

A Biological Treatment Technique for Wool Textile

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ABSTRACT

A biological treatment technique for wool textile was carried out by enzymes degradation coupled with H₂O₂ oxidation. The results demonstrated that the technique had ideal effects on wool textile such as better softness, plump and less loss of bursting stress. Because of mild reaction conditions, less textile damage and less environmental pollution, this technique for wool textile treatment could have promising prospect.

Key words: Wool textile decrement, oxidation pretreatment, enzyme degradation, L86 enzymes

INTRODUCTION

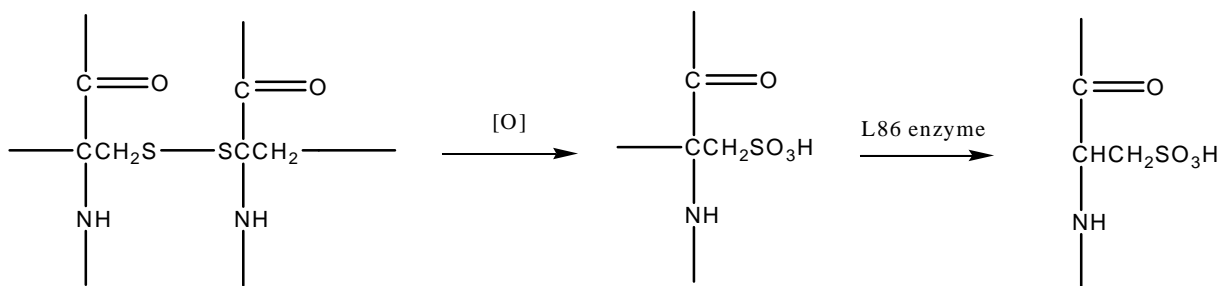
It is necessary for the wool industry to use more environmentally friendly finishing processes due to the pollutant in the process of chemical treatment. Wool mainly consists of scaly layer and cortex layer, both adhering to each other through cellular matrix carboxymethyl cellulose (CMC). Scaly layer is composed of surface layer, outer layer and inner layer, which is approximately 10% of total wool weight (Word et al., 1993; Messinger et al., 1994). During the processing the scaly layer of wool is peeled off partly or completely by digestion in order to raise the wool fineness shine, softness and elasticity. Surface layer and outer layer of wool contain abundant keratin protein, which are too tight to be degraded; whereas inner layer contains non-keratin protein, which are easy to be digested by protease; cellular matrix CMC is similarly easy to be degraded by cellulase (Leeder et al., 1968).

Traditional oxidizers such as NaClO and KMnO₄ are used to break the surface layer and outer layer of the scaly layer by oxidizing the disulfide bond in

keratin proteins. However, their strong oxidations are always difficult to control and often result in disproportion of the treatment. Moreover, NaClO reaction with wool produces halogenide. Thus, chemical oxidizers are not suitable. Experimental results in this paper proved that H₂O₂ was a suitable oxidizer, since it could give oxygen smoothly with moderate oxidation. The mechanism of oxidation is shown in scheme 1.

Therefore, less aggressive chemical processes and environmentally friendly methods such as enzyme based processes, as well as combination treatments have gained widespread acceptance (Cortez et al., 2002; Jose et al., 1996; Manjrekar, 1995; Shridhar et al., 1995), which impart desirable properties, such as improving handle properties and imparting shrink-resistance and produce less pollution (Breier et al., 1999; Bishop et al., 1998; Heine et al., 2001). Generally H₂O₂ is applied to break the surface layer and outer layer of the scaly layer; Then, *Aspergillus usarii* L86 enzymes including acid protease and CMCCase (Yongquan Li, 2001) are added to degrade inner layer and outer layer in order to peel off the scaly layer effectively.

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Scheme 1 - The mechanism of oxidation by H_2O_2 and enzymes.

MATERIALS AND METHODS

Experimental Materials

Knitted fabric was made from 100% Australia wool, whose size was 22cm*16cm, transverse 54 needles/cm and longitudinal 78 lines/10cm.

Process of treatment

After H_2O_2 oxidation pretreatment, the wool textile was degraded with L86 enzymes, followed by neutralization with alkali, washing and aminosilicone oil Umd softening treatment (18g/L of Umd, pH5-6, 20-30°C for 10min), and finally, the treated wool textile was washed and dried at 80°C.

H_2O_2 oxidation

All experiments were carried out under the conditions of the dissolvent proportion of 1:30 and 2.0g/L of penetrate reagent. For observing influence of H_2O_2 oxidation on wool textile, reaction temperature and pH were at 20°C, pH 4.0 for 40 min; H_2O_2 concentration 40g/L, pH 4.0 for 40 min, and at 20°C, H_2O_2 concentration 40g /L and ratio at 6.0%.

Biological treatment with respectively enzymes

Under the conditions of dissolvent proportion of 1:30, reaction temperature 40°C and pH 4.0 according to the enzymatic characteristics of acid protease and CMCase (Xinghua, Wen, 1999), the L86 enzymes containing acid protease and CMCase were added to degrade the inner layer, and add NaHSO_3 at the same time.

Acid protease measurement

Folin method was applied in the enzyme activity assay (Yongquan Li, 1999). Under the conditions

of pH3.0 and 40°C, one unit of acid protease was defined as 1 μg tyrosine produced by hydrolysis of casein per minute.

CMCase measurement

CMC saccharimetry was applied in the enzyme activity assay (Shuzheng Zhang, 1984). Under the conditions of pH5.0 and 50°C, one unit of CMCase was defined as 1 μg CMC hydrolyzed per minute.

Bending stiffness

Bending stiffness was measured with Instron 1122 Strength Electronic Instrument.

Bursting Strength

The strength of wool textile (measure unit N/cm^2) was determined with Textile Bursting Strength Instrument.

Decrement ratio

$$\text{Decrement ratio} = \frac{\text{Dry weight before treatment} - \text{weight after treatment}}{\text{Dry weight before treatment}} \times 100\%$$

Untreated wool textile was dried at 105°C. Then, it was treated with decrement and dried. The decrement ratio was calculated:

Each test was conducted at least three times. Data are the means of three replications. Significantly different from replications was at $p < 0.05$.

RESULTS AND ANALYSIS

Technique of oxidation pretreatment

The relationships between the concentration of H_2O_2 and bursting strength loss ratio, decrement ratio are illustrated in Fig. 1. The results indicated that when the concentration of H_2O_2 was between 40 and 50g/L, the decrement ratio arrived was

6-8% with the textile bursting strength loss ratio within 10% and the wool textile was soft, plump and smooth.

The experiment about effect of reaction temperature on decrement ratio showed (Fig 2) that the speed of H_2O_2 oxidation was slow below 20°C.

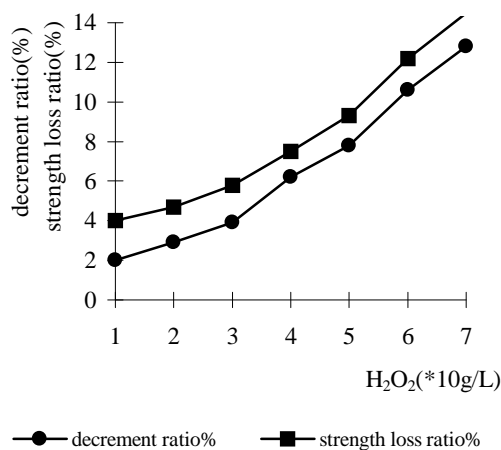


Figure 1 - Effects of H_2O_2 concentration on the pretreatment of wool textile. The reaction conditions were at 20°C, pH 4.0 for 40 min.

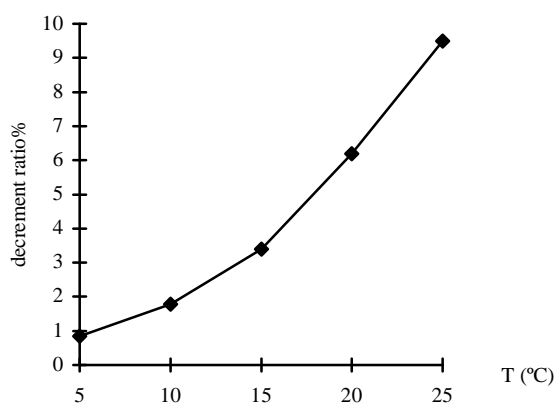


Figure 2 - Effects of reaction temperature on decrement ratio. The reaction conditions were at H_2O_2 concentration 40g/L, pH 4.0 for 40 min.

However, the reaction speed was increased above 20°C, but it damaged the strength of wool textile intensively and made the wool textile fragile and

faint, so the temperature should be controlled strictly at 20°C in pretreatment process.

Fig. 3 showed the pH effect on pretreatment reaction. The results revealed that the H_2O_2 oxidation reaction was hardly processed at $pH > 6.5$. While at $pH < 2.0$, H_2O_2 reaction finished completely within 20 min (decrement ratio at 6.0%); and if the reaction time was beyond 30 min, the effects of the treatment were not fairly

proportioned (decrement ratio $> 10\%$, bursting strength loss ratio $> 12\%$). However, controlling pH 4.0 and reaction time 45min, the decrement ratio also could reach at 6.0%. Thus, the pretreatment condition was selected as 40g/L of H_2O_2 concentration, reaction time 45 min and pH 4.0.

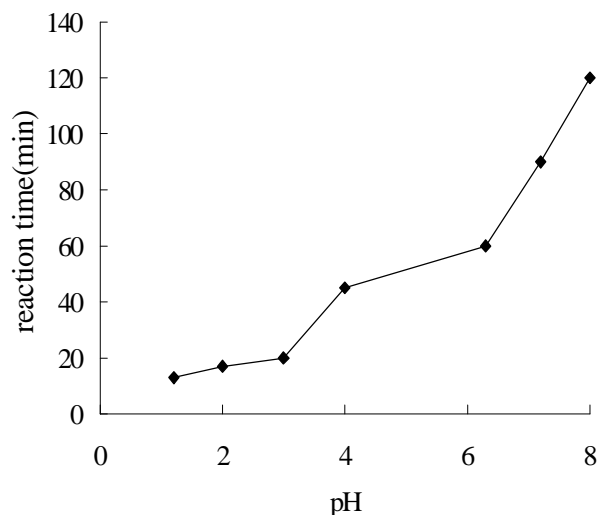


Figure 3 - Effects of pH on time of H_2O_2 oxidation reaction. The reaction conditions were at H_2O_2 concentration 40g/L, $20^\circ C$, and ratio at 6.0%.

Enzymatic degradation

The supernatant from *Aspergillums usamii* L86's fermentation broth containing acid protease (10000U/ml) and CMCCase (3600U/ml) was used as treating reagent. After the oxidation pretreatment at the conditions of 40g/L of H_2O_2 , pH 4.0, $20^\circ C$ and 45min of reaction time, the L86 enzymes containing acid protease and CMCCase were added to degrade the inner layer. CMCCase acted on the cellular matrix between scaly layer and cortex layer, which could help peeling off the scaly layer, so as to reinforce the effect of acid protease degradation. In order to optimize the enzyme degradation process, an L9 (3^4) orthogonal test was carried out, in which the amount of enzyme solution, the concentration of $NaHSO_3$ and the reaction time were taken as experimental parameters.

The results are shown in Table 1, which showed that reaction time influenced the results most significantly and the enzyme concentration

followed. The reaction time represented the influence of enzyme degradation on the decrement ratio, the longer the treatment time, the stronger the degradation reaction.

While it was treated for 60 min, the effect of decrement was quite good, but too much loss of textile strength, so the suitable reaction time was selected as 45 min. $NaHSO_3$ in solution had two functions, one was to decompose the disulfide bond in the wool, which would raise the speed of enzyme degradation; the other was to reduce residue of H_2O_2 in the solution, because the residue of H_2O_2 would injure the wool gradually and influence the whiteness of textile. The results demonstrated that the suitable concentration of $NaHSO_3$ was 60g/L, and increasing the concentration of protease could increase the textile decrement ratio with bursting strength decreased. However, there was a two-phase reaction of solid-liquid on wool surface, when the enzyme concentration reached at a certain amount, the wool surface was saturated and

reaction was efficiency. By adding more enzymes into solution, the reaction speed could not be increased. Considering the reaction effect and the material cost, the suitable amount of enzymes was selected as 1.5 ml of per liter solution.

The optimum conditions of enzyme degradation process were 1.5ml of enzymes of per liter solution and its final concentration arrived at 15U/ml of acid protease and 5U/ml of CMCase, 60g/L of NaHSO₃, the reaction time 45min, dissolvent proportion 1:30, 40°C, pH 4.0.

Table 1 - Orthogonal Test of enzyme degradation and extreme value analyses

N°	Test factors			Experiment results	
	Enzymes (ml)	NaHSO ₃ (*10g/L)	Time (min)	Bursting Strength (N/cm ²)	Decrement ratio (%)
1	1.0	4.0	30	57.18	5.8
2	1.0	6.0	45	49.02	7.4
3	1.0	8.0	60	38.34	7.6
4	1.5	4.0	45	52.18	7.9
5	1.5	6.0	60	45.42	8.7
6	1.5	8.0	30	47.21	7.2
7	2.0	4.0	60	40.68	8.5
8	2.0	6.0	30	52.07	7.4
9	2.0	8.0	45	34.96	8.3
K ₁	20.8	22.2	20.4		
K ₂	23.8	23.7	23.6		
K ₃	24.2	22.9	24.8		
R	3.4	1.5	4.4		

Table 2 - The conditions and results of contrast experiment

N°	Test Method	Experiment Results		
		Decrement ratio (%)	Bending stiffness (N/cm)	Bursting strength (N/cm ²)
10	Enzyme degradation ^a	4.5	0.305	63.68
11	H ₂ O ₂ oxidation ^b	7.2	0.274	50.97
12	Coupling treatment process ^c	8.8	0.213	46.52

Experimental conditions : ^a1.5ml/L of enzymes per liter solution, NaHSO₃ 60g/L, pH 4.0, 40°C, dissolvent proportion 1:30 for 90min;

^b H₂O₂ 40g/L, penetrate agent 2.0g/L, 20°C, pH=4.0; dissolvent proportion 1:30 for 90min.;

^c H₂O₂ oxidation conditions were like No11, for 45min;enzyme degradation conditions were like No10, for 45min

Contrast experiment

In order to show the characteristics of enzyme degradation coupled with H₂O₂ oxidation, the contrast experiment about enzyme degradation, H₂O₂ oxidation pretreatment and enzyme

degradation coupled with H₂O₂ oxidation were carried out and the decrement ratio, bending stiffness and bursting strength were selected as responsive values. The test conditions and results are shown in Table 2.

Apparently the coupled treatment process provided better decrement effect with satisfying decrement ratio, bursting strength and softness than that of H₂O₂ oxidation or enzyme degradation alone. Furthermore, after coupling treatment, washing and drying, the treated wool textile showed good strength and softness, and clear printing pattern. While treated with H₂O₂ oxidation or enzyme degradation alone, the textile showed relatively bad strength, softness and feel of handle.

After the treatment by enzyme degradation coupled with H₂O₂ oxidation, the wool textile should be washed, avoiding the peptides and carbonaceous matters adhering to textile, which were produced by enzyme degradation. Then, temperature should be raised to 80°C so as to deactivate enzyme and dry wool textile. When the scaly layer of wool was peeled off, the wool textile showed plump and softness but bad elasticity, and the cortex layer would be influenced easily by many chemistry reagents and weather conditions, therefore softener with affinity to wool, amino-silicone oil Umd, had to use to form a protective membrane covering the wool surface.

The technique of biological treatment was studied according to the subtle structure of wool. The enzyme degradation had mild reaction conditions and could be controlled easily. The enzymes from strain *Aspergillus* L86, whose components (two enzymes) interrelated with the structure of wool closely and had the same pH of decrement process, improved the effects of treatment remarkably (Yongquan Li, 2001). Hence the effect of coupling treatment process was better than that of traditional chemistry treatment. For example, it greatly improved the quality of treated textile, and produced less environment pollution.

Since H₂O₂ oxidation and enzyme degradation required the same pH, when these two processes were combined, the solution needed not be changed during process. Thus, using this technique could cut down the material cost and manpower.

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REFERENCES

- Bishop, D.; Shen, J.; Heine, E. and Hollfelder, B. (1998), The use of proteolytic enzymes to reduce wool-fibre stiffness and prickle. *J. Text Inst.*, **89**, 546-553.
- Breier, R. and Eugen, P. (1999), *Felt-free finishing of wool using proteolytic enzyme, useful for flocks, slubbing, yarn and fabric*. DE19807456.
- Cortez, J.; Bonner, P. L. R. and Griffin, M. (2002), *A method for enzymatic treatment of textiles*. WO0204739.
- Heine, E.; Hartwig, H. and Lone, D. (2001), *Method for enzymatic treatment of wool*. US2001003220.
- Jose, C. (1996), The state of the art in textile biotechnology. *J. Soc. Dyers and Colorists*, **112**, 326-329.
- Leeder, J. D. and Bradbury, J. H. (1968), Conformation of epicuticle on keratin fibres. *Nature*, **218**, 694-695.
- Manjrekar, S. G. (1995), Application of enzymes in wet process an overview. *J. Textile Assn.*, **60**, 79-87.
- Messinger, H.; Hocker, H. and Zahn, H. (1994), Covalently linked fatty acids at the surface of wool: part of the cuticle cell envelope. *Textile Res. J.*, **64**, 554-555.
- Shridhar, V. C.; Samina, K. and Mehta, R. D. (1995), Effect of bio-finishing on cotton/wool blended fabrics. *Textile Res. J.*, **65**, 564-569.
- Shuzheng Zhang (1984), *Enzyme preparation industry*, Beijing: Science Press. pp. 387-413.
- Word, R. J.; Willis, H. A.; George, G. A.; Guise, G. B.; Denning, R.; Evans, D. J. and Short, R. (1993), Surface analysis of wool by x-ray photoelectron spectroscopy and static secondary mass spectrometry. *Textile Res. J.*, **63**, 362-368.
- Xinghua Wen; Yongquan Li and Chenming Xu (1999), Studies on the kinetic property of acid protease from *Aspergillus usamii* mutant. *Mycosystem*, **18**, 66-71.
- Yongquan Li (2001), Screening of compound enzymes high productive strain L86 for wool textile decrement by laser irradiation *Mycosystem*, **20**, 196-200.
- Yongquan Li; Xinghua Wen and Xiaolong He (1999), Studies on the screening high yield acid protease producing strain L336 by combining microwave irradiation with chemical inducing. *Acta Microbio. Sinica*, **39**, 181-184.

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