HIGH EXHAUSTION SYSTEM (HES) FOR LEATHER PROCESS: ROLE OF BIOCATALYST AS AN EXHAUSTIVE AID FOR WET-END

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Abstract. Application of biocatalyst becomes an imperative due to their eco-friendly advantages. Enzymes in pre-tanning for unhairing, fibre opening, defleshing and bating are well reported and practiced. However, the role of enzymes as a chemical aid is less explored and consider as secondary applications. Leather enzymes are known for their hydrolytic behavior which makes it more suitable for pretanning operations. However, typical chemical exhaustive aids acts as a vehicle for the diffusion of chemicals, whereas enzymes aids in the splitting of fibres which facilitate the diffusion of chemicals and create more functional sites for the tanning and post tanning chemicals to interact. In this research, pickled pelts are treated with acid protease and subsequently tanned using chrome tanning agent. Enzymatic treated pelts resulted in better uptake of chromium as compared to conventionally processed leathers. Similarly, after neutralization, chrome tanned leathers are pretreated before post tanning process. Enzymatic treated wet blue leathers showed higher uptake of post tanning chemical, uniform dyeing and reduction in the pollution load. From the preliminary research, an interesting finding has augmented that application of enzymes at an optimized concentration would lead to better uptake of chrome which reduces the pollution and minimization pollution load in post tanning. This study, emphasize on the application of enzymes in tanning and post tanning for higher diffusion of chemicals.

1 Introduction

Application of enzymes in leather processing finds an inevitable role due to eco-benign aspects. Conventionally, protease is commonly used in bating process for the opening up of fibres and removal of short hairs which are left after liming process. Recently, many attempts have been made to use enzymes in different stages of leather processing. Enzymes such as protease, amylase and lipase are commonly used in the tannery for various functions. Protease aids in scissoring proteoglycans and non-collagenous proteins from the skin. Amylase split the inter-fibrillar proteins and proteoglycans whereas fats and tri-glycerides are removed using lipase. Though, enzymes are eco-friendly and replace the conventional chemicals like lime and sodium sulfide. It also limits the practical application due to several factors, such as concentration, pH, temperature and time. Overexposure of enzymes to skins would lead to complete depletion of the materials. Application of enzymes during tanning and post tanning is less explored owing to its limited activity on leather. Recently, novozymes have introduced enzymes to treat tanned leathers which relax the fibres that enhance the area yield. Similarly, acid protease has been used as an auxiliary agent for better uptake of dyes. In the present study, a novel attempt has been made to maximize the utilization of enzymes in tanning and post tanning process for better area yield and uptake of chemicals.

2 Material and Methods

2.1 Materials

Wet salted goat skins were chosen as raw materials for the study. All chemicals used for leather processing were of commercial grade while the chemicals used for the analysis of spent liquors were of analytical grade. Chemicals used for analysis were of analytical grade.

2.2 Combination tanning trials

Conventional chrome tanning was followed as given in Table 1. Control trial was processed without protease treatment and experimental trials were done with protease treatment before chrome tanning.

Table. 1. Application of enzyme during chrome tanning.

Process	Chemicals	% offered	Time (minutes)	Remarks
Pickling	Water	100		
	Salt	10	10’	pH-2.8 to 3
	Formic acid	1	3x10’+20’	
	Sulfuric acid	0.5	3x10’+20’	
Tanning	Pickle bath	50		
	Protease	X	60’	Check
	BCS	6	Y	penetration
Basification	Water	100		
	Sodium formate	1	3x10’+20’	
	Sodium bicarbonate	1	3x10’+20’	pH-3.8 to 4
Drain/Wash/Drain				

After neutralization, chrome tanned leathers were treated with protease as given in Table 2 and conventional post tanning process was followed. Control trial was carried out without protease treatment.

Table. 2. Application of enzyme during post tanning.

Process	Chemicals	% offered	Time (minutes)	Remarks
Wetback	Water	100	15’	Drain out
	Wetting agent	0.5		
Neutralization	Water	100		pH 5.3-5.5
	Sodium formate	1	45’	D/W/D
	Sodium bicarbonate	0.5		
Enzyme Treatment	Protease	X	30’	
Washing	Water	100	10’	D/W/Pile
Retanning	**Protease**	1.0	30’	Check
	Acrylic resin	2	20’	penetration
	Veg fatliquor	2	15’	
	Replacement Syntan	3		
	Melamine	5	120’	
	Wattle	3		
	Dye	2	60’	
Fatliqouring	Synthetic	6		
	Semi synthetic	2	60’	
	Vegetable	2		
Fixing	Formic acid	3	3x15’	D/W/Pile

2.3 Determination of hydrothermal stability of leather

The hydrothermal stability of leather was determined by Theis shrinkage tester. The shrinkage temperature test was carried out as per SATRA STD 114 method. A strip of about 2 by 3 leather and a thermometer were suspended in the sight glass filled with water, the upper end of the leather was fixed and the position of the lower end was indicated by an adjustable marker outside the tube to help judge when shrinkage occurs. The system was heated and the temperature at which leather shrinks to one third of its original length was recorded as a shrinkage temperature, which connotes hydrothermal stability.

2.4 Physical testing

Leather samples were subjected to physical testing to determine the influence of enzyme on physical properties of leather. Tear strength water vapour permeability tests were carried out using SATRA TM 162:1992. All test samples were conditioned at 20℃ and 65% relative humidity. Control samples were tested in the same way. All analyses were done in duplicate.

2.5 Scanning Electron Microscopic Analysis of Leather Samples

Samples from control and experimental pelts/tanned leathers were cut from the official sampling position. Samples were then dehydrated gradually using acetone as per standard procedures. The micrographs for the grain surface and cross section were obtained by operating the SEM at an accelerating voltage of 10 KV.

3 Results and discussion

In the present study, biocatalyst, protease enzyme is used as an exhaustive aid during tanning and post tanning (schematic representation is shown in Fig.1). Pickled pelt has been treated with different concentration of protease before chrome tanning as given in Table.1. Chrome content and hydrothermal temperature of wet blue leathers are estimated and results are shown in Fig.2.

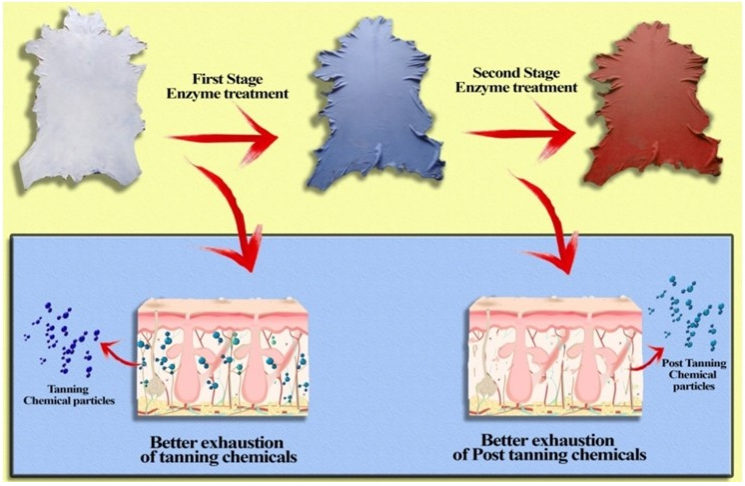

Fig. 1. Schematic representation of enzyme treatment at tanning and post tanning.

From the results, it can be inferred that chrome content in wet blue at 1% protease treated leathers showed better uptake of tanning chemicals. Similarly the shrinkage temperature of wet blue is found to be higher for protease treated leathers.

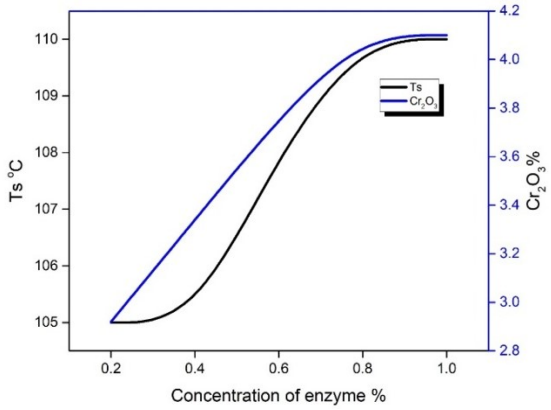

Fig. 2. Chrome content and hydrothermal stability of wet blue leathers.

Though, enzyme treatment might lead to relaxation of fibres which in turn could lead to better exhaustion of tanning chemicals. From the results, it can be ascertained that enzymatic treatment has not affected the quality of leathers in terms of wet resistance which is a primary quality measurement of wet blue leathers. Microscopic images of wet blue leathers provide topographical information on surface and compactness of fibres. Enzymatic treatment has not deteriorated the surface and makes it more compact.

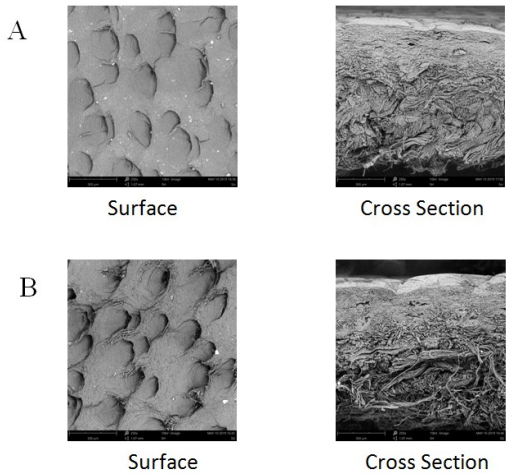

Fig. 3. Scanning electron micrograph of wet blue leathers A-Control wet blue leather and B-Experimental leather (1% protease treated).

The study further extended for treating wet blue leather using protease during neutralization process as given in Table 2 and subsequently processed into crust leathers.

Table 3. Physical strength characteristics.

Sample	Tensile strength (Kg/cm^2)	Elongation @ break (%)	Load @ grain crack (Kg)	Distension @ grain crack (mm)
Control	116.52	48.77	6.19	7.06
Experimental	162.77	56.27	6.65	7.14

Though, enzymatic activity on the leather is minimal, however, the relaxation of fibres would lead to better uptake of post tanning chemicals. After neutralization the wet blue leather is treated with 1% protease and thoroughly washed and post tanning process has been carried out. Crust leathers are evaluated for physical strength characteristics and microscopic images have been obtained to understand the influence of protease on post tanning process.

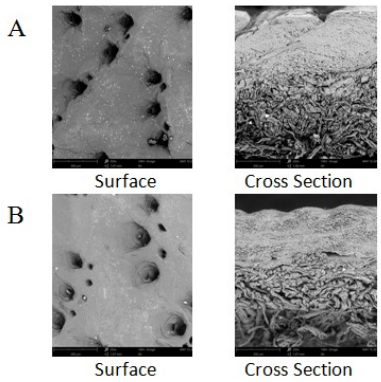

Fig. 4. Scanning electron micrograph: A-Control crust leather and B-Experimental leather (1% enzyme treatment).

From the physical strength results, it can be inferred that that strength has significantly enhanced for the enzyme treated crust leather. This might be due to better uptake of post tanning chemicals and uniform distribution. The data is in-line with microscopic image of crust leather as shown in Fig.4.

4 Conclusion

The present study provides a new insight on application of enzyme during tanning and post tanning processes. Interesting result has been obtained from the enzymatic treatment process. Enzyme treated wet blue leathers shows higher uptake of chrome tanning agent and slight increment in the hydrothermal resistance. Similarly, enzyme treatment during neutralization, the leather has shown better physical strength characteristics and compact fibres due to better uptake of post tanning chemicals. The study can be extended further to understand the kinetics of enzyme on leather substrate during pickling and neutralization.

5 Acknowledgements

Authors acknowledge the financial support from Department of Leather Technology, Anna University, India.

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