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Research Paper

Investigation of clay minerals (Kaolinite and halloysite) as a green leather tanning agent

Nelly Maina[1*], Douglas Onyancha[2], Paul Sang[3]

[1,2,3]Chemistry department, Dedan Kimathi University of Technology, Private bag – 10143, Dedan Kimathi, Nyeri – Kenya

**Corresponding Author: wmainanelly@gmail.com*

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Abstract— Tanning involves the stabilization of hides and skins with the use of organic or inorganic chemicals. Inorganic tannings include chromium tannage, alum tannage, zirconium tannage, etc. Among these, chrome tannage is the most preferred tanning method due to the superior properties it impacts on leather. Despite its popularity, there has been a rising concern about the environmental impact brought about by chromium tanning and as a result, researchers have embarked on a search for a more suitable alternative to chromium tanning. This study explored the use of clay as an economical and eco-friendly tanning agent. XRD and XRF analysis was done to identify the type of clay obtained from Murang'a quarry, Kabuta region in Kenya, and determine its physical and chemical composition. The finding indicated that the two clays were kaolinite and halloysite. Their XRD peaks were observed at a basal spacing of 7.14º and 7.2º respectively with SiO_2 and Al_2O_3 being the major elements with percentages ranging between 50%-40% and 40%-25% respectively. The clay samples were then modified using concentrated formic acid and used to tan goat skin. The physical properties of leathers obtained were analysed using IUP standard method which included the tensile strength and elongation at break, shrinkage temperature, tear strength, grain crack, and grain burst tests. From the results, both leathers tanned with kaolinite and halloysite had attained the minimum recommended values for all the tests. Moreover, leather tanned using halloysite had better physical properties compared to that tanned using kaolinite. From this study, clay can be used as an alternative tanning agent to chromium.

Keywords— X-ray diffractometer (XRD), X-ray fluorescence (XRF), kaolinite, halloysite.

1. Introduction

Collagen which is a natural material that has good biological compatibility and well characterized low astringency is a major component of the skin [1]. Its constituent is a triple helix that is made up of three polypeptide chains enfolded together in a coiled form that sums up into a dense structural level of microfibrils, fibrils, fibres and tissues[2].

Collagen is the main type of protein used during leather production where the appropriate tanning agent is used to stabilize it [3]. Raw or untreated hides and skin have diminutive value as they are more prone to putrefaction due to bacterial attack. As a result tanning is necessary where raw hides and skins are converted into a more a durable material [4, 5]. A variety of tanning agents such as vegetable tanning, oil tanning, chrome tanning, aldehyde tanning, zirconium tanning, and aluminium tanning among others are used during the tanning process [6]. Each of the tanning agent links with a functional group of collagen differently from the other and thus exhibit different physical and chemical properties[7].

Different types of mineral tanning have been used for centuries but chromium III salts have been dominant occupying about 90% of the world's tanning practices [8]. It is preferred by most tanners because of its ability to impart superior properties such as high thermal stability, flexibility and its ability to penetrate easily to the skin even at low applications [9]. This is achieved because chromium is a transition element and has 3d orbitals which give extra room for electrons to form coordinate complexes which then react with ionized carboxyl groups of the collagen to form strong covalent bonds [10]. However, there have been serious concerns regarding the environmental pollution caused by the use of chrome III salt during tanning. If the chrome tanning waste is not well managed, the Cr (III) and undergoes oxidation to Cr (IV) which is highly carcinogenic and may cause serious health issues to human beings [11]

New and eco-friendly methods of leather tanning have been researched and applied in an attempt to mitigate the environmental effects caused by the leather industry. Aluminium sulphate has been used as a tanning agent as it has less effect on the environment compared to chrome tanning. It is known to have lower thermal stability compared to other tannages as it does not form strong covalent bonds and its interaction with the collagen is based on electrostatic interaction [5]. Zirconium IV salts have also been used in tanning. The zirconium salts interact with the amino groups of the collagen creating more stable coordinate bonds. [12] They are however expensive and are limited in application due to its hydrophilic nature.

Phosphonium compounds(Tetrakis (hydroxymethyl) phosphonium sulphate (THPS)) are also a possible metal-free alternative used in leather tanning and is mostly used in production of orthopaedic leather[13]. It forms stable covalent links with the amino groups of the collagen as well as hydrogen bonding with the hydroxyl groups [14].

In this study, the possibility of using clay mineral as an alternative to chrome tanning was explored in a quest to utilize its environment friendly properties compared to chrome. The composition of clay consists of aluminium and silicon among other elements that have been used in tanning.
Clay is a group of hydrated aluminosilicates that have a similar chemical and structural composition which originate from the earth's crust as a result of weathering [15]. The use of clay in most industries has been rampant due to its economic benefits, availability, and its environmental friendliness in comparison to other raw materials [16]. Clay also possesses great physical and chemical properties that can be modified through thermal and acid treatments and as a result diversifying its uses.[17]

2. Related Work

Natural tanning agents have been employed in leather processing. For example, zeolites haves been investigated for their possibility to be used as a cleaner tanning agent [18]. In this study, combined tanning of zeolite-chrome tanning was done on sheepskin and calfskins pelts which resulted to improved float exhaustion, higher shrinkage temperature and reduced leather processing time for chrome tanning.

Clay materials such as kaolin have been used as a source of aluminum sulphate which is then used for leather tanning [19]. China *et al* explored the use of the prepared aluminum sulphate from kaolin in combined tannage with mimosa vegetable tannins. The leather obtained from this research exhibited excellent physical properties and a thermal stability of above 100ºC while using 2% concentration of aluminum sulphate. Better fiber separation was also observed during processing making it a suitable material to be used in the leather industry.

Laponite clay nanoparticles have also been used to reduce probable HCHO hazard and improve leather performance. Tetrakis (hydroxymethyl phosphonium sulphate) [THPS] was used together with clay laponite nanoparticles in tanning which resulted to improved thermal stability and reduced HCHO levels which was attributed to the conjoint effects of THPS and clay laponite [20].

Marukhlenko *et al*. investigated the capability of chromium-modified montmorillonite diffusions in fixing the collagen which resulted in better float exhaustion of up to 30% of chromium complexes and improved physical and mechanical properties [21].

3. Materials and Methods

3.1 Materials and chemicals

Pickled skins from Sagana tanners, Kirinyanga County, Kenya were used for this experiment. Clay samples from, the Kabuta region in Murang'a County of Kenya were sourced in two distinct layers namely: the top layer (mined three feet to the ground), and the bottom layer (mined seven feet to the ground). The chemicals used in all stages of the leather processing were of commercial grade and were purchased locally.

3.2 METHODS

3.2.1 Characterization of clay

Determination of the chemical composition of the clay samples was done using X-Ray Fluorescence (XRF) spectrometer, S1 TITAN 500 S model with an SDD silicon drift detector and a resolution of 145 eV.
The physical properties of the clay samples were carried out using a Rigaku MiniFlex II X-Ray diffractometer in Bragg-Brentano (configuration 2θ), 1.540598 A Cu-Ka 1 radiation.

3.2.2 Modification of clay

The clay was crushed into Powderly form, sieved using a 300 µm sieve, and purified by washing it with distilled water through filtration. It was then placed in the oven at 103˚c for 12 h to remove any moisture content after which it was cooled to room temperature in a desiccator.
Concentrated formic acid in the ratio of 1:3 (v/w) was sprayed slowly and continuously while mixing the resulting mixture. The mixture was left to dry before subsequent use.

3.2.3 Clay tanning

The tanning of the pickled skins was done according to process described in Table 1.
Both the modified and unmodified clay samples were used for tanning. Two pickled skins were cut in two halves (from the head to the tail). The four halves that were obtained were labelled I, II, III and IV. Each halve was tanned using the following different clay tanning agents respectively:

I. Modified top-layer clay
II. Unmodified top-layer clay
III. Modified bottom layer clay
IV. Unmodified bottom layer clay

A common tanning recipe was followed during the tanning process which is outlined in Table 1.
Chemicals were administered based on the weight of the pickled skins.

Table 1. Clay tanning process for both modified and unmodified clays on goat skin.

PROCESS	PRODUCT	PERCENTAGE (%)	RUN TIME (MINUTES)	pH	REMARKS
Wetting	Water	100			D/W/D

agent	Wetting agent	1	30		
Depickle	Water Sodium formate Sodium bicarbonate	100 2 0.5	30 Added 5 times with intervals of 20 minutes each	7	D/W/D For 15 minutes
Tanning	Water Formic acid Formic acid Sulphuric acid Clay Clay	100 1 1 0.2 1 2	 30 30 60 60 60	2.7-3.0	Penetration was checked from the neck region
Activation	Sodium formate Sodium bicarbonate	1.5 2.0	An addition was done in 4 batches with intervals of 60 minutes	4.2-4.8	Activation allowed the clay to be fixed in the leather and had a tanning effect

3.2.4 Physical testing of clay-tanned leather

The physical testing of the tanned leather was done as follows:
First, conditioning of the leather was done at a temperature of 25 ± 2°C and humidity levels of 65 ± 2% for 48 hours according to IUP 3 (2001) followed by sampling and cutting for physical tests according to IUP 2 (2001). Cutting was done parallel and perpendicular to the backbone. The physical properties tests done were: tensile strength and elongation at break done according to IUP 6 (2001) tear load IUP 8 (2001), shrinkage temperature IUP 16 (2001), grain crack and grain burst IUP 9 (2001) which were analysed in triplicates [22].

4. Results and Discussion

4.1 Sample characterization

The analysis of the clay samples using XRD was done and the spectra are shown in Figure 1 and 2. Figure 1 from the top layer clay sample displayed prominent diffraction peak of 2θ,12.38° corresponding to a d-spacing of 7.14, a second peak was observed at a 2θ, 20.36° corresponding to a d-spacing 4.359 and the third peak at 2θ, 25.1° corresponding to a d-spacing 3.55. From the finding this layer was identified to be kaolinite. These findings correlate well with the report of Kim H. Tan [23] who analysed the principles of soil chemistry including clay minerals such as kaolinite which were identified by a d-spacing of 7.14 during the XRD analysis.

Figure 2 showed a diffraction peak at 2θ,12.3° corresponding to a d-spacing of 7.2 and a second peak at 2θ, 20.7° which corresponds to a d-spacing of 4.30. This was identified as halloysite. The findings are similar to the reports of [23, 24] who analyzed halloysite clay samples for their properties and morphology.

Both, kaolinite and halloysite have a similar molecular structure i.e., $Al_2O_3.2SiO_2:2H_2O$ but the main difference lies in their crystal structure. Halloysite has disorderly layers of aluminum octahedral and silicon tetrahedral layers stacked together and an interlayer of water present between them [25]. Halloysite also has a unique nanotubular structure whose length can be 0.02µm to >30µm, [26] the external diameter is nearly 30-190 nm, and internal diameter 10-100nm [27] while kaolinite has a pseudo-hexagonal plate structure that has a diameter of 1µm [28]

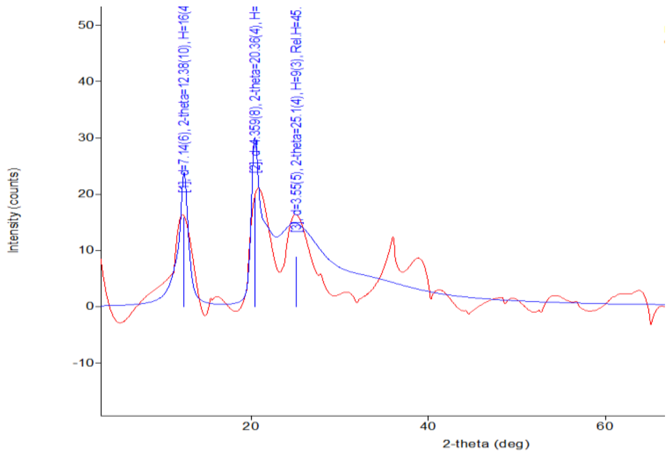

Figure 1. XRD peaks for the top layer

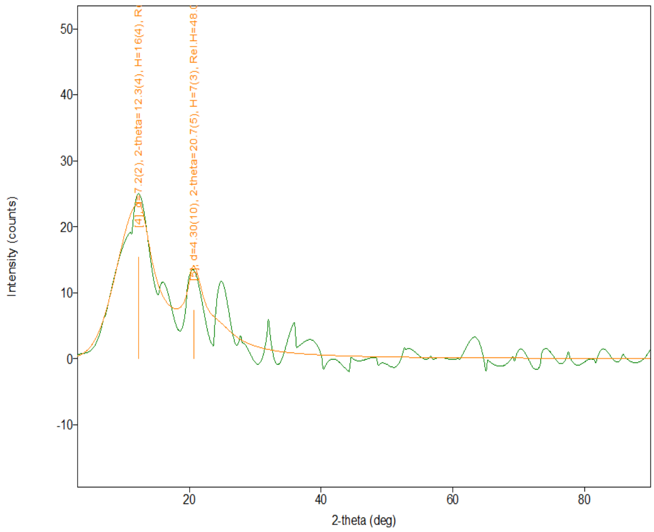

Figure 2. XRD peaks for the bottom layer

The chemical composition of the clay was analysed by XRF and the percentage compositions are shown in Table 2. The SiO_2 quantity was 50.203% for kaolinite clay and 42.915% for halloysite clay. Al_2O_3 was found to be 37.090% and 30.690% for kaolinite and halloysite respectively. The two compounds were found to be more dominant in the clay minerals. Significant amounts of iron and titanium were also present especially for the halloysite. Calcium oxide, potassium oxide, and manganese composition are also shown in Table 2. These results are in agreement with the results reported in the literature by Ombaka who carried out a study on characterisation and classification of clay minerals in Rugi Ward Kenya and found comparable mineral composition [29].

Table 2. Chemical composition of the unmodified clay samples

Elements	Unmodified top layer (kaolinite)	Unmodified bottom layer (halloysite)
SiO_2	50.203	42.915
Al_2O_3	37.090	30.690
CaO	0.379	0.549
K_2O	0.213	0.0216
Fe	8.532	21.171
Ti	3.063	3.459
Mn	0.211	0.280

4.2 Modified clay samples

The modified clay samples were subjected to an XRF analysis and a difference in chemical composition of the clay was observed as indicated in Table 3. For kaolinite, the SiO_2 quantity dropped from 50.203% to 49.174% while the Al_2O_3 reduced from 37.090% to 34.055%. Halloysite's SiO_2 quantity increased from 42.915% to 48.856% but the Al_2O_3 quantity reduced from 30.690% 28.612%.

The variation in the chemical composition of the modified clay was attributed to leaching of some minerals during the acid treatment. This has been observed by Panda *et al* during a study on effects of acid treatment on the physio-chemical characteristics in kaolin where a decrease in the mineral composition of kaolin due to leaching was observed when subjected to different acid concentration [30].

However, modification does not interfere with the clay's crystallographic structure but increases the specific surface area which was observed by Santos and Ferreira during functionalization and characterization of clay mineral [17]. The increased surface area of clay is important during leather tanning as it increases the reactive sites for bonding with the collagen.

Table 3. Chemical composition of the modified samples

Elements	Modified top layer (kaolinite)	Modified bottom layer (halloysite)
SiO_2	49.174	48.856
Al_2O_3	34.055	28.612
CaO	0.458	0.384
K_2O	0.243	0.579
Fe	11.481	16.787
Ti	4.120	3.696
Mn	0.253	0.666

4.3 Clay tanning

The clay minerals were used for tanning of goat skins.
Unmodified kaolinite and halloysite clay samples did not have a tanning effect as they did not penetrate into the skin's cross-section but the modified clay samples penetrated into the skin and therefore had the tanning effect on the pickled skins.

Non-penetration of the unmodified clay samples was attributed to lack of acid treatment which allows increased specific surface area and functionalization that in turn facilitates the diffusion, absorption and interaction of the tanning material with the collagen [30]. The use of concentrated formic acid increased the surface area of the clay as well as providing effective acidity that gives a tanning response. Modification also allowed the removal of mineral impurities and disintegration of external layers on the clay samples which then facilitated penetration [31].
Due to no penetration of the unmodified clay samples, they were not subjected to further tanning experiments.

A brownish colour was observed on the tanned skins due to the presence of iron in the clay as depicted in Figure 3 and 4.

Figure 3. Halloysite tanned leather (Bottom layer modified)

Figure 4. Kaolinite tanned leather (top layer modified)

4.4 Physical properties of clay tanned leather

Physical properties of the goat skin tanned using the modified kaolinite and halloysite were investigated and the results tabulated in Table 4.

The leather samples were subjected to tensile strength analysis using an Instron machine with the force of 500N pulling at 100nm/min. The tensile strength of the kaolinite tanned leather was 15.36 ± 0.43N/mm² and 13.29 ± 0.29N/mm² (samples cut parallel and perpendicular to the back bone respectively) while that of halloysite tanned leather was 22.91 ± 0.72N/mm² and 19.58 ± 0.36N/mm² (samples cut parallel and perpendicular to the backbone respectively). The leather obtained from both tanning agents attained values above the minimum recommended value for tensile strength i.e. >12 N/mm² [32]. Samples cut parallel to the backbone of the skin had superior tensile strength compared to the samples cut perpendicular to the backbone for both tanning agents as indicated in Table 4. High tensile strength from the samples cut parallel to the backbone was contributed by the collagen's fiber orientation. When the fibers are aligned parallel to the backbone there is minimal frictional damage compared to the perpendicular alignment [22].

Table 4. Physical properties of clay tanned goat tanned leather

Physical properties	Fiber's orientation	Top layer clay (kaolinite)	Bottom layer clay (halloysite)	Minimum recommended value
Shrinkage temperature		78.03 ± 0.41	89.33 ± 0.76	>75
Tensile strength (N/mm²)	↑	15.36 ± 0.43	22.91 ± 0.72	>12
	→	13.29 ± 0.29	19.58 ± 0.36	
Elongation at break (%)	↑	73.33 ± 2.49	45.26 ± 1.99	> 40
	→	63.33 ± 3.39	44.13 ± 7.20	
Tear strength (N)	↑	41.82 ± 0.74	57.32 ± 0.50	>20
	→	39.87 ± 0.73	46.74 ± 0.27	
Ball burst extension (mm)	Grain crack	7.49 ± 0.43	8.54 ± 0.64	6.50
	Grain burst	13.08 ± 0.58	10.06 ± 0.50	7.00

The degree to which a material stretches before fracture expressed in percentage is defined as its percent elongation. Both tanning agents attained values above the minimum recommended for percentage elongation i.e. >40 % [32]. Samples cut parallel to the backbone for the kaolinite tanned leather had a percentage elongation of 73.33 ± 2.49 % which was higher compared to samples cut perpendicular to the backbone which had a percentage elongation of 63.33 ± 3.39 %. Similarly, samples cut parallel to the backbone for halloysite tanned leather had a higher percentage elongation compared to those cut perpendicular to the backbone as shown in Table 4. Kaolinite tanned leather had significantly higher elongation compared to halloysite tanned leather. This indicated that halloysite tanned leather was more compact compared to kaolinite tanned leather making it stretch more.

The shrinkage temperature for the kaolinite and halloysite was found to be 78.03±0.41ºC and 89.33±0.76ºC respectively. The minimum recommended value for shrinkage temperature was attained by both tanning agents. Shrinkage temperature indicates the extent to which the collagen has been crosslinked with the tanning agents used [33]. From the results in Table 4, halloysite had higher amount of cross-linking's with the collagen compared to the kaolinite.

The leather obtained from both tanning agents had achieved the minimum recommended tear strength i.e. > 40N [32]. The results for the tear strength for both kaolinite and halloysite tanned leathers are indicated in Table 3. This test was carried out evaluate the materials resistance to tear force[34]. As observed on both tanning materials the samples cut parallel to the backbone had higher tear strength compared to the samples cut perpendicular to the backbone. This variation on the different fibre orientations was as a result of the angle at which the collagen fibres interweaves [35].

The ball burst test was performed to evaluate the grain's ability to resist cracking when subjected to force to evaluate its strength[36]. Both tanned leathers had attained values above 6.5mm and 7.0mm which are the minimum required values for grain crack and grain burst respectively [32]. The kaolinite tanned leather had lower grain crack compared to halloysite tanned leather however, it had greater grain burst compared to the halloysite tanned leather. This indicated that kaolinite had a better filling effect compared to the halloysite.
Both kaolinite and halloysite have similar structure and composition. They belong to the phyllosilicate group of clay and are dimorphic (1:1 layer of aluminium octahedral sheet stacked above one silica tetrahedral sheet) [28]

However, leather tanned using halloysite (bottom layer) had better physical properties compared to the leather tanned using kaolinite (top layer) which was attributed to kaolinite having low cation exchange capacity, low plasticity, and shrinkage properties, restricted surface area which limits interaction with the collagen and it's not easily broken down due to the tightness of the structural bonds [25]. As mentioned before, halloysite has a nanotubular structure while kaolinite has a platy morphology making halloysites to penetrate easier into the skin compared to kaolinites. Halloysite also have a higher iron content in the octahedral sheet compared to kaolinite which may have contributed to a higher tanning power [28].

The thermal stability of kaolinite and halloysite tanned leather was lower compared to that of chrome-tanned leather which 100 ^{0}C [37]. The tensile strength and elongation at break of both kaolinite and halloysite tanned leather is comparable to that of chrome-tanned leather. However, kaolinite had greater percentage elongation of 68.33±0.45% compared to that of chromium tanned leather 45.21% according to [38]. Halloysite-tanned leather had a tensile strength of 21.25±0.18 N/mm^2 which was higher compared to that of chrome-tanned leather 15.55 N/mm^2 according to Chakraborty *et al.,* but kaolinite-tanned leather had slightly lower tensile strength of 14.33±0.06N/mm^2 compared to both halloysite and chrome tanned leathers.
From the results, the physical properties of the clay-tanned leather had attained the minimum recommended values and were comparable to those of chrome tanned leather.

5. Conclusion and Future Scope

The natural clay mineral collected from Kabuta region in Murang'a county in in Kenya, was successfully characterised using the XRD and XRF by determining the physical properties as well as the chemical composition. XRD peaks were observed at a basal spacing of 7.14º which gives the identity of the clay material to be kaolinite and 7.2º to be halloysite. SiO_2 and Al_2O_3 were the major elements present with the percentage composition ranging between 50%-40% for kaolinite clay and 40%-25% for halloysite clay. Modification of the clay was achieved using concentrated formic acid in the ratio of 1:3 (v/w). The unmodified clay did not show any appreciable tanning. On the other hand, modified clay tanned the skins to leather, which was attributed to modification with formic acid which allowed faster and better penetration into the skin's cross-section as a result of increased surface area. The modified clay had a tanning effect on the pickled skins which had a thermal stability of 78.03 ± 0.41 and 89.33 ± 0.76 for kaolinite tanned leather and halloysite tanned leather respectively. The tanned leather using modified kaolinite and halloysite had achieved the minimum recommended values for (Tensile strength, elongation, ball burst and tear strength) making it a suitable alternative to chrome tanning. From the results obtained it can be inferred that clay tanning can be used to replace chrome in tanning processes, moreover, it is environmentally friendly and cheap. Further studies need to be done to investigate the performance of the clay-tanned leather in post-tanning processes as well as its affinity to dyes during the dying process.

Conflict of Interest

Authors declare that they do not have any conflict of interest.

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AUTHORS PROFILE

Nelly Maina earned her Bachelor of Science in Leather Technology from Dedan Kimathi University of Technology and graduated in 2020. She is pursuing a Master of Science in Leather Technology at Dedan Kimathi University of Technology at the same time serving as a Graduate assistant at the institution. Her research is focused on ecofriendly tanning methods. She has 2 years of teaching experience and 1 year of research experience.

Douglas Onyancha earned his Bachelor of Science from Egerton University and graduated in 2002. He later pursued a Master of Science in Chemistry from the same university and graduated in 2006 before joining Nelson Mandela metropolitan University for his PhD in Chemistry, where he graduated in 2010. His research interest is focused in organometallic compounds and their applications in materials industry including leather, drug delivery and catalysis. He has served as a lecturer in the department of chemistry at Dedan Kimathi University since 2012. He has more than 13 years of research experience, and has published more than 15 peer referred articles. His main focus area is organometallics and their applications in material development. In addition, cleaner production technologies to come up with alternative substitutes to toxic chemical in materials development forms part of his research.

Paul Sang holds a PhD. in Chemistry from Louisiana State University. He is currently a senior lecturer in the Department of Chemistry at Dedan Kimathi University of Technology. His current research is mainly in the broad area of green chemistry with a focus on waste minimization by converting waste generated to useful substances.