Effect of Enzymatic Treatment in Leather Manufacture at Different Processing Stage

by

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Abstract

The use of cleaner leather processing technologies is of great interest today due to the global trends favoring environmentally friendly manufacturing. Modernization and implementation of new technologies, like enzyme-driven catalysis instead of conventional inorganic catalysis, can improve the quality and reduce the cost of leather manufacturing while making the leather more environmentally sustainable. The use of enzymes in pre-tanning operations is a well-known technology. However, a holistic view of the effect of enzymes at various stages of leather processing is limited. We attempt to bridge this gap by studying the influence of enzymes on the characteristics of crust leather at multiple locations of leather processing. Trypsin was used to assess the enzymatic action on delimed pelts, while pepsin was used to evaluate the impact of enzyme treatment on a pickled pelt that was later chrome tanned.

Similarly, papain was used to study enzymatic activity on neutralized, chrome-tanned leather. The selection of enzymes for three different materials was guided by the optimal activity behavior of the enzymes. It is observed that the physical strength characteristics of the enzyme-treated leathers show minor differences. Hence, this study aims to explore the unconventional application of enzymes at various stages of leather processing.

Introduction

The leather industry is a traditional manufacturing sector but one that constantly adopts newer technologies to achieve sustainability.[1] The invention and implementation of cleaner technologies are essential to meet new environmental norms and meet the ever-changing requirements of consumers. Several cleaner practices including zero liquid discharge, effluent treatment through various techniques, mineral-free tanning systems, high exhaust tanning systems, aldehyde-free syntans, enzyme-assisted beam house operations, natural dyes, solvent-free finishing systems, etc. have been reported.[2-10] Of all clean manufacturing practices, enzyme-assisted processing has always been an exciting topic of study for the leather fraternity. Enzyme-assisted unhairing, fiber opening, defleshing, and scuds removal are processes where hydrolytic enzymes have been used. Proteases, amylases, and lipases are the most widely used classes of enzymes in leather processing for unhairing, fiber opening, and defleshing, respectively.[11-14] The use of protein-digesting enzymes (proteolytic enzymes) during leather processing to remove unwanted proteins other than collagen is also common. In this study, proteolytic enzymes of different specificities and functions, trypsin, pepsin, and papain, have been employed. Pepsin is an aspartic protease, while trypsin is a serine protease. Papain, a well-reported enzyme in leather processing, is very active in the neutral pH range, whereas pepsin and trypsin are in acidic and basic pH ranges respectively. The present study discusses the effect of enzymatic treatment on delimed pelt, pickled pelt, and chrome tanned leather using trypsin, pepsin, and papain, respectively.[15] The study is exploratory, and the characteristics of enzyme-treated crust leather were evaluated using a combination of tensile testing, grain crack measurement, and microscopic imaging.

Materials and Methods

Materials and Chemicals

All leather chemicals were of commercial-grade, and analysis chemicals were of analytical grade. The raw material used for leather processing was wet salted goat skins. Leather processing trials are detailed in Tables I-III.

Table I

Process Recipe for Trypsin Treatment

Process	Conc.	
Delimed Pelt		
Water	100%	
Trypsin	**0-1.0%**	**45-60 min**
Washing I	100	15 min
Washing II	100	15 min
Pickling		pH 2.8-3.0
Chrome Tanning	6%	
Basification		pH 3.8-4.0

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Table II

Process Recipe for Papain Treatment

Process	Conc	
Chrome tanned leather		
Neutralization		pH 5.5-6.0
Papain	**0-1.0%**	**45-60 min**

Table III

Process Recipe for Pepsin Treatment

Process	Conc	
Delimed Pelt		
Pickling		pH 2.8-3.0
Pepsin	**0-1.0%**	**45-60 min**
Chrome Tanning	6%	
Basification		pH 3.8-4.0

Table IV

Process Recipe for Post Tanning

Process	Chemicals	% of Chemicals	Duration (min)	Remarks
Wet Back and Acid Wash	Water	100		
	Acetic Acid	0.5		
	Wetting Agent	0.5	30	Adjust pH 2.8-3.0
Rechroming	Water	100		
	BCS	4		
	Cr. Syntan	4		
	Acrylic Syntan	2		
	Fish Oil F/L	1	40	
Basification	Water	100		
	Sodium Formate	0.5		
	Sodium Bicarb	0.5	2 × 10 + 20	Adjust pH 3.8-4.0
Neutralisation	Water	100		
	Neut. Syntan	2	20	
	Sodium formate	2	20	Adjust pH 5.5-6.0
Drain / Wash / Drain				
Retanning	Water	100	20	
	Acrylic Syntan	2		
	SMA Syntan	2	30	
	Polymeric/Phenolic Syntan	3		
	Melamine Based Syntan	2		
	Fillers	2		
	Wattle GS	2		
	Synthetic F/L	1	60	
Dyeing	Anionic Dye	X	30	
Fatliquoring	Water	100		
	Synthetic Fatliquor	2		
	Polymeric / Semi-Synt F/L	2		
	Veg based F/L	1		
	Fish Oil F/L	1		
	Preservative	0.1	60	
Fixing	Formic Acid	3	3 × 5' + 30	
Top Fatliquoring	Cationic F/L	1	20	
Drain / Wash / Drain				

Physical testing of leather samples

The samples for physical testing were obtained as per IULTCS methods.[16] The samples were conditioned at 26°C and 65% R.H. for 48 hours. Tensile strength[17] and grain crack[18], were measured as per standard procedures.

Microscopic Evaluation

Scanning electron microscopic techniques were used to understand the grain and surface characteristics of the leathers.

Determination of Hydroxyproline

To determine the effect of enzymes on collagen fibers, hydroxyproline content was estimated in the processed liquor using Woessner's method.[19] The quantity of hydroxyproline present was calculated by using the standard equation obtained by plotting standard curve.

Result and Discussion

Enzymatic processing is gaining interest owing to its cleaner manufacturing methods. Conventionally, proteases, amylases and lipases are the three enzymes used in the pretanning process. However, the influence of the enzyme on the skins at different processing stages is less explored and recently use of elastase in wet end processing was found to enhance area yield.[20] In the present study, three model enzymes were chosen to understand the leather Characteristics, viz., Trypsin on delimed pelt; Pepsin on the pickled pelt and papain on the chrome tanned leather. The selection of enzymes and the suitable substrate have been chosen based on the optimum enzyme activity. Enzymatic treatment of all the three enzymes on the skins has been studied as given in Table I-III. For Pepsin and Trypsin trials, conventional chrome tanning and post tanning have been carried out as given in Table IV after the enzymatic treatment. Whereas, for papain trials, after enzymatic treatment, the post-tanning process has been carried out at pH 5.5-6.0, as given in Table IV. After completing the post-tanning processes, the leather was tested for its physical strength properties, and the leather images are shown in Figure 1.

The images of processed crust leathers are shown in Figure 1. The leathers are found to be smoother with higher concentration of enzymatic treatment in all the trials. This might be due to the enzyme activity on the fibers which aids in smooth characteristics. Moreover, leathers are found to be soft in the enzyme treated trials.

Topological Images of the Enzyme Treated Crust Leather

The SEM images of the control post tanned leather and the experimental post tanned leather using 1% trypsin on delimed pelt, 1% pepsin on the pickled pelt and 1% papain on the chrome tanned leather are shown in the Figure 2, 3 and 4 respectively.

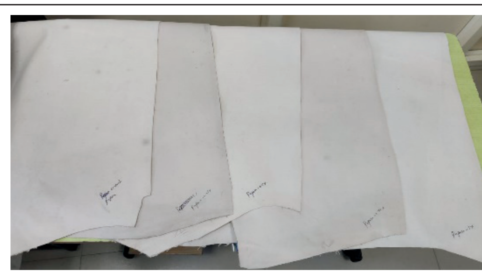
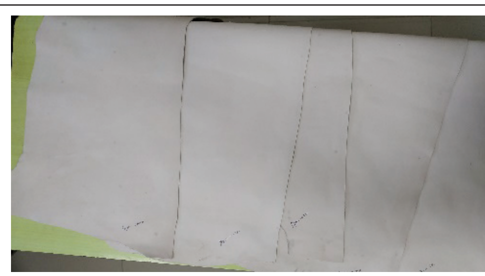
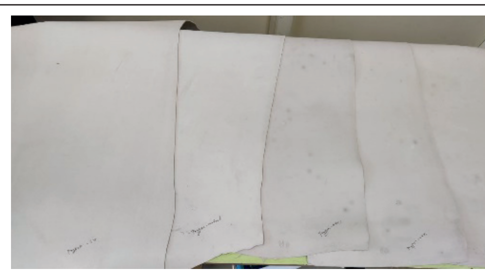
Papain-Neutral pH	
Pepsin-Acidic pH	
Trypsin-Alkali pH	

Figure 1. Images of enzymatic treated post tanned leathers

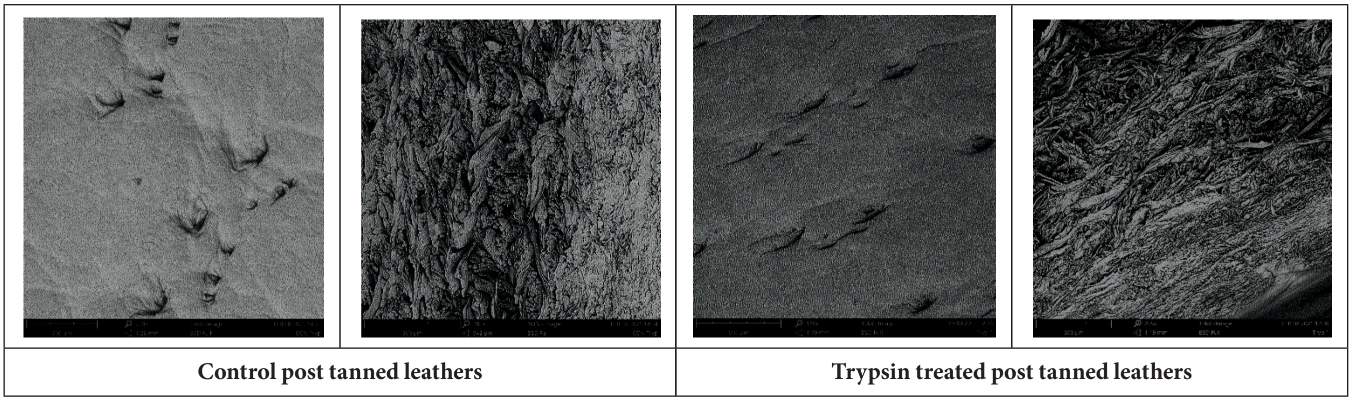


Figure 2. SEM images of control and trypsin treated crust leathers

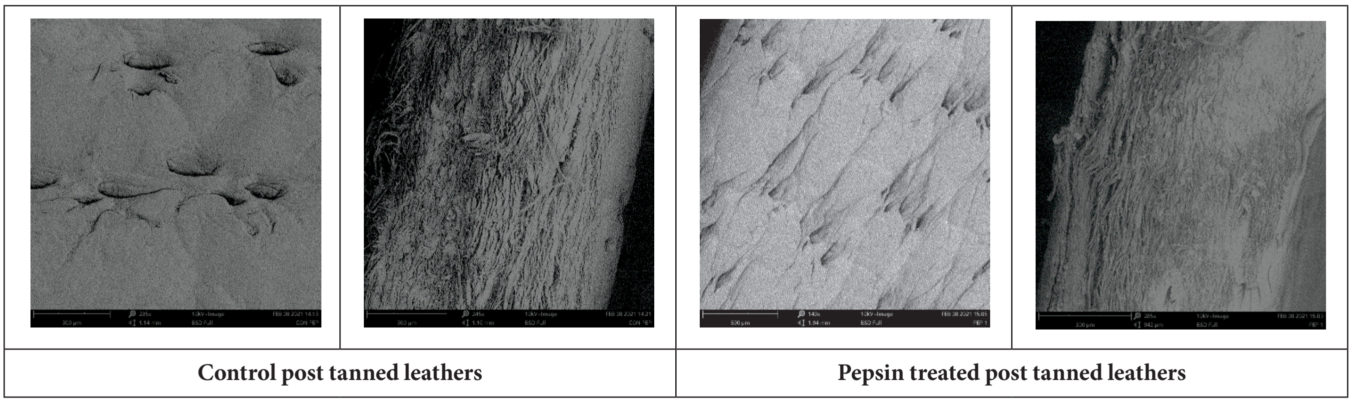


Figure 3. SEM images of control and pepsin treated crust leathers

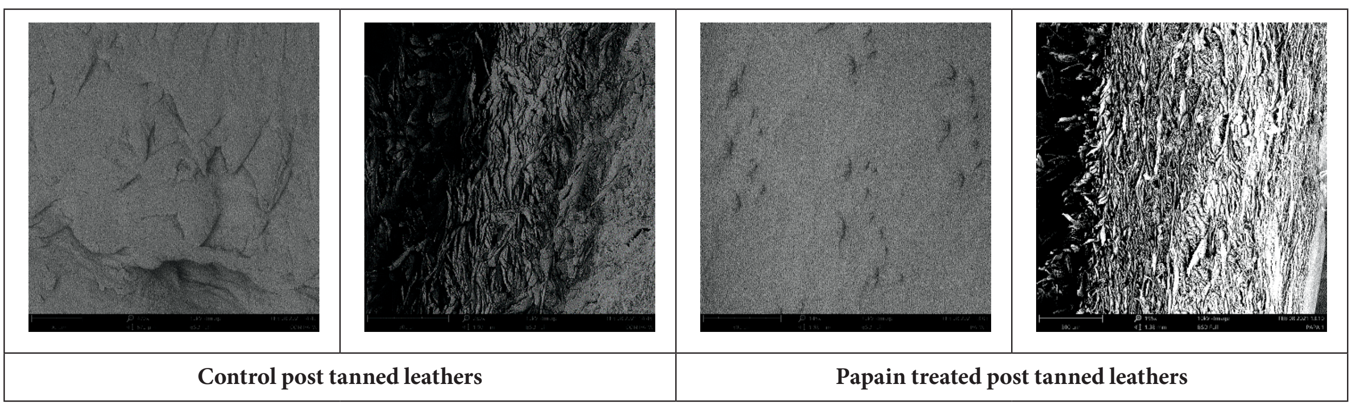


Figure 4. SEM images of control and papain treated crust leathers

The micrographic images of the crust leathers (Grain surface and Cross section) are shown in the Figure 2-4. Cross section images of the control and experimental leathers are found to be similar. Moreover, there is no disfigurement have been inferred on the grain surface due to enzymatic treatments.

Physical characteristics of the crust leather

The physical characteristics such as tensile strength and the tear strength were determined for the enzyme treated leathers and the results are given in the Table V-VII.

The pepsin treated crust leather has shown some varying result. The use of 0.25% and 1.0% of enzyme has shown a decrease in strength properties.

Treatment of trypsin on the delimed pelt has given a variation in strength characteristics. However, the tear strength has been reduced by the trypsin treatment with respect to the conventional processed crust leather.

The papain treated crust leather has also shown some varying result. The concentration of papain at 0.50% on the chrome tanned leather has shown a significant enhancement in the strength characteristics,

Table V

Pepsin treated crust leather physical characteristics

S. No.	Enzyme %	Tensile Strength (MPa)	Tear Strength (N/mm)
1.	0.25	24	66
2.	0.50	37	90
3.	0.75	38	104
4.	1.00	28	63
5.	Control	33	64

Table VI

Trypsin treated crust leather physical characteristics

S. No.	Enzyme %	Tensile Strength (MPa)	Tear Strength (N/mm)
1.	0.25	35.9375	79.5825
2.	0.50	38.0225	105.1275
3.	0.75	36.4725	80.3875
4.	1.00	38.175	110.835
5.	Control	37.5425	131.8175

Table VII

Papain treated crust leather physical characteristics

S. No.	Enzyme %	Tensile Strength (MPa)	Tear Strength (N/mm)
1.	0.25	29	91
2.	0.50	44	136
3.	0.75	36	83
4.	1.00	38	117
5.	Control	38	117

while the use of 0.25% and 0.75% of enzyme has shown decreased strength properties.

Grain crack properties

The crust leather treated with the enzymes were subjected to the lastometer test to determine the grain crack properties and the results are given in the Table VIII-X.

From the results (Table VIII-X), it can be established that enzymes have influenced the grain surface on the leathers, enzyme treated leathers have shown lesser distention at grain crack as compared to the control leathers. However, 0.5% papain treated leathers have higher distention grain crack which is in accordance with the higher strength properties of the leathers.

Table VIII

Lastometer test for pepsin treated leather

S. No.	Enzyme %	Load at Grain Crack (Kg)	Distention at Grain Crack (mm)
1.	0.25	45.91	7.95
2.	0.50	54.94	7.52
3.	0.75	50.1	7.26
4.	1.00	36.62	7.56
5.	Control	54.55	8.03

Table IX

Lastometer test for trypsin treated leather

S. No.	Enzyme %	Load at Grain Crack (Kg)	Distention at Grain Crack (mm)
1.	0.25	56.42	7.78
2.	0.50	64.42	8.09
3.	0.75	61.69	7.71
4.	1.00	73.86	8.32
5.	Control	80.04	7.92

Table X

Lastometer test for papain treated leather

S. No.	Enzyme %	Load at Grain Crack (Kg)	Distention at Grain Crack (mm)
1.	0.25	48.80	7.50
2.	0.50	78.05	8.76
3.	0.75	53.41	7.47
4.	1.00	43.48	7.58
5.	Control	49.45	7.36

Hydroxyproline assay

To assess the impact of enzymes on collagen, hydroxyproline assay was carried out separately for the liquors collected during leather processing treated with respective enzymes. The hydroxyproline estimation helps us to understand whether the collagen structure is damaged and indicates impairment in mechanical strength of leather.

The hydroxyproline results were given in table XI. Based on the results obtained, it has been observed that papain did not have any kind of impact on collagen fiber. Whereas, the trypsin and pepsin at the concentration of 0.25% and 0.5% did not show any hydroxyproline release. Although, when the concentration of trypsin and pepsin was increased, there was an increment in the hydroxyproline release. However, the release of hydroxyproline depends on several factors such the substrate, temperature and duration.

Significance of Enzymatic Treatment

Enzyme driven leather processing technologies gains significant attention amidst leather manufacturing owing to eco-acceptance. Conventionally as shown in Figure 5, enzymes have been used in the bating operation to remove scuds and open up the fiber bundles for better exhaustion of chemicals. However, the present research focused on using unconventional enzymes in leather to enhance the physical properties of the leathers. Leathers treated with enzymes have shown smoothness in grain as compared to the control process. Similarly, enzyme treated leathers were more pliable than the control processed leathers. Though, tanned leathers show resistance to the enzymatic treatments, however from the current research it is evident that fiber relaxation can be achieved using enzymes which enhances the smoothness and pliable properties of the leathers.

Conclusion

Enzymatic processing is a way forward towards cleaner and sustainable leather processing method. The present research focused on understanding the influence of enzymes at varied leather processing stages and corroborate with the strength characteristics

Table XI

Hydroxyproline Assay for liquor collected during leather processing treated with respective enzymes

	Hydroxyproline (μg/mL)			
S No	**0.25%**	**0.5%**	**0.75%**	**1%**
Trypsin	0	0	2.023	5.745
Papain	0	0	0	0
Pepsin	0	0	1.518	2.641

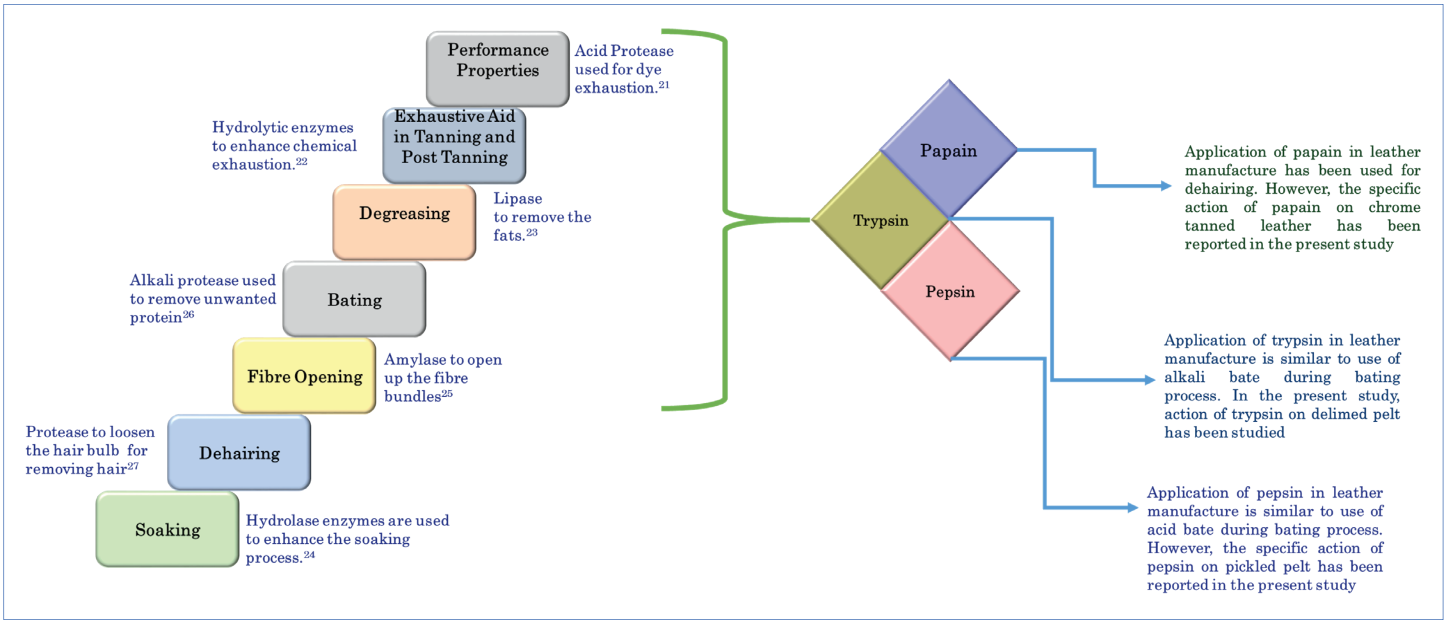


Figure 5. Significance of enzyme in leather manufacture

of the crust leathers. Influence of protease, amylase and lipase have been well reported on the leather characteristics. However, unconventional enzymes like pepsin and trypsin impact on leather have been reported in this study. Moreover, enzymes are also looked upon as an auxiliary aid to improve exhaustion of chemicals to endorse that this study would provide an insight on the strength properties.[21] The results have shown there is no significant influence on the strength properties, whereas there is marginal decrease in the distention at grain crack which is possibly due to the enzymatic interaction on the grain surface which in turn provides the smooth surface to the experimental leathers.

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