Studies on the Henna-Glutaraldehyde Combination Tanning System

by

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Abstract

An organic combination tanning process for the production of upper leathers based on henna and glutaraldehyde was demonstrated in this work. Extract from the leaves of Henna *(Lawsonia inermis)*, widely distributed in Sudan, has been evaluated for its utilization in the combination tanning system based on henna and glutaraldehyde syntan. It was observed that the henna-glutaraldehyde combination tanning system employing 20% Henna extract and 3% Glutaraldehyde syntan provided a shrinkage temperature of 100°C. The Differential Scanning Calorimetric (DSC) data is in accordance with the observed shrinkage temperature. The characteristics of the leathers indicate that the henna-glutaraldehyde combination tanning system provided leathers with good organoleptic properties and comparable strength properties. The leathers were further characterized by chemical analysis and Scanning Electron Microscopy (SEM). The leathers obtained from the combination tanning system were lighter in color compared to control leathers as observed from the color measurement. Thus the possibility of making upper leather using henna-glutaraldehyde combination tanning appears to be promising.

Resumen

Un proceso de curtido orgánico combinado para la producción de cueros para capellada basado en jena [henna] y glutardialdehído se demostró en este trabajo. Extracto de las hojas de jena *(lawsonia inermes)*, ampliamente difundida en El Sudán, se ha evaluado para su utilización en un sistema de curtido combinado. Se observó que un sistema de curtición combinada basado 20% de extracto de jena y un 3% de un recurtiente de glutardialdehído resulto en un cuero con una temperatura de encogimiento de 100°C. Los datos obtenidos por Barrido Diferencial Calorimétrico (DSC) concuerdan con la temperatura de encogimiento observada. Las características del cuero indican que el sistema combinado de curtición por medio de jena-glutardialdehído provee cueros con buenas propiedades de tacto y correspondientes propiedades de resistencias físicas. Los cueros fueron también caracterizados por análisis químico y Microscopía por Barrido Electrónico (SEM). Los cueros obtenidos por el sistema de curtición combinado fueron más pálidos en comparación a los cueros del control tal cómo observado por determinación colorimétrica. La posibilidad, entonces, de producir cuero para capelladas por un curtido combinado de jena-glutardialdehído, parece promisoria.

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INTRODUCTION

Recent developments of processes like chrome recycling and high uptake chrome tannages have greatly reduced the chromium concentration in the tannery effluents.[1,2] In spite of all the developments it is difficult to achieve chromium concentrations in the tannery effluent as per discharge norms stipulated in various countries. Also, the disposal of chromium containing solid wastes is of great concern. Besides these problems, chromium is preferred over other new tanning systems because of the versatile properties it imparts to the final leathers. Thus the prerequisite for any chrome-free tannage is that it should impart to the final leather at least equivalent properties as that of chrome-tanned leathers.[3] Well documented mineral tannages, like zirconium, aluminium and iron require strong masking to prevent precipitation of metal hydroxide because these metal ions hydrolyze at low pH values.[4] Also, the hydrothermal stability of the leather tanned using these tanning materials are less than that of chrome tanned leather. Pure vegetable tannages are not suitable as chrome replacements, while combination tannages employing vegetable tannins and metal salts or aldehyde compounds are potential alternatives to chrome tanning, capable of producing hydrothermally stable leathers.[5] Usage of Glutaraldehyde, Oxazolidine and (bis)-tetrakishydroxymethyl phosphonium sulphate (THPS) have recently gained commercial significance as tanning agents, although their individual tanning abilities were identified several decades ago.[6] Glutaraldehyde in the form of syntan has been used in a wide variety of situation to improve the quality of leather. It increases the perspiration resistance and softness of the leather and improves its response to dyeing. At present three forms of glutaraldehyde are commercially used for leather making viz., glutaraldehyde (unmodified), glutaraldehyde modified with alcohols and glutaraldehyde modified with alcohols and polymer (eg. Relugan™ GTW). All of the modified versions of glutaraldehyde in the market are an attempt to solve two very different problems associated with the use of glutaraldehyde alone; the unpleasant odor and the rapid reactivity of the glutaraldehyde, which causes it to react superficially with collagen matrix thereby hindering further penetration.[7]

Recently, henna *(Lawsonia inermis)* has been established as an alternative retanning material for wattle.[8] *Lawsonia inermis* is a member of the family Lythraceae widely spread in tropical regions with relatively few species in temperate region.[9] It is widely available in Sudan, India and Egypt. *Lawsonia inermis* has been well investigated phytochemically by various researchers. The occurrence of β- sitosterol glucoside, flavonoids, quinoids, naphthalene derivatives, gallic acid, coumarins and xanthones in Lawsonia leaves have been reported.[10-15] Owing to the abundant availability of henna and the presence of mixture of several polyphenolic compounds with varied molecular weight, an attempt has been made in this study to utilize them in combination tannage with glutaraldehyde.

EXPERIMENTAL

Materials

Conventionally processed pickled goat skins were used for tanning studies. Henna leaves were sourced from Sudan. Glutaraldehyde syntan (Relugan™ GTW) was procured from BASF India Ltd. Chemicals used for post tanning were of commercial grade. Chemicals used for the analysis of spent liquor were analytical grade reagents.

Aqueous Extraction of Henna Leaves

Aqueous extraction of henna leaves has been carried out as reported elsewhere.[16] The required amounts of ground henna leaves from Sudan were soaked in water at 80°C (1:10 w/v) for an hour. The resultant solution was filtered through a cotton cloth and the supernatant was concentrated to 1/3rd of its volume and used for tanning studies. The solid content of the henna extract was determined to be 35±1%.

Henna–Glutaraldehyde Combination Tanning

The tanning experiments were carried out using pickled goatskins. Experimental tanning trials employing glutaraldehyde syntan followed by henna (Glu-Henna) were carried out as per the process mentioned in Table I and combination tanning based on henna followed by glutaraldehyde (Henna-Glu) was carried out as per the process mentioned in Table II. Control henna tanning trial was carried out as per process given in Table III. The post tanning process mentioned in Table IV was followed for both experimental and control leathers. The shrinkage temperature of both control and experimental leathers were determined using the Theis shrinkage tester.[17]

Visual assessment of the crust leather

Experimental and control crust leathers were assessed for softness, fullness, grain smoothness, grain tightness (break), general appearance and dye uniformity by hand and visual examination. Three experienced tanners rated the leathers on a scale of 0-10 points for each functional property, where higher points indicate better property.

Physico chemical analysis of leathers

Physical testing

Samples for various physical tests from experimental and control crust leathers were obtained as per IULTCS methods.[18] Specimens were conditioned at 20±2°C and 65±2% R.H over a period of 48 hrs. Physical properties such as tensile strength, percentage elongation at break, grain crack strength and tear strength were measured as per standard procedures.[19-21] Each value reported is an average of four samples (2 along the back bone, 2 across the back bone). Softness measurement of

TABLE I
Formulation of Glu-Henna Combination tanning process for pickled goat skin

Process	%	Product	Duration (min)	Remarks
Adjustment of the pH	50	Water		
	0.75	Sodium bicarbonate	3 x 15	pH 4.5-4.7
Tanning	3	Glutaraldehyde syntan (Relugan GTW, BASF)	90	
Henna tanning	2	Phenolic syntan (Basyntan P, BASF)	30	
	10	Henna extract	120	
	10	Henna extract	120	
Fixing	1.0	Formic acid	3 x 10 + 30	pH 3.5
Washing	300	Water	10	Drain the bath and pile overnight. Next day sammed and shaved to 1.2 mm. The shaved weight noted.

TABLE II
Formulation of Henna-Glu Combination tanning process for pickled goat skin

Process	%	Product	Duration (min)	Remarks
Adjustment of the pH	100	Water		
	0.75	Sodium bicarbonate	3 x 15	pH 4.5-4.7
Tanning	2	Phenolic syntan (Basyntan P, BASF)	30	
	10	Henna extract	120	
	10	Henna extract	120	
	3	Glutaraldehyde syntan (Relugan GTW, BASF)	90	
Fixing	1	Formic acid	3 x 10 + 30	pH 3.5
Washing	300	Water	10	Drain the bath and pile overnight. Next day sammed and shaved to 1.2 mm. The shaved weight noted.

TABLE III
Formulation of Henna tanning process (control) for pickled goat skin

Process	%	Product	Duration (min)	Remarks
Adjustment of the pH	100	Water		
	0.75	Sodium bicarbonate	3 x 15	pH 4.5-4.7
Tanning	2	Phenolic syntan (Basyntan P, BASF)	30	
	10	Henna extract	120	
	10	Henna extract	120	
Fixing	0.25	Formic acid	3 x 10 + 30	pH 3.5
Washing	300	Water	10	Drain the bath and pile overnight. Next day sammed and shaved to 1.2 mm. The shaved weight noted.

TABLE IV
Formulation of post tanning process for experimental and control

Process	%	Product	Duration (min)	Remarks
Washing	200	Water	10	
Neutralization	0.75	Sodium bicarbonate	3 x 15	pH 4.8-5.0
Retanning, Dyeing and Fatliquiring	100	Water		
	2	Acrylic syntan (Relugan RE, Clariant)	40	
	2	Synthetic fatliquor (Lipoderm liquor SAF, BASF)	40	
	2	Phenol-naphthalene condensate syntan (Basyntan DI, BASF)	30	
	3	Acid dye brown	30	
	3	Synthetic fatliquor (Lipoderm liquor SAF, BASF)		
	4	Semi synthetic fatliquor (Balmol BL II, Balmer & Lawrie)	40	
	3	Phenol-naphthalene condensate syntan (Basyntan DI, BASF)		
	4	Melamine resin syntan (Basyntan FB6, BASF)	40	
Fixing	1	Formic acid	3 x 10 + 30	pH 3.5
Washing	300	Water	10	Drain the bath and pile overnight. Next day sammed and set, hook to dry, toggled, trimmed and buffed.

experimental and control crust leather was carried out as per standard method.[22] Samples were conditioned at 20±2°C and 65±2% R.H over a period of 48 hrs before the measurement. Circular aperture of diameter 35 mm is used for the softness measurement.

Chemical Analysis

The chemical analysis of the leathers viz. for total ash content, % moisture, % oils and fats, % water soluble, % hide substance, % insoluble ash and degree of tannage were carried out for control and experimental leathers as per standard procedures.[23] Analyses were carried out in triplicates for each sample and the average values are reported.

Reflectance Measurement

The leathers made in this study were subjected to reflectance measurement using a Miton Roy Color Mate HDS instruments. Color measurements *viz.* L, a, b, h and C were recorded for the control and experiment leathers. 'L' represents whiteness on a scale of 0-100. Higher value means lighter shade. ΔL represents lightness difference, Δa and Δb are the differences in a and b values, respectively, where 'a' represents red and green axis, ('a'>0 means red and 'a'<0 means green) and 'b' represents yellow and blue axis('b'>0 means yellow and 'b'<0 means blue) and 'C' represents the chromaticity or intensity of the color. Change in lightness is represented as 'ΔL', which provides the depth of the shade; positive value of 'ΔL' represent lighter shade, ΔH, hue difference, ΔC chromaticity difference. Other parameter such as ΔL, Δa, Δb and ΔC were calculated by subtracting the corresponding values for leather made from that of control leather.

Scanning Electron Microscopic Analysis of Leather Samples

Samples from experimental and control crust leathers were cut from official sampling position. Samples were directly cut into specimens with uniform thickness without any pretreatment. All specimens were then coated with gold using Edwards E306 sputter coater. A Leica Cambridge Stereoscan 440 Scanning electron microscope was used for the analysis. The micrographs for the grain surface and cross section were obtained by operating the SEM at an accelerating voltage of 20 KV with different lower and higher magnification levels.

Differential Scanning Calorimetry (DSC)

The thermal analysis of the leather samples from experimental and control crust leathers were carried out using Dupont 2910 DSC instrument. The heating rate was maintained at 10°C per minute in nitrogen atmosphere.

Analysis of spent liquor

The spent liquor from control and experimental tanning processing were collected, filtered and analyzed for chemical oxygen demand (COD), Biochemical oxygen demand (BOD5), and total Dissolve solids (TDS) as per standard procedures.[24] The presence of henna in the spent liquor from control and experimental tanning processes were collected and quantified by measuring the optical density of the spent liquor at a λ_{max} of 267 nm using UV–visible spectrophotometer (Hitachi, Japan), after suitably diluting the spent liquor.

RESULTS AND DISCUSSION

Combination tanning trials using henna and glutaraldehyde syntan were carried out with 3% offer of glutaraldehyde syntan and 20% offer of henna. The shrinkage temperature data of leathers tanned with Henna-Glu and Glu-Henna combination along with henna control is given in Table V. From the table it is seen that both the combinations resulted in leathers with better shrinkage temperature than control leathers (henna tanned). The shrinkage temperature of leathers obtained from Henna-Glu combination tanning (100°C) is higher than Glu-Henna (91°C), which is much better than the Ts of control henna leather (84°C).

Organoleptic properties of crust leathers for experimental and control

The organoleptic properties (visual assessment) of crust leathers from experimental and control is given in Fig.1. From the figure, it is observed that experimental crust leathers from Henna-Glu tanning exhibited good softness, fullness, smoothness, general appearance and dye uniformity compared to Glu-Henna crust leathers and control leathers from henna tannage.

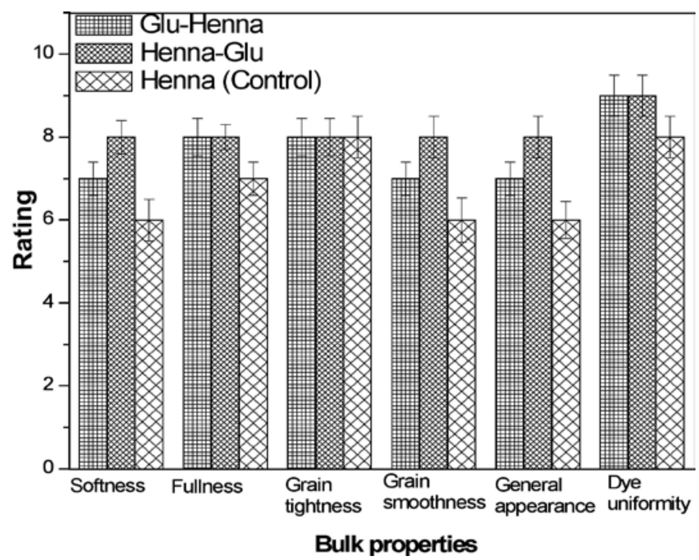

Figure 1: Graphical representation of organoleptic properties of the Experimental and control leather

TABLE V

Shrinkage temperature, physical strength characteristics and softness data for experimental and control leathers

Parameter	Glu-Henna	Henna-Glu	Henna (control)
Shrinkage temperature, T_S (°C)	91±2	100±1	84±1
Tensile strength (Kg/cm^2)	230±2	250±2	210±3
Elongation at break (%)	56±0.71	47±0.71	56±1.58
Tear strength (Kg/cm)	65±1.58	54±1.58	47±0.71
Load at grain crack (kg)	41±0.71	37±0.71	25±0.71
Distention at grain crack (mm)	10±1.58	10±1.41	10±0.71
Softness Value	4.60 ±0.43	4.80±0.45	3.40±0.47

TABLE VI

Characteristic of spent liquor for experimental and control

Experiment	COD(mg/l)	BOD_5(mg/l)	TDS (mg/l)	% Exhaustion
Glu-Henna	103000±2500	16000±1300	72500±2500	85±2
Henna-Glu	101000±2000	13500±1400	63000±2000	86±3
Henna (control)	117800±2950	24000±950	91140±1550	75±2

TABLE VII
Color Measurement Data for control and Experimental crust leathers

Sample	L	a	b	c	h
Control(Henna)	3.089	0.303	- 0.022	0.304	355.939
Glu-Henna	11.002	-5.337	-3.498	6.381	213.241
Henna-Glu	3.677	-0.773	-2.129	2.265	250.047

Sample	ΔL	Δa	Δb	Δc	Δh	ΔE
Glu-Henna	7.912	-5.640	-3.476	6.077	-2.639	10.320
	Lighter	Greener	More blue	Stronger	Decrease	
Henna-Glu	0.587	-1.076	-2.107	1.961	-1.324	2.438
	Lighter	Greener	More blue	Stronger	Decrease	

Physical strength characteristics of crust leathers for experimental and control

The physical strength measurements of matched pair experimental (Glu-Henna and Henna-Glu) and control leathers (henna) are given in Table V. The physical strength measurements viz., tensile strength, elongation, tear strength, load at grain crack and distension at grain has been found to be comparable. The experimental tanning resulted in leathers with good physical strength characteristics compared to control leathers. The softness values for the experimental and control leathers are given in Table V. It is seen that the softness of experimental leathers are better than that of the henna tanned control leathers. This is in accordance with the observations of organoleptic properties.

Analysis of Spent liquor

The COD, BOD_5 and TDS of the spent liquor for both experimental and control trials were determined and are given in Table VI. From the table it is observed that the COD, BOD_5 and TDS of the spent liquor processed using Henna-Glu and Glu-Henna tanning system (experimental) are lower than that of control Henna tanning trial. The COD, BOD_5 and TDS of the spent liquor analyzed from Glu-Henna tanning have been observed to be slightly higher than Henna-Glu system.

Analysis of Henna Extract Exhaustion

The exhaustion of henna extracts for both experimental and control (henna tanning) trials were determined and are given in Table VI. It could be observed that the % exhaustion of henna is better for experimental (Glu-Henna tanning and Henna-Glu tanning) compared to control leathers (Henna tanning). The exhaustion of the Glu-Henna tanning is 83% compared to Henna-Glu tanning (86%), whereas for the control the exhaustion is only around 75%.

Reflectance Measurement

The color measurement data for the control and experimental leathers are given in Table VII. It is observed from the table that the L value on treatment with Glu-Henna combination tanning is higher than the henna treated control and Henna-Glu tanned experimental leathers, which is clearly indicative of the lightness of the leathers. The 'a' value on treatment with Glu-Henna is less than control and Henna-Glu treated leathers. This indicates that the Glu-Henna treated leathers (experimental) are greener as compared to control and Henna-Glu treated leathers. The 'b' value on treatment with Glu-Henna is found to decrease which is clearly indicative that the Glu-Henna treated leather is bluer than the control and Henna-Glu treated leathers. The variations in the shade and intensity of color have been clearly observed from the L, a, b, h and C values obtained.

Scanning Electron Microscopic Analysis of Leather Samples

The scanning electron micrographs of crust samples from control (henna) and experimental tanning process (Glu-Henna, Henna-Glu) showing the grain surface at magnification of X100 are given in Figs. 2a-c, respectively. It is seen that the grain surface of sample from experimental tanning process is clean without any damage and foreign particle. The hair pores are clearly visible without any surface deposition of tannins. Scanning electron micrograph of crust samples from control (henna) and experimental tanning process (Glu-Henna, Henna-Glu) showing the cross section at magnification of X300 are given in Figs. 3a-c, respectively and shows well separated and opened up fibers. The Henna-Glu combination provides better fullness as seen from the scanning electron micrograph.

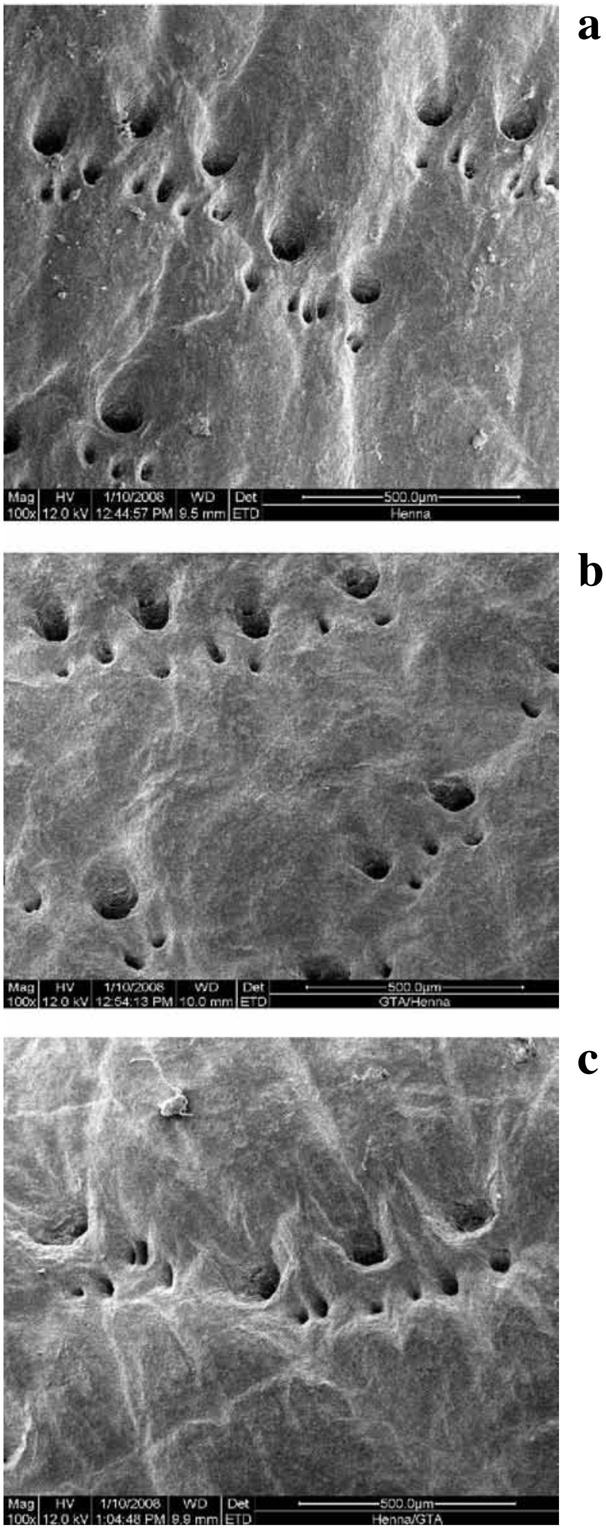

Figure 2: Scanning electron micrographs of (2a) control (henna), (2b) experimental (Glu-henna) and (2c) experimental (Henna-Glu) samples showing the grain surface at magnification of x100 after tanning.

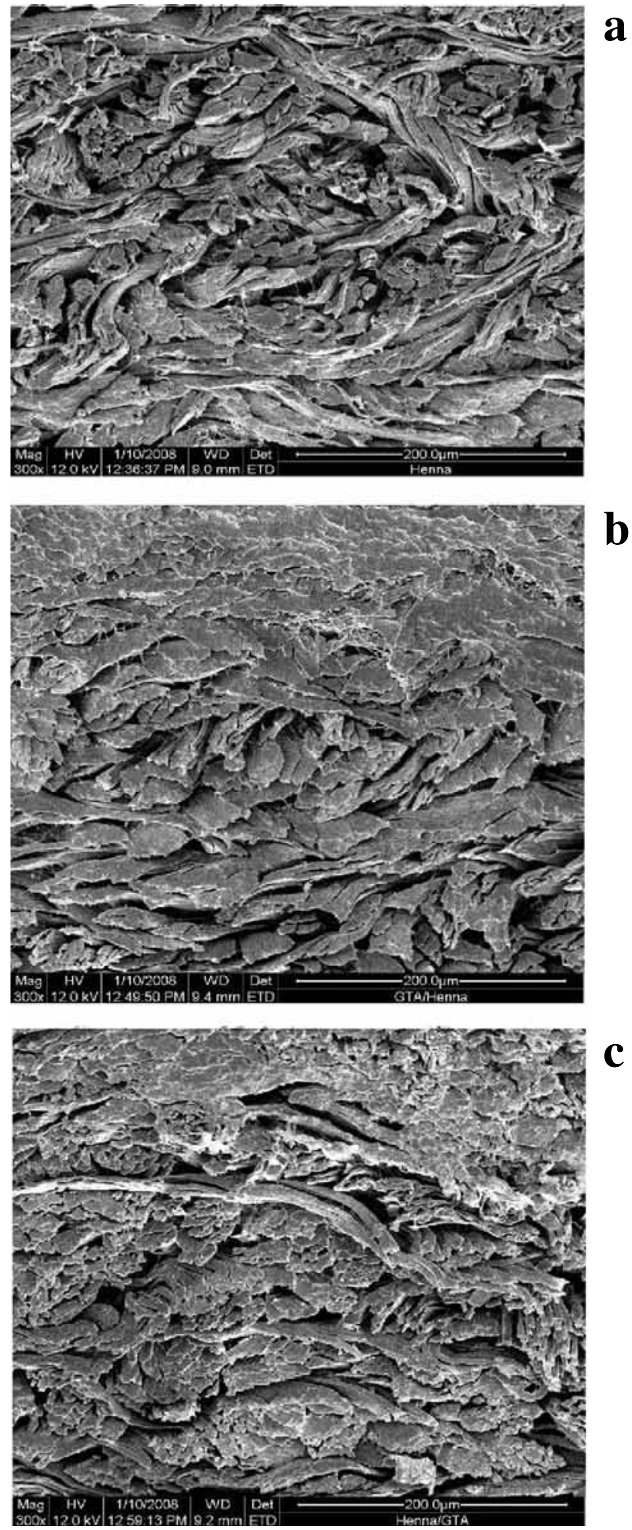

Figure 3: Scanning electron micrographs of (3a) control (henna), (3b) experimental (Glu-Henna) and (3c) experimental (Henna-Glu) samples showing the cross section at magnification of x300 after tanning.

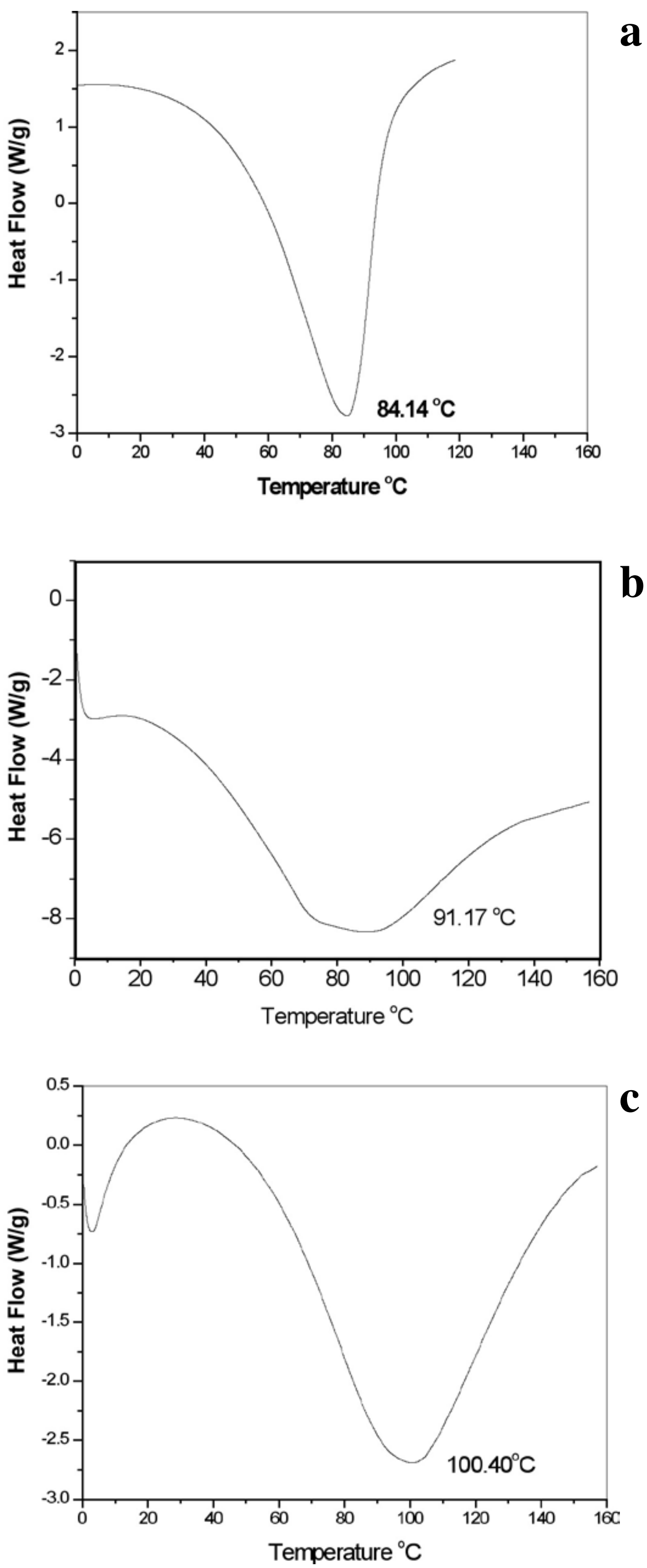

Figure 4: DSC for (4a) Control leather (henna), (4b) Experimental leather (Glu-Henna), and (4c) Experimental leather (Henna-Glu)

DSC Determination

The DSC technique as a tool provides rapid determination of changes in the collagenous structure of leather. The onset temperature of the DSC curve is defined as shrinkage temperature of the leather or the temperature of phase transformation, higher the onset, better the hydrothermal stability of collagen.[25] The DSC spectra of the experimental (Glu-Henna and Henna-Glu) and control (henna) crust leathers are given in Figs. 4a-c. It is seen from the figure that the peaks appear at 100.40°C for Henna-Glu, 91.17°C for Glu-Henna tanned crust leathers. This is in accordance with the shrinkage values obtained for the experimental leathers. It is seen that the order of addition of henna and glutaraldehyde syntan has effect on the thermal stability of the final leathers. The control leathers exhibits transition at 84.40°C. The higher thermal stability in the case of Henna and Glutaraldehyde could be attributed to complementary nature of interaction of henna and glutaraldehyde with collagen. However the thermal stability of the leathers is higher for henna followed by glutaraldehyde tanning compared to glutaraldehyde followed by henna. This could be possibly due to the decrease in the availability of the sites in the skin matrix for the interaction of henna after pretreatment with glutaraldehyde syntan as the later is known to form cyclic polymeric networks. The same may not be true in the case of henna followed by glutaraldehyde tanning where glutaraldehyde can manage to find sites for interaction even after henna treatment as henna binds with collagen through non covalent interactions. The possibility of interaction of covalent linkage of aldehydic functionalities with polyphenolic aromatic rings of henna similar to Mannich reaction is not ruled out.

Chemical Analysis of the crust leather

The chemical measurements of matched pair experimental crust leather (Glu-Henna, Henna-Glu) and control (henna) are given in Table VIII. The chemical analysis data for the experimental leathers is comparable to the control leathers. However, the water soluble matter for the control leathers is more than the experimental leathers with glutaraldehyde combination.

Henna and Glutaraldehyde Combination Tanning: An alternative viable tanning option for leather manufacture

In recent years research is focused on the development of chrome free alternative tanning systems, which would result in leathers with good thermal stability. In the present study, leathers with shrinkage temperature of around 100°C have been produced by employing henna-glutaraldehyde combination tanning system. Glutaraldehyde can exhibit binding with side chain amino groups of lysine and arginine of collagen and polyphenolics present in henna will have non-specific electrostatic and hydrophobic interactions. The complimentary nature of this combination tanning system facilitates the enhancement of hydrothermal stability of the resulting leather. Owing to the wide availability of henna in

TABLE VIII

Chemical Analysis of crust leather of experimental and control

Parameter	Henna (control)	Glu-Henna	Henna-Glu
Moisture %	13.30	14.00	13.00
Total ash content %	2.70	2.20	2.30
Fats and oils %	3.60	2.40	2.70
Water soluble matter %	5.10	2.80	3.50
Hide substance %	52	53	52
Insoluble ash %	1.20	1.40	1.30
Degree of tannage %	47.70	50	52.88

tropical regions of the world it can be a suitable vegetable tanning material for exploitation in developing combinations systems for the manufacture of leathers.

CONCLUSION

In the present study, an attempt has been made to produce upper leather using a combination tanning process based on henna and glutaraldehyde tannage. It is seen that Henna-Glu combination tanning system with 20% henna extract and 3% glutaraldehyde syntan produced leathers with shrinkage temperature of 100°C, which is 16°C more than control leathers. This is in accordance with the DSC measurement data. The exhaustion of henna for the combination system was 15% more than the henna treated leathers. The color measurement data indicates that Henna-Glu combination provides leather lighter in shade as compared to the control. The physical and chemical analysis indicates that the experimental leathers were comparable to control leathers in terms of all the properties. The Henna-Glu tanned leathers were softer than control. The bulk properties for the experimental leathers were better than control leathers. Scanning electron microscopic analysis of both control and experimental leather samples showed clean grain surface devoid of any foreign particles and good separation of fiber bundles. It is possible to manufacture lighter shade upper leathers from Henna-Glu combination with a shrinkage temperature of 100°C.

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