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E-mail: bjsir07@gmail.com

Tannin agents from native *Swietenia microphylla* (sky fruit) for leather processing

M. A. Hashem*, S. Payel, M. S. Ali, P. Bhowmik and M. S. Sahen

Department of Leather Engineering, Khulna University of Engineering & Technology, Khulna-9203, Bangladesh

Abstract

In leather processing, retanning is considered one of the most important steps which play a key role in the final leather. The retanning agent improves the required physicomechanical properties of the final leather. In this study, an alternative retanning agent is extracted from the native *Swietenia macrophylla* (sky fruit). The solvent extracted tannin from the sky fruit was characterized by Fourier Transform Infrared (FT-IR) speactroscopy. The tannin content of the sky fruit was 8.09%. The leather retanned with tannin extracted from sky fruit was compared with the conventional one. The physicomechanical properties-tensile strength, elongation at break (%), stitch tear strength, and shrinkage temperature fulfilled the requirements. The organoleptic properties of the retanned leather e.g., softness, fullness, grain smoothness, grain break, general appearance, and uniformity were evaluated in comparison with the conventional retanned leather. The extraction of retanning agent from the native sky fruit could be an alternative source of vegetable tannin which is locally and available.

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Introduction

In leather manufacturing, in post tanning generally after shaving pelts are with different retanning agents e.g., resin, syntan, vegetable, aldehyde, etc. to improve the roundness, fullness, softness, grain firmness, filling, and suppleness of the final leather. About 80-90% of global leather products are tanned with chromium(III) salts (Manfred *et al.* 2012). Although chrome tanning is a popular method in leather production for its excellent physicomechanical properties: alternative vegetable tanning agents are preferred due to some environmental impacts of chrome tanning agents. Both valences (trivalent and hexavalent) of chromium are potentially harmful but hexavalent chromium compounds are acutely and chronically toxic, mutagenic, carcinogenic, and teratogenic (Altaf *et al.* 2008).

Vegetable tanning agents are bi-active materials that are found in the bark, wood, leaves, root, fruits, fruit pods, plant galls and some of the plants can impart a tanning effect to leather (Mane *et al.* 2007; Riccim *et al.* 2015). The main components of vegetable tannins are polyphenolic constituents with a medium molecular weight fraction and the molecular weight range is 500-3000 Daltons (Balfe, 1948; Sundara *et al.* 1982). According to the chemical structure, vegetable tannins are classified into hydrolysable tannins and condensed tannins. Hydrolysable tannins are saccharide-based compounds in which aliphatic hydroxyl groups are esterified by carboxylates specificallycarrying pyrogallol groups such as 1, 2, 3, 4, 6-Pentagalloyl glucose (Fig. 1).

Hydrolysable tannin is found in myrobalan extract, tara extract, chestnut, etc. Numerous molecules of catechol unit together in condensed tannins and ultimately separate from the aqueous solution in the form of sludge (Hemingway *et al.*1989) whichis found in the wattle, quebracho, babul tree, etc. The flavonoid ring structure and their oligomers and polymers forming flavan-3-ol structure i.e. epicatechin and catechin are shown in Fig. 2.

*Corresponding author e-mail: hashem_518@yahoo.com, mahashem@le.kuet.ac.bd

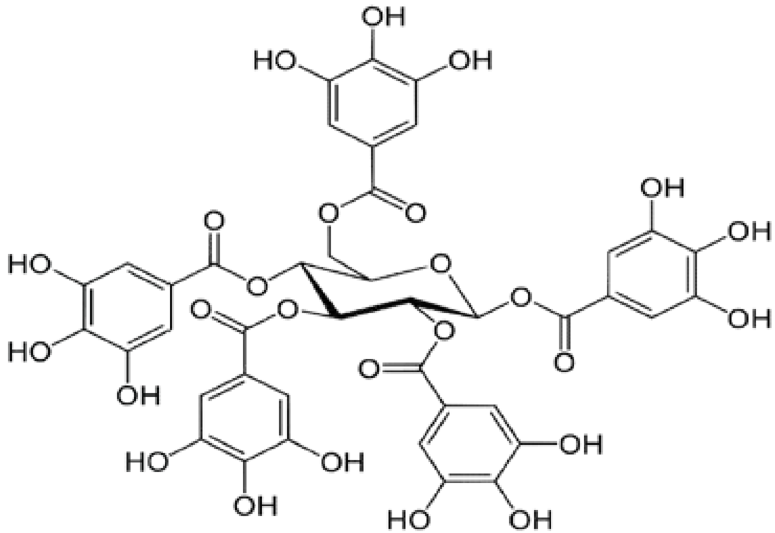

Fig. 1. 1, 2, 3, 4, 6- Pentagalloyl glucose

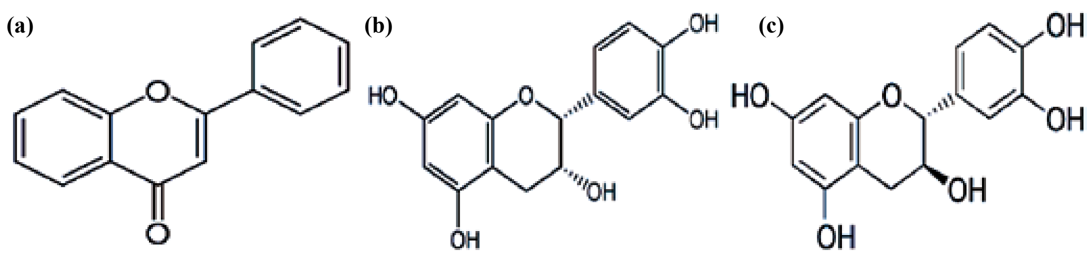

Fig. 2. Structure of flavonoid (a), Epicatechin (b), and Catechin (c)

Vegetable tanning agents propose natural products which are widely used for fancy and luxury leather goods production (Sundar *et al.* 2013). During tanning with vegetable tanning agents, the polyphenolic compounds crosslink with the active groups of collagen through the hydrogen bond. Therefore, the tanned leathers become endurable with an increase in hydrothermal stability and resistance to microorganisms.

For leather processing, Bangladesh invests a huge amount of foreign currency in importing vegetable extracts (Quebracho, Mimosa, Tara, Wattle, Chestnut, etc.) from different parts of the world. The sky fruit (mahogany tree) is available in Bangladesh and could be a source of vegetable tannin extract. It is also found in Europe and America. The major ingredients found in sky fruit derived from *Swietenia macrophylla* are saponin, flavonoid, and alkaloid (Arumugasamy *et al.* 2004). They contain a polyphenolic structure and their molecular weight range is found in the tannin range. It also contains anti-bacterial and anti-fungal agents (Eid *et al.* 2013) which can overcome the problems of fungal and bacterial growth during the storage of finished leather and leather products.

In this study, retanning agents extracted from the sky fruit ofthe native mahogany tree (*Swietenia microphylla*) have been tried as an alternative source of tannin agents. The extracted tannin agent was characterized by Fourier Transform Infrared (FT-IR) spectroscopy. The physicochemical properties of the retanned leather were compared with conventional retanned leather.

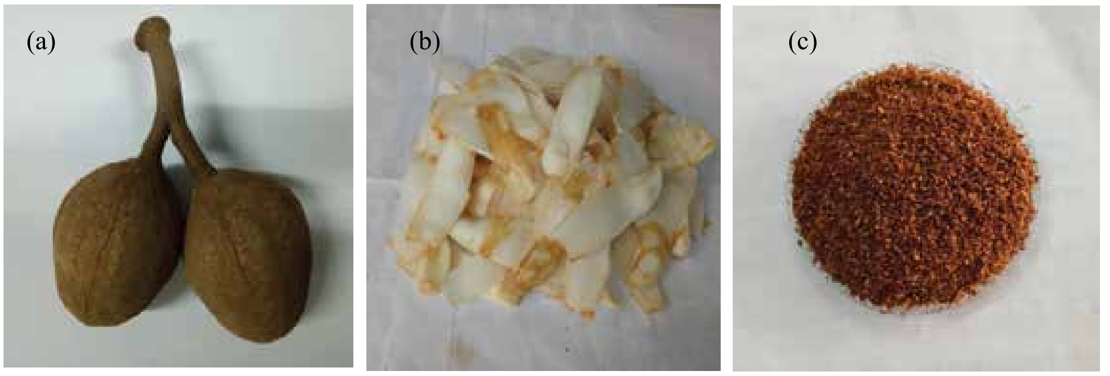

Fig. 3. (a) Sky fruit, (b) Seeds of sky fruit, (c) Extracted powder from sky fruit

Materials and methods

Materials

Sky fruit of the mahogany tree (*Swietenia microphylla*) were collected from the campus of Khulna University of Engineering & Technology (KUET), Khulna, Bangladesh. Freshly flayed goatskin was collected from the local slaughterhouse in Khulna, Bangladesh.

Vegetable tannin extraction

Powder preparation

At first, the seeds were separated from the sky fruit and cleaned and sun-dried well. Then, it was dried in the oven at 105ºC temperature. After drying, the seeds were ground using a laboratory grinder (Fritsch, Pulverisette 14, Germany). Fig. 3 (a-c) shows the *Swietenia macrophylla* (sky fruit), its seed, and the extracted sky fruit powder. The colour of the powder was dark brown. Half of the powder was stored for the tanning of pickled pelt. The rest of the powder was used for extraction of the tanning agents by the solvent extraction method.

Extraction of tannin in aqueous phase from sky fruit powder

The tannin was extracted from sky fruit powder in the hot water extraction process. About 50 g of powder was mixed with 800 mL of water, and heated in a water bath for two hours. The aqueous phasewas stirred during heating to ease the extraction process uniformly. The extracted aqueous solution was finally filtered through a cotton filter cloth and noted down the volume of the extracted solution.

Retanning process

The previously chrome-tanned goat wet blue was used as a basic raw material for retanning process. The sammying and shaving operation was conducted on the goat wet blue. Before starting the retanning, the pelt was divided into two parts along the backbone. One part was retanned with 10% (w/w) tannin extracted from sky fruit powder (experimental) and the other part was retanned with the conventional mimosa vegetable tannin (control). Table I represents the retanning processing of goat wet blue. Fig. 4 (a, b) represents the retanned experimental and control leathers. The cross-section penetration and shrinkage temperature were measured.

Physicomechanical properties

The moisture content of the tanning agent was determined using the Dean and Stark method (BIS, 1971). The sample was weighed in a crucible and then heated in an oven at 105±1ºC for 3 h. After that, they were cooled in a desiccator and weighed again. The heating was continued until the weight was constant. The process was followed three times simultaneously. The pH of the powder was measured using calibrated pH meter (UPH-314, UNILAB, USA) at a 1:10 ratio.

Table I. A typical recipe for retanning process

Operation	Name of chemicals	Chemical (%)	Remarks
Wet back	Water at 35°C	150	Run 20 min
	Wetting agent	0.25	Drain the float
Neutralization	Water at 40°C	100	
	Sellasol NG	1.5	
	Sodium formate	0.5	Run 60 min, pH 5.0
Drain and wash	Water at 40°C	200	Run 10 min
Retanning	Water at 40°C	60	
	Intan TP340	3.0	
	Relugan RE	1.5	Run 25 min
	Relugan D	4.0	
	Tanigan OS	3.0	
	Tannin (Sky fruit extracted)*	10.0	60
Dyeing	Brown Dye	2.0	Run 60 min
Fat liquoring	Water at 60°C	100	
	Lipsol BSFR	3.5	
	Pefectol HQ	2.0	
	Neopristol SWK	2.5	
	Formic acid	1.5	Run 30, pH 3.9
Drain and pile			

Setting out, Vacuum drying, Natural drying, Vibrating staking, and Toggle drying
* For experimental, retanning was done by sky fruit extracted tannin
* For the conventional retanning process, sky fruit extracted tannin was replaced by conventional vegetable tannin (mimosa)

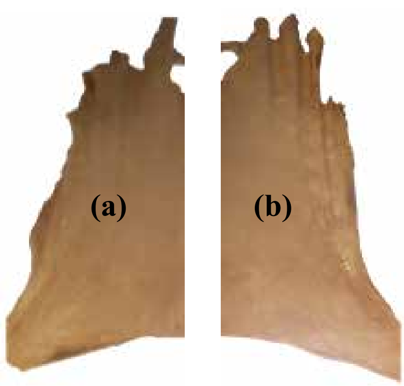

Fig. 4. Leather tanned with (a) 10% (w/w) tannin extracted from sky fruit and (b) conventional vegetable tannin extract

Tannin content analysis

The tannin content of the sky fruit extract was determined following the International Pharmacopoeia (2003) and the AOAC standard (1965). A 25 mL of the extracted tanning solution wastaken in a 1 L flask along with 25 mL of indigo solution and 750 mL of deionized water. Then, titration was performed with a 0.1 N aqueous solution of $KMnO_4$ until the blue solution turns green. Later, a few drops more were added at a time until the solution becomes golden yellow. The tannin content was measured using the following equation (i):

$$\text{Tannin content (\%)} = \frac{(V - V_o) \times 0.004157 \times 250 \times 100}{m \times 25} \quad ...(i)$$

Where V and V_o are the volumes of 0.1 N aqueous solution of $KMnO_4$ for the titration of the sample and blank solution in mL, 0.004157 is the tannin equivalent of 1 mL of 0.1 N aqueous solution of $KMnO_4$, m is the mass of the sample taken for the analysis in g.

FTIR analysis

The solvent-extracted tannin sample was analyzed using Fourier transform infrared spectrometer (FTIR, Spectrum 100, PerkinElmer, USA) where data was recorded at (4000–400 cm^{-1}) on potassium bromide (KBr) discs.

Morphological analysis

The morphological analysis was conducted by performing Field Emission Scanning Electron Microscope (FESEM) test. The leather samples were taken approximately from a similar area of the sky fruit leather and conventional vegetable-tanned leather and the test was performed by placing it on leading carbon tape. Leather samples were analyzed on a Field Emission Scanning Electron Microscope (FESEM, ZEISS Sigma 300 VP, UK). Images of the surface were taken with the magnification of 3000X at an accelerating voltage of 5 kV.

Determination of shrinkage temperature

Shrinkage temperature was determined according to the ISO 3380 standard (SATRA, ISO 3380, 2015) using a shrinkage tester (SATRA, STD 114, UK). The sample was cut into the required shape (50 mm × 3 mm) using a standard die and placed in the clamp. Then, the test sample was immersed in the water and the temperature of the water was gradually increased. The temperature at which the sample visibly shrank was noted as the shrinkage temperature. The shrinkage temperature was determined every day during the tanning operation.

Physical strength determination

At first, the test specimens were cut according to ISO 2418: 2002/IUP 2 (ISO 2418, 2002) and were conditioned at 23 ± 2ºC temperature and 50 ± 5% relative humidity as per ISO 2419: 2002/IUP 3 (ISO 2419, 2002) standard method. Then the physical properties such as tensile strength and percentage elongation at break were determined as per standard method EN ISO 3376:2002. The stitch tear strength was measured following ASTM D4705-18 (2018) standard methods. ISO 3379:2015 was followed to measure the ball bursting strength.

Results and discussion

Physical characteristics

The moisture and pH of the extracted power were 16.4% and 5.05, respectively. Marzalina and Normah (2001) explained that immature seeds have >45% moisture content. This indicates that the extracted seed was matured as it had only 16.4% moisture. The pH indicates that the powder is in an acidic range which can facilitate fungal growth. But Woodard and Milner (2016) stated that fungal decay occurs in the presence of oxygen when the moisture content is more than 20% and the temperature is in the range of 25-40ºC. Since the moisture content of the extracted powder was only 16.4%, it can be said that the proposed retanning agent could be stored in powder form for a long time.

Tannin content

Table II indicates the tannin content present in the sky fruit extract and conventional tanning agent (mimosa). It can be seen that the tannin percentage in mimosa was about 29.5%, whereas the tannin content in sky fruit was around 8.09%. This indicates that the waste sky fruit contains a significant amount of tannin which can be utilized as an alternative vegetable tanning agent.

Table II. Tannin (%) of sky fruit and conventional tanning agent (mimosa)

Tanning agent	Tannin (%)
Sky fruit	8.09
Mimosa (Conventional)	29.5

FT-IR analysis of tannin

Fig. 5 and Table III depict the FT-IR analysis of the solvent-extracted tannin. The figure shows various peaks at different wavelengths (cm^{-1}) indicating the presence of different functional groups.

The peak at 805, 1025, and 1224 cm^{-1} wavelength expresses the presence of =C-H, C-F, and C=O functional groups, respectively. The stretch between 1727 and 2856 cm^{-1}

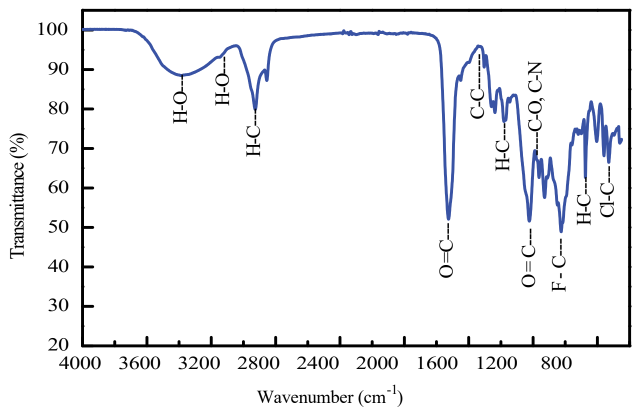

Fig. 5. FT-IR analysis of solvent-extracted tannin agent from sky fruit

represented in Fig. 6. It indicates that the fiber orientations of both the leathers were almost similar and there was no breakdown in the fibres of both samples. This notifies that the proposed sky fruit could be applied as a native alternative tanning agent without affecting the fibre strength of the leather.

Hydrothermal stability

The hydrothermal stability of a material is the measurement of resistance to wet heat. The shrinkage temperature of raw goatskin, pickle pelt, and vegetable-tanned leather is shown in Table IV.

Table III. Functional group analysis of sky fruit

Absorption (cm^{-1})	Functional Groups	Intensity	Type of vibration
622	Alkyl halide (C-Cl)	strong	stretch
805	Alkene (=C-H)	strong	bending
1025	Alkyl halide (C-F)	strong	stretch
1130	Alcohol (C-O), Amine (C- N)	strong, weak medium	stretch
1224	Acid (C=O)	strong	stretch
1382	Alkane (-C-H)	variable	bending
1437	Aromatic (C=C)	medium-weak, multiple bands	stretch
1727	Carbonyl (C=O)	strong	stretch
2856	Alkane (C-H)	strong	stretch
2929	Acid (O-H)	strong, very broad	stretch
3234	Alcohol (O-H)	strong, very broad	stretch, H-bonded

indicates strong interaction of C=O and C-H functional groups. Moreover, at 2929 cm^{-1} wavelength, a strong, broad O-H group was found. Also, the figure implies the presence of the H-bonded O-H group at around 3234 cm^{-1} wavelength. The analysis ensures the presence of the O-H and C=O groups which helps in bonding with collagen during the retanning process. Mavlyanov *et al.* (2001) explained that the O-H and C=O groups of the tannin content is responsible for the cross-linking with collagen through hydrophobic and hydrogen bonding.

Morphological analysis

The fibre orientation of the sky fruit and vegetable tanned leather was observed from the FESEM tomography

In raw goatskin, shrinkage temperature was 64.95ºC but in pickle pelt, it was 52.05º C. This is due to the breaking of the hydrogen bond of triple helices allowing the protein to undergo the transition from helix to a random coil (Covington, 2009). On the other hand, during retanning operation tanning agent changes the collagen structure through crosslinking and prevents the helices from unravelling which means an increase in shrinkage temperature. Therefore, the pickle pelt retanned with the vegetable-tanning (sky fruit) agent increased the shrinkage temperature. It seems that the shrinkage temperature (71.95ºC) was enough compared with the standard value. Therefore, it could be said that the sky fruit has the tannin power to stabilize the collagen and improve stability.

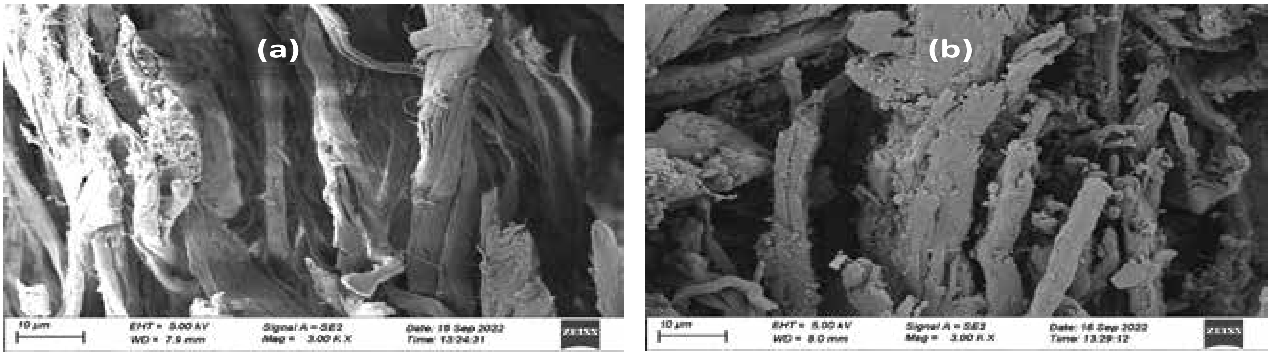

Fig. 6. Morphological analysis of sky fruit leather (a) and conventional mimosa leather (b)

Table IV. Shrinkage temperature

Sample	Experimental (ºC)	Standard (ºC)
Raw skin	64.93 ± 0.5	65
Pickle pelt	52.05 ± 0.4	40-60
Tanned	71.95 ± 0.6	70-80

Table V. Physical properties of sky fruits tanned leather

Sample	Experimental value	Standard value	Reference
Tensile strength (kg/cm^2)	64.93	200	Hashem *et al.* 2017
Elongation at break (%)	52.05	40-65	Hashem *et al.* 2017
Stitch tear strength (kg/cm)	105.01	100	Dutta, 1990
Load at grain crack (kg)	22	20	Kanagaraj *et al.* 2006
Distension at grain crack (mm)	7.7	7	Kanagaraj *et al.* 2006

Physical strength

Sky fruits tanned leather provides excellent physical properties. The most important physical properties are tensile strength and percentage of elongation of leather where tensile strength and percentage of elongation for the powder and aqueous solution treated tanned leather was determined in parallel and perpendicular directions. Both samples showed greater strength of physical property than the standard (Table V).

Conclusion

Retanning operation is the most important process in leather manufacturing. It improves stability and makes the leather: fullness, softness, and grain tightness. The present investigation offers a chrome-free tanning process using natural materials which is available in Bangladesh. Every year Bangladesh imports vegetable tannins from abroad. The sky fruit has a significant amount of retanning agent, which improved the physical properties, and hydrothermal stability of the retanned leather. It could be an alternative source of retanning agents in leather making.In leather processing, Bangladesh could use sky fruit extract, as a retanning agent to save the import cost, which will play important role in the economy of Bangladesh.

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