

Application of Enzymes and Chitosan Biopolymer to the Antifelting Finishing Process

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ABSTRACT: We surveyed environmentally friendly chemicals and mild processes that could be used to avoid the high absorbable organic halogen compounds (AOX) load and damage to the environment from the waste of wool plants. In this research, we sought to achieve a new zero-AOX processing alternative to conventional processes such as chlorine/Hercosett processing and thus use environmentally friendly enzymes and chitosan as a biopolymer. We studied enzymatic, oxidative, and additive processes and various combinations of them to improve the shrink-proofing and antifelting properties of wool. We performed our

experiments with enzymatic treatments using commercial protease preparations, such as Perizym AFW, Alcalase 2.5L, Savinase 16L, and papain. The oxidative agents were hydrogen peroxide and sodium hypochloride, and the additive agents were based on polyurethane, polysiloxane, and silicone, as well as chitosan, a hydrophilic and natural polymer. We attempted to determine the agent or combination that best improved the shrink-proofing properties. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2903–2908, 2004

Key words: biopolymers; chitosan; wool; enzymes

INTRODUCTION

Wool is about 97% protein, 2% lipids, and 1% minerals. The cuticle is 10% of the weight of wool, and the cortex is 90%.¹ The fiber is surrounded by cuticle cells that overlap in one direction and consist of at least four layers: the epicuticle, the A and B layers of the exocuticle, and the endocuticle. The cuticle and cortical cells are separated by a cell-membrane complex comprising internal lipids and proteins.² Enhancing the smoothness of the cuticle scales results in a reduction of the fiber friction when the fibers move against the cuticle scale direction (fiber root) and to the fiber tip. The hydrophobic character and scaly structure of the surface of wool are the main factors behind the differential frictional effect, which causes all the fibers to move toward their root end when mechanical action is applied in the wet state.³ Consequently, the tendency of the fibers to move in one direction (e.g., during scouring) is reduced, and a certain antifelting effect is achieved. The detached chlorinated protein residues contribute to the wastewater load (AOX) of textile plants. Therefore, it is ecologically and economically reasonable to develop alternative wool treat-

ments and to transfer them to the textile industry.⁴ As forward-looking technologies, enzymatic and biopolymer treatments of wool are to be considered. The mathematical difference of the dry friction coefficient can be reduced by an enzymatic treatment.

Enzymatic treatment not only is an environmentally friendly shrink-proofing process but can also retain the natural aspect of wool. The enzymatic treatment of wool can partially remove the lipid layer and also cause some oxidation of the underlying cystine and peptide links. Three distinct enzyme groups are particularly important for processing wool: proteinase, lipase, and lipoprotein lipase. Of these, protease is the most widely used. An ideal antifelting effect should be achieved with an enzymatic process alone without the application of a synthetic resin, but this kind of process has not yet been developed. As a result, some combined enzymatic processes (i.e., oxidative, reducing, alkaline, acidic, solvent, and additive processes) using new polymers such as chitosan or physical types with various forms of radiation, such as high-frequency waves and cold discharges, have been studied and developed.⁵

Chitosan is a polysaccharide-based cationic biopolymer and a suitable candidate for replacing some synthetic polymers that produce AOX in wool finishing. In aqueous solutions at pH < 6.5, chitosan is in its protonated form and behaves like a cationic polyelectrolyte, forming viscous solutions and interacting with oppositely charged molecules and surfaces.⁶

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TABLE I
Enzymes, Additive Agents, and Oxidative Agents Used for the Antifelting Finishing Process of Wool

Enzymatic process		
Enzyme	EC no.	Source
Perizym AFW	—	Highly specific combination of proteases
Alcalase 2.5L, type DX	EC 3.4.21.62	A serine-type protease produced by the submerged fermentation of a genetically modified <i>Bacillus</i> microorganism. Declared activity = 2.5 AU/g.
Savinase 16L, type EX	EC 3.4.21.62	A serine-type protease produced by the submerged fermentation of a genetically modified <i>Bacillus</i> microorganism. Declared activity = 16 KNPU/g.
Papain	EC 3.4.22.2	A protease enzyme from <i>Carica papaya</i> . 3.1 U/mg
Additive process		
Additive agent	Properties	
Dicrylan WSR	Aqueous solution of a modified polyurethane and a poly(dimethylsiloxane). Nonionic/anionic.	
Dicrylan 7702	Aqueous dispersion of a crosslinkable silicone. Nonionic/slightly cationic.	
Prodotto ST 40	Aqueous dispersion of a reactive polysiloxanes. Nonionic.	
Argosil 30	Microsilicon-based softener agent	
Chitosan	A polysaccharide-based cationic biopolymer. Deacetylation = 85%/min.	
Oxidative process		
Oxidative agent	Properties	
Hydrogen peroxide	50% solution	
Sodium hypochloride	Liquid material containing 140 g/L active chlorine.	

The influence of proteases and chitosan on the dyeability of wool fibers has been investigated for the last several years. Previous studies have used only an enzymatic process or various combinations of enzymatic, oxidative, additive, and physical processes to improve the antifelting properties of wool materials.

Riva et al.⁷ applied a proteolytic enzyme derived from the bacterium *Streptomyces fradiae* to wool in an attempt to improve its shrink-resistance properties. They determined the influence of the enzyme concentration and the treatment time on the improvement of felting shrinkage in different washing cycles.

Levene et al.⁸ reported that the activity of an alkaline bacterial protease in conferring shrink resistance to wool tops and woven cloth was enhanced by the

pretreatment of wool with sodium sulfite at pH 8.5–9.0. Among the 16 proteases whose activities were compared, esperase was the most active and caused the least damage when applied after a sulfite treatment. None was found to confer adequate shrink resistance to tops under these conditions without causing excessive damage.

Heine et al.⁴ studied the influence of a proteolytic pretreatment with papain and pronase on the dyeability and shrink-proofing properties of wool. The shrink-proofing properties of wool fabrics with an enzymatic treatment were improved.

Breier⁹ compared the area shrinkage results from the Petry–Lanazym process and from a process using 1.5 g/L Perizym AFW and chlorine with 3% Basolan

TABLE II
Recipes for Additive Processes

No.	Concentration	Chemical Agent	Bath uptake	Padding temperature (°C)	Drying	
					Temperature (°C)	Time
1	40 g/L	Dicrylan WSR	70	20	130	60 s of drying
	80 g/L	Dicrylan 7702			150	5 min of curing
	4 g/L	Sodium bicarbonate				
2	75 g/L	Dicrylan 7702	70	20	130	60 s of drying
	15 g/L	Phoboton catalyst 7639			150	4–5 min of curing
3	15 g/L	Prodotto ST 40	70	25	160	4 min of drying
	70 g/L	Prodotto 2/11				
4	15 g/L	Phoboton catalyst 7639	80	25	100	3 min of drying
	1 g/L	Chitosan			150	3 min of drying
5	5%	Acetic acid	80	25	130	3 min of curing
	7 g/L	Argosil 30				

TABLE III
Recipes Used for Enzymatic and Oxidative Processes

Process	No.	Concentration	Chemical Agent	pH	Liquor ratio	Temperature (°C)	Time (min)
Oxidative process	1	10–20 mL/L 0.5–1 g/L 0.5 g/L	Hydrogen peroxide Gemstap 624 Gemsol HRK	8.5	15:1	55–60	60
	2	10.08 g/L 5 g/L	Sodium hypochloride Hydrogen chloride	2	15:1	30	60
Enzymatic process	3	2 g/L 0.5 g/L 0.8 ml/L	Perizym AFW Perlavin NIC Sodium hydroxide	8	10:1	70	60
	4	4% 0.8 ml/L	Alcalase 2.5L Sodium hydroxide	8.5	10:1	55–60	60
	5	4% 0.8 ml/L	Savinase 16L Sodium hydroxide	9	10:1	45–50	60
	6	6.7 g/L 1% X%	Papain Sodium bisulfide Sodium bicarbonate	6–7	10:1	65	60

DC (dichloroisocyanuric acid) for knitwear wool worsted yarn, carded yarn, wool/silk, and an untreated sample after multiple home washings. The enzymatically finished wool showed a good improvement in the felt shrinkage in comparison with untreated natural wool.

El-Sayed et al.¹⁰ reported that the efficiency of the proteolytic enzyme papain (EC 3.4.22.2) in conferring shrink resistance to wool tops and woven fabrics was enhanced by the pretreatment of the wool with lipase (EC 3.1.1.3), sodium monoperoxyphthalate (SMPP), and sodium sulfide. A treatment with lipase, SMPP, and sodium sulfide enhanced the efficiency, with respect to the shrink-proofing process, of the subsequent treatments.

Cardamone¹¹ studied the proteolytic activity of *Aspergillus flavus*, *Aspergillus oryzae*, and *Subtilisin* proteases on wool to determine their effects on the scales and mechanical and physical properties of wool. He treated the wool fabrics with different concentrations and treatment times. *A. oryzae*, when applied at 1% owf (on weight of wool fabric), caused scale smoothing and produced a tougher, softer fiber with increased strain, a slight loss in strength, and little change in the coefficient of friction, geometric roughness, and bending rigidity. *A. oryzae* had little effect on the shrinkage (7.37% shrinkage). Higher enzyme concentrations of *A. oryzae* should be examined. The digestion of wool fibers with *A. flavus* should be restricted. Although the *Subtilisin* protease concentration of 10% owf was higher than recommended for its suggested use, it resulted in aggressive attack, causing the disorientation and removal of scales, with penetration of the inner cortical cells and a concomitant decrease in the mechanical properties. However, the recommended dosage of 2% was effective for shrinkage control after 12 h of exposure at 40°C without appreciable damage to the structural integrity of wool.

El-Sayed et al.¹² described an enzyme-based process used to improve the felting resistance of wool top. This process used lipase in the pretreatment step, glutathione reductase in the reduction step, and papain in the posttreatment step. They used glutathione reductase as a catalyst to reduce the disulfide bonds in wool keratin along with nicotine amide adenine dinucleotide phosphate in the reduced form. Wool fibers treated with this system showed good felting resistance in comparison with untreated wool, but they still were inferior to that treated with the chlorine/Hercosett process. They also reported the tenacity and weight loss of treated wool. Scanning electron microscopy showed an insignificant attack of papain at the surface of wool.

Yoshimura et al.¹³ developed new shrink-resistance finishing with enzymes and studied the promoting

TABLE IV
Loss of the Tensile Strength, Weight Loss, and Alkaline Solubility of Wool

	Loss of tensile strength (%)	Weight loss (%)	Alkaline solubility (%)
Cont	18.81	1.57	8.5
Per	24.31	2.16	7.5
Alc	28.63	2.88	10
Sav	73.88	14.9	12.5
Pap	76.96	12.38	13
Cont + Chi	22.66		
Per + Chi	21.16		
Alc + Chi	35.41		
Sav + Chi	74.75		
Pap + Chi	80.6		

Cont = control (pretreatment without enzyme); Per = perizym AFW; Alc = alcalase 2.5L; Sav = savinase 16L; Pap = papain; Cont + Chi = control + chitosan; Per + Chi = perizym + chitosan; Alc + Chi = alcalase + chitosan; Sav + Chi = savinase + chitosan; Pap + Chi = papain + chitosan.

TABLE V
Relaxation, Felting, and Total Shrinkage Values in the Warp and Weft Directions

		Shrinkage in warp direction (%)			Shrinkage in weft direction (%)		
		Relaxation shrinkage	Felting shrinkage	Total shrinkage	Relaxation shrinkage	Felting shrinkage	Total shrinkage
Enzymatic process	Control	1.71	6.11	7.71	1.58	5.88	7.36
	Per	0.22	0.04	0.25	0.11	0.48	0.59
	Alc	0.29	-0.84	-0.55	0.98	-1.48	-0.49
	Sav	0.11	-1.42	-1.31	-0.22	-2.20	-2.41
	Pap	-0.79	-0.60	-1.39	-0.74	-1.42	-2.17
Oxidative process	H ₂ O ₂	0.60	4.72	5.28	1.45	5.08	6.46
	HYPO	0.93	0.04	0.97	0.44	1.56	2.01
Additive process	Chi	0.92	1.54	2.46	1.45	1.16	2.59
	DicWSR	0.46	1.20	1.65	1.36	0.52	1.87
	Dic7702	0.78	4.52	5.27	1.08	3.60	4.64
	ProdST40	0.46	3.14	3.58	1.19	2.76	3.92
	Argo	0.18	0.39	0.57	0.95	0.36	1.31
Enzymatic-additive process	Per-Chi	0.74	0.75	1.48	1.89	1.22	3.09
	Alc-Chi	1.05	0.08	1.13	1.33	0.80	2.12
	Sav-Chi	0.18	-1.16	-0.98	1.00	-2.41	-1.40
	Per-DicWSR	1.93	-1.82	0.15	2.41	-0.22	2.19
	Alc-DicWSR	0.75	-0.31	0.44	1.97	1.27	3.21
	Sav-DicWSR	0.56	-0.36	0.20	2.31	0.86	3.14
	Argo	0.57	0.56	1.13	1.54	1.45	2.97
Oxidative-additive process	H ₂ O ₂ -Argo	0.75	0.71	1.46	0.93	2.31	3.22
	H ₂ O ₂ -ProdST	0.45	-0.04	0.41	1.89	1.39	3.25
	HYPO-Argo	0.74	0.19	0.93	2.00	1.27	3.25
	HYPO-ProdST	0.68	-1.32	-0.63	1.43	0.31	1.73
Enzymatic-oxidative process	Per-HYPO	0.81	-0.19	0.63	1.39	0.67	2.06
	Sav-HYPO	0.33	0.48	0.81	0.84	0.30	1.14
	Per-H ₂ O ₂	2.34	0.61	2.93	2.45	0.26	2.70
	Alc-H ₂ O ₂	1.68	1.16	2.81	2.57	1.59	4.11
	Sav-H ₂ O ₂	0.88	3.16	4.01	1.90	3.17	5.01

Cont = control (treatment without enzymes); Per = Perizym AFW; Alc = Alcalase 2.5L; Sav = Savinase 16L; Pap = Papain; HYPO = sodium hypochloride; H₂O₂ = hydrogen peroxide; Argo = Argosil; DicWSR = Dicylan WSR; Chi = chitosan; ProdST = Prodotto ST40; Dic7702 = Dicylan 7702.

effect of surfactants on the enzymatic treatment of wool. Wool fabric was pretreated with anionic surfactants. This pretreatment accelerated the following enzymatic treatment remarkably, and high weight losses (>30%) were obtained within 3 h. The typical anionic surfactants, fatty acid sodium salts and sodium dodecyl sulfate (SDS), showed different promoting effects. Oleic acid sodium salt worked in the center of the wool fiber and hydrolyzed the cell membrane complex in the cortex. SDS worked in the scale on the wool surface. SDS depressed the fibrillation of the wool fiber and improved the fiber strength.

Julia et al.¹⁴ recommended an alternative zero-AOX treatment to replace the chlorine/Hercosett process. The Hercosett resin was substituted by a chitosan biopolymer. Moreover, wastewater AOX requirements could be fulfilled if hypochloride-containing agents were replaced by chemicals, such as hydrogen peroxide, that were less harmful to the environment. The shrink-resistance properties of the wool treated with chitosan were influenced by the pH and temperature of the pretreatment with hydrogen peroxide.

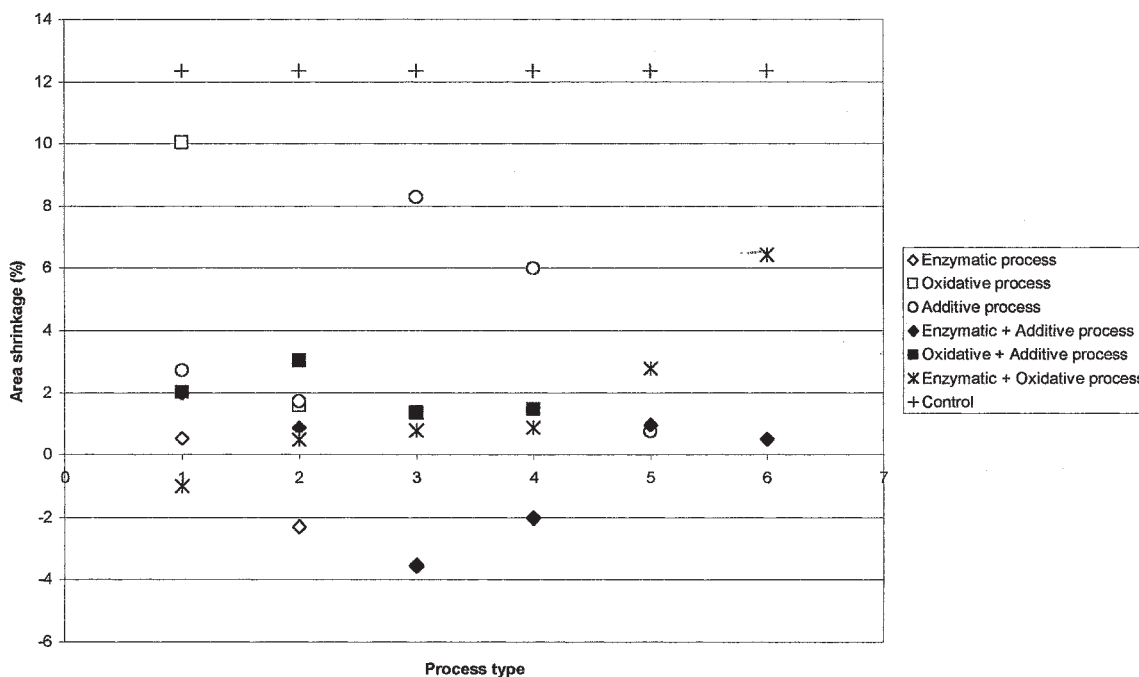
Jovancic et al.⁶ demonstrated that a commercial enzyme preparation could be successfully incorporated

into an alkaline hydrogen peroxide bath to promote the shrink-resistance properties of wool and the effectiveness of subsequently applied chitosan biopolymer. Moreover, the presence of an enzyme in the alkaline peroxide bath increased the wettability and whiteness of wool, and this could be interesting for subsequent dyeing, particularly with pastel shades.

In this research, we used enzymatic, oxidative, and additive processes and their various combinations to improve the shrink-proofing and antifelting properties of wool. We performed our experiments with enzymatic treatments using commercial protease preparations such as Perizym AFW, Alcalase 2.5L, Savinase 16L, and Papain. The oxidative agents were hydrogen peroxide and sodium hypochloride, and the additive agents were based on polyurethane, polysiloxane, and silicone, as well as chitosan, a hydrophilic and natural polymer. We attempted to determine the agent or combination that best improved the shrink-proofing properties.

EXPERIMENTAL

The textile material was 100% wool fabric (plain-weave, 173 g/m², 29 ends/cm, and 27 picks/cm).



Process type	Enzymatic process	Oxidative process	Additive process	Enzymatic + Additive process	Oxidative + Additive process	Enzymatic + Oxidative process
1	Per	H2O2	Chi	Per-Chi	H2O2-Argo	Per-HYPO
2	Alc	HYPO	DicWSR	Alc-Chi	H2O2-ProdST	Alc-HYPO
3	Sav		Dic7702	Sav-Chi	HYPO-Argo	Sav-HYPO
4	Pap		ProdST40	Per-DicWSR	HYPO-ProdST	Per-H2O2
5			Argo	Alc-DicWSR		Alc-H2O2
6				Sav-DicWSR		Sav-H2O2

Figure 1 Area shrinkage from enzymatic, oxidative, and additive processes and their combination.

Commercial proteolytic enzymes, oxidative agents, and synthetic polymers based on polyurethane, polysiloxane, and silicone, as well as chitosan, were used for the antifelting finishing processes in this study and are described in Table I.

Antifelting finishing processes with proteases and oxidative agents were performed with an exhaustion method, whereas those with additive agents were performed with a padding method, as shown in Tables II and III.

The alkaline solubility, weight loss, and loss of tensile strength for the samples treated with proteases and chitosan were determined. The tensile strength (in the warp direction) was evaluated according to ASTM

D 5035-90 (West Conshohocken, PA) with an Instron 4411 tester (Jena, Germany) and was calculated as the percentage of the tensile strength loss. The weight-loss percentage was calculated as follows:

$$[(W_1 - W_2) \times 100] / W_1 \tag{1}$$

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

Moreover, the relaxation, felting, and total shrinkage values in the warp and weft directions of wool samples treated with enzymes, oxidative agents, additive agents, and their various combinations were

measured according to IWTO TM 31. The area shrinkage was measured as follows:

$$\text{Area dimensional change (\%)} \\ = WS + LS - (WS \times LS)/100 \quad (2)$$

where WS is the mean width dimensional change (%) and LS is the mean length dimensional change (%)

A statistical analysis of the results was evaluated with the SPSS statistics program (Chicago, IL, U.S.A.) with a 95% confidence interval. A one-way analysis of variance, for the comparison of felting shrinkage values, was used ($\alpha = 0.05$).

RESULTS AND DISCUSSION

Tensile strength loss

The tensile strength losses of samples treated with alcalase and perizym and control samples were similar, and the losses of savinase and papain reached 70%. The highest loss of tensile strength was caused by the savinase–chitosan and papain–chitosan treatments. After a proteolytic treatment, a chitosan treatment caused an increasing loss of tensile strength.

Weight loss

The protease type affected the weight loss according to the results of the analysis of variance. Significant differences were obtained between samples subjected to proteolytic treatments. The highest loss of weight was caused by the treatment with savinase and papain (Table IV).

Alkaline solubility

The alkaline solubility of wool fabrics indicates the extent of the modification of the chemical properties. The higher the change is in the alkaline solubility, the greater the modification is of the fabrics.¹⁵ The alkaline solubility values of the fabrics treated with perizym and alcalase resembled those of the control samples, despite the higher values of approximately 13% from the treatments with savinase and papain. The proteolytic treatments did not cause significant chemical damage of the wool fabrics (Table IV).

Felting shrinkage

The felting shrinkage of the samples treated with proteases, oxidative agents, additive agents, and various combinations of them was determined. The values of the shrinkage in width and length after relaxation, the felting, and the total shrinkage are shown on Table V.

The felting behavior was improved by the proteolytic treatments. Moreover, the best treatments for the antifelting processes used perizym and hypochloride according to a one-way analysis of variance ($\alpha = 0.05$). Thus, an enzymatic treatment could provide antifelting values comparable to those of a chloride treatment and still be environmentally friendly and produce zero AOX.

Figure 1 shows that the processes with hypochloride and enzymes and combinations of the processes could provide sufficient shrink-proofing properties, whereas hydrogen peroxide and Dicrylan 7702 could not.

CONCLUSIONS

For improved antifelting, protease enzymes were used in textile finishing processes; they provided a completely zero-AOX treatment of wool and did not significantly change the nature of the wool fiber. The felting shrinkage properties were improved by all the proteolytic treatments, and the values resembled those of conventional processes with chloride. We recommend that proteolytic processes be used as alternatives to conventional chloride processes, which cause high-load AOX and serious damage to the environment.

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