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A SYSTEMATIC STUDY ON NILE CROCODILE (CROCODYLUSNILOTICUS) SKINS FOR THE PREPARATION OF LEATHER PRODUCTS

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ABSTRACT

Leathers made from crocodile skins have very good market value. The beauty, durability, texture, and extraordinary properties of these leathers have fascinated more people. As a result of increased popularity and use, there is a critical need for baseline information so that the industry can effectively market exotic leather products. In Ethiopia, crocodiles are available in good numbers in the rivers, lakes,and inthe ranch. Ethiopia is considerably exporting the raw crocodile skins to other countries from Arba Minch Crocodile farm. This is due to lack of awareness and technology among the Ethiopian tanners to convert the unique skin into high-value leather products. Exporting crocodile leather products will add manifold foreign exchange earnings compared to raw skins. Hence, in this research, an attempt was made to investigatethe processing technology to convert the Nile crocodile skins into finished leather and leather products by developing suitable process technology. Tanning studies werecarried out on raw skins to standardize the process technology for the conversion of the unique skin into the leather using chrome, mimosa, and combination type procedures. The physic-chemical properties of the resulting leathers were analyzed using standard procedures.The combination tanning method shows better shrinkage temperature ($108.83+0.73^{o}C$), tensile strength ($34.42\underline{+}0.26 N/mm^2$), % elongation ($56.71\underline{+}0.17$), and tear strength ($82.39+0.12 N/mm$) compared to other tanning methods. This study reveals that chrome, mimosa, and combination (Veg-Al, Al-Veg) tanned leather are all exhibit satisfactory quality and performance. Vegetable and combination tanning methods are environmentally friendly and promising options.So, among the exotic skins, crocodile skins are considered as promising raw materials for making leather on large scale in the Ethiopian scenario.

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INTRODUCTION

Leathers made from exotic skins have very good market value. The unique beauty, durability, texture, and extraordinary properties of exotic leathers have fascinated more and more people. As a result of increased popularity and use, there is a critical need for baseline information so the industry can effectively market exotic leather products. In most African countries conversion of snake and crocodile skins into leather is legally allowed for the manufacturing of leather products stated by Karthikeyan *et al*. (2013) and Rajan (2016). Since the back of the crocodile/alligator skins is heavily scaled, coarse, and horny, only their bellies with striking patterns are used. Crocodile/alligator skins, finished unattractive colours, Lizard skins, tanned and finished with characteristic grains in charming shades, Python skins, which are finished with 4 meters long and 20 cm wide, Cobra skins tanned and finished with beautiful scale patterns and attractive colours are used for making exclusive leather goods such as wallets, sophisticated ladies handbags, jeweller's boxes, watch straps, ties, and belts,etc,as stated by Schlaepfe (2005). Traditionally, the domestic demand for leather**,** particularly exotic leather**,** has been for masculine products such as boots, belts, and small goods. Fueled by fashion emphasis, the demand has changed dramatically. Consumers, particularly females, are now seeking apparel products made from *exotic* leather. However, there are only a few domestic manufacturers of such products. Emus, flightless birds that adapt to a wide variety of climates, are another source of exotic leather for the marketplace. Exotic leather such as American alligator and emu are relatively new to the apparel product arena. While cowhide and lambskin been found in other applications such as boots, belts, handbags, and other small goods, specifiedby Belleau (2001). Crocodile leather is exotic leather which as a group, makes up less than 1% of the world's leather production. It is rare compared to other hides such as sheep or cow and requires high levels of craftsmanship to prepare it for use in the consumer industry. Crocodile leather is rare and expensive because of limited numbers of crocodiles, their relatively small size, and the scarcity of dependable farms and tanning facilities to process and prepare the product for the market, indicated by Croco World (web), Exotic (web), Goulding *et al.,* (2007). Crocodile skin is primarily used in the production of handbags and other luxury items such as shoes, belts, wallets, upholstery, and furniture. For these products, Freshwater, Saltwater, and Caiman are used because of the superior quality of skin which when tanned has an aesthetic finish, by and About Crocodile (web). All these skins are valued the same. As one of the largest crocodile species, the Australian Saltwater Crocodile has a reputation for having the most desirable and high-quality hide. This makes it more popular than the smaller Caiman skins which, as a more common species, is a cheaper option noted by Hawkins (2004). The value of a skin is dependent on what it will be used for. Freshwater Crocodile, particularly from New Guinea, is known for its flexibility which allows processors to skive it down to thinness suitable for clothing whereas Nile crocodile, mostly available across Africa, is durable, making it desirable for heavy-duty items such as footwear and beltsgiven by Thorbjarnarson (1999).

The tanning process is the stabilization of the collagen matrix to retain a separated fiber structure and to increase the hydrothermal stability. This is the stage at which the pelt becomes 'leather' and is then resistant to putrefaction or rotting. Organic or inorganic based materials thatcan crosslink with reactive groups of the collagen are used in the tanning process stated by Özgunay *et al*., (2009), Alex *et al*., (2016). Chrome tanning is currently the most popular tanning system in the leather industry because of the excellent qualities of chrome-tanned leather-like high hydrothermal stability, good dyeing characteristics as well as softness defined by Zhou *et al*. (2012). Nowadays, more than 90% of the world's leather is tanned with chromium, which is a consequence of the easy processing, the broad achievability, and the excellent properties of leather. Tanning using Chromium (III) sulphate can achieve shrinkage temperatures above 120°C. However, it also has considerable potential for environmental pollution. The interactions of collagen with chrome have been extensively investigated since the end of the nineteenth century. The fundamental reaction is the formation of complex bonds with the ionized carboxyl groups of aspartic and glutamic acid residues on collagen fibersreferred by Covington (1997). The Nile crocodile's skin is often compared to the American alligator because of its low bone content. It is relatively long compared to its width and it has a particularly long, narrow tail. One of the very distinct features of the skin is the tiny follicle on each of its scales. The scales on this croc are very large and more square than round towards the corners of the tiles stated by Mark (Web). Matte black Nile crocodile leather and polished black Nile crocodile leather are mentionedin Figures 2 (a & b). This research study was undertaken to resolve some of the practical problems that arise when working with exotic leather, in the hope that such an effort would serve to promote the leather industry domestically, particularly in luxury goods and apparel applications. All these aspects put forward to make Research and Development on Crocodile skins using different tanning methods such as: - vegetable, chrome, and combination.

MATERIALS AND METHODS

The fresh Nile crocodile skins were collected from Arba Minch crocodile ranch, Gomo-Gofa zone, South Nation Nationality People Region, Ethiopia. Crocodile the skin was cleaned thoroughly with water and cured with sodium chloride for preserving and to avoid the generation bacteria and micro-organisms.

Processing of Crocodile Skin: The tanning process was carried out in processing wet salted Crocodile skin, using chrome, mimosa powder, and a combination of mimosa and basic aluminiumsulphate. The formulation of the tanning process is given by Kasmudjiastuti *et al*., (2015 and 2017) and Rajan, (2016)

Beam house operation

Trimming and green fleshing: The crocodile skins were trimmed and green fleshed to remove unnecessary parts like edges (legs, tails, backs, etc.), flesh, and non-fibrous protein adhered to the skin.

Pre-soaking: The trimmed Nile crocodile skins were soaked with 2000% water, 0.1% non-ionic wetting agent at 25^0c temperature based on dry salted weight and the skins will be left over the night in the bath and the next day it was washed thoroughly and drained by Kasmudjiastuti *et al*., (2015 and 2017) and Rajan. Karthikeyan (2016)

Main Soaking: With 1500% water, 0.5% non-ionic wetting agent, and 1% preservative (tannic acid) the skins were soaked for the period 48h with frequent handling then it washed thoroughly and drained by Kasmudjiastuti *et al*., (2015 and 2017) and Rajan. Karthikeyan (2016)

Liming (De-Scaling): Skins were treated to remove scales with 300% water, 5% sodium sulphide and 7% of slaked lime for 2 hours at a temperature of 25-30^0C. Then 1.5% sodium sulphide and 4% of slaked lime were added for 2 hours. Next 1.5% sodium sulphide and 4% of slaked lime were added for 1 hour with 300% of water. Between additions, the skins were agitated for 10min and allowed to remain in the bath for 15-18 hours by Kasmudjiastuti *et al*., (2015 and 2017) and Karthikeyan (2016).

Re-liming: After de-scaling the stock was re-limed with 600% water, 10% lime and treated for 24h, then the skins flashed and washed thoroughly then drained by Kasmudjiastuti *et al*., (2015 and 2017) and Rajan. Karthikeyan (2016)

De-liming and Bating: With 400% of water and 0.5% formic acid the crocodile skin was de-limed and hand hauling is done for 25minat 28^0c temperature. Then the skins were treated with 1% of lipase (enzymatic bate) and 0.3% of ammonium sulphate for 60min and washed thoroughly by Kasmudjiastuti *et al*., (2015 and 2017) and Rajan. Karthikeyan (2016)

Bleaching: The dark brown colored pigment adhered to the skin of crocodile is not removed by liming and re-liming process.

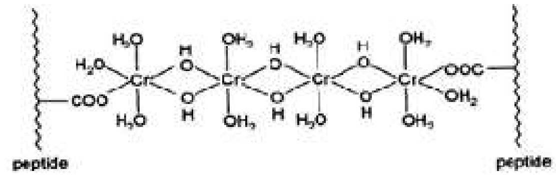

Figure 1. Chrome tanned cross-linkages with collagen (protein) of the skin /hide [Covington (1997), Hussein(2017)]

a)Matte black Nile

b) Polished black Nile

Figure 2. Crocodile leather[Exotic(web)]

To remove the adhered pigment potassium permanganate/sodium sulphite/ chemicals containing chlorine were used. After bating, bleaching of crocodile skin was carried out with 10% Brine solution: 800% water at 5min, 10% Formic acid at 15min, 1.7% Formaldehyde at 20min, and 20% Sodium hypochlorite at 10min. The stock is treated with occasional agitation for every 1hr 10min. Then 1% sodium thiosulphate at 10min was added at skin PH of 4.5 by Kasmudjiastuti *et al*., (2015 and 2017) and Karthikeyan (2016)

Pickling: The bated skins were pickled in a bath containing 100 % water, and 10% common salt (% based on the skin weight) for 10 minutes. Then extra pickling was kept by adding 0.5% formic acid for 15 minutes and 1 % hydrochloric acid 3 times in 10 minutes interval, thenthe bath was left overnight. Next day 1 % of HCl (1 % HCl in 10 % water) was added 2 times for 10 minute's interval, and it was left for 30 minutes. During this process pH of the bath was maintained at 2.9 for chrome tanning by Kasmudjiastuti *et al*., (2015 and 2017) and Karthikeyan (2016)

Chrome Tanning of Nile crocodile Skin: Tanning of skins was carried out in 2 groups and these groups were tanned with 33% basic chromium sulphate in proportions of 6% and 8%. With 50 % pickled water, 8 % basic chromium sulphate (% based on the skin weight), and 1 % Lipsol 622 (Cationic fatliquor) the pickled Nile crocodile skins (PH 2.9) were tanned for 60 minutes in drum running with 8 rpm. Further tanning was kept by adding 8% basic chromium sulphate and 1 % Lipsol 622 (Fat-liquor) for 60 minutes. Then 50% of water is added and the drum runs for 30min. To the running drum, 1% sodium formate (mix with 10% water) is added for 30 minutes. After 30 min 1% sodium bicarbonate (mix with 10% water) is added in 3 feeds at 10-minute intervals and finally, the drum runs for 2hrs maintaining PH at 3.8. Then skins were drained, washed, and piled for 2 days packed in polythene sheet to avoid edges drying out hard. A similar procedure was carried out for 6% basic chromium sulphateby Kasmudjiastuti*et al*., (2015 and 2017) and Karthikeyan (2016).

Vegetable Tanning of Nile Crocodile Skin: The previously pickled pelt wasde-pickled for 1hour in 50% water, 5% sodium bicarbonate (the percentage is based on the weight of the pickled pelt). The pH of the de-pickled skin was maintained at 4.5. Then the de-pickled skins were tanned with vegetable tannin (mimosa) powder by adding 8% tannin and drumming for 60 minutes, followed by 8% tannin for 60 minutes and a further drummed until penetrated. After tannage, a small percentage of 0.1% EDTA (ethylenediaminetetraacetic acid) was added to sequester any iron present, followed by acidification with formic acid to a pH of 3.5. The leather was then given a light wash and dried.A similar procedure was carried out for 6% mimosa powderby Kasmudjiastuti *et al*., (2015 and 2017) and Karthikeyan (2016).

Combination tanning: Initially, the de-pickled skins were treated with 20% tannin and drumming for 60 minutes, followed by 20% tannin for 60 minutes and a further drummed until penetrated. After tannage, a small percentage of 0.1% EDTA (ethylenediaminetetraacetic acid) was added to sequester any iron present, followed by acidification with formic acid to a pH of 3.5. Then the mimosa tanned crust leather was re-tanned with 2% basic aluminiumsulphate for 60 minutes. The stock is washed at 300% water for 10min and piled overnight, a similar procedure was also carried out for 6% byKasmudjiastuti*et al*., (2015 and 2017) and Karthikeyan (2016).

Post tanning operation

Neutralization: After the tanning process the wet blue leathers were neutralized about one hour in a drum containing (150% water, 1.5 % sodium formate), and 1% sodium bicarbonate for 60 minutes in three intervals at rpm of 8 at 30^0c. Then the processed leather was washed and drained. Also, re-tanning, dyeing, and fatliquoring were carried out according to the recipe given by Kasmudjiastuti*et al*., (2015 and 2017) and Karthikeyan (2016). Determination of thickness, Tensile Strength, Percentage elongation at break, tear strength, Ball burst test, hydrothermal stability of leathers, moisture content, Fat Content, Ash Content, Protein (collagen) content of Raw

Aluminum content in Nile crocodile leather were done using standard testing procedures.

Data analysis: The data collected from experimental results were analyzed using descriptive statistics such as mean, percentage, and standard deviations. The data were subjected to analysis using the statistical package for social science (SPSS). A student t-test ANOVA was used to test the level of significance for the means of the resultant physical properties of the chrome, vegetable, and combination tanned leathers at the different concentration levels of the tanning agents.

RESULTS AND DISCUSSION

The parameters of the chemical and physical properties were determined and used to describe the quality and tanning effects in this investigation shown in Table 1.

The moisture content of raw and crust Nile crocodile skin

The average moisture content of the presently studied raw Nile crocodile skin is found to be about 61.45+_0.53% and of crust leather ranges (14.51+0.13- 16.45+0.32 %) as shown in (Table xx).Therefore the raw skin/hide should be preserved after removal to protect it from the bacterial attack. If the skin/hide is not preserved, the various bacteria (aerobic, anaerobic, and facultative) will grow and are involved in the degradation of collagen stated by Kanagaraj (2002). Also in crust leather to facilitate the mechanical operations, the moisture content of the dried leather should be around 12-18%. If the moisture content is above the standard values the resultant leather becomes looser, causesthe formation of mould and increasing flabbiness, and below the standard values will result in susceptible to embrittlement and crankiness of the grain defined by Liu (2011).

The fat content of raw and crust Nile crocodile skin: The amount of natural fat present in various animal skins and hides varied depending on the age, sex, and breed of the animals. As indicated by different researchers, it varies between 3 -50% in sheep-skins, 0.5 -12% in cattle and horse hides, 7.14-8.44% in ostrich skins, 0.24 - 44.07% in fish skins, 4% - 40% in pig-skin, and 3% - 10% in goat-skin over dry weightsdescribed by Ozgunay(2007), Belleau (2001), Pratama (2018) and María (2017). So, the evaluation of natural fat in presently studied raw Nile crocodile skin was 2.94± 0. 16% and the fat contents crust leather ranges between (3.2±0.33 -4.2+0.51%) which had lower values compared to sheep, fish, ostrich and pig skins whereas, it shared similar values with cattle hides, horse hides, and goat skins. It revealed that the obtained result was quite normal. So, if the fat in rawhide and skin structure is not removed, it affects other processes adversely by prohibiting the penetration of chemicals into the skin/hide in further processes, and may also cause a strong smell, an increase in micro-organism activity and defects like spew on leathers and it also prevents the hydrophilic activities of chemicals (liquoring agents) and, therefore, some undesirable quality problems such as hardness to touch, loss of some physical strength, and dyeing imperfection occurs in the finished product. For this reason, the excess amounts of fat in skins and hides are removed before tanning by applying a degreasing process byFasil (2015).

Ash content of raw and crust Nile crocodile skin: The ash content of the raw Nile crocodile was 1.43+0.12. And the ash of crust leather with different tanning concentrations chrome (6 and 8%), mimosa (6 and 8%), combination tanning 20% mimosa with aluminium (5 and 10%) and aluminium (5 and10%) with 20% mimosa ranges (1.84 - 2.81) as indicated in table 1. However, all values obtained are quite normal and realize the minimum requirements standards set by UNIDO (1996) and comparable to those reported by Musa *et al*., (2011), Ebtesam *et al*., (2014),and Musa*et al* (2013). In contrast, a very wide range of ash content (1-75%) was obtained by Haroun *et al*., (2012).

The protein content of raw Nile crocodile skin: The crude protein (collagen) content in the samples of the present study was found to be 28.69+0.38 %. This reveals that a maximum amount of leather forming collagen exists in the skin tissue which is the true leather making protein present in the skin, and the skin isused to produce exotic leather and leather products by tanning with various tanning methods. It is also shown that the skin of crocodiles iscomposed of higher proportions of leather forming material called collagen, in comparison to other structural proteins such as elastin, keratin, and reticulin reported by Karthikeyan (2016).

The thickness of raw and tanned Nile crocodile leather: In the presently studied, the thickness of raw skin and crust leather was determined. The thickness of raw skin was 2.83+0.41mm and crust leather produced to the different Chrome, mimosa, and combination tanning concentrations used to range between 3.13±0.21-3.82±0.11mm. As many properties will depend on the thickness, it is measured to express the test results concerning the thickness as a means of production control and determining the conformance of specifications. Animal skins or hides are not uniform, which means there isa big difference in thickness and type of fibril weaving existing in different areas of a hide or skin. This shows that the hide or skin does not have the same thickness overall its cross-section reported by Ebtesam*et al*, (2014).

Determination of chrome and Aluminium oxides in crust leather: In the presently studied the result of chrome content of crust leather with the concentration of (6 and 8%) showed 1.62+0. 32 % and 1.96+0. 11% respectively. While 20% vegetable (mimosa) pre-tanning with (5 and 10%) BAS re-tanning and (5 and 10%) BAS pre-tanning with 20% vegetable (mimosa) re-tanning showed 2.56±0.31%, 2.79±0.42%, 2.45±0.16% and 2.64±0.05% respectively. The obtained result is quite normal and fulfils standard set by UNIDO which stats max. 2.5% for chrome oxide and min. 2% for Aluminium oxide. The physical properties that were determined are: tensile strength, tearing strength, distension at grain cracking, shrinkage temperature, and thickness, and shown in Table 2.

Tensile strength test: In the present study tensile strength of chrome, Vegetable (mimosa), and combination (mimosa-Al, Al- mimosa) tanned leathers were determined and compared. The mean values corresponding to each experiment are given in Figure 4. The tensile strength of leathers tanned with different chrome and vegetable (mimosa) concentrations of (6%, and 8%) offers 28.74±0.53 N/mm^2, 27.32±0.59 N/mm^2, 22.80±0.14 N/mm^2 and 24.92+0.66 N/mm^2 respectively. The obtained values are quite normal.The strength of chrome-tanned leather is close to the mimosa-Aluminium combination of tanned leather. According to the results, values of chrome-tanned leather were higher in tensile strength values compared to the vegetable (mimosa) tanned and Aluminium -Vegetable tanned leathers. The tensile strength of 20% vegetable (mimosa) pre-tanning followed by 10% aluminum re-tanning was (34.42±0.26 N/mm^2) and 20% vegetable (mimosa)

Table 1.Chemical analysis of rawskin and crust Nile crocodile leather

Test parameter	Raw skin	Mimosa (8%)	Mimosa (6%)	Chrome (8%)	Chrome (6%)	20%Mimosa-10%Aluminium	20% Mimosa-5% Aluminium	10%Aluminium -20% Mimosa	5%Aluminium-20% Mimosa
Thickness	2.83±0.41	3.82±0.11	3.61±0.41	3.24±0.02	3.13±0.21	3.77±0.32	3.63±0.51	3.58±0.35	3.47±0.43
Moisture content %	61.45±0.53	16.45±0.32	16.41±0.12	14.82±0.56	14.51±0.13	16.26±0.38	16.21±0.26	16.32±0.13	15.62±0.54
Ash content %	1.43±0. 12	1.84±0.36	1.92±0.43	2.532.63±0.34	2.52±0.48	2.81±0.52	2.42±0.27	2.63±0.14	2.482.63±0.82
Fat content %	2.94±0.16	3.4±0. 21	3.7±0. 12	3.2±0. 33	3.5±0. 13	4.1±0. 14	3.6±0. 02	3.9±0. 19	4.2±0. 51
Protein content %	28.69±0.38	-	-	-	-	-	-	-	-
chrome content %	-	-	-	1.96±0. 11	1.62±0. 32	-	-	-	-
Aluminium content %	-	-	-	-	-	2.79±0. 42	2.56±0. 31	2.64±0. 05	2.45±0. 16

Table 2.Physical Analysis of chrome, vegetable, and combination tanned leather

Tanning concentration	Shrinkage Temperature (ºc)	Tensile strength (N/mm^2)	Elongation at break (%)	Tear strength (N/mm)	Distension at grain cracking (mm)
Mimosa (8%)	83.34±0.81	24.92±0.66	44.34±0.43	53.65±0.92	11.43±0.13
Mimosa (6%)	78.45±0.12	22.80±0.14	41.57±0.82	51.31±0.78	10.66±0.11
Chrome (8%)	108.56±0.35	28.74±0.53	53.23±0.35	75.43±0.39	13.17±0.09
Chrome (6%)	101.28±0.46	27.32±0.59	50.60±0.65	65.69±0.95	12.75±0.15
20% Mimosa- 10% Aluminium	108.83±0.73	34.42±0.26	56.71±0.17	82.39±0.12	14.35±0.41
20% Mimosa- 5% Aluminium	104.79±0.51	32.17±0.19	54.56±0.55	78.14±0.19	13.57±0.62
10%Aluminium-20% Mimosa	92.92± 0.21	24.63±0.37	43.34±0.84	56.71±0.52	11.83±0.59
5%Aluminium-20% Mimosa	94.38±0.52	26.52±0.15	48.81±0.96	62.12±0.49	10.91±0.28

Figure 3. The presently tanned leather products

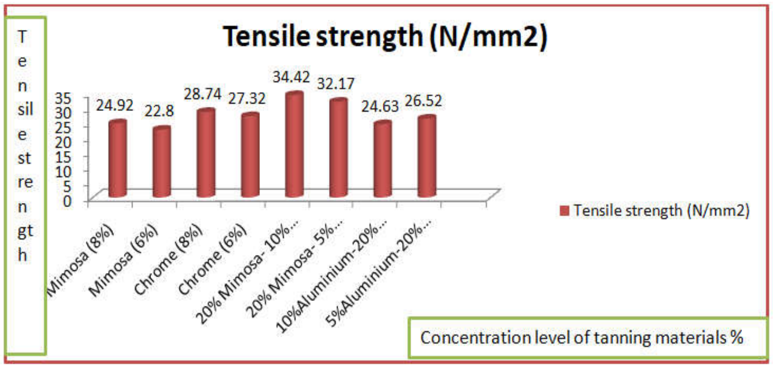

Figure 4. Tensile Strength of the Treated Leather

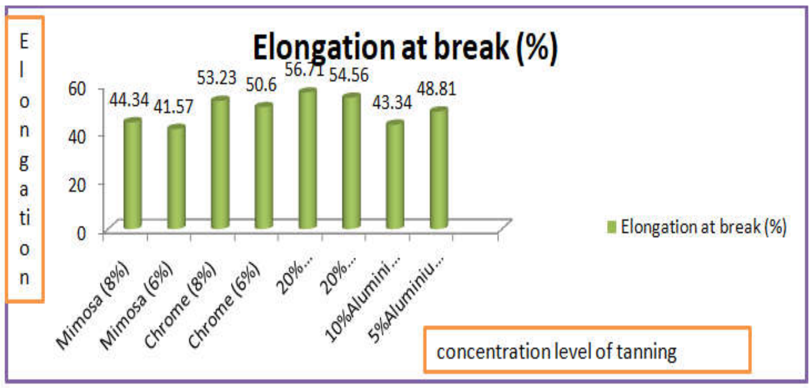

Figure 5.Elongation of Leather

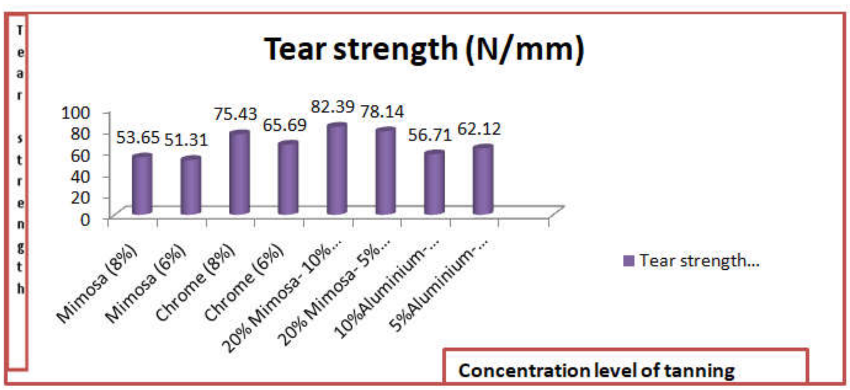

Figure 6. Tear Strength

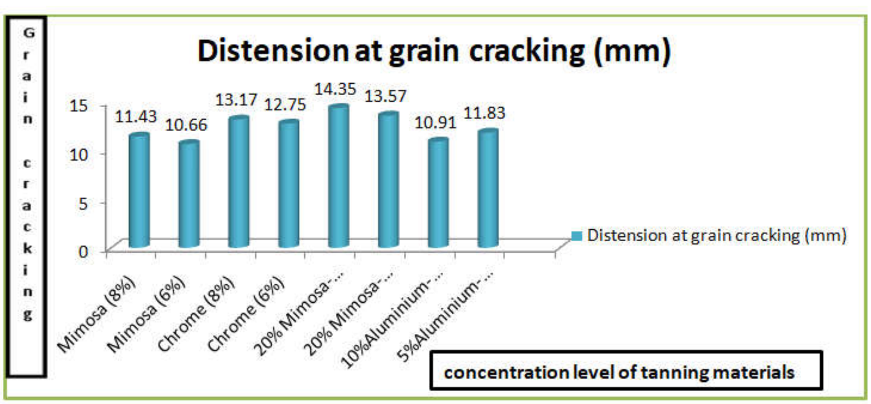

Figure 7. Distension at grain cracking

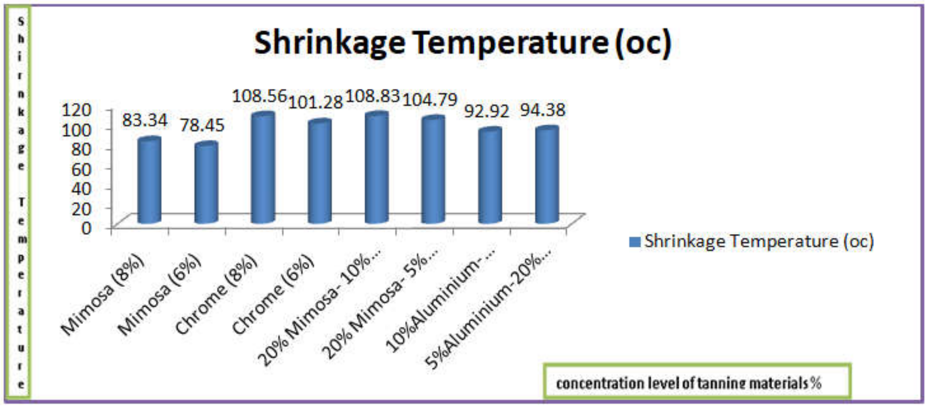

Figure 8. Shrinkage Temperature of Leather

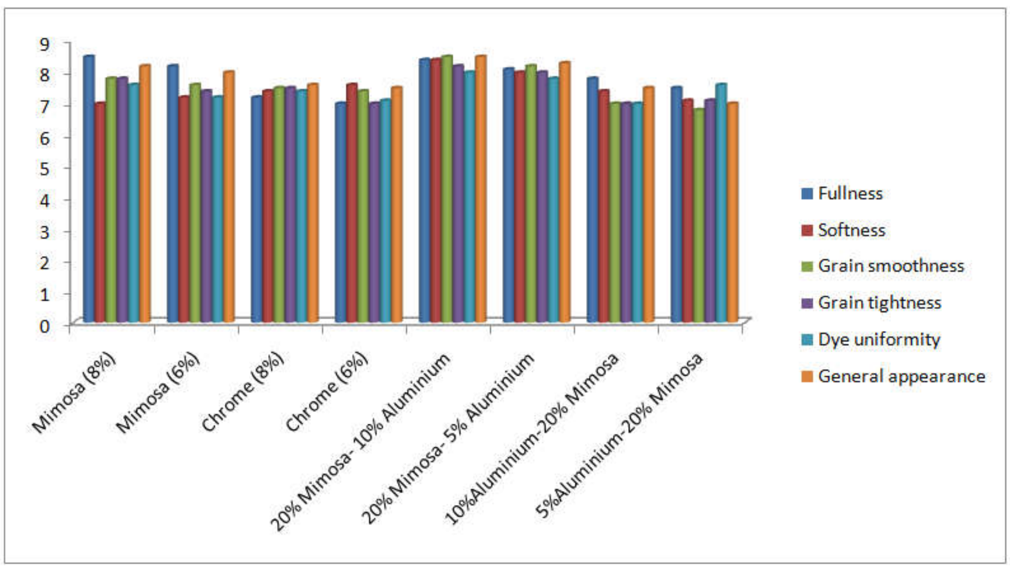

Figure 9. Functional Properties of Leather

pre-tanning followed by 5% aluminum re-tanning (32.17±0.19N/mm^2) showed higher values compared to 10% aluminum pre-tanning followed by 20% vegetable re-tanning (24.63+0.37 N/mm^2) and 5% aluminum pre-tanning followed by 20% vegetable re-tanning (26..52±0.15N/mm^2) (Fig. xx). As indicated in research conducted by Musa *et al.*(2011), the introduction of basic aluminiumsulphate into the tanning system as a re-tannage agent produces a definitive improvement in the strength properties of the leather and the fiber bundles are well separated in the case of Al-Vegetable tanned leather; while Vegetable -Al tanned leather shows cemented fiber bundles. This reveals that Vegetable-Al tanned leather would show evidence of high tensile strength with low softness whereas Al-Vegetable tanned leather would exhibit low strength with high softness. The value tensile strength increased as long as the increased tanning agent concentration. The highest value of tensile strength was obtained by using 20% mimosa pre-tanned and re-tanned with (5 and 10%) basic Aluminiumsulphate tanning agent. The increase of tensile strength value probably was due to the reactivity of tanning agents to the collagen fibers. The presence of –OH functional groups in vegetable tanning agents that reacted completely with NH_2 functional groups from collagen can alter the

More tanning agents added would give higher crosslink density into leather, thus gives better tensile strength.Also, the results of tensile strength measurement were affected by fiber tissues of skin collagen, physical structure, rawhide chemical substance, and the tanning agents. UNIDO offers a minimum of 10N/mm^2, 15 N/mm^2, and 20 N/mm^2 of tensile strength for chromium tanned garment leathers, linings, and shoe upper leathers respectively. The tensile strengths of the leathers tanned by all the three (chrome, vegetable, and combination) tanning materials in the current study were above the expected minimum of 20N/mm^2 shoe upper leathers stated in UNIDO (1996). So, the experimental result shows that in each method the value of tensile strength is higher than the standard value. An increase in the tensile strength can be interpreted in terms of the number of covalent cross-links formed during the tanning processes. However, a decrease in the tensile strength at a higher concentration of aluminium re-tanning (10%) may be due to the increased stiffness which is shown by the decreasing elongation and results in a brittle fiber; consequently, it breaks more easily at a reduced load stated by Mahdi (2012). The results revealed a significant difference ($p < 0.05$) in tensile strength. Leathers tanned with a mimosa (6%) had the lowest tensile strength of 22.80±0.14N/mm^2 while strength of 34.42±0.26N/mm^2. The results of elongation test of crocodile leather tanned by using chrome (6 and 8%) and mimosa (6 and 8%) tanning agents obtained were 50.60±0.65, 53.23±0.35, 41.57±0.82 and 44.34±0.43 %) respectively. While elongation of leather tanned using 20% vegetable (mimosa) pre-tanning with (5 and 10%) BAS re-tanning and (5 and 10%) BAS pre-tanning re-tanning with 20% vegetable (mimosa) re-tanning showed 54.56+0.55, 56.71+0.17, 48.81+0.96 and 43.34+0.84 % respectively. In this study, it was observed that leathers tanned with 20% vegetable (mimosa) pre-tanning re-tanning with 10% BAS re-tanning showed the maximum percentage of elongation whereas leather tanned with a mimosa (6%) had the lowest percentage of elongation (41.57±0.82 %) compared to the rest of experimental results (Fig 5). The obtained result is quite normal and fulfils the expected minimum of 40-75% set by BIS (1992) for resin finished shoe upper leather from goat and sheep skins reported in BIS (1992). The result revealed that the elongation of leather has increased along with an increase of tanning agent concentration except for 10% BAS pre-tanning with 20% vegetable (mimosa) re-tanning method which is stiff and resulted ina brittle fiber. So, it is concluded that the value of elongation is related to leather elasticity.

Tearing strength: The tearing strength indicates the strength of the fibers and their cohesive force. It is the maximum limit of the skin to be torn reported by Dutta(1999). A minimum standard value offered by UNIDO is 15N/mm, 25 N/mm, and 30 N/mm of tear strength for chromium tanned garment leathers, linings, and shoe upper leathers respectively. From the above figure 6, it has been found that the tear strength of tanning methods wasquite higher than the standard of the upper leather. The result of the current study of tear strength using chrome (6 and 8%) and mimosa (6 and 8%) tanning agent showed 65.69±0.95N/mm, 75.43+0.39 N/mm, 51.31+0.78 N/mm and 53.65+0.92 N/mm respectively. While tear strength of leather tanned using 20% vegetable (mimosa) pre-tanning with (5 and 10%) BAS re-tanning and (5 and 10%) BAS pre-tanning with 20% vegetable (mimosa) re- tanning showed 78.14±0.19 N/mm, 82.39±0.12 N/mm, 62.12±0.49 N/mm and 56.71+0.52 N/mm respectively. It is suggested that the tear strength of leather is affected by the change in skin structure and high protein fiber composition. The tear strength will be lower during liming and fleshing and will have high value when the collagen fiber is held and bonded strongly with the tanning materials reported by Indri Hermiyati *et al*., (2017).

Ball burst test: The ball burst test is another physical property for testing the quality of leathers. It is intended to indicate the grain resistance to cracking during top lasting of the shoe uppers. The distention grain crack values for chrome (6 and 8%) were12.75±0.15 mm and 13.17±0.09 mm, for vegetable (mimosa) was 10.66±0.11mm and 11.43±0.13 mm respectively. while the distention grain crack of 20% vegetable (mimosa) pre-tanned and re-tanned with (5 and 10) and (5 and 10%) basic Aluminiumsulphate pre-tanned and re-tanned with 20% vegetable (mimosa) was 13.57±0.62 mm, 14.35±0.41 mm, 11.83±0.59 mm and 10.91±0.28 mm respectively. All the leathers tested had more than 7.0 mm of the minimum recommended value for distention grain cracking tests of UNIDO (1996) as indicated in figure 7 below.

Shrinkage temperature (Ts) ^{0}c: In the present study, it has shown that the shrinkage temperatures of tanning using chrome salts (6%, 8%), mimosa (6%, 8%) and combination of mimosa (20%) and aluminium salts (5%, 10%) and vice versa were measured using shrinkage tester. The shrinkage temperature data for chrome, mimosa, and combinations of mimosa and aluminium combination tanning methods are given in Fig 8. The shrinkage temperature for the chrome (6%, 8%) and mimosa (6%, 8%) tanned crust leather was found to be 108.56^{o}C, 101.28^{o}C, 83.34^{o}C and 78.45^{o}C respectively (Table 6). This is because the shrinkage temperature tendto increase with the increase of tanning (chrome and mimosa) concentrations. The skin fibers treated with vegetable as a pre-tanning agent exhibited stability against wet heat and the shrinkage temperature for 20% mimosa pre-tanning with different aluminiumre-tanning percentages (5%, 10%) was found to be 104.79^{o}C and 108.83^{o}C respectively. This due to the increased formation of cross-links and the effects of aluminium, as one of the vegetables– aluminium combination tanning systems, on the stability of the complexes and bond formation, thus increasing the hydrothermal stability of the resultant leathers stated by A.E Musa *et al*., (2011). On the other hand, the skin fibers treated with aluminium as a pre-tanning agent (5%, 10%) produced a shrinkage temperature of 94.38^{o}C and 92.92^{o}C, respectively. Therefore, it can be concluded from the result that vegetable pre-tanning reveals an increase in the shrinkage temperature when compared with aluminium pre-tanning. This improved hydrothermal stability of vegetable pre-tanning is due to new cross-links formed and consequent changes in the tertiary structure of the skin collagen.

The shrinkage temperature of chrome-tanned leather is the same asthe veg -Al tanned leather. According to the results obtained vegetable -Al tanned leathers were the alternative option replacing chrome tanning. It is observed that leathers treated with 20% mimosa retanned with 10% Basic Aluminiumsulphate exhibits higher shrinkage temperature. The shrinkage temperature of leathers obtained from combination tanning of mimosa-Al is slightly higher than Al-mimosa combination tanning methods. Both the combination tanning systems mimosa-Al and Al-mimosa resulted in leathers with shrinkage temperature above 90°C. As indicated in combination tanning, vegetable tannins can penetrate the collagen inter-fibrillar space making the collagen peptide groups more accessible to aluminium tannins. In contrast, in the present study using aluminium as a re-tanning agent is much better than pre-tanning; this is because aluminium possibly tightens the collagen fiber network, preventing high molecular weight vegetable tannins from interacting with collagen fibers. The other possibility is that the free amino acid side chains of collagens are exhausted on pre-tanning with aluminium, reducing the number of collagen–aluminium-vegetable tannin cross-links when vegetable tannins are introduced reported by Mahdi *et al*., (2008). The higher the thermal stability or shrinkage temperature confirms the higher amount of cross-links in the collagen matrix. In combination-tanning using metals and vegetable tanning agents, the order of tanning is important concerning hydrothermal stability of the leather. Re-tanning of metal- tanned leather with vegetable tannin confers lower shrinkage temperature, while re-tanning of vegetable tanned leather with metal salt results in a synergistically increased shrinkage temperature. So, in regards to the mechanism of re-tanning of vegetable tanned leather with metal salts, metal ions form complexes with the already bound tannin molecules and form covalent links with the carboxyl groups of collagen by Duki *et al*., (2013).

On the other hand, the hydrothermal stability of the leather was not improved by using aluminium as pre-tanning agent this because the synergistic interaction between the polyphenol and the aluminium may arise from one of the following options:

Collagen-Al-Veg-Al-Collagen
Collagen-Veg-Al-Veg-Collagen
Collagen-Veg-Al-Collagen

It is known that applying the aluminium salts before the vegetable tannins produce only moderate shrinkage temperature, with characteristics of aluminium salts alone. Therefore, the first and third options are unlikely. The most probable mechanism is for the aluminium salts (III) to crosslink the vegetable tannins. The cross-linking polyphenol on collagen is itself cross-linked; to form a matrix within the collagen matrix, to stabilize the collagen by a multiplicity of connected hydrogen bonds in the new macromolecule explained Mahdi *et al*., (2009). So, the use of a combination tanner using mimosa and aluminium is recommended in the process of leather tanning to improve and enhance the quality of the raw material of leather, to reduce the environmental pollution generated by chrome (chromium III salts) and results in leathers with good thermal stability and organoleptic properties that areimportant for commercial viability of the tanning system.

Crust leathers from experimental processes have been evaluated for various bulk properties by hand and visual evaluation. The crust leathers were rated (on a scale of 1-10 where 1 is the poorest and 10 is the best) for each functional property by three professional tanners and two researchers. The average rating for the leathers has been calculated for each functional property and is given in and figure 9. Higher numbers indicate better property. From the figure, it is observed that mimosa pre tanned and re-tanned with basic Aluminumsulphate experimental crust leathers exhibited good softness, smoothness, general appearance, and dye uniformity compared to leathers from mimosa, chrome, and basic Aluminumsulphatetannage pre tanned and re-tanned with a mimosa. The organoleptic properties of the mimosa -Al crust leathers are better compared to mimosa, chrome, and Al-mimosa crust leathers.

Conclusion

This study indicates that chrome, mimosa, and combination (Veg-Al, Al-Veg) tanning agents are better and exhibit satisfactory performance in the production of crocodile leather and leather goods. The combination tanning method shows better shrinkage temperature (108.83+0.73^{o}C), tensile strength (34.42$\pm$0.26N/mm^2), % elongation (56.71$\pm$0.17) and tear strength (82.39+0.12N/mm) as compared to Basic Chrome sulphate and Vegetable (mimosa) tanning methods. The physical and chemical characteristics of experimental leathers are quite normal and fulfil the minimum requirements. It was also observed that mimosa pre-tanned and re-tanned with basic Aluminiumsulphate experimental crust leathers exhibited good softness, smoothness, general appearance, and dye uniformity compared to leathers from mimosa, chrome, and basic Aluminiumsulphatetannage pre-tanned and re-tanned with a mimosa.Vegetable and combination tanning methods are the best and one of the most promising options as they are an environmentally benign process.

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