Evaluating Suitability of Glutaraldehyde Tanning in Conformity with Physical Properties of Conventional Chrome-Tanned Leather

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ABSTRACT

Leather manufacturing involves a number of unit processes, out of which tanning is the most important in so far as it converts the putrescible hides/skins into non-putrescible leather. In this study, glutaraldehyde has been exploited as a means to reduce the use of basic chromium sulfate for the production of quality shoe upper crust leather. The paper consists in studying the physical properties of aldehyde-tanned leather and chrome-tanned leather. The aim is to find out the possibility of replacing the wet-blue leather, containing Cr(III) salts, with the glutaraldehyde-tanned wet-white leather. The physical properties of the aldehyde-tanned leather were evaluated, analyzed and compared with the conventional chrome-tanned shoe upper crust leather. Statistical analysis illustrated that the tensile strength, the percentage of elongation, stitch tear strength, Baumann tear strength and grain crack strength of the leather was 211±1 kg/cm^2, 38±0.5 %, 89±0.11 kg/cm, 63±0.4 kg/cm and 23±0.4 kg respectively. It was observed that the property of the experimental leather was quite comparable with the conventional chrome-tanned leather and able to meet the requirements of the shoe upper crust leather after re-tanning. The shrinkage temperature of the experimental tanned leather was found to be 87 °C, lower than that of corresponding control, which indicates lesser tanning power of aldehyde. However, the morphology of the aldehyde-tanned leather was quite akin with the conventional leather. This study suggests that using glutaraldehyde in the tanning process in order to minimize the chromium load in the tanning and the re-tanning process during the production of shoe upper crust leather reduces the generation of toxic waste and its impact on the environment.

KEYWORDS

Glutaraldehyde, tanning, wet-white leather, physical properties

INTRODUCTION

In regard to export earnings in Bangladesh, leather comes in second, after readymade garments. It is one of the oldest and fastest growing industries in South and Southeast Asia. Tanning is the process of converting putrescible hide or skin into leather, which is durable and less prone to deterioration [1]. This process in the leather industry is a critical step towards protecting leather from microbial decay, heat, sweat and humidity [2]. During leather manufacturing, raw hides/skins undergo several chemical and mechanical operations.

Among all these operations, tanning is the most important one [3]. Tanning agents are considered as the most significant material in the leather making process. About 90% of the tanning industries use basic chromium sulfate (BCS) during tanning [4]. At present, basic chromium sulfate is the most popular of among all tanning agents, as it provides unique properties and good hydrothermal stability to tanned leather [5]. Chrome tanning was first introduced in the 19th century [6]. At that time, tanning processes were based on salts of different metals e.g. aluminium [7], sodium [8], titanium [9], iron [10] etc. It has been reported that only 60-70% of chromium used in tanning is consumed by the pelt in the traditional chrome tanning process and the rest is discharged into spent chrome tan liquor, causing severe environmental pollution and a great waste of chrome as well [11, 12]. Nowadays, high exhaust chrome tanning procedure has been developed; though that is not practiced widely yet [13]. The ultimate fate of this waste chromium is to be deposited in soil or water and to accumulate in various plant parts, e.g. leaves, roots, stems and fruits, and finally introduced to the food chain through their consumption [14]. Therefore, it has become essential to introduce an alternative to the chrome tanning agent for the minimization of environmental pollution and health hazards. Many alternative processes, like vegetable tanning, aluminum tanning, aldehyde tanning, etc., have been taken into consideration to produce chromium-free leather for some ecological benefits, however could not achieve the characteristics of the chrome-tanned leather [15]. Due to stricter requirements for leather production and leather waste recycling, the production of chromium-free or, more specifically, inorganic salt-free leather becomes essential. That's why demand for metal-free leather is being increased and promoted [16]. Different organic compounds are being considered as tanning agents. Among them, aldehyde alone or in combination with other tanning agents has been found to produce considerably good properties of leather [17]. The use of aldehyde in combination with chromium as a less-chrome approach has been shown to exhibit better leather characteristics. Aldehyde is rarely used as a tanning agent alone. However, aldehydes have been used in the pre-tanning and the re-tanning process. The use of formaldehyde as a tanning agent is rare as it had been included in the group of hazardous materials due to its toxic, mutant and carcinogenic nature [18]. Glutaraldehyde and some of its modifications have proved to be more competent tanning agents than others [19]. Using optically active unnatural D-Lysine (diamino compound) with Glutaraldehyde (GTA) for tanning is an effective method of eco-friendly processing [20]. Chromium can form certain compounds, which are toxic to humans, animals, and plants [21]. Glutaraldehyde is extensively used as crosslinking agent for the preparation of collagenous biomaterials [22]. It reacts with the alpha amino group of collagens and creates stable pyridinium-ring crosslinks rather than unstable double-Schiff base like other aldehydes [23]. Exposure to glutaraldehyde may lead to irritation in the skin, eyes and the nose among the workers. It may also cause coughing, nausea, headaches, dizziness and problems in the respiratory tract. The toxicity level of glutaraldehyde is not widely known [24]. Toxicity level of glutaraldehyde should be investigated in comparison with chromium before it to be used in the leather making process. In this work, glutaraldehyde was used in tanning for the reduction of chromium content and the physical properties of glutaraldehyde-tanned leather have been compared with the conventional chrome-tanned leather with a view to stimulate further studies.

EXPERIMENT

Materials and Methods

Twenty pieces of wet salted goat skins, 5 sq. ft. in size on average (weight of each being 1 kg), were collected from the hide market in Posta, Lalbagh, Dhaka, Bangladesh. Glutaraldehyde and basic chromium sulfate powder, along with other chemicals for leather processing, were obtained from local chemical dealers at Hazaribagh, Dhaka, Bangladesh. All the chemicals used in leather processing were of commercial grade.

Method of leather processing

Leather processing consisted of three stages. The skins were processed in the conventional way from soaking to pickling, stated in Table 1. The pickled pelts were processed through trials for the optimization of tanning, shown in Figure 1, and then the final tanning experiment with glutaraldehyde and basic chromium sulfate is cited in Table 2 and Table 3, respectively. Both the experimental and the control tanned leather were processed into shoe upper crust leather, following the same post-tanning method mentioned in Table 4.

Table 1. Process for pickled pelt production from wet salted goat skins

Process	Chemicals	% Offer[a]	Time	Remarks
Desalting was carried out by a nylon brush and trimming was done by a hand knife. Then, salt weight was noted.				
Pre-soaking	Water	500		
	Soda ash	0.2		
	Wetting agent	0.2	30 min	Drained
Main Soaking	Water	500	Run 30 min, rest 60 min and then run 5 min per hour for 10 hours	pH adjusted to 8.5-9.5 and then washed for 10 min and drained.
	Soda Ash	0.4		
	Wetting Agent	0.3		
	Preservative	0.2		
Liming	Water	300		
	Liming auxiliary	1.0		
	Sodium sulfide	2.0		
	Lime	2.0	Run 30 min, rest 60 min	
	+ Sodium sulfide	1.0		
	+ Lime	2.0	Run 30 min, rest 60 min	pH adjusted to 12.5-13.0
	+ Wetting agent	0.2	Run 5 min/hr. for 12 hours	Drained, unhaired, fleshed and took pelt weight.
Chemical wash	Water	200	20 min	Drained
	Sodium-meta-bi-sulfite	0.25		
Deliming	Water	80	60 min	pH adjusted to 8.3-8.4 pH checked with phenolphthalein indicator and drained.
	Ammonium sulfate	2.0		
	Sodium-meta-bi-sulfite	0.5		

Bating	Water at 37 °C	100	90 min	pH adjusted to 8.0-8.2. Checked by thumb test. Scudded and cleaned the pelt.
	Bating agent	2.0		
	Wetting agent	0.5		
Pickling	Water	80		
	Salt	8.0		
	Imprapell CO	0.2	Run-15 min	
	Formic acid (1:10 dilution)	0.5	Run-30 min	
	Sulfuric acid (1:20 dilution)	+1.0	Run 3 x 10 min	pH was checked 2.8 with bromocresol green. Left overnight.
	Sodium hypochlorite	0.5	Run-30 min	After that, half of the pickled bath was drained.

[a]Note: All percentage of chemicals were calculated based on pelt weight.

Table 2. Recipe for glutaraldehyde tanning

Process	**Chemicals**	**% Offer[b]**	**Time**	**Remarks**
Tanning	+ Sodium thio-sulfate	0.5	20 min	
	+ Glutaraldehyde	3.0	30 min	
	Phenolic syntan	4.0		
	Sodium formate	1.0	180 min	At morning drained, piled up and aged for 2 weeks.
	Fatliquor	1.0		

[b]Note: All percentage of chemicals were calculated based on pelt weight.

Table 3. Recipe for chrome tanning

Process	**Chemicals**	**% Offer[c]**	**Time**	**Remarks**
Tanning	+ Basic chromium sulfate	4.0	30 min	
	+ Basic chromium sulfate	4.0		
	Sodium formate	1.0		Penetration of chromium sulfate was checked ok.
	Chrome stable fatliquor	0.5	60 min	
Basification	+ Water	50		
	+ Sodium bi carbonate	1.2	90 min	pH adjusted to 3.7-3.8. Drained, piled up and aged for 2 weeks.
	+ Preservative	0.2	60 min	

[c]Note: All percentage of chemicals were calculated based on pelt weight.

Table 4. Recipe for post tanning

Process	Chemicals	% Offer[d]	Time	Remarks
Acid wash	Water	200		
	Oxalic acid	0.3	30 min	
	Wetting agent	0.3		Washed and drained,
Neutralization	Water at 45 °C	100		
	Neutralizing syntan	2.0	30 min	pH adjusted to 4.0-4.5 and checked with BCG indicator.
	Sodium formate	1.0		
	Sodium bi carbonate	0.8	30 min	Drained and washed.
Re-tanning and dyeing	Water at 50 °C	100	20 min	
	Resin syntan	2.0		
	Fat liquoring agent	4.0		
	Dye	3.0	20 min	Checked dye penetration.
	Dye leveler	1.0		
	Mimosa	8.0	30 min	
	Quebracho	8.0		
	Replacement syntan	3.0	60 min	
	Formic acid	2.0	2 x 20 min	Washed and drained.
Fatliquoring	Water at 55 °C	100		
	Synthetic oil	2.0		
	Semi-synthetic oil	2.0	60 min	
	Raw oil	0.5		
	Fungicide	0.2		
	Formic acid	1.5	30 min	Washed and drained.
Top dyeing and fatliquoring	Water at 55 °C	200	30 min	
	Dye	1.0		
	Formic acid	1.0	30 min	
	Resin syntan	1.0		
	Raw oil	0.5	30 min	
	Cationic fat	0.5		Washed, drained and horsed up for overnight.

[d]Note: All percentage of chemicals was calculated based on shaved weight. Next day, after setting out and the vacuum-drying operation, leather was hung for natural drying. After a proper drying and conditioning, the vibrating, staking, toggling, trimming and plating/ironing were carried out for completion of the crust leather production.

Preliminary experiment for tanning agent optimization

Four goat skin samples were collected for the experiments and various percentages of glutaraldehyde (1%, 2%, 3% and 4%) were prepared to optimize the amount of glutaraldehyde requirement. The efficacy of the tanning method was assessed by determining the shrinkage temperature of the produced leather after tanning.

Organoleptic assessment of crust leather

Glutaraldehyde-tanned (experimental) and chrome-tanned (control) crust leather were assessed by fullness, grain tightness, softness, grain smoothness and dye uniformity through visual examination. Three experienced tanners rated the leather on a scale of 0-10 points for each functional property, where higher points indicated better result.

Determination of shrinkage temperature

The SATRA STD 114 apparatus for leather shrinkage temperature determination was used to measure the shrinkage temperature by following the standard operating procedure [25]. The samples were taken according to the sampling location of leather. All the experiments were performed in triplicate and reported the average value.

Analysis of discharged liquor

The discharged liquor both from the experiment and the control tanning process were collected, filtered and analyzed for the pH, total solids (TS), total dissolved solids (TDS) and chromium content in accordance with the standard procedures [26].

Physical tests

The produced leather was conditioned at 20±1 °C and 65±3 % relative humidity over a period of 48 h; the samples were taken from the specified sampling location. The physical properties of produced leather, e.g. tensile strength, the percentage of elongation at break, stitch tear strength, Baumann tear strength and grain crack strength were determined following standard methods set up by IULTCS allowing the assessment of the capacity of the leather to withhold the wear and tear properties [26-29].

RESULTS AND DISCUSSION

Hydrothermal stability analysis of produced leather

It has been reported that the addition of glutaraldehyde in increased amount considerably increases the shrinkage temperature [30-32]. In this study, it was found that the shrinkage temperature of leather increases gradually up to a certain level with the increase of glutaraldehyde percentage and after that it becomes unchanged with the increasing percentage of doses (Figure 1).

At 3 %, the shrinkage temperature of wet white leather was found 87 °C after aldehyde tanning and there was no increase of shrinkage temperature, although the percentage was increased to 4 %. After observation, the wet white leather tanned with a 3 %-glutaraldehyde dose was taken as experiment and made ready for final post-tanning operations along with the chrome-tanned (wet blue) leather as control.

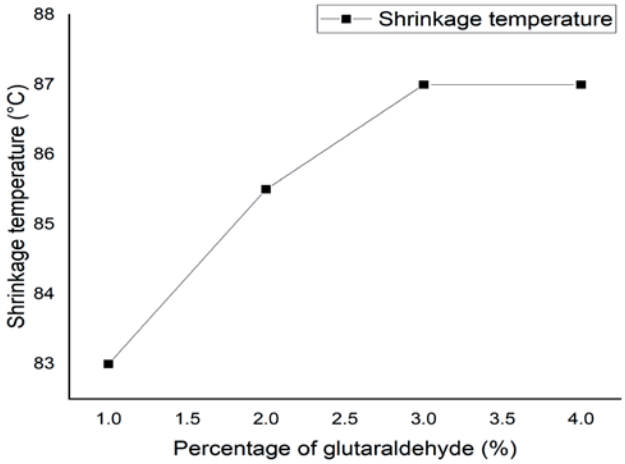

Figure1. Shrinkage temperature of wet white leather with different percentage of glutaraldehyde

The shrinkage temperature of the glutaraldehyde-tanned (wet white) leather (87 °C) was observed to be lower than that of the conventional chrome-tanned (wet blue) leather (104 °C). This is because of weak and less number of cross-linkages formation in the case of aldehyde tanning.

Table 5. Resultant shrinkage temperature of produced leather (experiment vs. control)

Type of leather	Shrinkage temperature (Ts)
Glutaraldehyde (experiment)	87 °C
Chrome tanned leather (control)	104 °C

SEM analysis

The Scanning Electron Microscopic (SEM) images of the conventional chrome-tanned leather and glutaraldehyde-tanned leather were investigated to assess the effect of tanning on the fiber structure of leather. The images (Figure 2 and 3) were captured at magnification of x200 and x500.

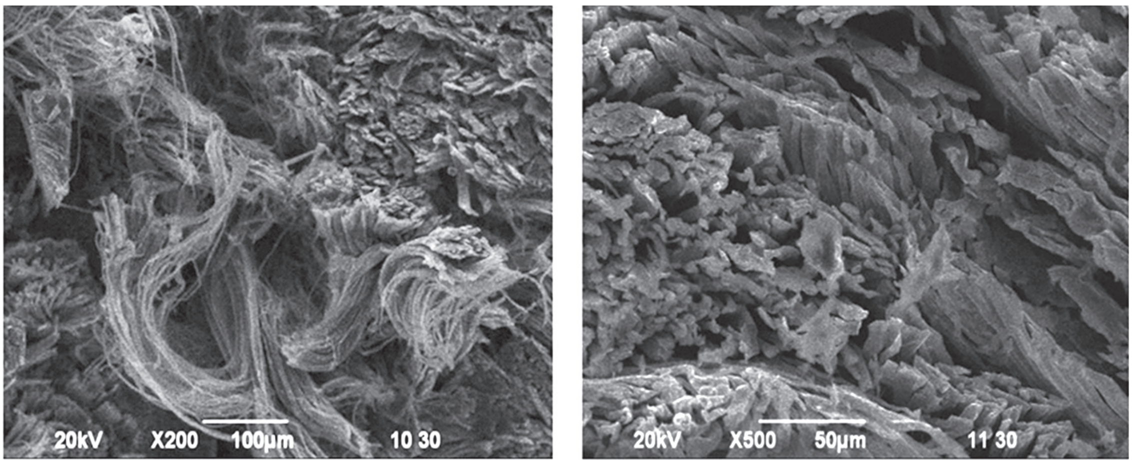

Figure 2. Cross section (a) (X200) and (b) (X500) of glutaraldehyde-tanned leather (experiment)

It was observed from the images that the fiber structure of glutaraldehyde tanned leather is comparable with that of the conventionally processed chrome-tanned leather.

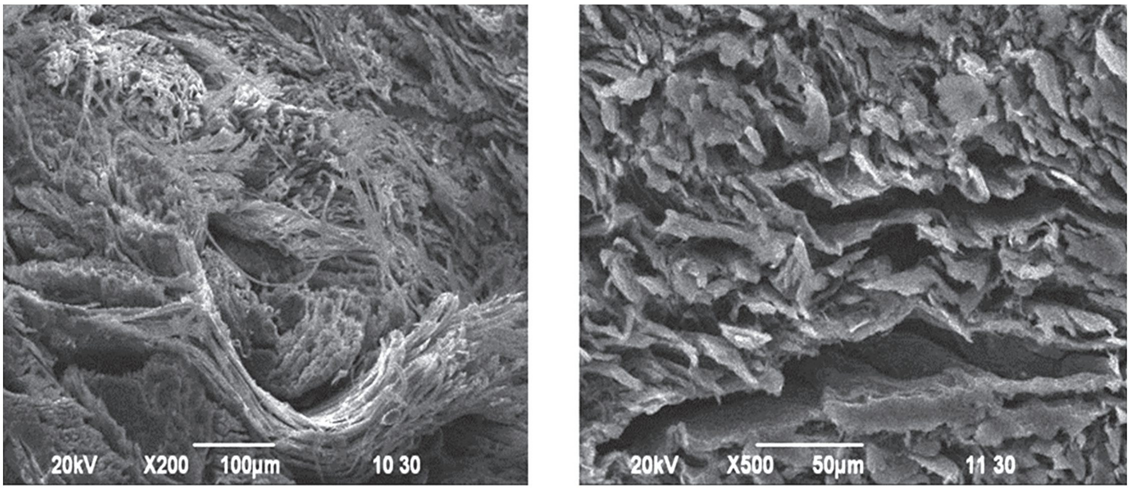

Figure 3. Cross section (a) (X200) and (b) (X500) of chrome-tanned leather (control)

Organoleptic analysis

The produced crust leather from the experimental and control method have been evaluated for various properties by both tactile and visual evaluation. The average rating for the leather has been calculated for each property and is presented in Figure 4. Higher number denotes better property. The figure shows that the organoleptic properties of the glutaraldehyde-tanned crust leather are comparable to those of the conventional chrome-tanned leather. The glutaraldehyde-tanned (experimental) crust leather exhibited good fullness, grain tightness and grain smoothness compared to the leather produced from the conventional chrome tanning.

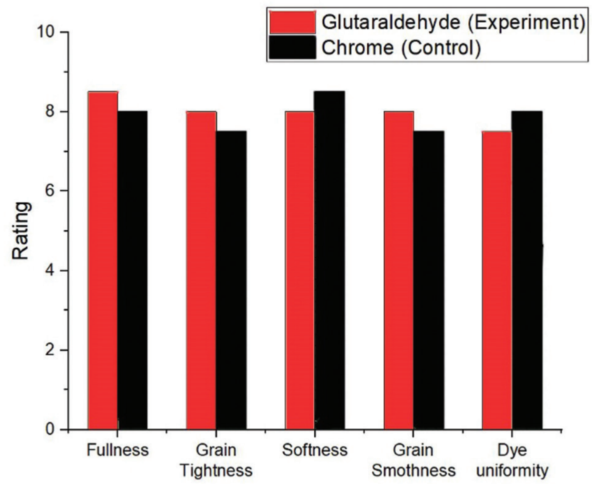

Figure 4. Graphical representation of organoleptic properties of produced leather

Physical properties analysis

The results of physical properties analysis of produced leather have shown that despite having lower shrinkage temperature, the glutaraldehyde-tanned leather had high tensile strength, stitch tear strength, Baumann tear strength, grain crack strength and elongation at break compared to that of the chrome-tanned leather (Table 6). The data indicated that the physical properties of the experimental leather were quite comparable with that of the corresponding control samples. It was found that almost all properties were above the minimum requirements of shoe upper crust leather standard [31-32].

Table 6. Physical properties of control and experimental crust leather

Parameter	Glutaraldehyde-tanned (Experiment)	Chrome-tanned (Control)	Minimum requirements for shoe upper crust leather [7, 30]
Tensile strength (Kg/cm2)	211±1	243±1	200
Elongation at break (%)	38±0.5	43±0.8	40-65
Grain crack strength (Kg)	23±0.4	27±0.4	20
Stitch tear strength (Kg/cm)	89±0.11	98±0.67	80
Baumann tear strength (Kg/cm)	63±0.4	68±0.25	30

Tanning discharge liquor analysis

The discharged liquor from chrome tanning and glutaraldehyde tanning was analyzed for the parameters which are listed in Table 7. The table shows that total solids and total dissolved solids are lower in the discharged liquor of experimental tanning than control tanning. However, the pH of the glutaraldehyde tanning effluent was slightly lower than that of the conventional chrome-tanning effluents.

Table 7. Characteristics of tanning discharged liquor

Parameter	Glutaraldehyde-tanned (Experimental)	Chrome-tanned (Control)
pH	3.5	3.8
Total solids (TS)	43990	57550
Total dissolved solids (TDS)	39500	51130
Chromium content	0	4330

[e]Note: All the values except the pH are expressed in mg/L

Besides lesser TS and TDS, no chromium is present in the discharged liquor of glutaraldehyde tanning. Hence, glutaraldehyde tanning is better in view of environmental aspects.

CONCLUSION

The environmentally compatible tanning method is a dire need for the sustainable development of leather industries throughout the world. This investigation explored the potential of glutaraldehyde as a pre-tanning and re-tanning agent for the production of various types of leather. The reported data i.e. different strength properties, leather morphology, etc. have indicated the eligibility of glutaraldehyde to be used as a pretanning and post-tanning agent. However, gluteraldehyde alone cannot be a suitable tanning agent for the shoe upper crust leather production since the shrinkage temperature was lower than the boiling point of water. The lower shrinkage temperature of upper leather may require different machineries for shoe manufacturing. The conventional shoe manufacturing process requires steaming at 100 °C which is not possible with the usual glutaraldehyde-tanned leather. Although the strength properties were found comparable with those of the chrome-tanned leather, that may be attributed to the use of syntan and other post-tanning chemicals. Gluteraldehyde could be used in combination tanning to produce quality leather with a reduction in the chromium load both in leather and effluents, which in turn contribute to reduction in the environmental impact.

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