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Treatment of Wool with Laccase and Dyeing with Madder

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Abstract This research has explored the effect of laccase (Denilite II S) on the physical properties of the wool fabric and confirms the anti-felting of wool. In the experiment, laccase was applied to a wool fabric and different characteristics including weight loss, strength, alkali solubility, felting shrinkage, water drop absorption, and dye ability with madder were studied. The surface morphology of the wool fabrics was also observed by scanning electron microscope. The results indicated that the wool fabric treated with laccase has a higher water drop absorption, lower felting shrinkage, and lower values of a^* and b^*. Treatment of a wool fabric with 10% or lower percentage of laccase reduced the fabric weight but increased the tensile strength. However, using higher concentration of laccase reduced fabric weight and tensile strength. The dyeing of laccase pre-treated wool fabric with madder indicated a lower lightness.

Keywords Wool · Laccase · Tensile strength · Alkali solubility · Absorption

Introduction

Biotechnology offers enzymes for the production of goods to meet various human needs. These products can accelerate the chemical reactions by reducing the activation energy needed to make the reaction start [1–6].

These enzymes that are applied on textile are from hydrolytic reactions. In the case of wool, they are capable of providing the fabric with the characteristics of anti-felting, dye take-up, increasing the anti-shrinking, reducing the dead fiber, fabric whitening, and removing the protein stains [2].

Cuticle and cortex cells in wool fibers can also be modified with the proteolytic enzymes. In addition, these treatments alter the surface properties of the fiber by reducing

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its hydrophobic nature and enhancing its textile properties such as dye uptake, shrink resistance, and electrical conductivity [2].

Laccases (EC 1.10.3.2) are oxidoreductases which contain copper. In laccases, there are four copper atoms distributed in type 1, type 2, and type 3 sites. The type 1 site is the one wherein the oxidation of substrate takes place, then the electrons jump to the trinuclear cluster. This resulted from the reduction of oxygen to water. Laccase exists in many plants, fungi, and microorganisms. It can oxidize some of the phenolic and mineral compounds with the reduction of oxygen to water [6–15]. As biocatalysts, laccases are useful for replacing expensive and harmful chemicals with saving energy. These are good compounds for the formation of new functional groups and reducing the negative impact on environment [6–15].

In textile processing, laccase has been used for improving the fabric whiteness in bleaching process, decolorization of dyed textile materials and colored effluent and scouring of fibers, wool dyeing, and wool anti-felting [11–12]. In one research, the treatment of wool with laccase was reported and it was shown that the treated fabric has a lower weight with reduced tensile strength. However, the dye ability and pilling of the laccase-treated fabric had improved [11].

The main objective of this study was to compare the behavior of different concentrations of laccase on wool fabric and to investigate the possibilities of eliminating anti-felting processing without the strength reduction.

Materials and Methods

The textile materials were raw wool fabric, 350 g/m^2, yarn count=30/2 Nm, 16 warp and 15 weft per centimeter. The twist was 550 per meter.

The laccases used were Denilite II S (EC 1.10.3.2) from Novozyme. Treatments were carried out at pH=4.5, L:G=40:1 (liquor to goods ratio) and 60 °C for 1 h. For enzyme deactivation, acetic acid was used.

To evaluate the alkali solubility of wool fabric, sodium hydroxide 0.1 N was prepared.

Scouring of the wool sample was carried out in the aqueous solution containing a non-ionic surfactant (Fluidol W100) and sodium carbonate.

The dyestuff was madder and aluminum sulfate used as mordant in the acidic media prepared by citric acid.

Weight Loss

The sample was prepared in dimensions of 15×15 cm^2. First, it was placed in an oven 150 °C, and then left in the desiccator, and then its weight was measured.

Weight loss (%) was calculated from the following equation:

$$\frac{W_1 - W_2}{W_1} \times 100$$

Where W_1 is the weight of the sample before treatment and W_2 is the weight of the sample after treatment.

Alkali Solubility

One gram of wool sample was treated with 1,000 ml NaOH solutions at 65 °C for 1 h. It was then rinsed with distilled water and dried in an oven at 110 °C for 1 h. After being desiccated, the alkali solubility of the samples was calculated as a percentage of the original weight according to the above equation.

Water Drop Absorption

The water drop adsorption experiments were performed before and after the enzymatic treatments. The sample is laid on a glassy surface and 1 cm above the surface; a dropper would discharge a drop of water on the sample. The required time for the sample to absorb the drop was measured. This experiment conducted 20 times and the mean values reported.

Tensile Strength

The tensile strength (in warp direction) was evaluated according to CRE with a Shirley (micro 250) tester. The samples had the size of 15×7 cm^2 and speed of 500 mm/min.

Anti-Felting

The samples in dimensions of 10×10 cm^2 were first marked, then soap milling was carried out manually in 1% soap bath with L:G=10:1. The temperature of the bath was 50 °C and duration of the process was 45 min.

Scanning Electron Microscope (SEM)

To observe surface changes of wool fibers caused by enzyme treatment, the SEM was used and some images from the wool fiber surface were provided with the enlargement of 30,000 and 2,000.

Abrasion

An abrasion tester for surface changes was used to observe the abrasion of the goods. A 250 g weight was used and the surface of the fabric was studied with two warps or wefts torn; the number of abrasion cycles was reported.

Reflectance

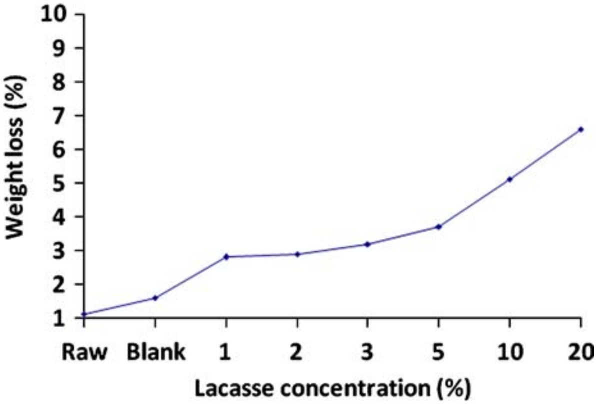
The reflectance spectra of the samples were measured using an ACS Spectro-sensor II integrated with an IBM personal computer. CIELAB color coordinates including L^* (lightness), a^* (redness–greenness), and b^* (yellowness–blueness) were calculated from the reflectance data for 10° observer and the illuminant D65.

Results and Discussion

Figure 1 compares the effects of laccase at 1, 2, 3, 5, 10, and 20% on weight of fabric on the weight reduction.

As it is shown, increasing the concentration of laccase raises the weight reduction value to 6.7%. The highest weight reduction is related to the highest concentration of laccase. The increasing of laccase to 5% has a slight influence on the weight loss but laccase above 5%

Fig. 1 Impact of laccase concentration on fabric weight loss



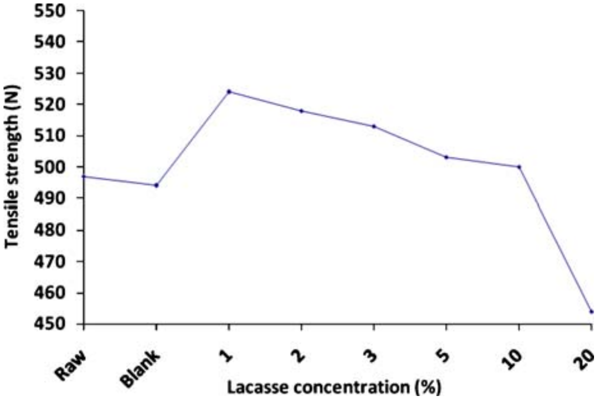
significantly reduces the fabric weight. The loss of weight by laccase can be depicted to removing some impurities from wool and to the oxidation of cystine and tyrosine in the wool fibers [14, 16].

The effects of different concentrations of laccase on tensile strength are shown in Fig. 2. It can be inferred that increasing the laccase concentration leads to a decrease in the strength tensile and the most changes occur in the range of 10% to 20%. There is a little increase in tensile strength on 1% of laccase but the tensile strength tends to fall by increasing laccase. This is in accordance with the results of weight loss. As the fabric loses more weight, the tensile strength decreases more. An increase in the tensile strength at 1% of laccase can be attributed to the formation of some covalent crosslinks between polypeptide chains due to the oxidation of thiol groups to disulfide bridges [15]. This is in accordance with the findings of Sorensen and McDevitt [15].

The effects of laccase at different concentrations of 1% to 20% laccase on the alkali solubility of wool fabric samples are indicated in Fig. 3. It can be observed that at higher concentrations of laccase the values of alkali solubility are greater. This may be related to the oxidation of the cystein leads to reduce of wool fabric resistance against alkali [14].

In Fig. 4, the effects of laccase at various concentrations on fabric felting shrinkage were compared. The scale structure of the wool cuticle and existence of hydrophobic substances are two main reasons for wool fabric felting shrinkage. During laundering, wool fibers

Fig. 2 Impact of laccase concentration on tensile strength



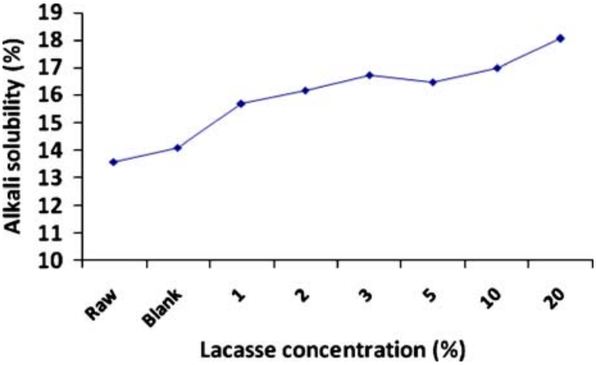


Fig. 3 Effect of laccase concentration on alkali solubility

move in the root direction and, as a result of different coefficient friction of fibers in the 'with-scale' or 'against-scale' directions, they entangle to each other. This progressive entanglement mechanism eventually leads to felting. In a commercial process, the surface scales degrade to only a limited extent and the reduction of the coefficient friction between fibers 'against-scale' without significantly reducing fiber strength and weight. However, proteases as a replacement of chlorination fail to fulfill the latter promise.

From Fig. 4, it can be inferred that laccase is a useful enzyme for reducing felting shrinkage. It can also be concluded that increasing concentration of laccase leads to a decrease in fabric shrinkage. A trend of decrease in felting shrinkage is the same for the wide range of laccase concentrations. This is an encouraging application of laccase on wool fabric for anti-felting shrinkage as alkali solubility improves and the negative impact on the tensile strength is negligible within 10% of laccase.

The influence of different concentrations of laccase ranging from 15% to 20% on the wool fabric abrasion can be seen in Fig. 5. It is obvious that the abrasion resistance of the sample treated with 1% laccase increases considerably but increasing the laccase concentration reduces the abrasion resistance. By using 1% laccase, the possible formation of disulfide bridges help to increase the abrasion resistance [14]. However, increasing the laccase concentration probably leads to oxidation of wool and results in progressive reduction of abrasion resistance. The results of abrasion resistance on different fabric samples confirm other results including tensile strength, weight loss, and alkali solubility.

The effects of laccase at different concentrations ranging from 1% to 20% on the water drop adsorption on the fabric surface are revealed in Fig. 6. The results showed that

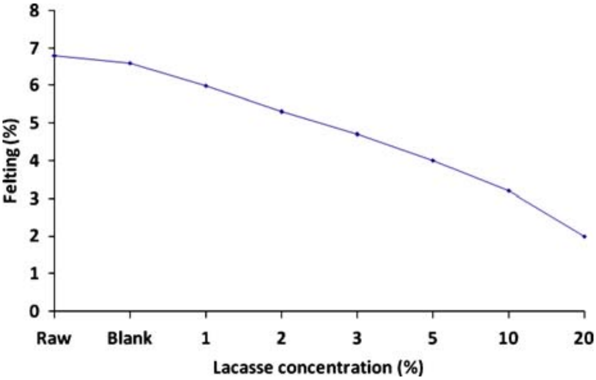


Fig. 4 Influences of laccase concentration on felting shrinkage

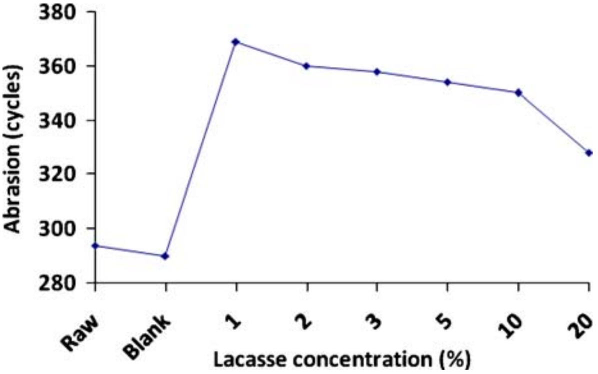


Fig. 5 Influences of laccase concentration on abrasion

increasing enzyme concentration leads to a decrease in the time of water adsorption. This means that wool fabric treated with high concentration of laccase has a higher water absorption rate. This can be a result of possible oxidation of wool by laccase [14]. Consequently, the fabric becomes more hydrophilic. This is a useful factor for reducing felting shrinkage of wool fabric. The results of felting shrinkage on the enzyme-treated fabric samples confirm this hypothesis.

Color Changes on Laccase-treated Wool Fabric

The results of color indices on the laccase-treated wool fabric samples are presented in Table 1.

It can be observed that increasing laccase causes a decrease in L^* value and an increase in a^* and b^* values. This means that the fabric becomes redder and yellower. It can be related to the oxidation of wool by laccase that becomes progressively higher with increasing concentration of laccase. The values of ΔE indicated similar trends; as the concentration of laccase increases, the value of ΔE increases. These results can also confirm the oxidation of wool fabric during treatment with laccase.

Dyeing With Madder

As illustrated in Table 2, treating the wool fabric samples with laccase causes a decrease in the L^* value. This means that the color of fabric becomes darker. However, the values of a^* (redness) and b^* (yellowness) are also marginally lower. It seems that pre-treatment of

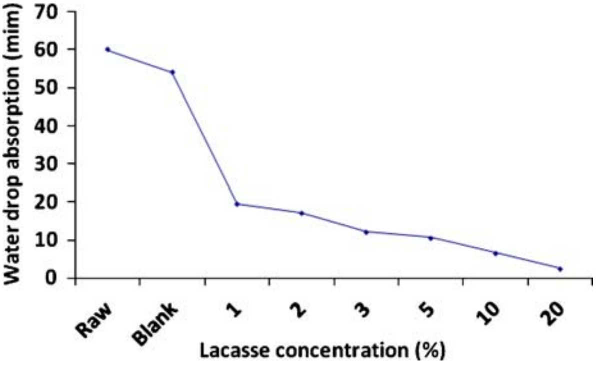


Fig. 6 Influences of laccase concentration on water drop absorption

Table 1 L^*, a^*, b^*, and ΔE values of treated samples with laccase.

Samples		L^*	a^*	b^*	ΔE
Raw	–	81.5	1.1	15.8	0
Laccase	1%	77.6	1.6	17.6	4.4
	5%	75.1	1.5	22.8	9.5
	10%	73.0	2.2	25.8	13.2
	20%	71.5	1.9	24.9	13.5

fabric samples with laccase reduces the fabric lightness. This can be influenced by the fabric color after dyeing with madder and produces a darker fabric with lower L^* value. This means that pre-treated wool fabric with laccase can be effective on the fabric color when dyed with madder. It can be suggested that those pre-treated wool fabric samples with laccase with more hydrophilic characteristics should adsorb higher amounts of water-soluble dye from a dye bath. Hence, madder is a natural dye which consists of different compounds, mainly alizarin, with low water solubility. Therefore, it cannot be expected to obtain a higher dye adsorption on the wool fabric by madder. This can be seen in the results as the values of a^* and b^* decrease marginally.

These results were perfectly compatible with observations. It was perceived that the sample treated with enzyme was darker than the two gray (raw) samples after dyeing.

SEM Pictures

Figure 7 depicts the effect of enzymatic treatment on the surface of the wool fibers. These microscopic images were taken from both enzyme-treated and un-treated samples with 2,000× magnification.

The presence of a porous and hydrophobic layer called epi-cuticle makes wetting of the wool fiber surface difficult. As it can be perceived from Fig. 7, the enzyme-treated samples have smoother scale tails. It can be inferred from Fig. 8 that there are some cracks on fiber surface of the raw wool and the laccase-treated wool. These cracks have not been altered after laccase treatments and laccase concentration had no significant impact on the cracks.

The results of weight reduction, strength, and abrasion tests were compatible with the microscopic images, as the samples treated with 20% laccase confronted a reduction in shrinkage.

Conclusions

The results unveil the fact that increasing the concentration of laccase in the following condition: pH=4.5, L:G=40:1 at 60 °C for 1 h decreases the strength, water drop

Table 2 L^*, a^*, b^*, and ΔE values of samples pre-treated with laccase and dyed with madder.

Samples		L^*	a^*	b^*	ΔE
Raw	–	38.7	41.5	34.5	0
Laccase	1%	35.6	41.9	32.3	3.8
	5%	35.2	40.3	32.6	4.1
	10%	35.3	41.9	31.4	4.6
	20%	33.9	40.8	30.4	6.3

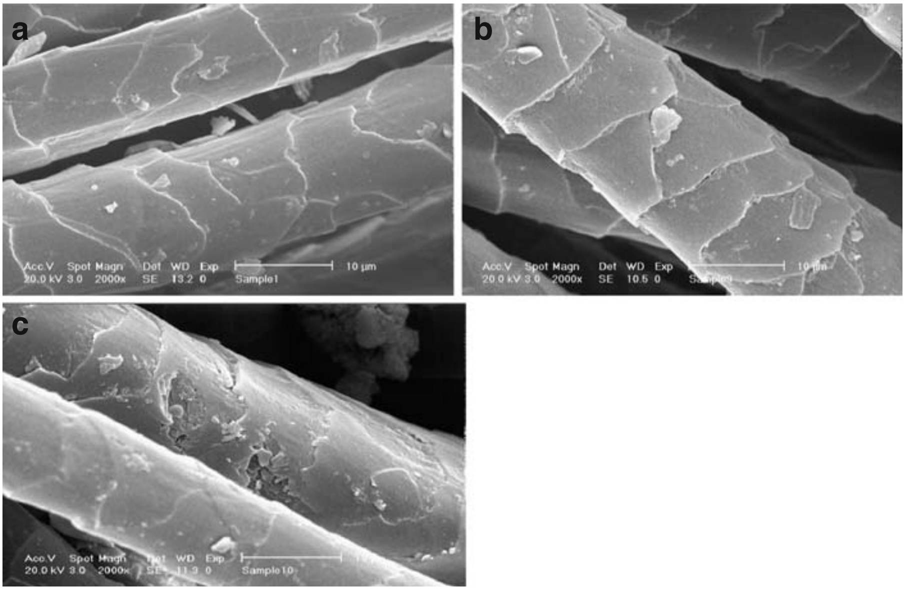


Fig. 7 SEM pictures of wool fibers: **a** raw wool, **b** 10% laccase-treated wool, and **c** 20% laccase-treated wool (×2,000)

absorption time, and shrinkage of the wool fabric samples. On the contrary, it increases alkali solubility, resistance to abrasion, and weight reduction percentage.

Deploying 5% of laccase with pH=4.5, L:G=40:1, at 60 °C significantly increases the strength. Moreover, water drop absorption time, shrinkage, and weight reduction percentages decreased as a result of which resistance to abrasion increased.

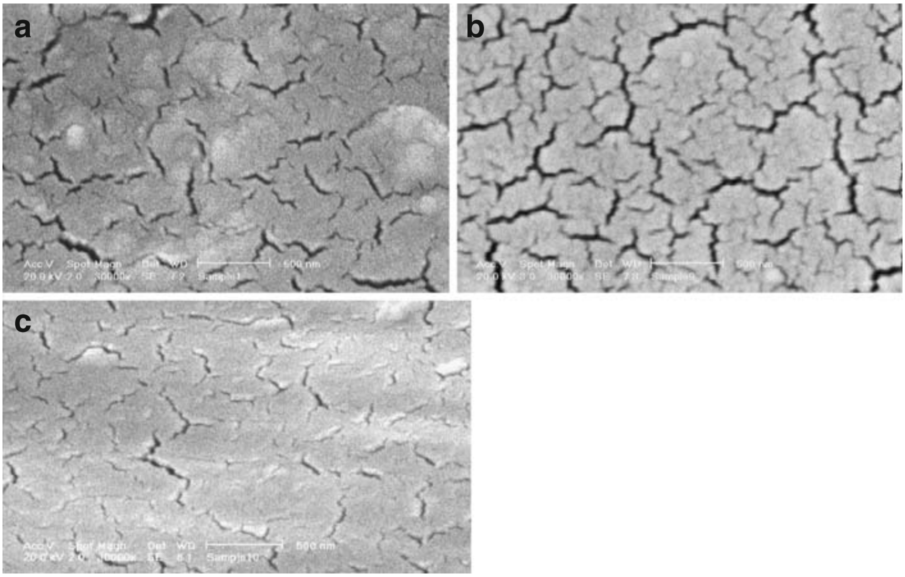


Fig. 8 SEM pictures of wool fibers: **a** raw wool, **b** 10% laccase-treated wool, and **c** 20% laccase-treated wool (×30,000)

Taking everything into consideration, it can be concluded that laccase can be applied on wool and can be a replacement for proteases. This is by reducing the felting without any significant impact on other properties of the wool fabric.

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