Substance improvement in Leather using Eco-benign materials

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Abstract

A large proportion of hides/skins especially of Asian origin lack substance and possess inherent defects leading to difficulty in producing high quality leathers. In this regard eco benign, simple and cost effective methodology has been developed to improve the substance (bulk properties) as well as surface characteristics of leather using selected polymers and bio-degradable materials. In this work, suitable formulation has been made using eco-benign materials and employed for leather substance enhancement. The effect of this treatment has been studied during various stages of leather processing. The substance improvement has been quantified. Strength property and pore-size analysis have also been studied. The results indicate that there is up to 30% improvement in substance for different types of substrates and end products. This methodology could be a lucrative way of upgrading low value leathers.

Keywords: Leather, Substance improvement, Bio-degradable, Eco-benign, Value addition

1. Introduction

Hides and skins are most commonly a by-product of meat, milk or wool production. The properties of leather vary considerably depending upon the type and quality of both the skins and the tanning process[1]. Since, skin/hide is anisotropic in nature in respect of matrix properties such as fibre diameter, fibre compaction, pore size with variations across the cross-section, one area to another and raw material[2]. Hence, predominant variation in material thickness is observed with belly area suffering most in terms of substance. Therefore, there is a need for bringing a sort of uniformity in substance by way of incorporating materials which do not affect the inherent properties of leather but also provide compatible matrix. This issue is being addressed to some extent by re-tanning step in conventional leather processing[3]. However, the problem has not been solved yet due to nature of re-tanning agents employed[4]. In this regard, some bio polymer formulation has been suggested. The advantages of using biopolymers in the leather are filling the loose portions such as belly, neck etc and impart fullness to the grain[5].

The objective of the present study is to improve the substance of low quality leather by using biodegradable polymers (BDP) which are water soluble in nature, for which product Patent is also pending at CSIR-CLRI. BDP has excellent film forming, emulsifying and adhesive properties. It is also resistant to oil, grease and solvents. It is odorless and nontoxic. It has high tensile strength and flexibility. Experiments were carried out with variations in offer of BDP, pore-size analysis and statistical analysis of substance improvement.

2. Materials and Methods

2.1. Chemicals and raw materials

Biodegradable polymers were purchased from Chennai based chemical company. The cow hide for the experiments were taken from tannery division of CSIR-CLRI. The hide was soaked in water for the rehydration of the skin. Then after liming (hair removal) and de-fleshing process the skin was cut into two pieces through the backbone and marked as left and right. Then the weights of hide pieces were taken. Then the skin was processed till pickling process and stored in pickling solution.

2.2. Biopolymer preparation

The % of biodegradable polymer (BDP) used for the treatment is based on % *w/w* of hide weight. The BDP were dissolved in 100% water (with respect to hide weight) which is heated up to 70°C by continuous mixing process. This solution was used for the treatment process.

2.3. Influence of BDP on cow hide at tanning stage

The left side piece of the cow hide was taken as control and right side was taken for experiment process, for the treatment with selected biodegradable polymer. Both the control and experiment process were carried out separately in different drums. For the control process conventional tanning process were carried out. For the tanning process 8% (% *w/w* w.r.to hide wt.) chromium sulphate was used. First 4% (% *w/w* w.r.to hide wt.) was taken and added in the drum. After 1 hr of treatment again 4% chromium sulphate was added in the drum and treated for 1 hr.

For the experiment process, polymer based (sandwich model) tanning process were carried out. For the tanning process 4% chromium sulphate (% *w/w* w.r.to hide wt.) was used and treated for 1 hr. After treating with chrome, prepared 5% (% *w/v* w.r.to hide wt.) BDP solution was added in the drum and treated the hide for 2 hrs. Then again hide is treated with 4% chrome for 2 hrs.

In control process, instead of BDP 100% water was added after treating with 8% chrome. After tanning process both the control and experiment process are treated with sodium formate (1%) and sodium bicarbonate (1%) in order to adjust the pH at 4. Then the both hides are taken out from the drum and kept for aging 36 hrs.

2.4. Influence of BDP on cow hide at pickling stage

The left side (control) and right side (experiment) of the hide pieces were treated in separate drums. In the control process, hide was treated with 100% pickle liquor (% *w/v* w.r.to hide wt.) for 15 minutes. For the tanning of the hide 8% (% *w/w* w.r.to hide wt.) chromium sulphate was used. First 4% (% *w/w* w.r.to hide wt.) was taken and added in the drum. After 1 hr of treatment again 4% chromium sulphate was added in the drum and treated for 1 hr.

For experiment process, once the hide is treated for 2hrs with 5% (% *w/w* w.r.to hide wt.) with BDP solution the hides were tanned using 8% chrome for 2 hrs.

Basification process is carried out in order to adjust the pH of the hide at 4 for both control and experiment process by adding 100% water (% *w/v* w.r.to hide wt.) is added to both the drums. And then sodium formate (1%) and sodium bicarbonate (1%) was added and treated for 2 hrs. Then the both hides are taken out from the drum and kept for aging 36 hrs.

2.5. Crusting process

During crusting process the tanned hide is re-tanned, dyed and lubricated. Crusting process is begins with neutralization process, in which tanned hide is treated with sodium formate (0.5%) and sodium bicarbonate (0.5%) in order make the pH of the hide at 5.5. This process is necessary for the leather in order to allow it to properly absorb the various chemicals that are used. Once the pH levels of hides are neutralized, retanning process is done by using syntans and hide is dyed at this stage. Once desired color is achieved, fat liquoring process is used to lubricate the leather fibres with wax and oils. Formic acid (3%) is used for fixation process, in which all the chemicals used previously are either bonded within the leather or removed from it.

During setting process, excess of water from the hide is removed and flatness of the hide is achieved. After setting process, leather is dried and then staking process has carried out in order to make leather softens and conditioned. The thickness of the hides of control and experiment are measured at this stage by using gauge machine and compared the results by calculating mean thickness and standard deviation.

Calculation

$$\text{Mean } (\overline{X}) = \frac{\Sigma X}{N}$$

Standard deviation

$$\sqrt{\frac{1}{N}\sum_{i=1}^{N}(X_i - \overline{X})}$$

N = Total no. of values
X = Each value in the population

2.6. Shrinkage temperature analysis

SATRA STD 114 shrinkage apparatus is used for the analysis. This apparatus enables shrinkage temperature to be measured up to 115°C. When leather is slowly heated in water, a sudden shrinkage occurs at a temperature which is characteristic of the tannage. If the shrinkage temperature is above 100°C it is necessary to use water pressure greater than atmospheric to determine its value. Tanning aims to bring about stability against thermal and enzymatic degradation of skin matrix properties. One of the characteristic features of skin is its dimensional change under the action of heat. Skin undergoes length reduction at a characteristic temperature to a level of one third of its original dimension.

2.7. Strength analysis

The hides were tested for various physical properties such as tensile strength and tear strength which are important for its application. Analysis were performed using *Instron* universal testing machine as per IUP method [6].

2.8. Pore size Analysis

Analysis of pore structure of skin is important to understand process of diffusion and adsorption involved during any application of the skin matrix. Pore structure renders skin many unique properties. Insight into the pore structure of the skin matrix is required to understand mass and heat transport properties as well as fracture mechanism of material under flexural stress [7,8]. The changes brought about in the pore structure have been studied using Capillary flow pore-size analyser [9].

3. Results and discussions

3.1. Influence of BDP on cow hide at tanning stage

Table 1 shows the mean thickness and standard deviation of the cow hides of both control and experiment from different regions of the hides. The results shows that 0.38 mm of substance have been increased in the belly region of experiment when compared with control. In the backbone region of the experiment also have 0.28 mm improvement in the substance compared to control. In case of butt region there is no improvement. This is may be because of the butt region is already filled there is no empty places so the polymer can go and attach.

Area	EXPERIMENT		CONTROL	
	MEAN	S.D	MEAN	S.D
Backbone	2.91	0.12	2.63	0.22
Butt	3.04	0.068	3.05	0.097
Belly	2.44	0.217	2.06	0.089

Table1. The mean thickness and its standard deviation in the different regions of cowhides.

Test	EXPERIMENT		CONTROL	
	Along	Across	Along	Across
Tensile strength (N/mm2)	**24.65**	**22.43**	**27.12**	**26.07**
Tear strength (N/mm)	**101.83**	**107.68**	**101.48**	**100.77**

Table 2. Comparative studies of strength properties polymer treated hide and control at tanning stage.

Shrinkage temperature analysis shows that experiment have shrinkage temperature of 101° C when compared to control which is 100°C. These results indicate that polymer treatment doesn't reduce any native properties of leather.

3.2. Pore-size Analysis

In the pore size analysis, the mean flow pore diameter of the experiment is 0.3006 microns and the control is 0.1793 microns. This study shows that the mean flow pore diameter of polymer treated experimental leather has not reduced indicating that present polymer treatment is not adversely affecting the pore structure and not function as that of conventional filling type of syntans.

3.3. Influence of BDP on cow hide at pickling stage

The thickness in the different regions of cow hides of experiment and control are given in the table 3. The results shows that there is no substance improvement in the cow hide when compared to control.

Table 3. The mean thickness and its standard deviation (S.D) for cowhides.

Area	EXPERIMENT		CONTROL	
	MEAN	S.D	MEAN	S.D
Backbone	1.20	0.010	1.22	0.0089
Butt	1.36	0.0134	1.34	0.012
Belly	1.26	0.020	1.27	0.034

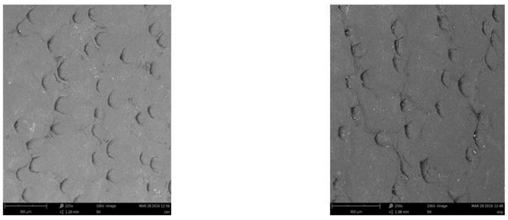
Table 4. Strength analysis results of polymer treated cow hide and control at pickling stage.

Test	EXPERIMENT		CONTROL	
	Along	Across	Along	Across
Tensile strength (N/mm^2)	15.75	16.87	13.75	12.26
Tear strength (N/mm)	80.14	88.44	104.21	105.32

Shrinkage temperature analysis shows that polymer treated hide can withstand the temperature up to 103°C where as control 102°C. And it also shows that the polymer didn't reduce the native properties of tanned leather.

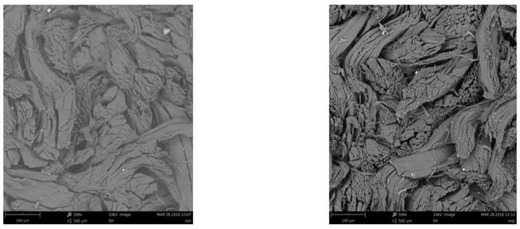
3.4. Scanning Electron Microscopic (SEM) Analysis

SEM analysis was made for experimental (5% BDP offer) and control leathers for both surface and cross section as shown in Fig.1 and 2 respectively. The images show more kind of compaction and coating over the fibres.



1a 1b

Figure 1 – Surface view of Control and Experiment. 1a- Control , 1b- Experiment



2a 2b

Figure 2 – Cross section view of Control and Experiment. 2a- Control , 2b - Experiment

4. Conclusion

In this present study, the hides treated with BDP at tanning stage (sandwich model) which indicates good substance improvement when compared to treatment at pickling stage. Strength properties of leather are not affected by treatment with BDP. The substance improvement has been quantified. The results indicate that there is up to 30% improvement in substance for different types of substrates and end products. This method could be used for upgrading the low value leathers. This method is simple, cost effective and eco-friendly and can be used to improve the substance of leathers for the production of high quality leather.

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References

1. Bienkiwicz K, Physical chemistry of leather making, R.E. Kriger publishing company, Malabar, Florida, 1983
2. Sivakumar V, Swaminathan G, Rao P G & Ramasami T. *Chem Eng Process. Process Intensification,* 47 (2008) 2076.
3. Dutta S S, An introduction to the principles of leather manufacture, Indian. Leather. Technol. Assoc., Calcutta, 1985.
4. Prentiss W C & Sigafoos C R, *J Am Leather Chem Assoc*, 70 (1975) 481.
5. Resmi Mohan, Sivakumar V & Muralidharan C, Substance improvement and value addition in leather through Eco-benign Approach, Poster Presentation, *Proceedings of the XXXIV* IULTCS, IVL- P35, Chennai, 2017
6. IUP, International union of leather chemists societies physical testing commission. Recommended physical test methods – IUP/1, *J Soc Leather Technol Chem Soc* **42** (1958) 382.
7. Stromberg R.R & Swerdlow M, *J Am Leather Chem Assoc*, , 47 (1954) 336.
8. Carter T J & Kanagy J R, *J Am Leather Chem. Assoc*, 49 (1954) 23.
9. Sivakumar V, Jena A, Gupta K & Mandal A B, *J Soc Leather Tech Chem*, 99 (2015)16.