect on the physicomechanical properties. A chitosan treatment before the enzymatic treatment additionally improves the shrink resistance and increases the weight loss. To better investigate the role played by the chitosan, surface-related properties, such as the friction coefficient, the compressional behavior (compressibility, linearity of compression, and thickness), the wearing resistance (weight loss after abrasion), the bursting resistance (bursting strength and deformation), and surface topography, have been studied. The results suggest that the chitosan pretreatment reduces the damage caused by the subsequent enzymatic treatment. They also imply a protective effect of the bursting and wearing resistance, which prevent excessive weight loss due to abrasion. A significant influence of the wool fiber cell membrane complex on the surface-related properties has been demonstrated through regression analysis and scanning electron microscopy observations. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 1938–1946, 2005

Key words: chitosan; degradation; enzymes

INTRODUCTION

There is increasing interest in environmentally friendly textile finishing as an alternative to the conventional processes that produce absorbable organic halogen compounds (AOX), such as chlorination. Enzymes have been considered appropriate alternatives because they can replace harsh chemicals, work under mild conditions, and are biodegradable.[1] An enzymatic treatment with protease generally reduces wool felting shrinkage, enhancing the whiteness degree and improving the dyeability.[2] However, if an enzyme is applied at levels that produce machine washability, wool fibers are frequently damaged.[3] Protease enzymes preferentially attack the highly swellable cell membrane complex (CMC) by penetrating cuticular scales, causing stripping and weakening of the wool fibers.[4] Consequently, it is essential to restrict the enzymatic action to the wool fiber surface or retard its action to avoid enzyme diffusion into the wool to control enzymatic treatment.

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Chitosan is a modified carbohydrate polymer derived from the chitin component of the shells of crustaceans. When chitin is deacetylated to about 50% of the free amino form, it is called chitosan [poly(1,4)-2-amino-2 deoxy-*b*-D-glucan; see Fig. 1]. Chitin and chitosan have different physical properties. Chitin is insoluble in most common solvents, whereas chitosan dissolves in many common aqueous acidic solutions. In aqueous media at pHs lower than 6.5, the amine group of chitosan acquires a proton and ionizes positively, and this gives the biopolymer a special capacity to fix anions and to fix itself to negatively ionized fibers.[5] Chitosan has several useful properties, such as nontoxicity, biocompatibility, biodegradability, antimicrobial activity, and chemical reactivity.[6] In the field of textiles, chitosan has been used as a shrink-resisting agent[7,8] and as an agent for improving the dyeability of wool.[9,10] Moreover, it has been used to improve dyeability, soil release properties, and the handle of cotton.[11] Chitosan, because of its polycationic character, has an affinity for interaction with oppositely charged molecules or surfaces, such as enzymes and wool, respectively. Because of its biocompatibility, biodegradability, water-binding capacity, and nontoxic properties,[12,13] it can be considered an environmentally acceptable substitute for synthetic polymers in textile finishing.[12,14,15]

A proteolytic enzyme used in experiments is an alkalophilic protease, which belongs to a subgroup of

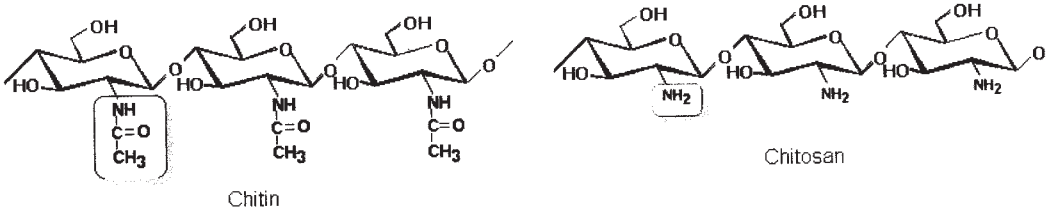

Figure 1 Structures of chitin and chitosan.

subtilisin enzymes with maximum stability in the range of pH 7–10 and high activity in the range of pH 8–12. Proteases or, more correctly, peptidases hydrolyze peptides bonds in soluble and insoluble peptides. Peptidases can be divided into endopeptidases and exopeptidases, which cleave peptide bonds within the protein or release amino acids sequentially from either the N or C terminus, respectively.[16]

In this work, wool was treated with chitosan before an enzymatic treatment in an attempt to efficiently control the enzymatic action. The enzymatic treatment was carried out at different concentrations with the monitoring of different parameters (weight loss, whiteness degree, and area shrinkage). These parameters were studied after chitosan, enzyme, and combined chitosan–enzyme treatments. The specific surface-related properties, such as the friction coefficient, compressional behavior (thickness, compressibility, and linearity of compression), wearing resistance (weight loss after abrasion), and bursting resistance (bursting strength and deformation) were evaluated. The obtained results reveal that a wool chitosan pretreatment reduces the fiber damage caused by the subsequent enzymatic treatment. Scanning electron microscopy (SEM) micrographs suggest that the enzymatic treatment is more uniform and regular if wool is previously treated with chitosan.

EXPERIMENTAL

Materials

The wool was a plain-weave woven fabric (345 g/m^2). The urea bisulfite solubility was 36.24%, the alkali solubility was 21.76%, and the pH of extracted water was 6.8. Chitosan of a known viscosity (775 cps) and degree of deacetylation (83.7%), kindly supplied by Vanson (Redmond, WA), was used without further purification. The proteolytic enzyme known as esperase was supplied by Novo Nordisk A/S (Bagsvaerd, Denmark). All other chemical and auxiliaries were laboratory-reagent-grade.

Chitosan treatments

Chitosan treatments were performed 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. Chitosan solutions (3 g/L) were freshly prepared by the dissolution of chitosan in distilled water containing acetic acid. After the treatment, the samples were run (3 m/min and 3 bar) through an HVF laboratory padder (Mathis, Zurich, Switzerland) to remove the excess solution and were finally dried at room temperature.

Enzyme treatments

Enzyme treatments were carried out by the exhaustion method for 30 min at a liquor-to-wool ratio of 15:1 with an OB 14 thermostatically controlled shaking bath (Memmert, Schwabach, Germany) at 55°C and pH 9 with a $Na_2CO_3/NaHCO_3$ buffer. After the treatment, the wool samples were hand-squeezed, rinsed in a pH 4 solution at 70°C for 5 min, rinsed in cold distilled water, and finally dried at room temperature.

Tests

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

The degree of whiteness (CIE Ganz 82) and the yellowness index (ASTM D 1925) were measured with a Color-Eye 3000 spectrophotometer (Macbeth, Regensdorf, Switzerland) with a D65 illuminant and a 10° observer. The higher the degree of whiteness was, the whiter the wool was.

TABLE I
Weight Loss of Treated Wool with Either the Enzyme or Chitosan+Enzyme at Different Enzyme Concentrations

Enzyme concentration (o.w.w.)	Weight loss (%)	
	Enzyme-treated	Chitosan+enzyme-treated
0.25	0	1
0.5	—	4.2
1	2.5	5
2	3.84	5.1
4	6	6.6

TABLE II
Whiteness Degree and Yellowness Index of Untreated Wool and Wool Treated Either with the Enzyme or Chitosan+Enzyme at Different Concentrations

Enzyme concentration (o.w.w.)	Whiteness (CIE Ganz 82)		Yellowness (ASTM D 1925)	
	Enzyme-treated	Chitosan+enzyme-treated	Enzyme-treated	Chitosan–enzyme-treated
UT	−27.43		33.02	
0.25	−17.91	−15.19	29.60	28.66
0.5	—	−2.62	—	25.11
1	−1.49	0.20	24.7	24.35
2	1.92	−2.65	24.03	25.28
4	5.35	2.65	23.09	23.77

The area shrinkage was determined according to Woolmark TM 31 with a Wascator model FOM 71 washing machine (Electrolux-Wascator AB, Ljungby, Sweden) with the ISO 6330 5A wash cycle program as a base to determine the total felting shrinkage of wool samples.

The surface friction was measured according to IUP Standard 51 with an MT-LQ tensile testing machine supplied by Stable Micro Systems (Godalming, UK). The dynamic friction coefficient between fabric/aluminum and fabric/Teflon was determined under 0.53 kPa of pressure with a contact area of 108.8 cm^2 and a relative displacement velocity of 8 mm/s.

The thickness was determined according to ASTM Standard D 1777 at 4.9 kPa, and the compressibility behavior was determined in accordance with the method of Kawabata.[17]

The bursting resistance was measured with the apparatus and conditions described in IUP (BS3144 Standard). A circular fabric sample 35 mm in diameter was pushed by a cylindrical probe 9 mm in diameter at a uniform speed of 1.7 mm/s up to breaking. The cylindrical probe had a hemispherical test head with a curvature radius of 20 mm; the breaking strength (N) and deformation (mm) were recorded. The abrasion resistance was measured with a Martindale abrasion tester (Stockport, England) in accordance with the British Standard method.[18] The mechanical properties of the fabrics were measured under standard laboratory conditions (22°C and 65% relative humidity).

SEM observations were carried out with a Hitachi 570 scanning electron microscope (Krefeld, Germany); the wool samples were previously sputter-coated with a thin layer of gold.

RESULTS

Table I shows the weight loss of wool samples treated either with enzyme only (enzyme) or pretreated with chitosan and subsequently treated with enzyme (chitosan+enzyme). The weight loss increases with increasing enzyme concentration. Because a weight loss of 3–4.5% could be excessive for wool,[19,20] it has been assumed that enzyme concentrations over 0.25% over weight wool (o.w.w.) for wool samples pretreated with chitosan should be avoided.

Table II shows the whiteness degree and yellowness index of untreated wool and wool treated under different experimental conditions. If we compare untreated wool and wool treated with the enzyme, there is an obvious improvement in the whiteness degree for all enzyme concentrations, regardless of the chi-

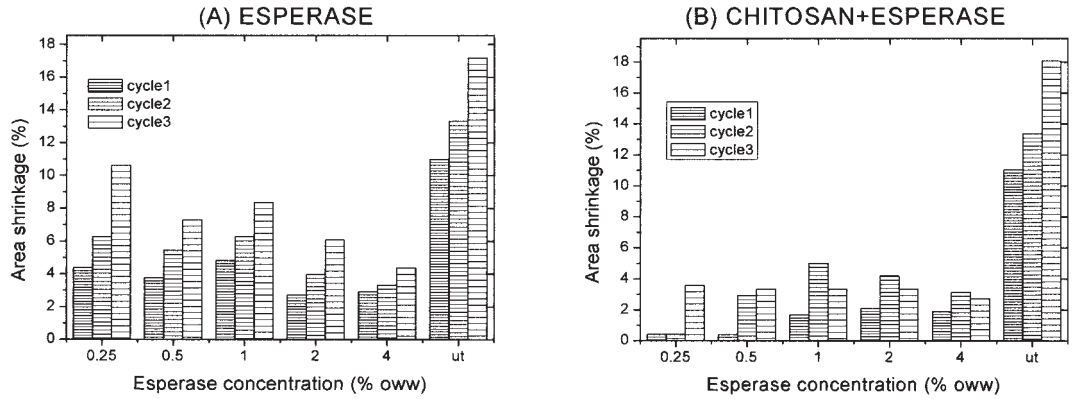

Figure 2 Area shrinkage (%) of untreated wool and wool treated with either (A) the enzyme or (B) chitosan+enzyme as a function of the enzyme concentration.

TABLE III
Friction Coefficients of Untreated and Differently Treated Wool Fabrics

Chitosan pretreatment	Friction surface			
	Teflon		Aluminium	
	No	Yes	No	Yes
Untreated	0.2345	0.2850	0.2274	0.2552
0% esperase[a]	0.3007	0.2778	0.2555	0.2600
0.25% esperase	0.2367	0.2403	0.2316	0.2281
0.50% esperase	—	0.2395	—	0.2309
1% esperase	0.2602	0.2586	0.2333	0.2347
2% esperase	0.2638	0.2564	0.2357	0.2372
4% esperase	0.2564	0.2626	0.2366	0.2350

[a] Blank enzymatic treatment (enzymatic treatment with no enzyme present).

tosan pretreatment. The higher the applied enzyme concentration is, the higher the obtained degree of whiteness is. This could be attributed to enzyme efficiency in eliminating the naturally colored pigments of the wool surface, which are bonded to the wool protein and lie mainly in the cuticle layer.[21] The chitosan pretreatment slightly degrades the whiteness degree of enzymatically treated wool, probable because of the natural coloration of the chitosan.

The area shrinkage percentage of untreated, enzyme-treated, and chitosan+enzyme-treated wool after the first, second, and third 5A Wascator shrinkage test cycles are presented in Figure 2. The area shrinkage of the enzymatically treated samples is slightly lower than that of the untreated one [Fig. 2(A)]. As we have reported elsewhere,[21] the shrinkage reduction tends to decrease slightly with increasing enzyme concentration. Nevertheless, at a higher enzyme concentration, the weight loss rises, and this indicates possible fiber damage. It has been already published that proteolytic enzymes promote the partial lifting of cuticle edges, the reduction of scale height, and the removal of the endocuticle.[22] Because of these effects, the natural tendency of wool to shrink is reduced. However, the area shrinkage tends to rise with an increasing number of washing cycles; this is also noted for the untreated sample.

When wool has been previously treated with chitosan [Fig. 2(B)], the area shrinkage is noticeably lower than that of enzyme-treated wool, even at the lowest enzyme concentration of 0.25%. Therefore, the pres-

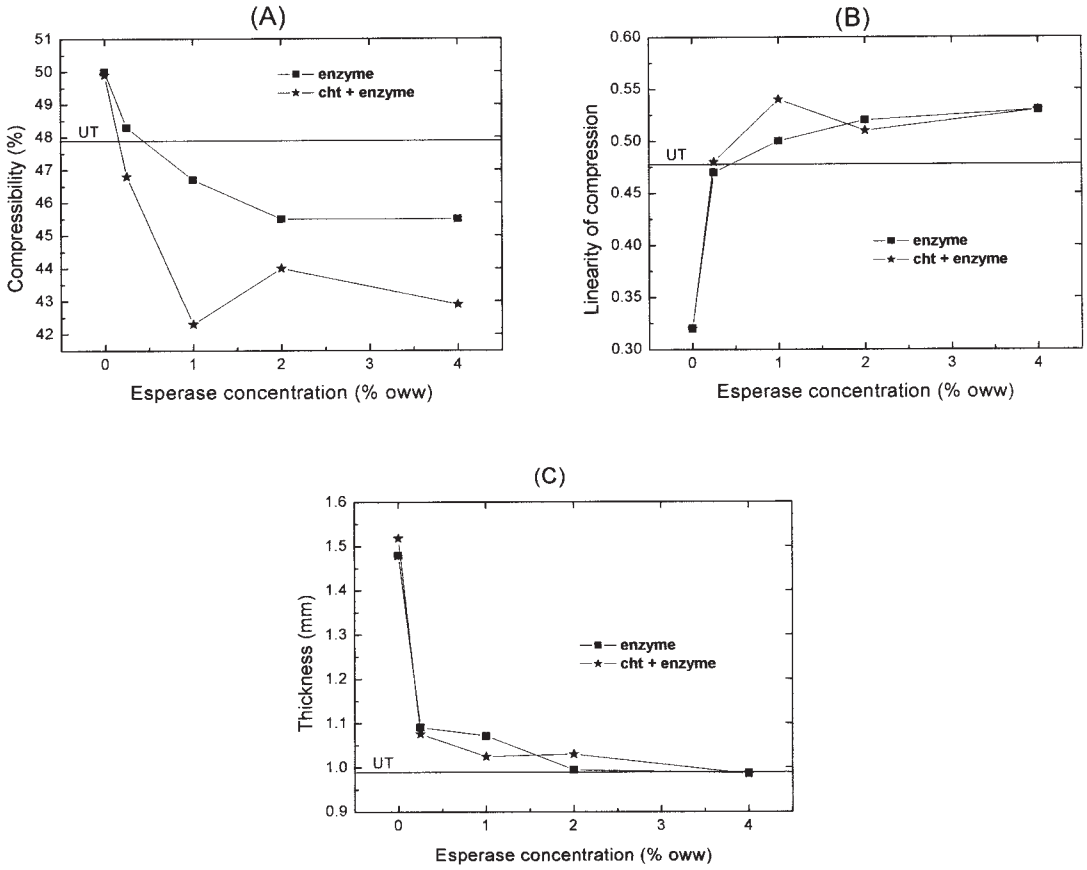

Figure 3 (A) Compressibility, (B) linearity of compression, and (C) thickness versus the enzyme concentration of differently treated wools.

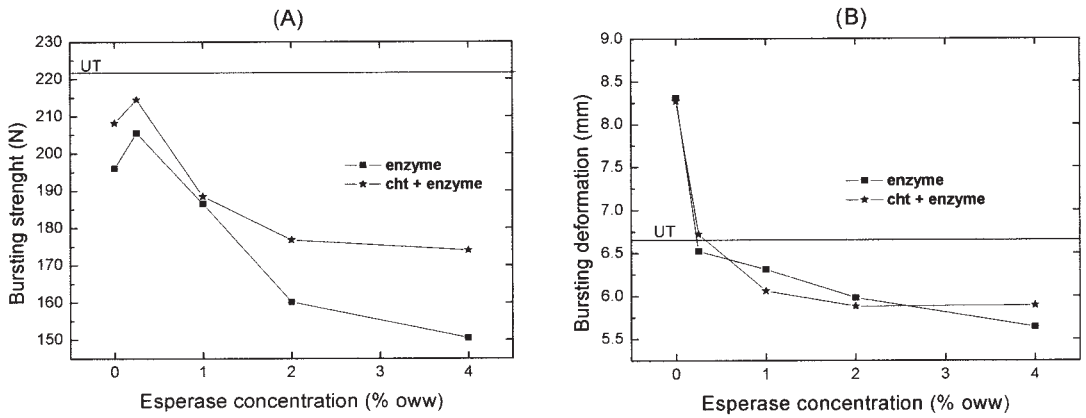

Figure 4 (A) Bursting strength and (B) bursting deformation versus the enzyme concentration of differently treated wools.

ence of chitosan has a positive influence on the wool shrink resistance. This effect of chitosan could be attributed to the swelling of the chitosan sorbed on the fiber surface during aqueous washing, which consequently reduces the frictional coefficient of the fibers. Although chitosan is not visible on the fiber surface by SEM observations, some interfiber chitosan bonds have been seen, preventing the movement of fibers and reducing the shrinkage.[23] It is also known that chitosan confers shrink resistance to wool previously treated with an oxidative agent such as hydrogen peroxide[5] or permonosulfuric acid[24] or submitted to an air, oxygen, or water-vapor low-temperature plasma treatment.[23,25] However, the presence of chitosan on the wool fiber surface positively affects the enzymatic treatment, as documented by an increase in the weight loss (see Table I).

To additionally evaluated the contribution of chitosan on the enzyme treatment, surface-related properties, such as the friction coefficient, compressional behavior (compressibility, linearity of compression, and thickness), wearing resistance (weight loss after abrasion), and bursting resistance (bursting strength and bursting deformation), have been studied.

The surface properties of a fabric can be represented by the friction coefficient, which is determined from the frictional effect of its fibers and yarns as well as the geometric roughness of its surface.[6] The frictional coefficient was determined from the frictional effect of the surface of the fabric treated with the enzyme or chitosan+enzyme in contact with Teflon or aluminum as a reference surface. The results are presented in Table III. In comparison with the untreated sample, the blank enzymatic treatment (0% esperase) produces an increase in the frictional coefficient, regardless of the reference surfaces applied. However, this increase is not definitely confirmed when the wool has been pretreated with chitosan. If we use Teflon as the reference surface, the frictional coefficient of wool treated with the enzyme tends to increase with increasing enzyme concentration. However, this trend is unclear in the case of chitosan-pretreated wool. Similar results have been obtained with the aluminum reference surface, although the differences between the values are less pronounced. It seems that the Teflon reference material allows more accurate results to be obtained than the aluminum reference surface.

Several physical properties, including compressibility, have been identified as potentially influencing the human interpretation of textile handle.[26] Compressibility evaluates the fractional compression (%) impaired to the fabric by a fixed load with respect to an initial thickness measurement. Figure 3(A) shows that the compressibility of enzyme-treated wool gradually decreases with increasing enzyme concentration until 2% o.w.w. The decrease in the compressibility is more pronounced when wool has been chitosan-pretreated, and an increase in the stiffness is revealed. The linearity of compression [Fig. 3(B)] confirms these results. It increases with increasing enzyme concentration, and this indicates the homogeneous, that is, more compact, fabric structure.

The thickness is the distance between the upper and lower sides of a textile fabric and is measured as the

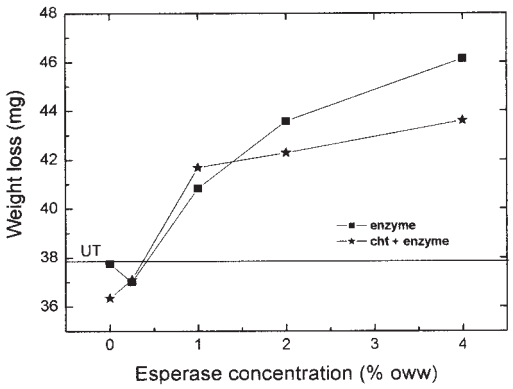

Figure 5 Weight loss after 30,000 abrasion cycles versus the enzyme concentration of differently treated wools.

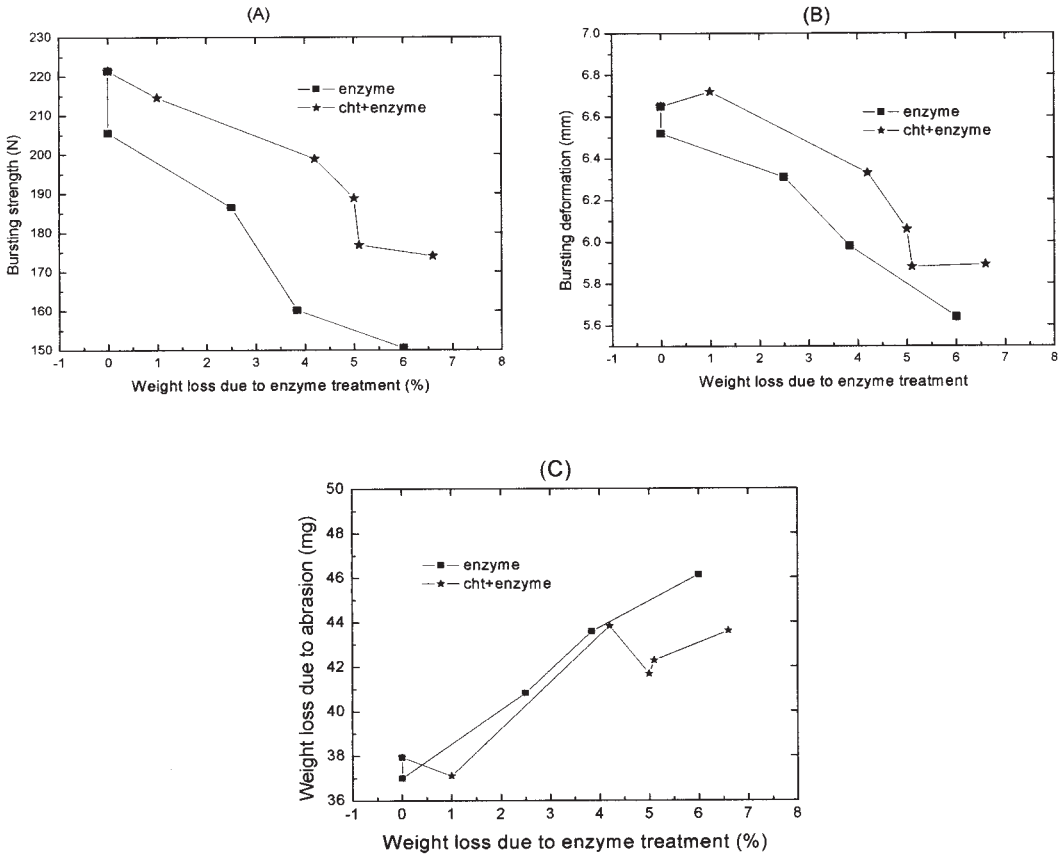

Figure 6 (A) Bursting strength, (B) bursting deformation, and (C) weight loss due to abrasion versus the enzymatic weight loss of differently treated wools.

distance of two plane parallel measuring plates of a certain size between which the textile fabric is located under a certain measured pressure. The fabric thickness decreases with increasing enzyme concentration, regardless of the chitosan pretreatment [Fig. 3(C)]. The blank enzymatic treatment causes an increase in the thickness that can be attributed to stress relaxation and to a felting effect. The values of the thickness after the enzymatic treatment are comparable to those of the untreated sample, probably because of swelling or protein removal during the course of the treatment.

Mechanical resistance properties such as the bursting strength and deformation were also evaluated. The bursting strength is defined as the multidirectional resistance to the rupture of a circular fabric specimen. The testing of wool was carried out under two-dimensional stress by the application of a load perpendicular to the test surface. Both the effective bursting strength (N) and the bulge height (bursting deformation; mm) were measured.

As we can see in Figure 4, the fabric bursting strength is negatively affected by the blank enzymatic treatment and by increasing enzyme concentration. However, a clear protective effect of the chitosan pretreatment on the bursting strength can be observed. The bursting deformation of the untreated sample increases after the blank enzymatic treatment, but it is negatively affected by an increase in the enzyme concentration even when the wool has been previously treated with chitosan. The treatments with more than 0.25% enzyme cause a significant decrease in the

TABLE IV
Regression Analysis Indicating the Level of Significance, Determination Coefficient, and Contribution of the Weight Loss and Chitosan Pretreatment to the Bursting and Abrasion Resistance

Regression coefficient	Bursting strength	Bursting deformation	Abrasion resistance
Constant	207.05	6.58	38.11
Weight loss	−9.01	−0.15	1.21
Chitosan	21.56	0.21	−1.46
Significance level	0.01%	0.00%	0.02%
Determination of coefficient	89.65%	92.46%	88.27%
Contribution to the determination coefficient			
Weight loss	69.02%	84.45%	82.80%
Chitosan	20.63%	8.01%	5.47%

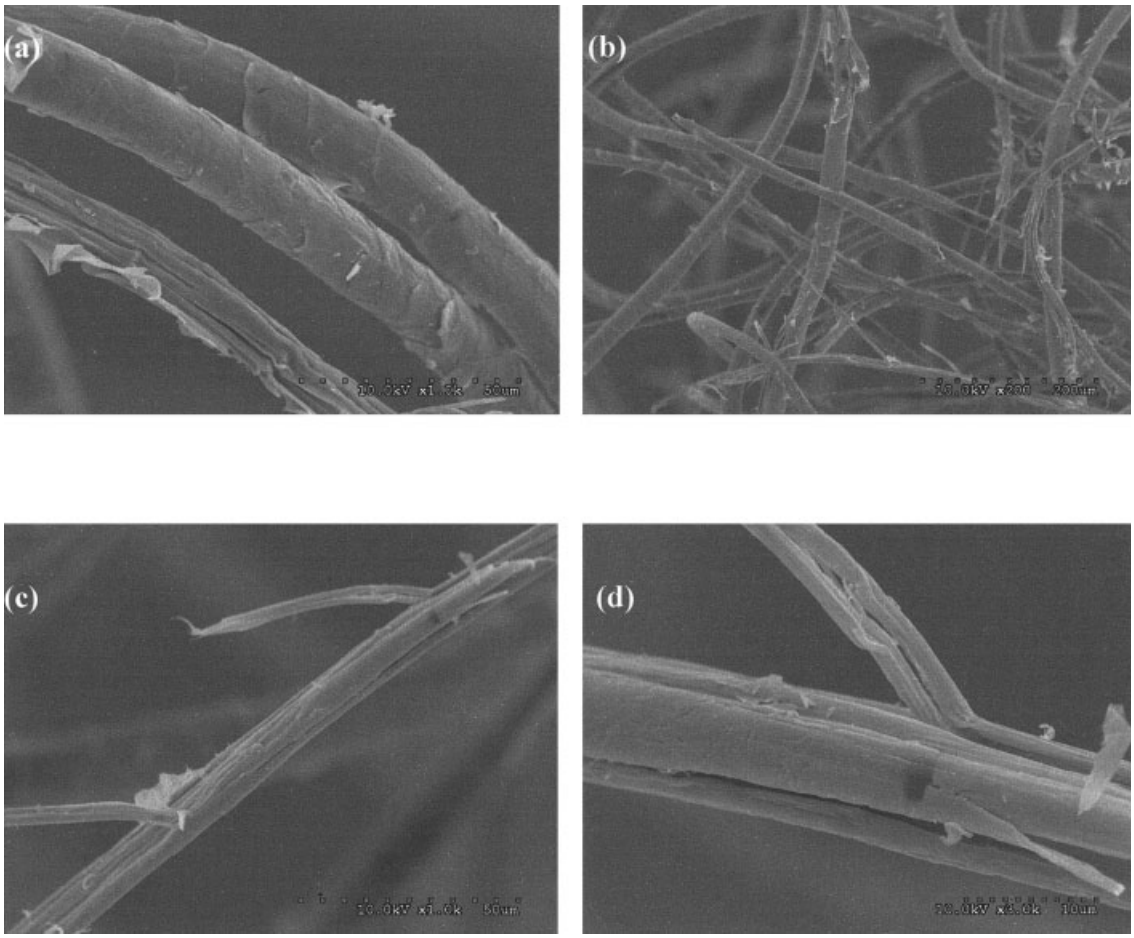

Figure 7 SEM images of wool treated with 0.5% esperase for 30 min.

bursting strength and deformation, and this indicates damage to the wool fabric.

Fabric rubbing, scrapping, and wearing against itself or against other abrasive surfaces produces abrasion in wear. As expected, the abrasion modifies the fabric surface and consequently affects the internal structure of the fabric. Abrasion resistance can be measured according to different criteria.[27] In this work, it has been measured by the weight loss of the fabric after 30,000 abrasion cycles (Fig. 5).

Because the abrasion resistance is directly related to the wearing properties of fabrics, a treatment with more than 1% enzyme should be avoided despite the excellent protective effect of the chitosan pretreatment (see Fig. 5)

It is widely accepted that proteases preferentially attack the highly swellable CMC and the endocuticle. This, in turn, should mean that higher values of the weight loss signify lower the wool fiber/CMC ratio. Moreover, the mechanical properties of the wool fiber are closely related to the structure of the CMC. If there is some dependence between the weight loss and the bursting and/or abrasion resistance, it should be possible to indirectly deduce the particular role played by CMC in the enzymatic treatment studied.

Accordingly, we graphically present the dependence between the weight loss and the bursting strength and deformation [see Fig. 6(A,B), respectively]. The wool treated with chitosan before the enzymatic treatment shows constantly higher bursting strength and deformation values than the wool treated with the enzyme only. The same effect takes place in the case of abrasion resistance [see Fig. 6(C)]. An increase in the enzyme concentration results in higher weight loss because of the treatment, and consequently, the abrasion resistance is decreased. The same trend is observed for wool previously treated with chitosan, although the abrasion resistance is quite better than that of enzymatically treated wool.

To better quantify the influence of the chitosan pretreatment as well as the enzymatic treatment on the bursting and abrasion resistance, a regression analysis was performed. The influence of the enzyme was measured by the weight loss produced during the enzymatic treatment, whereas the influence of the chitosan pretreatment was explained by the dummy variable chitosan,[28] which equals zero for wool without pretreatment and is unity for chitosan-pretreated wool. Table IV shows the results of the regression analysis.

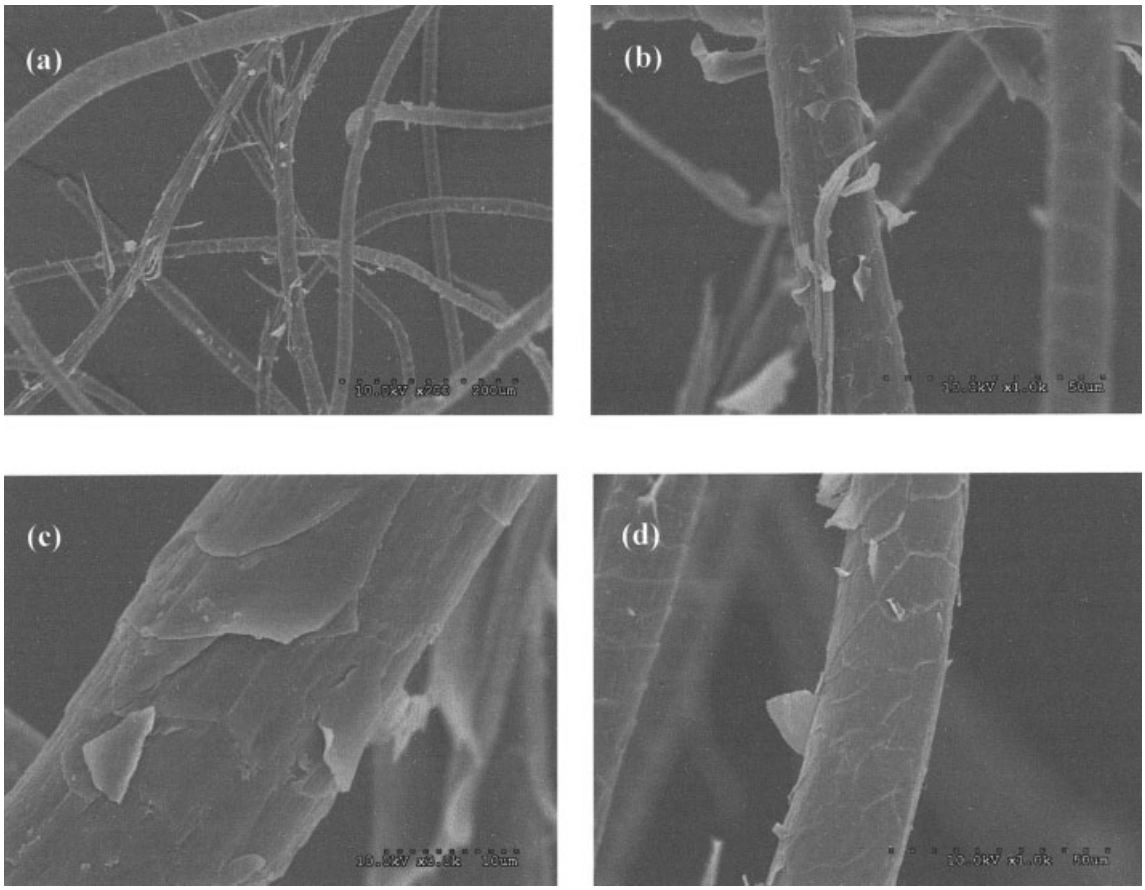

Figure 8 SEM images of wool treated with chitosan and then with 0.5% esperase for 30 min.

The enzymatic treatment has a significant influence on the bursting strength (69.02%), although it dominantly affects the bursting deformation (84.45%) and the abrasion resistance (82.80%). The protective effect of the pretreatment with chitosan on the bursting strength (20.63%), bursting deformation (8.01%), and abrasion resistance (5.47%) can also be observed. It seems that the enzymatic treatment only, depending on the treatment conditions, alters the CMC, which is visualized through the bursting and abrasion resistance loss. The chitosan pretreatment apparently preserves the structure of the CMC by improving the bursting and abrasion resistance.

The SEM observations confirm the results obtained by regression analysis. Figure 7 shows micrographs of wool treated with 0.5% o.w.w. enzyme, revealing a detrimental effect on the surface of the fibers. A majority of the wool fiber scales have apparently been modified or even removed. Also, the enzymatic treatment is not uniform because some fibers remain practically intact or slightly affected, whereas others are considerable damaged. Others authors have observed a similar effect by using specific enzymes.[3,19] However, when wool has been previously treated with chitosan, the cuticle cells are still visible, and subsequent enzymatic treatment seems to be more uniform and regular (Fig. 8).

CONCLUSIONS

It is reasonable to assume that the presence of chitosan on fiber surfaces increases the esperase efficiency, as revealed by the increase in the weight loss. The esperase could be adsorbed on the chitosan-coated wool fibers. The chitosan pretreatment improves the shrink resistance of wool fabrics, including when the wool is treated only with 0.25% esperase. At this esperase concentration, the shrink resistance is attained at the machine-washable level with an enhanced whiteness degree, and the values of the compressibility, linearity of compression, thickness, bursting strength, bursting deformation, and weight loss after abrasion are similar to those of an untreated sample. Enzyme concentrations over 1% o.w.w. should be avoided because of the excessive weight loss and impaired wearing properties of fabrics, despite the excellent shrink resistance achieved. However, at high esperase concentrations, the chitosan pretreatment also results in a protective effect on the wool fiber, reducing the damage caused by the subsequent enzymatic treatment. This has been confirmed by

the determination of the bursting and abrasion resistance. The regression analysis of these parameters with respect to the weight loss produced during the enzymatic treatment reveals that esperase preferably alters the CMC, and the chitosan pretreatment apparently preserves the CMC structure. SEM micrographs show the protective effect of chitosan and suggest that esperase treatment seems to be more uniform and regular if the wool has been previously treated with chitosan.

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