

Effect of Different Unhairing Methods on the Ionic Liquid Based Fiber Opening Process

by

Mohammad Jamal Azhar, Gladstone Christopher Jayakumar, Jonnalagadda Raghava Rao and Nishter Nishad Fathima*
*Chemical Laboratory, Council of Scientific and Industrial Research-Central Leather Research Institute,
 Adyar, Chennai-60002, India*

Abstract

Leather processing is known to impact the environment, especially the pre-tanning processes. Lime sludge is one of the major concerns for the industry. Application of ionic liquid (1-butyl 3-methylimidazolium chloride) instead of conventional reliming practice can reduce this problem to a large extent. In this study, the effect of different unhairing process on the fiber opening using ionic liquids has been studied. The extent of fiber opening was assessed for both control and experimental pelts through SEM analysis. The experimental pelts were found to have better fiber opening than the control. The ionic liquid fiber opened pelts were tanned and the spent liquors were assessed for the chrome content, COD, TDS. The results indicate that all the environmental parameters are better or on par with the conventional process. The final leathers made were also found to have physical characteristics similar to that of conventionally limed leathers.

Introduction

Pre-tanning processes contribute a large percentage of the total pollution from the tannery amounting to 60–70%. Among the pre-tanning processes, the liming operation raises more environmental concerns due to the poor solubility of lime resulting in generation of lime sludge. Also, the removal of lime in deliming process using ammonium salts leads to the emission of the ammonia and alters the NPK ratio of the soil. Hence, alternative to lime is being sought actively. In this direction, use of other alkalis like NaOH, enzymatic fiber opening have been reported.¹⁻⁴ Recently, ionic liquids (ILs), generally called as “task specific” or “designer solvents” are being explored for both stabilization and destabilization of protein.⁵⁻⁸

Ionic liquids are molten salts composed of bulky organic cations and small inorganic anions that have high tenability. Ionic liquids have non-flammability and outstanding catalytic properties. Several classes of ionic liquids are being explored for

its possible stabilization or destabilization of collagen.^{9,10} The effect of alkyl imidazolium based ILs on different hierarchical order of type I collagen has been studied recently.¹¹ This study led to the exploration of imidazolium based IL as a possible candidate for fiber opening agent.¹² In the present study, the effect of different unhairing processes on the fiber opening process using IL has been investigated to validate its application in industry. The IL fiber opened pelts were processed further as upper leathers and various properties of the leathers made are presented. The environment impact of the IL based fiber opening process has also been assessed.

Experimental

Materials

Wet salted goat skins of 4-6 sq. ft. were used as raw material. Chemicals used for the processing were of commercial grade, while the chemicals used for analysis of spent liquor were of analytical grade. Ionic liquid (1-butyl 3-methylimidazolium chloride) was procured from Sigma Aldrich.

Ionic Liquid Based Fiber Opening Process

Wet salted goat skins were cut into 2 sides. The left half was used for control and the right was used for experimental trials. First control was unhairing using lime and sodium sulfide followed by reliming using lime. Second control was unhairing using lime and sodium sulfide without fiber opening or reliming. Unhairing was done using 4 different techniques viz., enzymatic, enzyme sulfide, sulfide lime, sulfide lime & enzyme followed by fiber opening using ionic liquid. The conventional process and the various experimental processes followed for fiber opening using ionic liquid (1-butyl 3-methylimidazolium chloride) are given in Tables I to V. The control and experimental skins were tanned using 6% BCS and post tanned to make upper leathers using conventional process.¹³ The shrinkage temperature of the leathers were determined using a Theis shrinkage meter.¹⁴

*Corresponding author e-mail: nishad.naveed@gmail.com; nishad@clri.res.in, Fax: +91 44 24911589; Tel: +91 44 24411630

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Table I
Conventional control process for unhairing and fiber opening.

Process	Chemicals	%	Duration	Remarks
Liming	Water	300		
(Pit)	Lime	8		
	Sodium sulphide	3	1 day	The next day, the skins were dehaired using blunt knife.
Reliming	Water	300		
(Pit)	Lime	10	2 days	The pelts were fleshed, scudded and the fleshed weight in wet condition was noted.
Washing	Water	200	10	Bath was drained.
Deliming				
(Drum)	Water			Cross Section of the delimed pelt was checked for colorless using phenolphthalein indicator.
	Ammonium chloride	3	90 min	
Bating (Drum)	Alkali bate	0.5	30 min	Bath was drained.

Table II
Process of lime & sulfide unhairing followed by Ionic liquid fiber opening.

Process	Chemicals	%	Duration	Remarks
Liming (Paste)	Water	10		Formulation applied on flesh side and skins are piled flesh to flesh side.
	Lime	8		
	Sodium sulphide	3	1 day	The next day, the skins were dehaired using blunt knife.
Fiber Opening	Water	30		The pelts were fleshed, scudded and the fleshed weight in wet condition was noted.
(Drum)	Ionic liquid	0.2	4hrs	
Washing	Water	200	10	Bath was drained.
Deliming				
(Drum)	Water			Cross Section of the delimed pelt was checked for colorless using phenolphthalein indicator.
	Ammonium chloride	3	90 min	
Bating(Drum)	Alkali bate	0.5	30 min	Bath was drained.

Note: Ionic liquid - (1- butyl 3- methylimidazolium chloride)

Morphological Analysis

Samples from control and experimental crust leathers were cut from the butt portion and coated with gold using an Edwards E306 sputter coater. A Quanta 200 series scanning electron microscope was used for the analysis. The grain and cross-section was examined under the microscope at varying magnifications. The micrographs were obtained by operating the SEM at a voltage of 30KV with different zoom level.

Physical Characteristics Analysis

The samples for physical testing were obtained as per IULTCS methods.¹⁵ The samples were conditioned at 80±4°F and 65±2% R.H. for 48 hrs. Physical properties such as tensile strength, %

elongation, distension and grain crack strength were investigated.¹⁶⁻¹⁸ Each value reported is an average of four experiments.

Spent Liquor Analysis

The spent chrome liquor from the conventional and experimental tanning system were collected and filtered. The filtered liquor was then analyzed for chromium content, TDS and COD as per standard procedures.¹⁹⁻²⁰

Organoleptic Properties

Crust leathers were assessed for fullness, softness, roundness, smoothness, grain tightness, strength and general appearance by

Table III
Process of enzymatic unhairing followed by Ionic liquid fiber opening.

Process	Chemicals	%	Duration	Remarks
Enzymatic (Paste)	Water	10		Formulation applied on flesh side and skins are piled flesh to flesh side.
	Enzyme	3	1 day	The next day, the skins were dehaired using blunt knife.
Fiber Opening	Water	30		The pelts were fleshed, scudded and the fleshed weight in wet condition was noted.
(Drum)	Ionic liquid	0.2	4 hrs	
Washing	Water	200	10	Bath was drained.

Note: Ionic liquid - (1- butyl 3- methylimidazolium chloride)

Table IV
Process of enzyme & sulfide unhairing followed by Ionic liquid fiber opening.

Process	Chemicals	%	Duration	Remarks
Enzymatic (Paste)	Water	10		Formulation applied on flesh side and skins are piled flesh to flesh side.
	Sodium sulphide	0.75		
	Enzyme	3	1 day	The next day, the skins were dehaired using blunt knife.
Fiber Opening	Water	30		The pelts were fleshed, scudded and the fleshed weight in wet condition was noted.
(Drum)	Ionic liquid	0.2	4hrs	
Washing	Water	200	10	Bath was drained.

Note: Ionic liquid - (1- butyl 3- methylimidazolium chloride)

standard tactile evaluation technique. Experienced tanners rated the leathers in a scale of 0-10 points for each functional property, 0 being poor and 10 being best.

Results and Discussion

The application of ionic liquids for fiber opening will depend on the unhairing process employed and world over different types of unhairing methods are employed for different types of hides/skins. Hence, to ensure the practical applicability of the ionic liquids based fiber opening process, effect of different unhairing methods on this process has been investigated.

Effect of IL Fiber Opening on Shrinkage Temperature of Leathers

The ionic liquid based fiber opened chrome tanned leathers and conventionally limed and relimed chrome tanned leathers were tested for their shrinkage temperature to ensure that ILs do not lead to extensive fiber opening resulting in distortion of collagen fibers, which leads to lowering of shrinkage temperature of the leathers. It has been reported that few classes of ILs are capable of extensive destabilizing of collagen.⁹ Hence, optimization of the amount of IL and duration of treatment are important factors. It was found that the shrinkage temperatures of leathers fiber opened after following enzymatic, enzyme sulfide, sulfide lime, sulfide lime & enzyme are 103, 102, 102 and 104°C,

respectively as compared to 102°C for control leather. Hence, it can be seen that ILs does not affect the Ts of the leathers negatively though they are known to be protein denaturing agents. The amount and the duration has been such optimized that it does not affect the leathers negatively.

Effect of IL Fiber Opening on Physical Strength Characteristics of Leathers

Wet end finished leathers were primarily assessed based on their physical characteristics and organoleptic properties. Optimum utilization of ionic liquid for fiber opening was also assessed based on the final strength properties of the leathers. The physical strength characteristics like tensile, % elongation, load at grain crack and distention at break of both control and various experimental leathers are provided in the Table VI. Ionic liquids have a tendency to solubilize the protein when it used for excess concentration and treated for longer duration. Hence, optimum concentration was optimized in our earlier studies. However, the addition methodology in the conventional unhairing process might have influence with the ionic liquids. Therefore, combination of different unhairing method was followed with addition of ionic liquid to ensure that structural property of collagen fibers was retained after the treatment. It is seen that the ionic liquid ensures fiber opening without affecting not only the shrinkage temperature but also the physical strength properties of leathers made. From the results, it can be observed that the addition of ionic liquid in the system do not alter the

Table V
Process of enzyme, lime & sulfide unhairing followed by Ionic liquid fiber opening.

Process	Chemicals	%	Duration	Remarks
Enzymatic (Paste)	Water	10		Formulation applied on flesh side and skins are piled flesh to flesh side.
	Sodium sulphide	0.75		
	Lime	1		
	Enzyme	3	1 day	The next day, the skins were dehaired using blunt knife.
Fiber Opening (Drum)	Water	30		The pelts were fleshed, scudded and the fleshed weight in wet condition was noted.
	Ionic liquid	0.2	4hrs	
Deliming (Drum)	Water			Cross Section of the delimed pelt was checked for colorless using phenolphthalein indicator.
	Ammonium chloride	1	60 min	
Washing	Water	200	10 min	Bath was drained.

Note: Ionic liquid - (1- butyl 3- methylimidazolium chloride)

property of the leathers and all the leathers meet the standard norms as shown in the table. This is in accordance with the organoleptic properties. Moreover, the minor variation in the strength properties is probably due to piece to piece variation. Eventually, the concentration of ionic liquid and duration of treatment will have greater influence in the strength property. However, optimum utilization of ionic liquid results in the significant reduction of lime usage at reliming stage and replacement of fiber opening enzymes.

Effect of IL Fiber Opening on Fiber Structure of Leathers

Morphological structure of control and experimental crust leather are shown in Figure 1. Two controls were used in this experiment to study the influence of unhairing methods as well as the extent of fiber opening by IL. Control I was conventional unhairing using lime and sulfide and fibre opening using lime. Control II had unhairing using lime and sulfide but with no reliming. It is should read as clearly seen from Figure b2 that

there is no fiber splitting owing to the absence of fiber opening agent. Whereas cross section micrographs of all other leathers showed good fiber opening. The grain surface at 200x magnification shows no deposition for all the experimental leathers. Scanning electron micrographs of crust leather samples from control I and experimental processes showing the cross section at a magnification of 1000x clearly, show that fibers are well opened up. The fiber bundles exhibit fine splitting of fibers indicating that irrespective of the unhairing method followed, fiber opening using IL can be employed effectively.

Environmental Impact Analysis

The chrome content, TDS and COD level present in the spent liquor after tanning for control and experimental leathers are shown in Table VII. From the results, it can be observed that there is significant reduction in TDS as compared to control process. Also, COD is comparable with that of control process. Moreover, chrome content in the spent liquors is reduced

Table VI
Physical properties of Crust Leather.

Physical Property	Tensile Strength (N/mm ²)	Elongation at break (%)	Load grain crack (kg)	Distention at grain crack (mm)
Control	23±2	45±3	24±2	8.5±0.3
Experiment 1	24±1	44±3	22±1	9.2±0.2
Experiment 2	22±2	40±2	19±2	7.2±0.5
Experiment 3	21±2	40±3	20±1	7.2±0.5
Experiment 4	22±3	43±3	22±1	8.3±0.2
Recommended standard	15	45	20	7

Table VII
Pollution load from waste water.

Effluent Analysis	Control	Experiment 1	Experiment 2	Experiment 3	Experiment 4
TDS (kg/ton)	30	18	30	19	18
COD (kg/ton)	6.8	6.1	7.3	7.1	6.4
Chromium Content as Cr ₂ O ₃ (kg/ton)	13.6	11.08	4.0	9.2	5.6

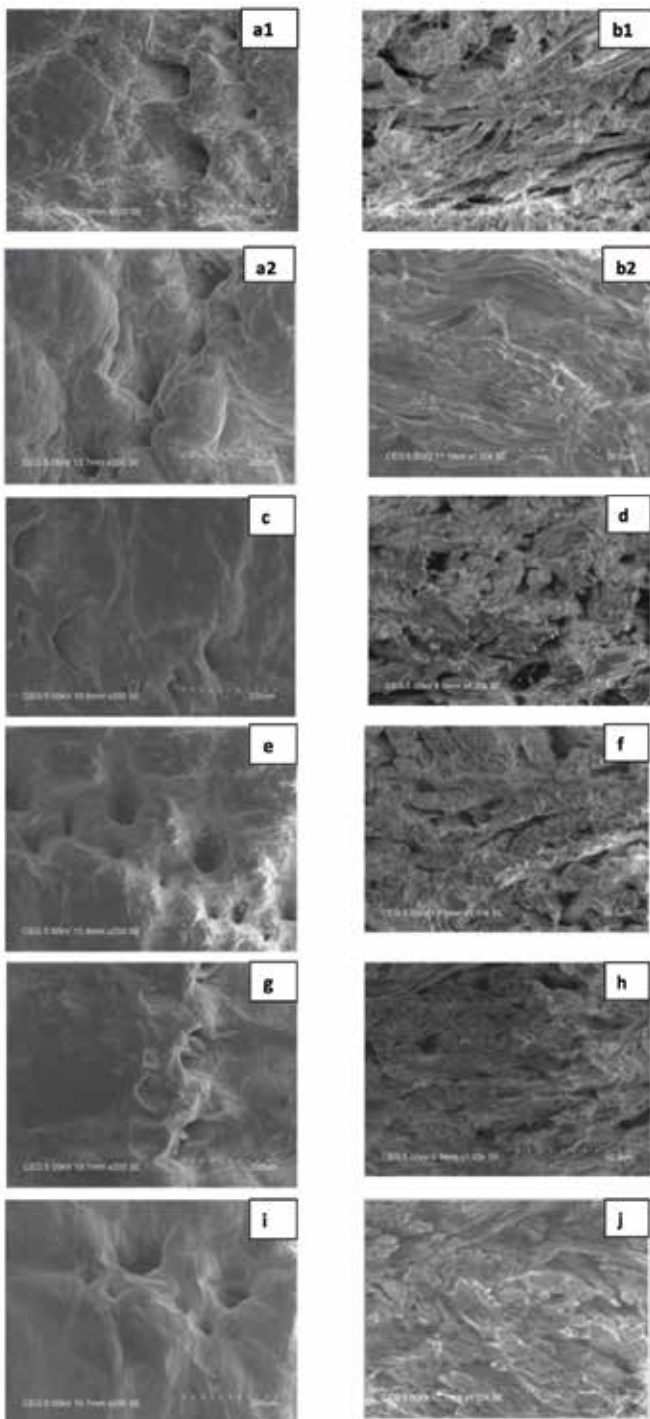


Figure 1. SEM images of a1) Grain surface (200x) and b1) cross-section of Control I (Liming & Reliming) fiber opened crust. a2) Grain surface (200x) and b2) cross-section of Control II (no reliming) crust. c) Grain surface (200x) and d) cross-section of Paste Liming & Ionic liquid fiber opened crust. e) Grain surface (200x) and f) cross-section of Enzyme - 3% & Ionic liquid fiber opened crust. g) Grain surface (200x) and h) cross-section of Enzyme - 2%, Na₂S - 0.75% & Ionic liquid fiber opened crust. i) Grain surface (200x) and j) cross-section of Enzyme - 2%, Lime - 1%, Na₂S - 0.75% & Ionic liquid fiber opened crust.

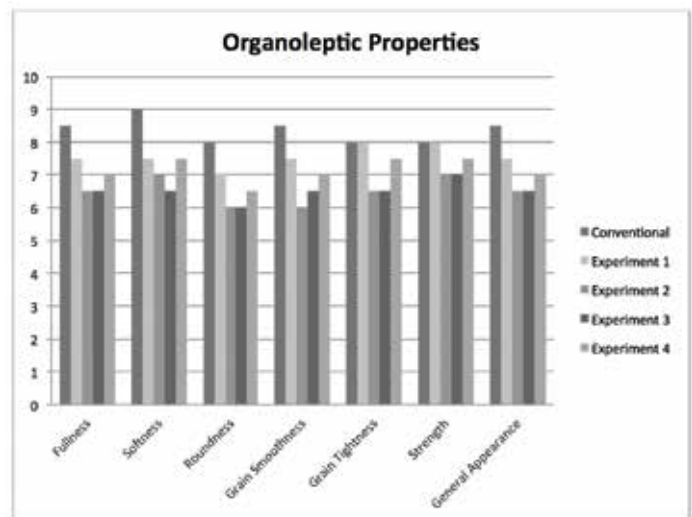


Figure 2. Visual assessment of leathers treated with different method of unhairing method followed by ionic liquid fiber opening.

considerably in the IL treated processes. This ascertains that there is higher uptake of chromium due to better fiber opening in the experimental trails. Though ILs are expensive in comparison to lime, the environmental benefits accrued will negate the cost increase. Also, ILs are considered as green solvents and are recyclable. Hence, they don't pose any negative environmental impact.

Organoleptic Properties

The bulk properties of upper leathers made were assessed by tactile evaluation by experienced tanners. The comparative ratings for each property of upper leather are given in Figure 2. The ratings are averaged values from different tanners. Conventional fiber opening process using lime was taken as control for comparison. It is evident from the figure that all the bulk properties are comparable to that of the control leathers.

Significance of the Study

There is a constant research for reducing the pollution load during leather manufacture. In current context, pretanning operations are known for its negative impact on environment. To combat this, several cleaner technologies have been developed with pros and cons. However, contesting existing technologies with modern science is always a challenging task. In continuation with this, molten salts, ionic liquids are chosen and studied for the fiber opening process during leather manufacture. The selection of ionic liquid has advantage as compared to their existing counterparts. The properties of ionic liquid can be altered and tuned based on their anions, cations and chain length. Hence, it is one of the widely explored materials for many applications like pharmaceutical, refinery, catalytic, etc. Application of ionic liquid can compared with the enzyme, amylase for fiber opening process. During amylase treatment,

proteoglycans are scissored to remove the unwanted interfibrillar materials. Similarly, ionic liquid creates an ionic effect among the interfibrillar materials, which results in the breakage of proteoglycans that result in the scissoring of proteoglycans (the effect of ionic liquid on collagen fibers is reported in our earlier studies).⁹⁻¹² Therefore, the optimum concentration and duration are the key factors in deciding the efficiency of ionic liquids for fiber opening. The effect of different unhairing methods, which is the operation prior to fiber opening, has been evaluated in this present study to ensure the compatibility of unhairing methods with ionic liquid treatment.

Conclusion

It can be concluded from the results that ionic liquid based fiber opening can be employed effectively irrespective of the unhairing method followed. From the various results, it is observed that the effect of unhairing method has not direct impact on the final quality of the leathers. Thus, use of ionic liquid not only leads to elimination of the lime sludge during reliming in the effluent but also produces leathers of quality on par with that of conventionally processed leathers.

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