Research Article

Preparation of aluminium sulphate from kaolin and its performance in combination tanning

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Abstract

Leather making commonly use chromium salts to produce high quality products. However, the use of chromium salts is compromised by environmental safety concerns. Combination tanning using vegetable tanning coupled with aluminium sulphate can sustainably replace chrome tanning system. Adversely, the use of commercial aluminium sulphate poses economic burden that entails for cost effective sources. Abundance of kaolin on earth's crust with scarce utilization is an opportunity towards cost effective aluminium sulphate for tanning. Therefore, in the present work aluminium sulphate was prepared from kaolin and its performance for combination tanning was studied. Diffraction and vibrational spectroscopic studies were carried out to confirm the prepared aluminium sulphate. Combination tanning was carried out with mimosa vegetable tannins. Leathers tanned with the combination of aluminium sulphate from kaolin and mimosa vegetable tannin exhibited hydrothermal stability of up to 118 °C as compared to mimosa alone that showed the average of 80 °C. Physical strength characteristics met the standard norms. Fibers separation was good as confirmed through microscopic studies. The study provides a new insight on accomplishing self-sustenance through available resources and eco-friendly manufacturing system.

Keywords Pugu kaolin · Combination tanning · Aluminium sulphate · Mimosa · Leather manufacturing

1 Introduction

In the process of making leather, the hide or skin is customarily tanned with mineral tanning materials such as basic chromium, aluminium or zirconium salts [1, 2]. Todays' leather manufacturing industry is dominated by the use of basic chromium salt, accounting for more than 90% of global leather tanning. Generally, the chromium salts tanned leather have good quality including high shrinkage temperature (hydrothermal stability), excellent handle feeling, good abrasion resistance and storage stability [3–5]. However, chromium tanning is being debatable owing to reported toxicity of chromium ions and associated disposal issues [6]. Furthermore, chromium sources are limited in the world. Development of chromium-free tanning agent is highly needed for sustainable leather production. Use of aluminium sulphate ($Al_2(SO_4)_3$) as tanning agent has a long history in the leather industry [1, 2]. It produces pure white finished leather with high softness, elongation, and fine grains [7]. However, hydrothermal stability of aluminium tanned leather is limited to 75 °C due to the weak nature of links with carboxyl

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groups of collagen molecule [8]. When used in combination with inorganic or organic tanning agent, the hydrothermal stability is significantly improved [8]. The combination tanning is tannage system in which two tanning agents with weaker crosslinking ability are used together [7, 9–14]. Combination tanning that involve blending vegetable tannins and $Al_2(SO_4)_3$ has been widely studied. Such studies include combination of commercial $Al_2(SO_4)_3$ with vegetable extracts from *Acacia mearnsii* [14], *Gardenia jasminoides* [15] *Acacia nilotica* [11] and *Caesalpinia spinosa* [16]. Such combination tannings are reported to produce leather with quality comparable to those tanned by chromium-based salts [11, 14, 16]. Normally, commercial $Al_2(SO_4)_3$ is industrially produced using bauxitic rocks as a raw material (20–30% of aluminium content) [17–19]. However, relying on bauxite has some limitations as it is globally diminishing and scarcely present in commercial quantity in most of the developing countries [20]. Hence, alternative source of $Al_2(SO_4)_3$ is an immediate need for sustainability of leather industry. Therefore, the work hereby reported was envisaged to prepare $Al_2(SO_4)_3$ from kaolin for application in combination tanning with vegetable tannins from mimosa.

Kaolin, an aluminosilicate clay with the molecular formula of $Al_2Si_2O_5(OH)_4$ containing 10–40% aluminium [21, 22], is regarded as a potential substitute of bauxite in the production of $Al_2(SO_4)_3$ [18]. Structurally, kaolin consists of repeated units of $Al(O_2OH)$ octahedral sheet coupled to a silica (SiO_4) tetrahedral sheet of which, one tetrahedral sheet of SiO_4 is linked through oxygen atoms to one octahedral sheet of $Al(O_2OH)$ [23, 24]. Within this structure two types of OH groups are present, one group extends from the layers and form hydrogen bonds to adjacent layers (surface OH group) and another OH group is situated within the empty spaces of the octahedral sheets (inner OH group) [24]. During the extraction process, kaolin is calcined at high temperature (usually 750–850 °C) to break hydrogen bond resulting into dehydroxylation and formation of metakaolin. The latter exhibits higher reactivity towards acid dissolution thereby aluminium can be easily leached out of kaolin structure and reacted with sulphuric acid to form $Al_2(SO_4)_3$ [22]. About 2.3 billion metric tons kaolin deposit of high standard, similar to Georgia kaolin, is located at Pugu Hills, 35 km from Dar es Salaam City, Tanzania [25–27]. The full potential of Pugu kaolin for industrial use is still untapped [25, 26]. So far its utilization is limited into ceramic industry indicating underutilization of such enormous resource [28].

The use of kaolin as the source of aluminium for the preparation of $Al_2(SO_4)_3$ has recently gained attention especially in application as a flocculant agent in water treatment due to both environmental concern and economic viewpoint [18, 29]. However, there is limited reports pertaining to the use of kaolin based $Al_2(SO_4)_3$ in combination tanning. Mimosa is well known vegetable tannin source cheaply available. Being a renewable resource, use of mimosa in combination with $Al_2(SO_4)_3$ from kaolin is foreseen to provide a sustainable combination tanning system. Thus, in the present work, we report the preparation of basic $Al_2(SO_4)_3$ from kaolin for application in combination tanning with mimosa vegetable tannins.

2 Materials and methods

2.1 Materials used

Kaolin was collected from Pugu hills, Kisarawe district, Pwani region, Tanzania. Quarter sampling technique was used as previously described [30]. Sulphuric acid (H_2SO_4), Sodium Carbonate (Na_2CO_3) and Trisodium citrate ($Na_3C_6H_5O_7$) used were of analytical grades purchased from Sigma Aldrich Ltd, India. Chemicals used in tanning trials were of commercial grade, provided by Council for Scientific and Industrial Research-Central Leather Research Institute (CSIR-CLRI) pilot tannery in India. Goat skins pelts were generously donated by CSIR-CLRI pilot tannery, pretanning section.

2.2 Characterization of kaolin

Three different techniques were used to analyze clay to ensure that clay used in the study was indeed kaolin. Crystalline phases and functionality of raw kaolin and calcined kaolin were determined by X-Ray Diffraction (XRD) analysis (SAXS Space) and FTIR (ABB-MB3000), while morphology of clay and mineralogical composition were determined by using Scanning Electron Microscopy (SEM) images (PhenonPro) and X-Ray Fluorescence (XRF) technique (Pw 4030), respectively.

2.3 Preparation and characterization of $Al_2(SO_4)_3$ from Pugu kaolin

Preparation of $Al_2(SO_4)_3$ from Pugu kaolin was carried out as previously described [18]. The kaolin sample passed through 250 µm sieve diameter was calcined in marble furnace at 750 °C for 120 min. Leaching experiment was done by contacting aqueous solution of 3 M Sulphuric acid (H_2SO_4) in 500 mL reaction flask. During leaching experiment, 300 mL of sulphuric acid solution was transferred into the reaction flask and heated under reflux condition until temperature reaches 90 °C. Then, 30 g of calcined clay was added into the reactor and the formed slurry was stirred at 150 rpm speed. After 120 min, the mixture was cooled and centrifuged at 4000 rpm speed for 5 min. The

supernatant was concentrated in water bath until white slurry formed. About 3 mg of formed slurry was taken for FTIR and XRD analyses. The rest was basified using 10% Na_2CO_3 and masked with $Na_3C_6H_5O_7$ at a ratio of 1:8 ready for use in combination tanning experiments with mimosa.

2.4 Combination tanning performance test

Sample of goat skins were treated with mimosa in combination with basified $Al_2(SO_4)_3$ from kaolin. The recipe for tanning process was adopted from CSIR-CLRI pilot tannery in India. In summary, 15% of vegetable tanning was used in combination with $Al_2(SO_4)_3$ of various concentration expressed as % Al_2O_3 (that is, 2, 5 and 10%). Amount of Al_2O_3 was quantified based on Al_2O_3 content present in the $Al_2(SO_4)_3$ (final product after extraction), because Al_2O_3 forms aluminium hydroxide complexes following basification with 10% Na_2CO_3, which in turn crosslink with collagen [31, 32]. Control trial was carried out by tanning goat skins with 15% mimosa alone. Resultant leather samples were tested for denaturation temperature using differential scanning calorimetry (DSC) technique (Perkin Elmer DCS Q200 V23) and conventional shrinkage temperature test (CST) (Theis shrinkage tester).

DSC technique measures the transformation of skin collagenous material as the function of time. The onset temperature of the DSC curve refers to the temperature of phase transformation, the higher the onset temperature, the better the hydrothermal stability of collagen [8]. About 3 mg of the sample was heated from 10 to 125 °C at 10 °C per minute heating rate under nitrogen atmosphere. Resultant thermographs were recorded for analysis. The shrinkage temperature test was carried out as per SATRA STD 114 method. A strip of about 2 cm by 3 cm leather and a thermometer were suspended in the sight glass filled with water, the upper end of the leather was fixed and the position of the lower end was indicated by an adjustable marker outside the tube to help judge when shrinkage occurs. The system was heated and the temperature at which leather shrinks to one-third of its original length was recorded as a shrinkage temperature, which connotes hydrothermal stability. All analyses were done in duplicate.

Leather samples were further subjected to physical testing to determine the influence of $Al_2(SO_4)_3$ from kaolin on physical properties of leather. Tear strength and water vapour permeability tests were carried out using SATRA TM 162:1992. All test samples were conditioned at 20 °C and 65% relative humidity. Control samples were tested in the same way. All analyses were done in duplicate. Characterization of microstructure of leather samples was performed using SEM technique. The samples were cut into predefined sampling position and shaped into uniform thickness. Thereafter, the samples were coated with gold using Edwards E306 sputter coater followed by scanning process. The images were obtained by operating the SEM at an accelerating voltage of 5 kV with 150× magnification.

3 Results and discussion

3.1 Characterization of kaolin

XRD spectrum of Pugu kaolin is shown in Fig. 1. Significant peaks of kaolinite is observed, similar to the previous work [22]. Results from XRF analysis of kaolin in Table 1 shows that the major content of kaolin are the oxides of aluminium (25.8%) and silicate (63.4%), which is the characteristic feature of kaolin clays, and are in agreement with the previous findings that reported 31.43% Al_2O_3 and 63.64% SiO_2 for same source of kaolin clay [30]. SEM images for the kaolin in Fig. 2 showed plate like layers stacked over one another, confirming morphological characteristic of kaolin clay as earlier reported [33]. Assemblage of plate-like hexagonal structures or book-like kaolinite stacks are common feature of kaolin clay observed under Scanning Electron microscope [34].

The FTIR analysis was applied to characterize the changes occurred upon calcination of kaolin, which is important step in preparation of $Al_2(SO_4)_3$ from raw kaolin. FTIR technique is related to the vibrations of molecular bonds in the minerals from which based on position of absorption peaks in the infra-red region of electromagnetic spectrum, an identity of mineral can be made [35]. An FTIR spectrum of Pugu Kaolin in Fig. 3 presents multiple absorptions related to Si–O bonds at 1005, 1026 and 1118 cm^{-1}. Absorption bands at 907 cm^{-1} corresponds to inner Al–OH. Presence of absorption bands at 3690 cm^{-1}

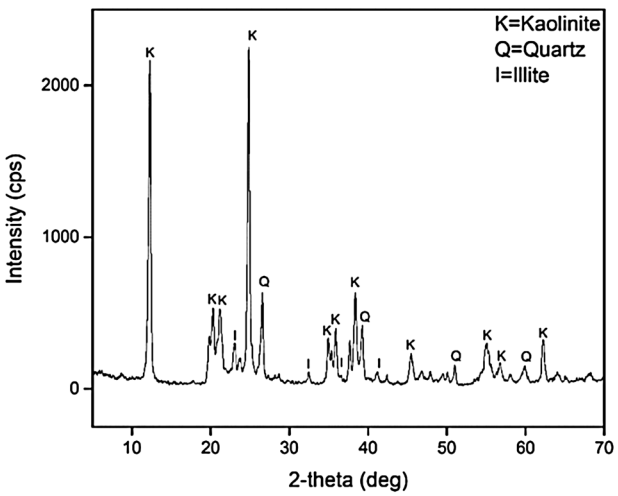

Fig. 1 XRD pattern of Pugu kaolin

Table 1 Chemical composition of Pugu kaolin

Chemical composition of kaolin sample (wt%)						
Oxide	Al_2O_3	TiO_2	CaO	Fe_2O3	SiO_2	K_2O
Quantity	25.8	2.88	0.39	2.89	63.4	3.19

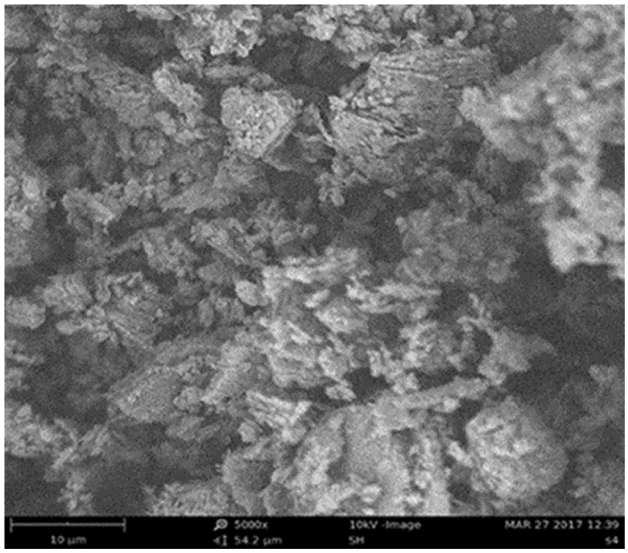

Fig. 2 Scanning Electron Microscopic image of Pugu kaolin

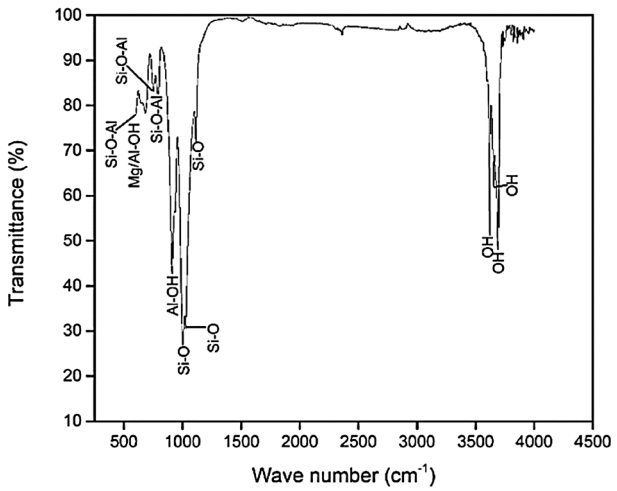

Fig. 3 FTIR spectrum of Pugu kaolin

corresponds to outer OH group while that at 3620 cm^{-1} is due to bonded molecular water [36].

For easy leaching of aluminium from kaolin aluminosilicate structure, the bonds holding structure must be broken down. This is achieved by calcinating kaolin, transforming its structure to amorphous metakaolin structure, which is more reactive form of kaolin towards dissolution agents than raw kaolin [37, 38]. Upon heating, kaolin structure breaks

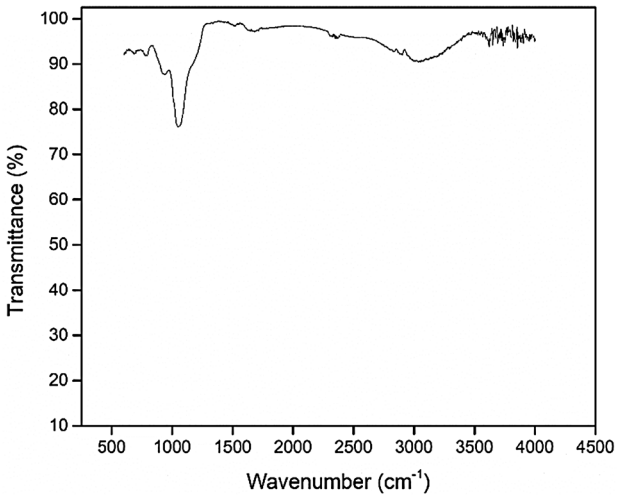

Fig. 4 FTIR spectrum of calcined kaolin

down into small pieces resulting into increased surface area for dissolution agents to react with aluminium oxide easily, as in bauxite rock [19]. In the low-temperature domain of the calcination reaction (500–800 °C), the transformation of kaolinite into metakaolinite is characterized by the removal of the chemically bonded water and the breakdown of the hydroxyl bonds [39]. Therefore, the main changes are related to the loss of OH groups that result into diminishing of the band corresponding to OH and Al–OH in calcined clay FTIR spectrum [36]. It is further elaborated that vanishing of Al–OH and immerging of Si–O band at 1047 cm^{-1} indicates destruction of octahedral sheet [40]. Similar observations were seen in the present work signifying the dehydroxylation and dehydration during calcination process (Fig. 4).

3.2 Preparation and characterization of $Al_2(SO_4)_3$ from Pugu kaolin

During extraction process, Al_2O_3 present in kaolin was leached and reacted with sulphuric acid used for dissolution to form $Al_2(SO_4)_3$ and water (Eq. 1). XRD spectrum of the prepared $Al_2(SO_4)_3$ is shown in Fig. 5. Most characteristic peaks for $Al_2(SO_4)_3$ [41] are reflected in the synthesized product from kaolin, suggesting that $Al_2(SO_4)_3$ is formed during extraction process.

$$Al_2O_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2O \quad (1)$$

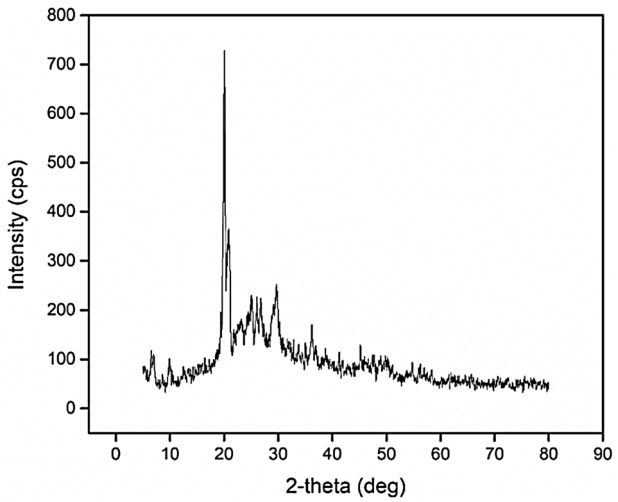

Fig. 5 XRD patterns of $Al_2(SO_4)_3$ prepared from Pugu kaolin

FTIR spectrum of $Al_2(SO_4)_3$ is shown in Fig. 6. The broad bands at 3255.5 cm^{-1} is due to OH stretching of molecular water and at 1658.8 cm^{-1} is due to OH bending of free water, revealing that the extracted salt is hydrated. The bands at 1171.1 and 1035.9 cm^{-1} correspond to SO_4 vibration. The bands at 868.4 cm^{-1} and 685 cm^{-1} are attributed to Al–O stretching and bending. The finding is corroborate with the absorption bands of $Al_2(SO_4)_3$ of commercial $Al_2(SO_4)_3$ previously reported [42, 43].

Therefore, based on diffraction patterns observed in XRD analysis and absorption bands in FTIR analysis, it can be concluded that Al_2O_3 from kaolin was successfully extracted and in presence the of sulphuric acid, it reacted to form $Al_2(SO_4)_3$.

3.3 Performance of $Al_2(SO_4)_3$ from Pugu kaolin on combination tanning

Leather tanned with combination of mimosa and $Al_2(SO_4)_3$ from kaolin demonstrated improved denaturation temperature as compared to control sample (Fig. 7). It was observed that addition of $Al_2(SO_4)_3$ resulted in significant increase in denaturation temperature. On addition of $Al_2(SO_4)_3$ (2% Al_2O_3 equivalent), sharp increase in denaturation temperature is observed, but further increase of $Al_2(SO_4)_3$ resulted into slight increase. This corroborates previous reports [8, 14, 44–46]. Denaturation temperature of leather is the maximum temperature at which wet leather can withstand shrinking, provides information about the amount of crosslinks introduced by tanning agent in skin matrix to stabilize the hide/skin structure against heat and thereby rendering hide/skin collagen less susceptible to denaturation [47]. Findings ascertained that Al_2O_3 from Pugu kaolin triggered chemical modification in collagen structure and raised the denaturation temperature.

The increase in denaturation temperature brought by combination tanning using aluminium sulphate and vegetable tannins was previous elaborated using various assumptions [8, 48, 49]. The most common and accepted assumption is that of link-lock [49]. According to link-lock assumption, increased denaturation temperature of treated collagen is due to creation of a matrix that become securely bound to collagen molecule. Matrix formation occurs in two steps, in first step (linking step) vegetable tannins bind with carboxylic group of collagen molecules, followed by second step (locking step) where aluminium ions crosslink with already bound vegetable tannins thereby creating strong network of tanning matrix that enables leather to withstand high heat. The values

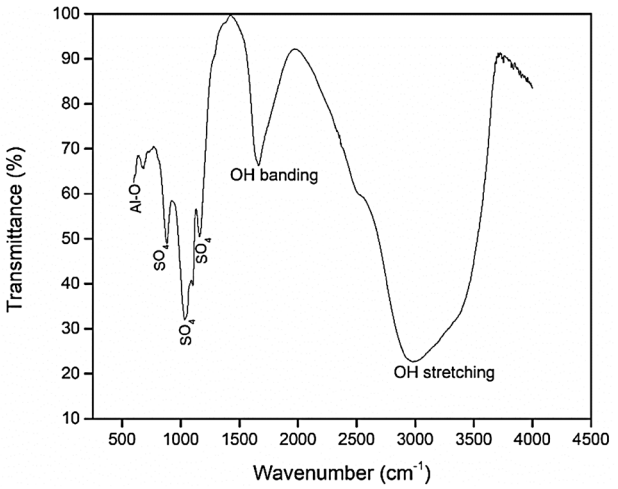

Fig. 6 FTIR spectrum of $Al_2(SO_4)_3$ prepared from Pugu kaolin

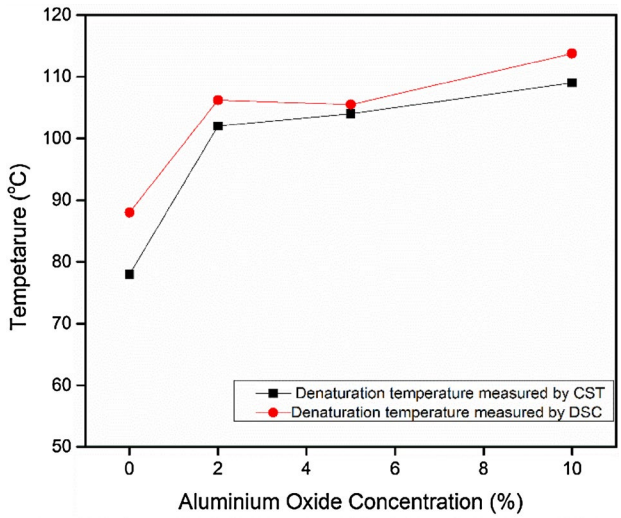

Fig. 7 Hydrothermal stability of leather samples

Table 2 Physical properties of leather tanned with the combination of Mimosa (15%) and Al_2O_3

Al_2O_3 (%)	0	2	5	10	CLRI recommended values	Testing method
Tear strength (N/mm)						
Along	59.0	63.4	66.5	65.6	0.7 mm min. 20	SATRA TM
Across	62.5	64.2	69.2	67.2	0.8 mm min. 25	162:1992
Average thickness (mm)	0.86	0.72	1.12	1.12	1.0 mm min. 45	
Water vapor permeability	10.5	10.4	11.1	10.4	Upper-min 0.8 Lining-min 2.0	SATRA TM 172:1993

of denaturation temperature measured by DSC method are generally greater than those measured by CST method (Fig. 7) due to the presence of other higher energy structures associated with side chain of collagen that is not observed on measuring denaturation/shrinkage temperature by using CST method as previously noted [8].

As the impact of strong bonds formed inside leather fiber matrix, the physical properties have been significantly improved. All samples have shown tearing strength and water vapor permeability better than recommended values (Table 2). Microstructure studies of collagen fibers have proven further that the combination tanning with

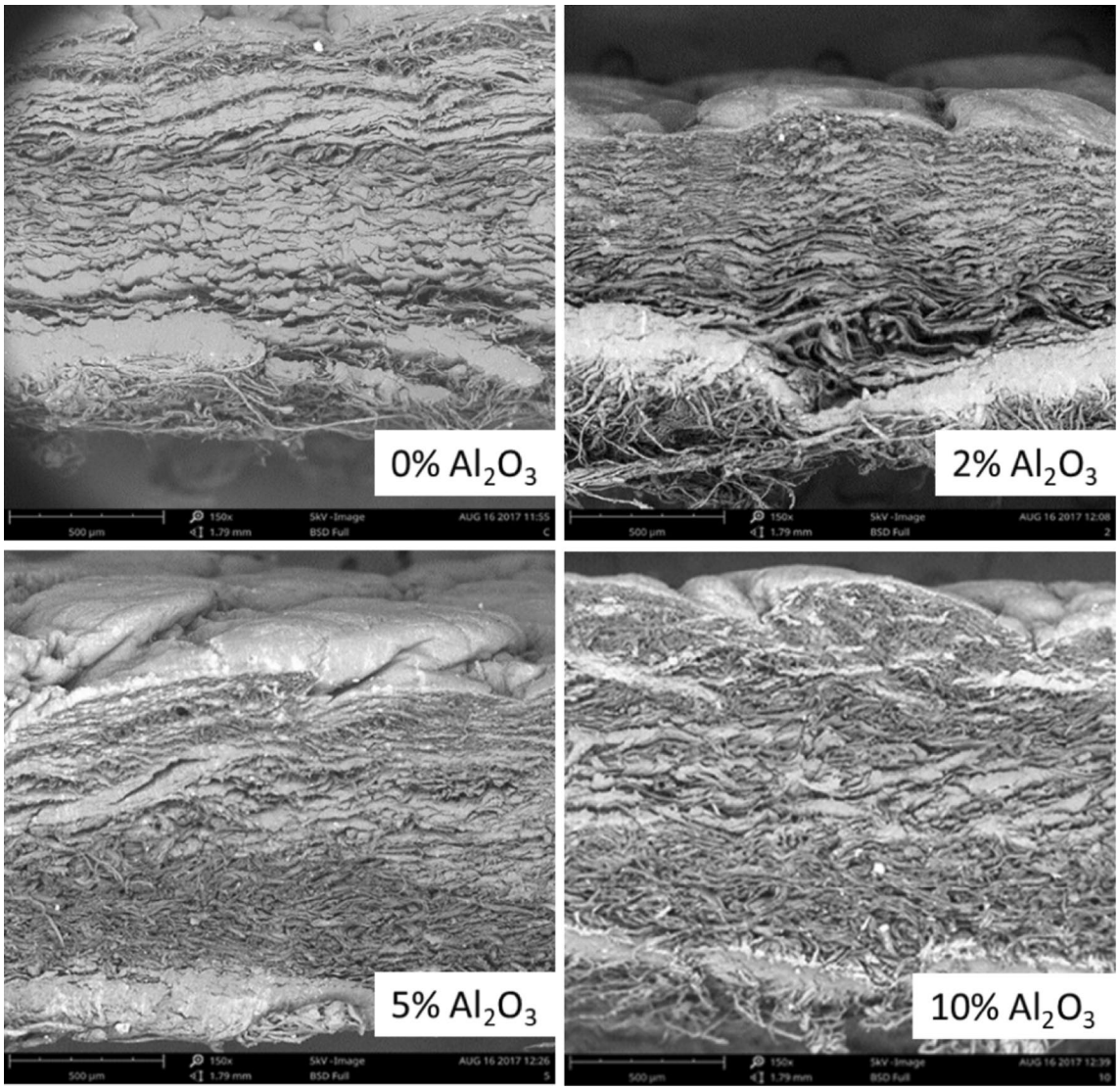

Fig. 8 SEM images of leather samples tanned with 15% mimosa and different concentration of Al_2O_3

$Al_2(SO_4)_3$ from kaolin can lead to higher fiber dispersion and clear spacing among collagen fibers, as it does commercial $Al_2(SO_4)_3$. Comparing with leather samples tanned with mimosa alone, combination tanned leather shown better fiber dispersion. Mimosa tanned leather displayed compact and tight fiber pattern, signifies that $Al_2(SO_4)_3$ is important to bring about good fiber separation that bring about strength and softness of leather (Fig. 8). It is earlier reported that penetration of tanning agent across the skin matrix results into good fiber separation and hence desired leather properties [50]. Therefore, it can be deduced that $Al_2(SO_4)_3$ from kaolin enhanced good penetration of both tanning agents hence produced leather with desired properties.

4 Conclusion

In the present work, $Al_2(SO_4)_3$ was prepared from Pugu kaolin for application in combination tanning. $Al_2(SO_4)_3$ was successfully obtained using sulphuric acid as dissolution agent, which was confirmed using spectra obtained from XRD and FTIR analyses. Its application in combination tanning with mimosa extract gave leathers with hydrothermal stability beyond 100 °C with 2% Al_2O_3 as a minimum concentration. More importantly, hydrothermal stability of up to 118 °C was attained upon increase in the concentration of Al_2O_3. Produced leather conformed to the recommended physical and mechanical properties signifying its durability and suitability in the leather products industry. SEM micrographs confirmed good fiber bundles separation, indicating sufficient interaction between skin collagen and tanning matrix formed by kaolin based $Al_2(SO_4)_3$ vegetable tannin, verifying link lock theory. This study provides useful information about possible utilization of kaolin abundantly available in Tanzania and probably elsewhere it is available in the world. In this way, kaolin can catalyse application of green chemistry through avoiding use of toxic chemicals such as chromium salts in leather industry, thereby bringing about sustainable leather production practices.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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