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A Comparative Study on Wool Bio-antifelting Based on Different Chemical Pretreatments

Qiang Wang, Ping Wang, Xuerong Fan*, Li Cui, Xianfei Zhao, and Xiaoxiao Gao

Key Laboratory of Science and Technology of Eco-Textile, Ministry of Education, Jiangnan University, Wuxi 214122, China
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Abstract: The enzymatic antifelting of wool with proteases, which is referred to as bio-antifelting, has become a promising eco-friendly alternative to conventional chlorination treatment. However, wool bio-antifelting in industrial scale has not been reached so far due to its unsatisfactory shrink-resistance and uncontrolled action in fiber damage. In this paper, the action and mechanism of two kinds of chemical pretreatments, i.e., hydrogen peroxide and dichlorodicyanuric acid pretreatments on the shrink-resistance of protease-treated wool fabrics were investigated and compared. The results show that although hydrogen peroxide treatment could decrease the shrinkage of wool in comparison with untreated one, its contribution to the enhancement of wool bio-antifelting with protease was not remarkable. An effective shrink-resistance can be obtained when the wool fabric was treated with dichlorodicyanuric acid and protease consecutively. Both of the two chemical pretreatments could improve the wettability and whiteness of protease-treated wool. The mechanism of different pretreatments for enhancing wool bio-antifelting with protease was further illustrated and compared via several microscopic analyses such as Allwörden's reaction, FTIR-ATR and SEM. The comprehensive comparison for wool bio-antifelting based on different chemical pretreatments reveals the difference of hydrogen peroxide and dichlorodicyanuric acid pretreatments in antifelting mechanism, which is valuable for getting a clear understanding and further modification of wool bio-antifelting.

Keywords: Wool, Bio-antifelting, Chemical pretreatment, Protease

Introduction

Wool is one of the most important fibers in textile industry and is commonly used for producing top-grade garments such as robes and business suits due to its special properties in fullness, elasticity handle, warmth retention and comfortability. However, the special scale structure in wool cuticle can easily cause felting shrinkage of wool fabrics subjected to mechanical action, most particularly during the laundering. A number of processes involving decreasing or eliminating the felting propensity have been extensively investigated for achieving machine washable wool [1,2]. To date, the chlorination/resin method (chlorine-Hercosett process) has been extensively applied for anti-felting finishing of wool fabrics to producing machine washable wool. However, this chemical treatment not only results in yellowing, strength loss, color fade and poor appearance of wool fabrics and garments, but also harms to human body and environment due to the release of absorbable organohalogens (AOX) in the effluents into the environment. Eco-friendly anti-felting techniques, i.e., AOX-free processes have been investigated in the last years [3-8].

Protease-based treatment of wool is one of the potential alternatives to chlorination antifelting [9-14]. It has some prominent advantages such as lower energy consumption and environmentally acceptable processing. However, in general the effectiveness of enzymatic antifelting of wool fabric is not very satisfactory due to the uncontrolled action between proteases and wool fibers. On one hand, this antifelting greatly depends on the type of protease used. On the other hand, proteases present lower accessibility to outer surface of wool fibers caused by hydrophobic lipid-like substances and the presence of a high degree cross-linkage of disulfide bonds among the cystines in wool exocuticle. This inability makes small protease molecules penetrate into overlapping cuticle cells and hydrolyze the proteins in cell membrane complex (CMC) and the cortex cells, causing high strength and weight losses [3,6,9].

Different pretreatment methods involving chloration, oxidation and reduction treatments as well as recently reported protease modification have been employed to improve the accessibility of proteases to the scale cells and enhance the effectiveness of enzymatic antifelting of wool fabric [3-5,13,15]. Chlorination pretreatment with dichlorodicyanuric acid (DCCA) followed by protease treatment has been actually used in textile industry, as recommended by Novozymes. Although it was claimed that chlorination-protease combined process could eliminate around half of the dosage of chlorination agents, AOX release problem still exists and devalues its actual application. Hydrogen peroxide pretreatment followed by protease treatment is an eco-friendly antifelting processing of wool fabric, but the effectiveness was conflicting according to limited reports [15-19]. The reason resulting in different results could be attributed to the composition of H_2O_2 treatment bath. The positive results for wool shrink-resistance had shown that hydrogen peroxide pretreatment in the presence of high concentration of salt (4 M NaCl) at high alkaline pH (11.5) could protect the wool fiber from internal damage by hydrogen peroxide and full shrink resistance of wool fabric

*Corresponding author: wxfxr@163.com

could be reached when combined with subsequent enzyme process [15]. Cardamone et al developed an ARS (activated peroxide system)-protease treatment to control felting shrinkage of wool [18,19]. The machine-washable wool fabric was obtained with the addition of dicyandiamide in alkaline hydrogen peroxide with the sodium salt of gluconic acid as well as the addition of a reducing agent (Na_2SO_3) in alkaline protease bath. Apparently, the utilization of H_2O_2 in wool processing has exceeded the bleaching, which was its primary function for wool in the past. Thus, to compare the action effectiveness and mechanism of the two chemicals is helpful for the improvement of wool bio-antifelting. In this paper, DCCA and H_2O_2 pretreatments followed by protease treatment of wool fabrics were detailedly investigated and compared in terms of the felting shrinkage, weight loss, wettability, whiteness and microcosmic changes of the wool fabrics.

Experimental

Materials

A hundred percent pure worsted wool fabric (33 tex ×33 tex, 325 g/m^2) was supplied by Wuxi Xiexin Group, China. Protease Savinase L (EC 3.4.21.62) was supplied by Novozymes (Shanghai, China). Dichlorodicyanuric acid (DCCA) was supplied by Shandong Yangguang Chemical Co., Ltd. (Shandong, China) and used as received. Other chemicals used in this work were all chemical grade without particular explanation.

Hydrogen Peroxide Pretreatment

Wool fabric was firstly incubated in hot water, and then moved into a solution containing hydrogen peroxide, 1.25 g/*l* sodium pyrophosphate, 1 g/*l* penetrating agent JFC (polyoxyethylene fatty alcohol) and treated at 50 °C and pH 8.0 for 60 min. The liquid ratio is 25:1 in this pretreatment. The pretreated wool fabrics were rinsed and dried for further experiments.

DCCA Pretreatment

Wool fabric was firstly incubated in cold water, and then moved into a solution containing DCCA and 1 g/*l* penetrating agent JFC and treated at 25 °C and pH 4.0 for 60 min. The pretreated wool fabrics were rinsed with warm water followed by an antichlorination treatment with 6 % owf (on weight of fabric) $NaHSO_3$ at 40 °C and pH 4.0 for 15 min. After that, the pH value of the solution was adjusted to 8 with 0.01 M Tris-HCl and the wool samples continued to be treated at 40 °C for 15 min followed by washing and drying. The liquid ratio is 25:1 in all these treatments.

Protease Treatment

Pretreated wool fabric was incubated in a solution containing 2.0 % owf of Savinase L and 1 g/*l* penetrating agent JFC and treated at 55 °C and pH 8.5 for 60 min with a liquid ratio of 25:1. The enzyme-treated fabric was heat deactivated followed by rinsing and drying.

Assessment of Wool Properties

Felting Shrinkage

Felting shrinkage was determined according to IWS TM No.31. The fabrics first underwent a 7A washing cycle according to ISO 6330 so that the stress formed in previous weaving and finishing processes could be relieved. The main condition of 7A washing cycle is as follows: 0.5 g/*l* detergent, 27 *l* of bath volume (high level), washing at 40 °C for 3 min, rinsing 3 cycles (3, 3 and 2 min, respectively) and laundry-drying for 5 min. The fabrics were washed with 5A procedure after above relaxation to test the felting shrinkage. The condition of 5A washing cycle is: 21 *l* of bath volume(low level), washing at 40±3 °C for 15 min each cycle, rinsing 4 cycles (3, 3, 2 and 2 min, respectively) and laundry-drying for 5 min. The fabric was subsequently dried below 60 °. The area shrinkage percentage of wool fabric was calculated in terms of the areas before and after washing.

Weight Loss

The average weight loss percentage (WL %) of each sample was calculated by following equation:

$$WL\ \% = (A - B)/A \times 100$$

where A is the weight of the sample before treatment, and B is the weight of the sample after treatment.

All samples were balanced at 25 °C and RH 60 % for 24 h before testing.

Wettability

The wettability of wool specimens (1 cm× 4 cm) was evaluated in terms of dynamic water adsorption mass, which was measured using an automated Dynamic Contact Angle Tensiometer (CDCA-100F, Camtel Ltd., UK) under room temperature.

Whiteness

The whiteness of wool fabrics was measured using WSD-II automated Whiteness Tester (Beijing Optical Instrument, Beijing, China).

Allwörden's Reaction

The wool fiber samples were spotted with bromine water for 90 s and the images were recorded with a DZ3 Ultra High Magnification Zoom Microscope (Union Optical Co., Ltd., Japan).

Fourier-transform Infrared (FTIR) Attenuated Total Reflectance (ATR) Spectroscopy

A Thermo Nicolet Nexus FTIR spectrophotometer (Thermo Electron Corporation, MA, USA) equipped with an OMNI-Sampler, a DTGS detector, and a Ge-on-KBr beamsplitter

(7800-350 cm^{-1}) was used for the FTIR-ATR measurements to indicate the changes of characteristic groups on the wool surface. The FTIR-ATR spectra (64 scans, 4 cm^{-1} resolution) were recorded using a single reflection horizontal ATR accessory with a spherical Ge crystal.

Scanning Electron Microscopy

The surface morphologies of the untreated and some of the treated wool samples were visualized using a FEI Quanta-200 scanning electron microscope (FEI Company, The Netherlands), operating at a typical accelerating voltage of 10 kV. The samples were sputter-coated with gold prior to the observation.

Results and Discussion

Effects of Hydrogen Peroxide and DCCA Treatments on Wool Felting Shrinkage

The wool fabrics were treated with various concentrations of hydrogen peroxide and DCCA at their optimal temperatures and pH values. The felting shrinkages of treated wool fabrics underwent different washing cycles are shown in Figure 1. Untreated and protease-treated wool fabrics were used as controls.

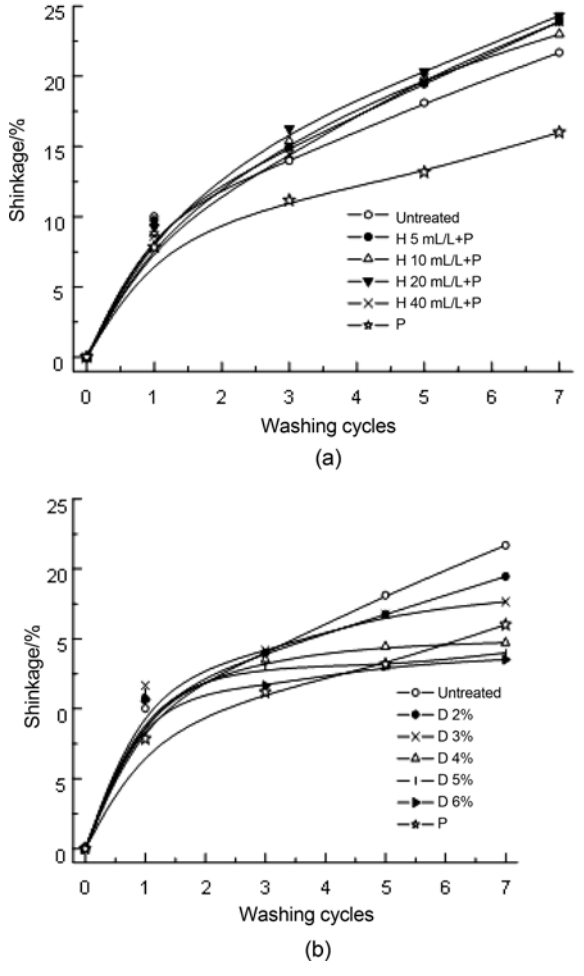

Figure 1. Effect of concentrations of (a) H_2O_2 (H) and (b) DCCA (D) on felting shrinkage of wool. Protease (P) concentration: 2 % owf.

Figure 1(a) shows that the felting shrinkage of wool fabrics treated with H_2O_2 undesirably increased compared with control samples. Some researchers had also found this phenomenon [16,17]. The shrinkages of wool fabrics treated with various concentrations of H_2O_2 presented unremarkable difference and increased with increasing washing cycles.

Figure 1(b) shows that the shrinkage of DCCA-treated wool samples all were decreased to some extent compared to untreated one. Moreover, these values gradually decreased with the increasing of concentrations of DCCA. The more effective antifelting of DCCA treatment than H_2O_2 treatment might be attributed to the different oxidation degrees of S (II) structure existing as disulphide cross-linkages in the wool scales. S (II) structure could be oxidized into S (VI) structure with DCCA, which mainly exists in sulfonic acid and sulfonyl chloride structure. It was reported that DCCA could oxidize more S (II) structure than H_2O_2 [20]. Therefore, the action of chemical antifelting finishing is not only related to the morphological deterioration of the wool scales, but also is affected by the newly developed ionized groups. The hydrophobic surface of the untreated wool with fewer ionized groups would lead very close contact between the wool fibers in the washing bath. Above-mentioned ionized and hydrated groups formed in antifelting finishing would produce a hydrophilic wool surface with an electric double layer. These changes of wool surface would reduce fiber contact in the finishing bath and weaken the differential frictional effect (DFE), which is responsible for the felting tendency of wool fabrics [21].

In addition, the shrink-resistance of treated wool was also associated to DCCA concentrations and washing cycles. The shrinkage of DCCA-treated wool reached equilibrium after one washing cycle when DCCA concentration was beyond 4 %.

Although DCCA treatment could make wool fabric obtain better anti-felting property, the severe pollution of AOX produced by the release of DCCA greatly devalue its industrial application. Figure 1 also indicates that protease could decrease wool felting propensity. Therefore, the combination of chemical and enzymatic treatments would not only enhance the anti-felting effectiveness of protease treatment, but also decrease the dosages of the chemicals used.

Effects of Hydrogen Peroxide/DCCA-protease Two-step Treatments on Wool Felting Shrinkage

Wool fabric samples were pretreated with various concentrations of H_2O_2 and DCCA followed by 2 % owf of protease treatment. Results of felting shrinkage of wool

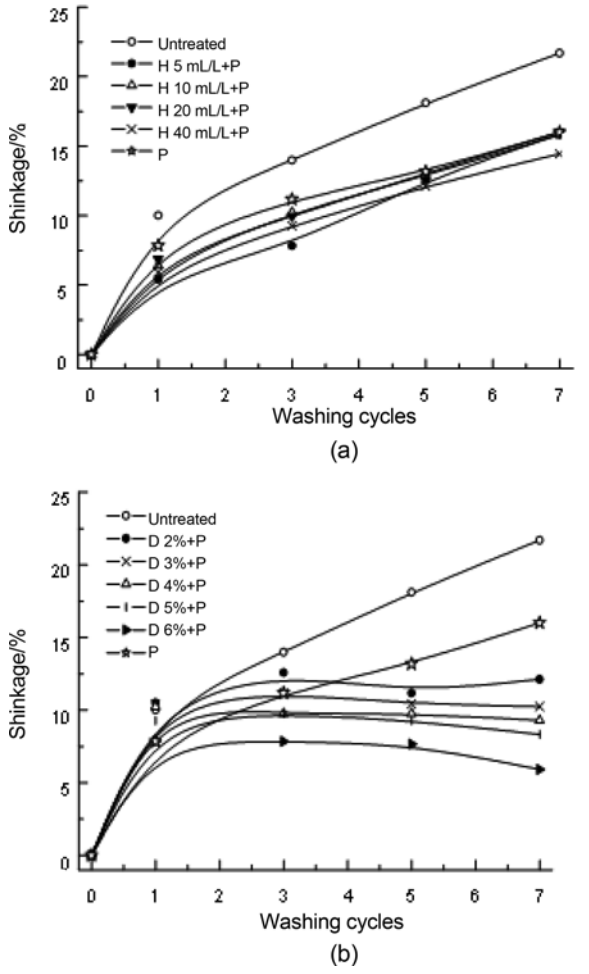

Figure 2. Effect of two-step treatment with (a) H_2O_2 (H) and protease and (b) DCCA (D) and protease on felting shrinkage of wool. Protease (P) concentration: 2 % owf.

samples underwent different washing cycles are shown in Figure 2.

Figure 2(a) indicates that the felting propensity of H_2O_2-protease treated wool fabrics gradually increased with increasing washing cycles. No remarkable difference in shrinkage was found among the treated samples. The shrinkage of wool samples successively treated with H_2O_2 and protease reached 13.97 % after seven washing cycles. Only a decrease of 2 % in felting shrinkage of wool fabric was obtained compared with wool samples treated with protease alone, although this value was lower than untreated sample. It is apparent that H_2O_2 pretreatment could not greatly improve the antifelting effectiveness of protease-treated wool fabrics.

Figure 2(b) shows that the felting propensity of wool fabrics treated with DCCA and protease in turn became stable even after one washing cycle. The shrinkage-resistance increased with the increasing of concentrations of DCCA. After seven 5A washing cycles, the decrease in the

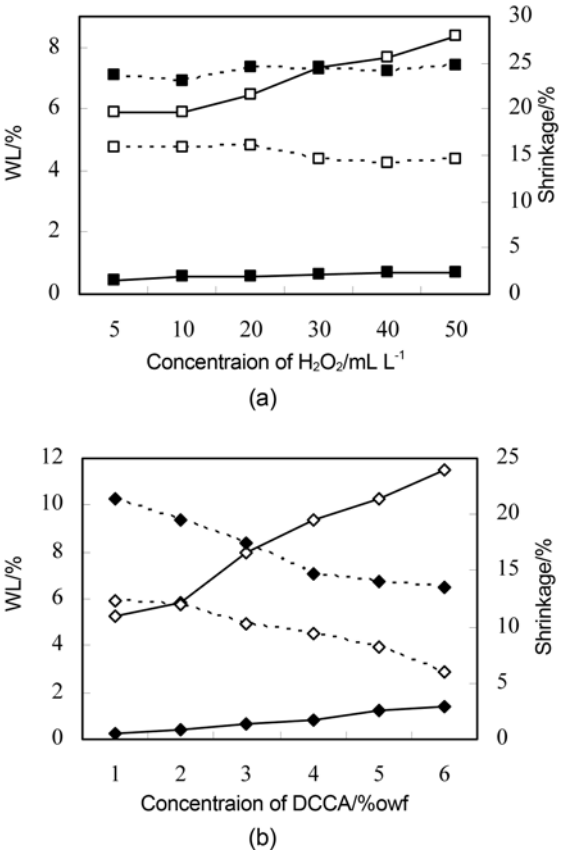

Figure 3. Effects of H_2O_2/DCCA concentration on wool WL% (—) and felting shrinkage (---). (a) H_2O_2 treatment alone (■) as well as H_2O_2 and protease combined treatment (□) and (b) DCCA treatment alone (◆) as well as DCCA and protease combined treatment (◇).

shrinkage of wool fabrics treated with 6 % of DCCA and protease was 15.77 % as compared to untreated wool samples, and 10.09 % as compared to the wool fabric treated with protease alone. In addition, it was obvious that the dosages of DCCA were decreased by using DCCA-protease combined treatment compared to individual DCCA treatment when they reached similar felting shrinkage.

Effects of H_2O_2/DCCA Concentration on Wool WL% and Felting Shrinkage

The WL% and felting shrinkage of wool samples underwent different treatments are shown in Figure 3. The WL% of H_2O_2-treated wool was less than 1 %, while their felting shrinkages are higher than 23 %. Moreover, the data of the WL% and felting shrinkage of treated wool changed less with the increasing H_2O_2 concentration. However, when the wool fabrics were treated with H_2O_2 and protease, the WL% of wool samples was increased gradually companying a remarkable decrease in felting shrinkages. It was obvious that H_2O_2 pretreatment increased the accessibility of subsequent protease action on CMC, resulting in an

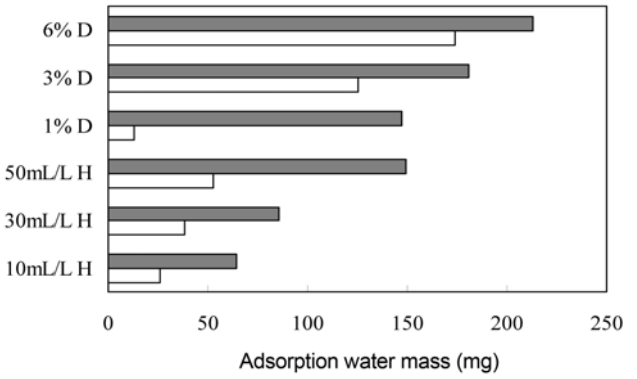

Figure 4. Effect of H_2O_2 (H) or DCCA (D) alone (□) and H_2O_2/DCCA-protease combined treatments (■) on wettability of wool. Protease concentration: 2 % owf.

enhanced internal damage of wool. Similarly, the felting shrinkage of H_2O_2-protease treated wool changed less with the increasing H_2O_2 concentration.

As shown in Figure 3(b), no matter whether DCCA treatment was followed by protease treatment or not, the increase in DCCA concentration enhanced the damage on wool fibers. Compared with H_2O_2 pretreatment, DCCA pretreatment remarkably enhanced the accessibility of protease to wool cuticle and CMC, resulting in higher WL % and lower felting shrinkage than H_2O_2 treatment. The data from WL% and felting shrinkage of treated wool further reveal that DCCA and H_2O_2 follow different mechanism when combined with proteases for wool antifelting finishing.

Wettability

The hydrophobicity of the wool fiber is due to the presence of hydrophobic lipids on the outmost layer (F-layer). These lipids are mainly composed of long chain fatty acids and the majority of these fatty acids are covalently bound to the underlying proteins *via* a thioester bond to cysteine residues [22]. Figure 4 shows that enzymatic, chemical or combined treatments can partially destroy or remove the covalently bound fatty layer in the surface of wool fibers, thus improving the hydrophilicity of wool fibers to a certain degree. Higher wettability of wool samples underwent chemical or combined treatments was reached with the increasing concentrations of hydrogen peroxide and DCCA. In general, hydrogen peroxide pretreatment shows lower improvement in wettability than DCCA, which was revealed by either water adsorption mass or the evenness of wettability in terms of the dynamic water adsorption curves.

The protease molecules not only hydrolyze the cuticle of the fibers but also penetrate into the fibers during wool processing, resulting in the removal of smaller peptide and protein segments with an increase of amorphous regions. The protease treatment with or without pretreatment increased the wettability of the wool fabrics to different extents. The pretreatments could facilitate the accessibility of protease onto the surface of wool fibers and promote the proteolytic reactions, making more underlying proteins (hydrophilic surface) exposed to the surface.

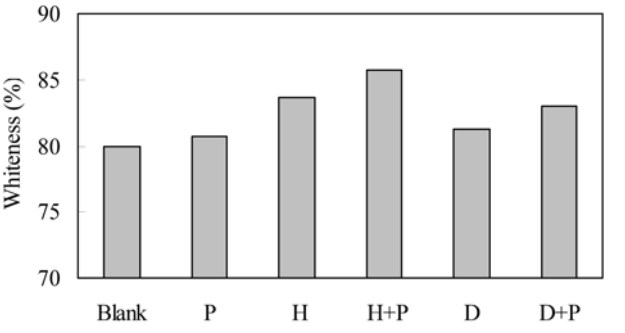

Figure 5. Whiteness of wool samples. Concentration: H_2O_2 (H), 40 m*l*/*l*; DCCA (D), 3 % owf; Protease (P), 2 % owf.

Whiteness

As seen in Figure 5, hydrogen peroxide-treated wool fabrics present higher whiteness than DCCA. Therefore, hydrogen peroxide is commonly used as a bleaching agent for wool. Moreover, although individual protease treatment of wool has lesser improvement in whiteness compared to the untreated wool, higher whiteness values were obtained after combined treatments of wool. This enhanced whitening effect could be ascribed to the fact that chemically pretreated-wool presents a more accessible surface for proteases, thus making more pigments being dislodged during protease treatment.

Allwörden's Reaction

Allwörden's reaction, which is also called as Elasticum

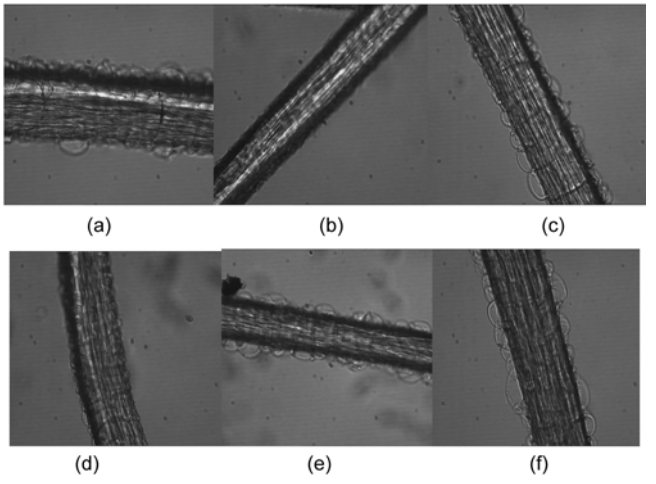

Figure 6. Pictures of wool fabric treated with (a) 40 m*l* l^{-1} H_2O_2 and protease, (b) 3 % DCCA and protease, (c) protease, (d) 3 % DCCA, (e) 40 m*l* l^{-1} H_2O_2, and (f) Untreated wool.

reaction, is a microscopic test for the scale structure of chemically damaged wool [23]. The undamaged wool would present strings of semi-circular pearl bead-like blisters over the entire fiber surface in this reaction. To chlorinated and alkali-damaged wool fibers, the reaction is either negative (due to the removal of wool epicuticle) or very weak. Figure 6 shows the images of Allwörden's reaction of wool fibers treated with different methods [24]. Untreated wool presents the most characteristic image of Allwörden's reaction, while protease-treated and hydrogen peroxide-treated wool fibers hardly show any change compared to the untreated one. H_2O_2 could break the cross-linking of disulphide bonds in scale exocuticle and has less action on amide linkages (peptides) in scale exocuticle, while the latter plays an important role for the formation of the blisters in Allwörden's reaction. As water-soluble high-molecular peptide fragments cannot pass the epicuticle, they would induce osmotic swelling of the scale cells as soon as the fiber is immersed in water. The combination of hydrogen peroxide and protease merely damaged the wool scales to some extent so that Allwörden effect still appeared. DCCA treatment could damage both the cross-linking of disulphide and amide bonds in scale exocuticle as well as the lipid-like substance in epicuticle. Therefore, DCCA-treated wool fiber only suggests very weak Allwörden effect. The combination of DCCA and protease further damaged the wool scales so that Allwörden effect disappeared.

FTIR-ATR Analysis

The finger range of 1000-1400 cm^{-1} in FTIR-ATR spectrum could reveal oxidation products of the cystines on wool surface (Figure 7). H_2O_2-treated wool presents a new adsorption at ca.1040 cm^{-1} compared with untreated wool, indicating the formation of final oxidation product (cysteic acid) of disulphide bonds. DCCA-treated wool shows adsorption peaks at 1023 cm^{-1}, 1040 cm^{-1}, 1075 cm^{-1} and 1190 cm^{-1}, indicating a stronger oxidation of the disulphide bonds [25]. No FTIR adsorption change between protease-treated and untreated wool fibers in above finger range indicates that protease has no action on the disulphide bond structure of the cystines in wool surface. However, the combination of DCCA or H_2O_2 pretreatment with enzymatic processes of wool fabrics could dislodge the oxidation products to varying degrees, thus resulting in the decrease in the absorbance at 1040 cm^{-1}.

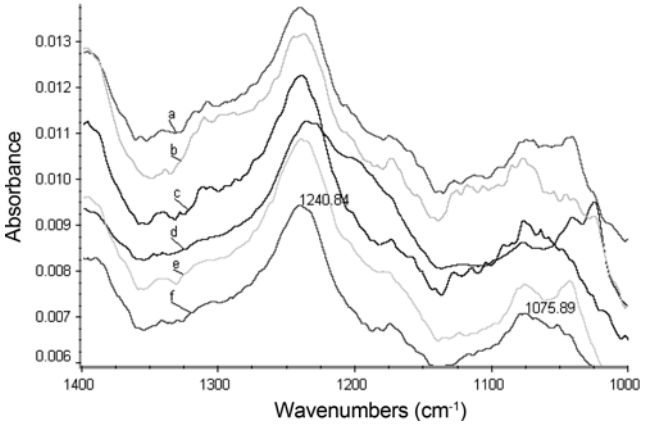

Figure 7. FTIR-ATR spectra of wool fabric treated with (a) 40 m*l* l^{-1} H_2O_2 and protease, (b) 3 % DCCA and protease, (c) protease, (d) 3 % DCCA, (e) 40 m*l* l^{-1} H_2O_2, and (f) untreated wool.

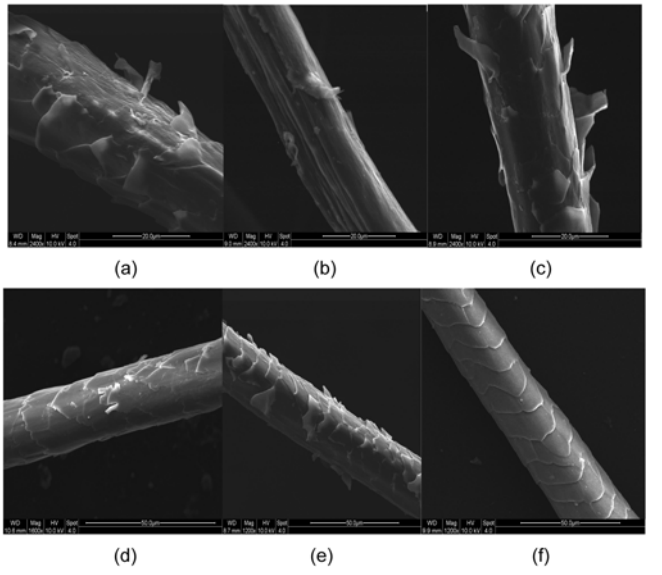

Figure 8. SEM images of wool fabric treated with (a) 40 m*l* l^{-1} H_2O_2 and protease, (b) 3 % DCCA and protease, (c) protease, (d) 3 % DCCA, (e) 40 m*l* l^{-1} H_2O_2, and (f) untreated wool.

SEM Observation

The surface morphology of wool samples was characterized by scanning electron microscopy (Figure 8). The untreated wool presents remarkable scale structure on fiber surface. The protease-treated wool fibers present patulous scales, which might be ascribed to the degradation of CMC with protease. The woolen fabrics, after being oxidized with H_2O_2 also show marks of scale damage to some extent. However, DCCA treatment produced the most remarkable damage to wool scales. DCCA-protease treated fiber had a smooth surface and the marks of wool scales almost disappeared, which could insure better antifelting effectiveness.

Conclusion

We compared the different effects of two representative pretreatments, i.e., H_2O_2 and DCCA treatments on wool bio-antifelting. Wool fabrics treated with H_2O_2 alone and H_2O_2 - protease combined treatment did not show a remarkable improvement in antifelting effectiveness. The felting shrinkage of wool fabrics treated with DCCA alone can be decreased effectively. DCCA-protease two-step treatment also reached

better antifelting effects and the dosage of DCCA could be greatly decreased. We revealed different mechanisms of H_2O_2 and DCCA pretreatments causing these differences through relevant microscopic analyses. These results will contribute to a better understanding of wool bio-antifelting based on chemical pretreatments. It should be noted that further research on dyeability and comprehensive mechanical properties such as bending, shear and surface properties by using KES-F (Kawabata Evaluation System-Fabrics) of the wool fabrics underwent above-mentioned treatments is ongoing, which would provide more extensive contrast beyond felting propensity and fiber damage.

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