A PROTEIN BASED POLYMERIC SYNTAN FROM LEATHER WASTE: RETANNING AGENT FOR SUSTAINABLE LEATHER PROCESSING

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Abstract. A copolymer has been synthesized from leather waste and monomer and its application has been studied for improved exhaustion in tanning and post-tanning processes. After synthesizing, the product has been analyzed and found to have particle size of 810 nm, pH of 4.0, relative viscosity of 0.8872 cp, polydispersity index (Mw/Mn) of 0.555 and percent solid as 23%. The weakly anionic character of the co-polymer is supported by zeta potential of –0.0403 mV. The stability of the particle was also studied using TGA, DSC. Functional groups of the polymer were analyzed by FT-IR which revealed the presence of carboxylic acid, amide I & II, hydroxyl groups and ester groups in the product. The product can be used for increasing exhaustion and leather-properties in chrome tanning and post-tanning processes. It improves belly filling, provides fullness, softness and dye exhaustion in post-tanning process. It also shows better fullness and body in chrome tanning processes. The color properties found to be better and strength properties were comparable in experimental leather as compared to conventionally produced leather. This product can be applicable for manufacturing different types of leather where fullness and tightness are necessary. The present process helps in mitigating pollution problem of liquid and solid wastes of leather industry. A cost benefit analysis shows that the process is feasible for up-scaling.

1 Introduction

About 0.6 million tonnes of solid wastes/annum are generated from leather industry globally. Out of this, 40-50% contribute raw trimming and chrome shaving waste. In India, there are about 2000 tanneries which process 700,000 tonnes of hides and skins per annum. During leather processing, 500-600 kg of the solid waste is generated per tonne of the raw material. In total, this contributes nearly 70.000 tonnes of trimming plus chrome shavings of solid wastes per annum. Hence, there is a need to develop a suitable technology from solid waste for minimizing the pollution problem. The leather industry requires a suitable technology/aid for increasing the chrome exhaustion in chrome tanning because conventional chrome tanning generates nearly 30-40% of chromium in the effluent that has to be addressed immediately. Application of suitable exhaustion aid to improve the exhaustion level more than 90% is the need of the hour.

Cr(III) is widely used in tanning process for tanning the pelt. The conventional process of chrome tanning employs Basic Chromium Sulphate (BCS) at the level of 6-10% in tanning process. In tanning process BCS at the level of 60-70% is absorbed while the remaining goes with effluent containing 2000-4000 ppm of Cr(III) which poses potential problems to environment. The efficiency of the tanning process could be increased by improving the exhaustion through employing high performance aids/ modifying the tanning process itself. The application of various aids/ compounds such as amino acids, fibrous sheets based on acrylate, polymeric materials (Phely-Bobin et al., 2002) , insulators or building material and then animal feed etc. while indirect use of these protein based wastes is used either to separate or to enhance exhaustion of Cr(III) on the collagen matrix for stabilization of leather (Kresalkova et al., 2002). It has been reported from literature that protein hydrolysate obtained from various leather wastes were also very useful for increasing the exhaustion of chrome tanning process. One of the major solid wastes of leather industry namely fleshing wastes were hydrolyzed and the hydrolyzates were copolymerized using acrylic acid for the application of enhancement of Cr(III) exhaustion while nano-particle based polymer was prepared from keratin hydrolyzate and acrylic ester for application in dyeing (Kanagaraj et al., 2008). In another approach, the chrome shaving wastes were used as reducing agent for Cr(VI) in preparation of chrome(III) tanning salt. The polymeric products obtained from leather wastes were also used after several hydrolysis for the preparation of tanning agent to provide a zero discharge of chrome in leather waste.

In the present approach, protein based retanning agent has been prepared from raw skin trimming wastes. Initially the wastes were hydrolyzed by alkali hydrolysis and then polymerized with poly ethylene glycol (PEG) to get low molecular weight retanning agent (Kanagaraj et al., 2015). This retanning agent was used as an exhaust aid in the tanning process and post tanning process and the leather properties were studied.

2 Materials and Methods

2.1 Materials

Raw skin trimming wastes were collected from the tannery division of CLRI. Basic chromium sulphate (BCS), PEG, acetone, potassium persulfate was purchased from Sigma Aldrich. The wet salted skins weighing 1.5kg/skin were procured from local vendor. Pelt (ready for tanning) and wet-blue were prepared from wet salted skin.

2.2. Methods

2.2.1 Synthesis of retanning agent from skin trimming wastes

Retanning agent from skin trimming wastes was synthesized as follows. 250 mL of distilled water was taken in a three necked round bottom reaction flask attached to magnetic heating system at 90°C with constant stirring. Then 20 g of skin hydrolysate (prepared by alkali hydrolysis using 4% sodium hydroxide followed by thermal heating at 90°C for 4 h) was added and stirred for 60 min with heating to make homogenous mixture. 40 g of PEG (was dissolved in sufficient amount of methanol) was added in drops through one of the necks of the flask while initiator, potassium persulfate weighing 1.5 g dissolved in 50 mL of water, was also added in installments through the other neck of the flask. The reaction was allowed to proceed for 3 h with constant heating at 85-90°C and with constant stirring. The pH of the resultant product was recorded as 2.5 which was adjusted further to pH of 4 with aqueous solution of sodium bi carbonate. Finally, the product was cooled (using desiccators) at room temperature and was stored. The characteristic feature of the product was analyzed for various parameters using standard methods.

2.2.2 Characterization of retanning agent

The product prepared from leather wastes was characterized for particle size, Differential scanning calorimetry (DSC) and Thermogravimetric analysis (TGA) using standard procedures. The % solid level was found out by conventional evaporation method.

2.2.3 Application of protein based retanning agent in chrome tanning and post tanning processes

The retanning agent prepared from the raw trimming wastes was applied at the level of 5% in the tanning process and the % uptake of chromium was studied. For this, the pickled pelt (with pH about 3.0) were treated with 6% of BCS (chromium (III) tanning agent) in a rotating drum/vessel for a period of 2 h and were followed by basification using sodium formate and bicarbonate where the pH of the leather was adjusted to 4.0. The spent liquors were collected. Then retanning agent at the level of 5% was added with the chrome-treated leather with constant stirring in the rotating vessel for a period of 1 h for completion of reaction and penetration. The collected spent liquors were recharged and the process was continued for another hour. The spent liquors were collected and analyzed for the % uptake of chromium. Similarly, the retanning agent was applied in post-tanning process along with dye, fatliquor and other retanning agents and the organoleptic properties of the leather were assessed.

2.2.4 FT-IR analysis

The sample after tanning was collected and dried in the water bath. They were mixed with potassium bromide (1:20; 0.02g of sample with KBr at a final weight of 0.4g) separately. The sample was then ground, desorbed at 60°C for 24 h and pressed to obtain IR-transparent pellets. The FT-IR was first calibrated for background scanning signal against a control sample of pure KBr. FT-IR Spectra of the samples was recorded using an FT-IR spectrum 2000 Perkin-Elmer spectrophotometer within the scanning range of 400-4000 cm^{-1}. Then the experimental sample was also scanned in similar way.

2.2.5 Color properties

The leather samples after tanning with retanning agent were processed into leather and were subjected to study difference in color properties using Gretag Macbeth Spectrolino Spectrophotometer with measurement geometry of $45^o/0^o$. The parameters L, a, b, c and H of the measurement were obtained using the standard procedures.

2.2.6 Physical testing

The experimental and control crust leathers samples were performed for various physical tests and the data were obtained as per IULTCS method. Specimens were conditioned at 80±4°C and 65±2%RH. Over a period of 48 hours, physical properties such as tensile strength, % elongation at break, tear strength and grain crack were examined for both experimental and control samples.

3 Results and Discussion

The retanning agent from raw trimming wastes has been prepared using suitable monomer through polymerization technique. PEG possess important characteristics such as good binder, high permeability and retention factor, good osmotic pressure, hydrophilic properties. Besides, it is also used as a preservative for many substances. These qualities have motivated the authors to select PEG as one of the monomer for the preparation of retanning agent. The retanning agent exhibited the following characteristics.

Table 1. Characteristics of Retanning agent.

Product characteristics	
pH	4.0
% solid content	23
Particle size	810 nm
Molecular weight	2490 D
Viscosity	0.8872 cp

The characteristic properties of the retanning agent is presented in Table 1. The retanning agent showed pH of 4.0, % solid of 23 %, particle size of 810 nm, molecular weight of 2490 D and viscosity of 0.8872cp. The above characteristics of retanning agent showed the possibility of better reactivity with collagen to bring about increased exhaustion. The retanning agent is readily soluble in aqueous medium as its low-viscosity helps in dispersing the co-polymer in water medium easily promoting better penetration of co-polymer to the leather matrix. Percent solid level of the product is found to be 23 which help the retanning agent for dispersing in aqueous medium speeding the diffusion. In the present investigation, retanning agent is added after the chrome tanning process in the same environment which helps to increase the uptake of chromium from the bath. This is due to plenty availability of reactive sites in the reatnning agent that helps to increase the uptake and reactivity of the collagen.

TGA and DSC analysis

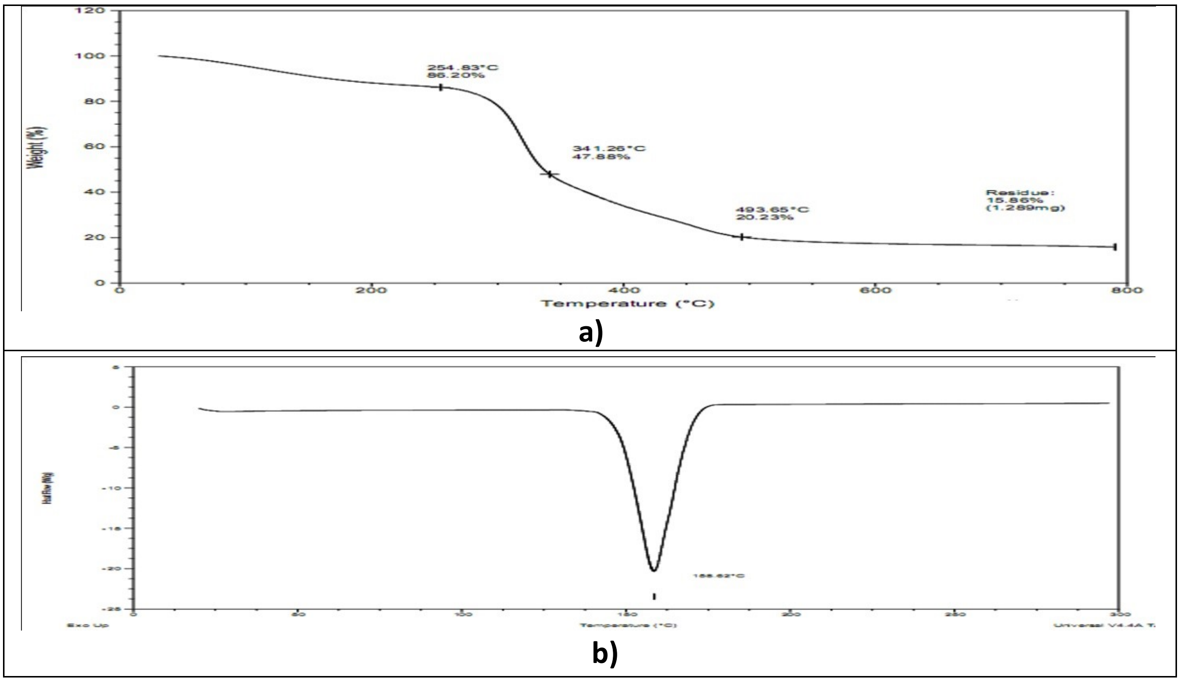

Fig. 1. Characterization of retanning agent a) TGA; b) DSC.

The stability of the retanning agent was tested by DSC and TGA analysis (Fig.1). DSC curve shows peak at 160°C where as TGA showed peak at 264, 341 and 493 °C. Weight loss of these materials as a function of temperature was recorded using this study. One can see that there are three stages in the curve. The first stage occurs between 100°C to 264°C indicating about 14 % losses in weight of the sample. The weight losses in this stage are because of loss in moisture. The second part of the curve represents the maximum weight loss because of the thermal degradation of the sample that happens at 341°C with weight losses of 52% for the copolymer sample. The third part of decomposition occurred at 493°C with a weight loss of about 80% which are mostly due to evaporation of volatile compounds. The final stage of decomposition curve is because of formation and evaporation of some volatile compounds from the sample.

Table 2. Chromium content in the tanned leather samples.

Raw material	Product offered		Chromium content		% Exhaustion	
	BCS	Retanning agent	Experiment	Control	Experiment	control
Cow	6%	5%	3.48	3.37	91%	74%
Goat	6%	5%	3.62	3.50	93%	77%

(Control: Absence of reatnning agent)

The retanning agent has been applied in the chrome tanning process at the level of 5% and the exhaustion of chromium has been studied and presented in the Table 2. The chrome content was found to be slightly higher in the leather obtained from goat as compared to cow sample. The chrome content is found to be 3.48 and 3.37 for the experiment and control cow-wet-blue leather samples. Similarly, the chrome content is found to be 3.62 and 3.50 for the experiment and control goat-wet- blue leather samples. The percentage exhaustion of the experimental tanned sample showed 91 and 93% (cow and goat respectively) as compared to 74 and 77% for the control sample. The reason for the increase uptake of chromium was due to free functional carboxylic groups present in the copolymer which helps for the exhaustion of chromium. The free carboxylic acids of retanning agent may form hydrogen bonding at multipoint in providing additional adsorption and exhaustion to the complex. The other reason behind this improved adsorption may be due to the fact that -OH groups of PEG that forms H-bonding with carboxyl groups of collagen. In addition to that a physiochemical property of ester is responsible for masking the Cr complexes that indirectly helps in stabilizing Cr complex in adsorption process. Masking reduces the potency of the chromium thereby increases the reactivity of chromium with the collagen matrix. Masking also favors in uniform distribution of chrome complexes and to stabilize all the reactive groups of collagen, thereby higher exhaustion of chrome is achieved.

Table 3. FT-IR findings.

Peaks	Functional groups
3390 cm^{-1}	Stretching frequency O–H and NH groups
1715 cm^{-1} and at 1650 cm^{-1}	C=O stretching and N-H bending frequency
1340 cm^{-1}	C-N stretching frequency of the amide group
1555 cm^{-1}	Amide-II
1644 cm^{-1}	Ester groups

The retanning agent was characterized for FT-IR and presented in the Table 3. It is seen from the table that the peak observed at 3390 cm^{-1} is due to presence of protein containing OH and NH groups for the reatanning agent. The peaks visible at 1715 cm^{-1} and at 1650 cm^{-1} are due to C=O stretching and to N-H bending frequency of the co-polymer. The functional groups present in the co-polymer envisaged that it is an amide co-polymer. It is further evident from the peak at 1340 cm^{-1} representing C-N stretching frequency of the amide group of the co-polymer. The C=O- and the N-H bonds present in the amide group provide stability to the collagen matrix by hydrogen bonding that is very helpful in the present investigation for the effective crosslinker of the chromium in the tanning process. Moreover, peak at 1555 cm^{-1} represents presence of amide-II and 1644 cm^{-1} represents ester groups.

Table 4. Color analyses of the leather sample.

Sample	L	a	b	c	H
Control (cow)	29.31	5.19	5.81	7.79	48.23
Experiment (cow)	20.45	3.45	2.66	4.35	37.6

The dyed crust leather produced using retanning agent was subjected to color analyses and presented in Table 4. The leather showed better uptake of dye that resulted in higher intensity of color as compared to control sample. The color values such as L, a, b,c and H values were better in the experimental leather indicating improved dyeing/ color properties.

Further, the leathers analysed for color fastness & resistance to hot contact and are presented in Table 5. The results indicated that color fastness and resistance to hot-contact of the experiment sample was comparable to control leather.

Table 5. Color fastness & resistance to hot contact.

S. NO.	Property	Result		CLRI recommendation	Test method
		Control	Experiment		
1.	Colour fastness circular to rubbing (Grey scale rate) Dry 512 rubs Wet 256 rubs	Grade 4/5 Grade 4/5	Grade 4/5 Grade 4/5	Min. 3.0	SATRA
2.	Resistance to hot contact	No finish damage at 175 °C Moderate finish damage at 225°C	No finish damage at 175 °C Slight finish damage at 250°C	No melting/fusing/ breaking of finish and no colour change upto 175 °C	SATRA TM 49 : 1995

The leathers obtained by the application of retanning agent were analyzed for the performance in terms of strength properties by standard physical testing methods and are presented in Table 6. The leathers obtained from experiment showed comparable strength values with that of control leather. Physical strength properties such as tensile strength, elongation at break, tear strength, load at grain crack and distension at grain crack were comparable to the control leather with repetition of 5 times for obtaining the standard results.

Table 6. Physical strength properties using retanning agent.

Parameters	Experiment	Control
Tensile strength (kg/cm^2)	246±4.0	222 ±4.0
Elongation at break (%)	56±1.0	55±1.0
Tear strength (kg/cm)	50±1.0	50±1.0
Load at grain crack (kg)	40±1.0	38±1.0
Distension at grain crack (mm)	14±0.2	12±0.1

4 Summary

A retanning agent has been synthesized from raw trimming waste and PEG for studying improved exhaustion of chromium in the chrome tanning process. Application of protein based retanning agent at the level of 5% showed 91 and 93% exhaustion of chromium for cow and goat sample respectively in the chrome tanning process. The FT-IR analysis confirmed the reason for improved exhaustion of chromium. It was due to the fact that the functional groups present in the retanning agent envisaged that it was an amide co-polymer. It is further evident from the peak at 1340 cm^{-1} representing C-N stretching frequency of the amide group of the retanning agent. The C=O- and the N-H bonds present in the amide group provide stability to the collagen matrix by hydrogen bonding that is very helpful in the present investigation for the improved uptake of the chromium in the tanning process. The main advantages of using the protein based retanning agent in the tanning and post-tanning processes are improved dye uptake, improved body and tightness in the belly area, good softness, spongy and fluffy leathers, improved fullness, smoother grain, excellent exhaustion of other post-tanning chemical. The color analyses also showed improved dye/color uptake in the experimental leather. The physical strength properties were also comparable to the control sample.

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