A Polymer-Based Preservation: A New Horizon in Leather Making

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Abstract: Salt-based preservation methods are commercially practiced around the world. The conventional method of preservation employs nearly 40-50% salt, which is subsequently removed during the soaking operation and thereby contributing to high total dissolved solids (TDS) in tannery wastewater. It accounts for nearly 40% of TDS load in tannery wastewater. This creates a major stumbling block to the tanners. Hence, an attempt has been made to replace the salt with a synthetic polymer to reduce the TDS in wastewater. Molecular weight and percentage offer of the polymer were standardized based on the rate of dehydration and rehydration of hide matrix. The effectiveness of preservation of goat skins has been visually assessed by experienced tanners and chemically assessed for hydroxyproline in the soaked liquors. The developed process results in significant reduction in total dissolved solids (TDS) and chlorides (Cl^-). Characteristics of the experimental crust leathers are shown to be on par with control crust leathers.

Keywords: preservation; salt free curing; polyethylene glycol; total dissolved solids

1 Introduction

The salt based curing is one of the steps in leather processing that contributes to 40% of total dissolved solids in the tannery effluent [1]. The application of salt during preservation provides bacteriostatic action on the putrescible skin/hide. The principle lies in the fact that the reduction of moisture content results in unfavorable condition for any microorganism to thrive. The higher salinity in the tannery effluent leads to an increase in the operating and maintenance cost of the treatment plants. Moreover the ground water pollution near the vicinity of tannery sectors forced tanners to opt for reducing/ avoiding the usage of salts for preservation [2, 3]. So a techno economically viable preservation method needs to be developed.

Polyethylene glycol is an inert, flexible, water soluble polymer of ethylene oxide having specific interaction with biological systems. It has a capacity to create very high osmotic pressures which helps as a precipitant for protein crystallization [4, 5]. In the present work, salt is completely replaced with polyethylene glycol for preservation of goat skins to achieve green leather processing. Different molecular weights of PEG are used in the preliminary trials and the best one is selected based on the dehydration and rehydration studies. Then the percentage offer of PEG of selected molecular weight was optimized. The effectiveness of the preservation of goat skin is analyzed by determining the hydroxyproline release in the soak liquor at various period of storage. Bulk trial trials were carried and the

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soak liquor was collected and analyzed for salinity, oxygen demand and chloride. Scanning electron micrograph and physical testing were carried on crust leathers.

2 Experimental

2.1 Materials

Raw goat skins with weight range of 1-2 kg were obtained from local slaughter house, Chennai, India. Skins were removed from the animal and transported through an ice packed container within 2 h. PEG and salt used for preliminary preservation trials were of laboratory grade. The chemicals used for bulk trial studies were of commercial grade. The chemicals used for the analysis of spent liquors were of analytical grade.

2.2 Selection and Optimization of PEG

Preliminary experiments were carried out employing different molecular weights of PEG ranging from MW 200 to 1000 with an offer of 5% (w/w on the weight of raw skins). The PEG was applied on the flesh side of each goat sides and allowed to dry at room temperature. For control, two goat sides were taken and salt 40% (w/w on the weight of raw skins) applied on the flesh side in one of the sides and the second side is dried at room temperature. Rate of dehydration of the skin samples were calculated by the difference in the moisture content taken at regular interval for a period of 24 hours. The preserved skin samples were stored for a period of twelve weeks. Then known weight of skin samples were cut and soaked to calculate the rate the rehydration. From the rate of dehydration and rehydration studies, a suitable molecular weight of PEG is taken for further optimization.

The amount of PEG of the molecular weight selected is optimized for concentration by varying the percentage offer 1, 2, 3, 4 and 5% on the weight of skin using the rate of dehydration and rehydration curves.

2.3 Efficiency of the Preservation Methodology

The efficiency of the preservation methodology is evaluated by determining the hydroxyproline content of the soak liquor, and soak liquor analysis.

Approximately 25 g of control and experimental samples were taken at various time periods up to 12 weeks of storage and soaked with 900% (w/w) water for 8 hours in a water shaker. The hydroxyproline content in the soak liquor was determined using the method of Woessner [6].

Spent liquors from soaking process were collected from control and experimental preserved skins. The spent liquors were analyzed for chloride (Cl^-), BOD, COD and salinity (TDS) as per the standard procedures. Effluent loads were calculated by multiplying the concentration (mg/L) with volume of spent soak liquor (L) from the soaking process per metric ton of preserved raw skins.

2.4 Characterization of the Final Leather

2.4.1 Scanning Electron Microscopy

Scanning electron micrographs of samples cut from the control (C) and experimental (E) crust leathers were conducted to examine grain surface and cross section at different magnifications.

2.4.2 Physical Testing and Hand Evaluation of Crust Leather

Samples for various physical tests from experimental and control crust leathers were obtained as per IUP method. Physical properties such as tensile strength, % elongation at break, tear strength and grain crack strength were examined as per the standard procedures. Experimental and control crust leathers were assessed for softness, fullness, grain smoothness, grain tightness (break) and general appearance by hand and visual examination. The leathers were rated on a scale of 0–10 points for each functional property where higher points indicate better property.

3 Results and Discussion

3.1 Selection and Optimization of PEG

The selection of molecular weight of PEG is based on the dehydration and rehydration rates. The dehydration and rehydration rates of the control and experimental samples are given in Figure 1 and 2. From the dehydration graph it is clear that PEG of different molecular weights namely 200, 300, 400 and 600 reduces the moisture content to below 20% but only PEG200 and 1000 follows a similar dehydration pattern to that of wet salted skins. From the rehydration graphs it is evident that the rehydration rates are comparable to that of the wet salted skins for all the molecular weight of PEG. Since PEG200 exhibited faster dehydration rates and similar rehydration rates it has been taken for further studies.

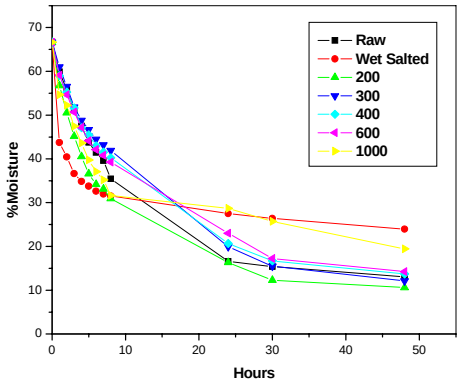

Fig 1 Dehydration profile of preserved skins

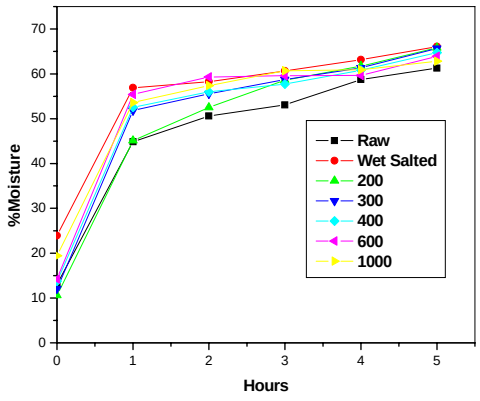

Fig 2 Rehydration profile of preserved skins

Various percentages of PEG200 were employed to optimize the amount required to preserve the goat skins. From the experimental studies it was clear that the offer of PEG200 above 2% exhibited similar dehydration and rehydration rate compared to that of wet salted skins. Hence, an offer of PEG200 at 3% has been optimized for bulk trials.

3.2 Comparison of Effectiveness of Preservation Method

3.2.1 Estimation of Hydroxyproline

The estimation of hydroxyproline in the spent soak liquors was carried out for the preserved samples and the hydroxyproline content was found to be 0.38, 0.07, 0.04 (g/kg of preserved skins) for dried, wet salted and PEG respectively during the twelfth week of preservation. The degradation of skin samples preserved by sodium chloride was found to be slightly higher compared to the PEG200 based

preservation. Hence, the PEG200 based preservation is found to be more effective as compared to salt based preservation.

3.2.2 Soak Liquor Analysis

The emission loads of the soak liquor are given in Table 1. Emission loads from spent soak liquor of experimental is lower compared to salt based preservation method. Salt based preservation method contributes to nearly 270 kg of salt for soaking per metric ton of preserved goat skins. This is primarily due to the removal of salt, which was used during the preservation process. From the table it is evident that the PEG based preservation method reduces the BOD, COD, Cl^- and salinity loads by 71, 34, 99 and 93%, respectively.

Table 1 Emission Loads of Control and Experimental Spent Soak Liquors

Sample	Emission loads (kg/metric ton of preserved skins)			
	BOD	COD	Cl^-	salinity
Wet salted				
1st soak	2.88	11.47	98.91	179.52
2nd soak	2.52	9.06	43.63	78.22
3rd soak	2.32	8.22	4.94	10.37
Total	7.72	28.75	147.48	268.11
PEG200				
1st soak	1.23	8.40	0.42	9.24
2nd soak	0.61	7.33	0.5	6.22
3rd soak	0.44	3.46	0.31	3.99
Total	2.28	19.19	1.23	19.45

3.3 Scanning Electron Microscopy Analysis

Scanning electron microscopy analysis of crust leather from control and experimental was carried out and from the figures obtained it was seen that the grain surface of both the samples were clean and visible without any damage. The cross sectional view of control and experimental crust leather samples showed that the fiber structure of both the samples exhibited uniform separation of fiber bundles. The filling and tightening of the fibers in the experimental sample appeared to be comparable with control sample.

3.4 Physical Testing and Hand Evaluation of Leather

The strength properties such as tensile strength, tear strength and grain crack strength values were obtained by standard physical testing methods. It was seen that the experimental leathers exhibit slightly higher strength properties. The organoleptic properties of the crust leather were examined and the experimental leathers exhibit better fullness compared to control leathers. Other properties such as softness, grain tightness and smoothness are comparable to that of conventionally processed leathers. In general, the appearance of experimental leathers is also similar to that of control leathers.

4 Conclusions

The development of a salt free curing system would go a long way in addressing the pollution problems faced by the leather industry. The PEG molecular weight of 200 at an offer of 3% has been standardized based on the dehydration and rehydration behaviour of the preserved skins. Scanning electron microscopy study reveals that the skins preserved by PEG shows well separated fibre bundles with uniform fibre structure and also clean, smooth grain without any damage. The degradation of skins preserved by sodium chloride is slightly higher compared to the PEG based preservation. Input-output analysis reveals that the PEG based preservation process reduces the chemical input by 92%. This method reduces the BOD, COD, Cl^- and salinity loads in the soak liquor by 75, 28, 98, 93% respectively. Thus the developed preservation process forms a techno-economically viable alternative for salt based preservation.

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