AN ECO-FRIENDLY TANNING METHOD USING PLANT BARKS AND THEIR COMBINATION WITH ALUMINIUM SULPHATE FROM KAOLIN FOR LEATHER INDUSTRY

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ABSTRACT

Chrome tanning has remained the most preferred tanning method worldwide in the leather industry because it produces leather of a high quality with all the desired features. However, environmental concerns of chromium shifted the focus of current research to chrome-free and greener chemical processing options. When used in combination with some eco-friendly metal salts, vegetable tannins are environmentally safe and manageable, while producing excellent quality leather, bearing shrinkage temperature above 100 °C as that of chromium tanned leather. As such, shortage of vegetable tannin supply requires characterization of non-commercialized sources locally available in Tanzania for cottage tanneries. In the present work, vegetable tannins from the stem barks of local plants namely *Acacia mearnsii (A. mearnsii), Acacia xanthophloea (A. xanthophloea), Euclea divinorum (E. divinorum)* and root barks of *Euclea racemosa (E. racemosa)* were prepared using a simple extraction technique at 30-80 °C. Extract yield, tannin, total flavonoid and phenolic content, cross-linking ability as well as properties of the tanned leather were determined. Results indicated that even at low temperature (50 °C) the barks yield vegetable tannins with features similar to that of a commercialized source of tannin. *Euclea racemosa* extract had low tannin, phenolic and flavonoid content and its crosslinking ability was poor; hence, was determined as an un-suitable tannin source. Despite recording less extract yield, tannin and other contents than that of *A. mearnsii*, the extract from *E. divinorum* bark demonstrated a substantial tanning ability, which is attributable to its high tannin strength. However, a broad interval between T_{onset} and T_{peak} of treated hide powder necessitated combination tanning with aluminium sulphate [$Al_2(SO_4)_3$] to lower the interval. About 2% (w/v) aluminium oxide (Al_2O_3) equivalent is an optimal dose of $Al_2(SO_4)_3$ for extract pre-treatment. Since the main source of $Al_2(SO_4)_3$, bauxite, is diminishing in the world, an alternative source of $Al_2(SO_4)_3$ was explored. The $Al_2(SO_4)_3$ was prepared from Kaolin of Pugu hill in Tanzania and applied for combination tanning. The study has proven the suitability of kaolin as an alternative source of $Al_2(SO_4)_3$ for combination tanning with vegetable tannins. Leather tanned with the combination of the prepared $Al_2(SO_4)_3$ and vegetable tannin exhibited the shrinkage temperature of up to 118 °C as compared to vegetable tannins alone that showed the average of 80 °C. Mechanical strength characteristics met the standard norms. Fiber separation was good as confirmed through microscopic studies. The study provides useful information and new insights on accomplishing self-sustenance through available resources and an eco-friendly manufacturing system for leather industries in Tanzania and beyond.

DECLARATION

I, Cecilia Rolence do hereby declare to the Senate of the Nelson Mandela African Institution of Science and Technology that this thesis is my own original work and that it has neither been submitted nor being concurrently submitted for a degree award in any other institution.

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CERTIFICATION

This is to certify that this thesis titled “An Eeco-friendly Tanning Method using Plant Barks and their Combination with aluminium sulphate from Kaolin for Leather Industry” is written by Cecilia Rolence under supervision of Prof. Askwar Hilonga, Dr. Swarna V. Kanth and Prof. Karoli N. Njau at the NM-AIST. We approve the thesis for submission to the NM-AIST senate for an award of the degree of Doctor of Philosophy in Materials Science and Engineering of the Nelson Mandela African Institution of Science and Technology.

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DEDICATION

I dedicate this work to my mother Valeria Anatory Kinolo in memory of her husband and my late father Mr. Rolence Leopard China.

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LIST OF ABBREVIATIONS AND SYMBOLS

Abbreviation/Symbol	**Description**
CD	Circular Dichroism
CLRI	Central Leather Research Institute
CSIR	Council for Scientific and Industrial Research
CST	Conventional Shrinkage Temperature
DIN	Deutsches Institut für Normung.
DNA	Deoxyribonucleic Acid
DSC	Differential Scanning Calorimetry
EN	European Standard
ETP	Effluent Treatment Plant
FAO	Food and Agriculture Organization
FILK	Forschungsinstitut für Leder und Kunststoffbahnen
FTIR	Fourier Transformer Infra-Red
HPLC	High Performance Liquid Chromatography
ISO	International Organization of Standardization
LCWS	Low Chrome Wet blue Scraps
NBS	National Bureau of Statistics
NEMC	National Environment Management Council
NMR	Nuclear Magnetic Resonance
PBS	Phosphate Buffer Saline
RTT	Rat Tail Tendon
ROS	Reactive Oxygen Species
RST	Raw Skin Trimmings
SATRA	Safety and Technical Rescue Association
SDS	Sodium Dodecyl Sulfate
SEM	Scanning Electron Microscopy
SLTC	Society of Leather Technologists and Chemists
SMEs	Small and Medium Enterprises
T/N	Tannin/Non tannin
TFC	Total Flavonoid Content
TNBS	2,4,6-Trinitrobenzenesulfonic acid
TPC	Total Phenolic Content
URT	United Republic of Tanzania

UV	Ultra Violet
UV-VIS	Ultra Violet Visible Spectroscopy
WHO	World Health Organization
WSD	Wet blue Shaving Dust
XRD	X-Ray Diffraction
XRF	X- Ray Fluorescence

CHAPTER ONE

INTRODUCTION

1.1 Background of the Problem

Leather is the natural material manufactured by processing animal hides/skins, and it has unique features unmatched by synthetic materials (Covington, 2009; Manfred *et al.*, 2012). The leather industry is one of the primitive industries of mankind designed to produce leather for various articles (Sathish *et al.*, 2016). Today leather is one of the essential lifestyle commodities in the world with the annual world production reaching 1.85 billion m^2 (Cao *et al.*, 2018). The industry contributes to the social-economic development of developing economies by creating employment. The export of finished leather and leather products increases foreign currency earnings (Muchie, 2000; Mwinyihija & Quisenberry, 2013).

Manufacturing of leather involves three steps. The first step being pre-tanning that consists of soaking, liming, unhairing, deliming and bating. The second step is tanning, that consists of the conversion of hide/skin substance into the leather. The final step is post-tanning, which confers the leather with customer desired properties such as softness, colour, to mention but a few. Tanning is the most critical step as it converts putrescible and heat prone biological materials (hides/skins) to durable, stable and non-putrescible material that can withstand heat, stress and bacterial attack (Yao *et al.*, 2019). The essence of tanning is to introduce potent/stable cross-links between collagen molecules so that the hydrothermal and mechanical stability of collagen fibrils can be improved. These cross-links are formed based on collective multiple site interactions between tanning agents and collagen fibrils, including hydrogen bonding, hydrophobic interactions, ionic interactions, and covalent bonds (Covington, 2009).

Several types of tanning agents, such as mineral tanning with metal salts, oil and aldehyde derivatives (Kite & Thomson, 2006; Krishnamoorthy *et al.*, 2013), synthetic tanning agents and organic tannages based on natural polyphenols (Covington, 1997) and synthetic organic oligomer (Zengin *et al.*, 2012) have been employed for tanning of leather. Except for chromium salt, other tanning agents do not confer leather all desired properties. Generally, chromium salts confer high shrinkage temperature of more than 100 °C. It alters the structure of collagen in only small way; hence, preserves the physical properties or the leather without restricting its application. Moreover, it gives a hydrophobic leather surface with the resultant leather becoming water resistance. The salts act as dye mordant thus impact light fastness to the leather. Therefore, chromium salts are considered as the most essential tanning agents used for all types of hides/skins. Owing to the extraordinary properties of finished leather, and convenient processing procedure, chromium tanning accounts for 90% of today's worldwide leather industry (Rao *et al*., 2004; Sathish *et al.*, 2016; Silambaras *et al*., 2015; Zhang *et al*., 2017).

However, despite its versatility, the use of chromium tanning is debatable due to reported toxicity of Cr (VI) and associated disposal issues (Madhan *et al*., 2006). Although tanning uses salt of Cr (III), change in pH during post-tanning processes and the presence of the oxidizing agents such as dissolved oxygen and MnO_2 in the tanning bath can influence oxidation of Cr (III) to Cr (VI). Moreover, the fluctuation in the temperature, humidity and UV light exposure to the leather and storage, may lead to the formation of free radicals, which in turn become the potential source of Cr (III) oxidation to Cr (VI) (Bayramoglu *et al*., 2012; Yılmaz *et al*., 2016). At high concentrations, Cr (VI) is mutagenic, carcinogenic and teratogenic (Nigam *et al*., 2015). The Cr (VI) compounds can enter the cell through the sulfate anion channel and then be exposed to reduction by a wide variety of cellular reductants, such as glutathione (GSH) and ascorbate, with the formation of highly reactive Cr (V/IV) intermediates and finally Cr (III) products (Kortenkamp *et al*., 1996; Zhang *et al*., 2011).

During this process, molecular oxygen gets activated and reduced to a superoxide anion ($\cdot O_2^-$) that is further converted to hydrogen peroxide (H_2O_2) via a dismutation process. The resultant intermediates further react with H_2O_2 to generate a spectrum of reactive oxygen species (ROS) containing hydroxyl radicals, singlet oxygen, superoxide, and hydrogen peroxide via the Fenton pathway (Cerveira *et al*., 2014). Subsequently, excessive ROS interaction with these intermediates may give rise to oxidative stress and DNA damage, including chromium–DNA adducts, DNA strand breaks, and DNA–protein cross-links (DPCs), all of which are unstable factors with mutagenic effects. Evidence from recent studies revealed the potential reproductive hazards of Cr (III) products on reproductive systems (Pereira *et al*., 2005; Marouani *et al*., 2012), as well as DNA damage by Chromium species contained in tanning effluents (Wang *et al*., 2017; Zhang *et al.*, 2011). In addition, women working in Cr industries and living around Cr-contaminated environment experience various reproductive problems such as abnormal menses, infertility, stillbirth, which are associated with high Cr (III) or (VI) levels in their blood and urine. Furthermore, various studies reported cases of lung cancer induced by Cr (VI) inhalation among workers in several industries (Hirose *et al*., 2002; Urbano *et al*., 2012; Proctor *et al*., 2014).

Owing to health hazards associated with chromium utilization in the tanning industry, ecofriendly and effective tanning technologies are needed to sustain the leather industry. Various eco-friendly tanning methods geared towards improving or replacing chrome-based technology without compromising the quality of the produced leather have been reported (Fathima *et al*., 2006; Roig *et al*., 2012; Valeika *et al*., 2010). These attempts include recycling of spent liquors, chromium exhaustion enhancement or total replacement of chromium salts. Total replacement of the chromium salts is ideal to elude adverse effects associated with chrome tanning. Chrome free combination tanning is reported to be an alternative technology to chrome tanning as it produces leather with properties matching those of chrome tanning (Madhan *et al*., 2006; Mahdi *et al*., 2009; Musa & Gasmelseed, 2013; Musa *et al*., 2009). In this regard, combination tanning provides a promising alternative chrome-free tanning technology.

Combination tanning involves the blending of vegetable tannins and $Al_2(SO_4)_3$, has thus far gained attention in several studies due to its outstanding efficiency compared to other tanning combinations (Musa & Gasmelseed, 2013; Slabbert 1981; Vitolo *et al*., 2003). The combination of commercial $Al_2(SO_4)_3$ with vegetable extracts from *Acacia mearnsii* (Slabbert, 1981), *Gardeni jasminoides* (Ding *et al.,* 2007), *Acacia nilotica* (Musa & Gasmelseed, 2013) and *Caesalpinia spinosa* (Vitolo *et al*., 2003) have been reported. However, the combination tanning with $Al_2(SO_4)_3$ from kaolin is scarcely known; hence, explored through research reported in this thesis. Overall, Tanzania is endowed with a large deposit of kaolin, which is a potential source of $Al_2(SO_4)_3$. Therefore, combination tanning based on vegetable tannins from local bioresources and $Al_2(SO_4)_3$ from kaolin is deemed a cheap environmentally benign alternative to commercial chrome-based tanning technologies as confirmed to be expensive for the local leather processing industries and SMEs.

Currently, there are limited studies pertaining to the suitability of vegetable tannins from local Tanzanian plants and their application in tanning leather, either individually, or in combination tanning. Thus, the present study was aimed at preparing vegetable tannins from local plant barks and investigating their suitability in tanning. Furthermore, the study was extended to prepare and investigate the application of $Al_2(SO_4)_3$ from Pugu kaolin in combination tanning.

1.2 Statement of the Problem

Leather industry is one of the priority industries identified to contribute to attaining the national development vision 2025 (Mrindoko, 2012; URT, 2015). Currently, there are nine tanneries and more than 50 SMEs engaging in leather manufacturing (URT, 2015). Like in other countries worldwide, chromium tanning is the most adopted method among Tanzanian leather manufacturers, leading to the environment pollution caused by chrome shavings, chrome trimmings and chrome rich wastewater from tanneries (Maziku, 2014; Mwandosya, 1995; Scheren *et al*., 1995). Piles of chrome shavings, trimmings and sludge are found around the tannery premises that end up in the landfills or dumpsites (NBS, 2017; China & Ndaro, 2016; Mkuula, 1993).

Disposal of chromium wastes in the landfills and dumpsites is not a permanent solution of managing chromium wastes as chromium can easily get into the ecosystems and cause harm (Lima *et al*., 2010; Mkuula, 1993; Parvin *et al*., 2017). Little has been done to manage chromium solid and liquid wastes in Tanzania and tanners' ability to afford modern ETP technologies to remove chromium in tannery wastewater is limited (Oruko *et al*., 2019; Kaseva & Mbuligwe, 2010; Mkuula, 1993). Chrome pollution challenge in Tanzania has led to the closure of some tanneries by environmental authority NEMC (China & Ndaro, 2015; Mkuula, 1993).

Apart from the environmental point of view, chromium salt is not locally manufactured. Since it has to be imported, its market price in Tanzania is too high for most small-scale leather enterprises to afford. Alternatively, cottage industries process leather by traditional means. Traditional tanning involves boiling plant barks and using the decoction for tanning. Boiling temperature leads to co-extraction of non-desirable compounds such as gums that negatively affect the quality of leather (China & Ndaro, 2016).

Thus, an eco-friendly and chrome-free tanning method is the current and continual need to sustain the leather industry of Tanzania. In this work, vegetable tannins from local plants barks and $Al_2(SO_4)_3$ from local kaolin deposits were prepared and tested for their suitability in combination tanning. Kaolin was chosen as a source of $Al_2(SO_4)_3$ because it's original source, bauxite, is diminishing in the world due to overutilization (Aderemi *et al*., 2009). The combination tanning using vegetable tannins and $Al_2(SO_4)_3$ prepared from locally available materials deemed environmentally friendly to sustain a leather industry of Tanzania.

1.3 Rationale of the Study

Tanzania is the second country in Africa after Ethiopia in terms of livestock population, which is the only source of hides and skin for leather manufacturing (Mbassa *et al*., 2014). Due to lack of appropriate processing technologies more than 80% of collected hides and skin are exported unprocessed (Ministry of Industry and Trade), depriving the country of employment creation and increased foreign income from export of finished leather and leather goods. In the present study, appropriate tanning agents prepared from locally available materials has been established to address underperformance issue in Tanzania leather sector. More importantly, this method is an eco-friendly and chrome-free tanning method which is deemed environmentally friendly to sustain a leather industry of Tanzania rather than the current chromium tanning method. Furthermore, this method has higher quality output as compared to traditional tanning which involves boiling plant barks and using the decoction for tanning. Boiling temperature leads to co-extraction of non-desirable compounds such as gums that negatively affect the quality of leather (China & Ndaro, 2016). Therefore, the study provides eco-friendly and affordable tanning agents to process hides and skins to the leather for sustainable manufacturing.

1.4 Research Objectives

1.4.1 General Objective

To develop environmentally friendly tanning method using vegetable tannins from the barks of plants plenty available in Tanzania and $Al_2(SO_4)_3$ prepared from Pugu kaolin.

1.4.2 Specific Objectives

(i) To establish the optimum extraction temperature for the recovering vegetable tannins from the barks of plants plenty available in Tanzania.
(ii) To investigate the binding/interaction mechanisms between vegetable tannins from local plants barks and the skin collagen.
(iii) To examine the combination tanning based on vegetable tannins from local plants barks and $Al_2(SO_4)_3$ prepared from Pugu kaolin.

1.5 Research Questions

(i) What is the optimum temperature for extraction of vegetable tannins from local plants' barks that can have all necessary ingredients for active tanning?
(ii) How do vegetable tannins from local plants' barks interact with skin collagen to impart stability to the leather?
(iii) To what extent is $Al_2(SO_4)_3$ prepared from Pugu kaolin suitable for combination tanning with vegetable tannins?

1.6 Significance of the Study

Tanzania is the second country in Africa after Ethiopia in terms of livestock population, which is the only source of hides and skin for leather manufacturing (Mbassa *et al*., 2014). However, more than 80% of collected hides and skin in exported unprocessed (Ministry of Industry and

Trade), depriving the country of employment creation and increased foreign income from export of finished leather and leather goods. Due to that, Tanzania is reported to be among countries with poorly performing leather sector (Wangwe *et al*., 2014). Lack of appropriate technologies contributes significantly to the underperformance of the leather industry of Tanzania.

In the present study, appropriate tanning agents prepared from locally available materials has been established to address underperformance issue in Tanzania leather sector. The tanning agents developed in this work are environmentally benign because they are non-toxic, to replace chromium salts that pollute the environment and affect the smooth running of tanneries due to environmental compliance issues. Moreover, the tanning agents are inexpensive because they are locally produced using local raw materials as opposed to chromium salt that has to be imported. Therefore, the study provides eco-friendly and affordable tanning agents to process hides and skins to the leather for sustainable manufacturing.

1.7 Delimitation of the Study

The study mainly focused on using the barks of four plants and kaolin available in Tanzania to develop an eco-friendly tanning method for leather industry. The plants used was collected from Kilimanjaro and Arusha regions because they grow largely in those areas of the country. Kaolin used was obtained from Pugu hills, Coast region, because compared to other sources, Pugu kaolin is the best in terms of quality and it has high aluminium oxide content. The temperature of extraction was the only parameter optimized for extraction of vegetable tannins from local plants because it is the main parameter that affects the quality of leather as stated in the problem intended to be solved by this study. Molecular characterization of extract was not considered in the present work as the focus was on checking suitability for tanning.

Apart from that, optimization of parameters to prepare aluminium sulphate from kaolin was beyond the scope of present study as the present study focused only on testing the feasibility of using aluminium sulphate from kaolin for tanning. Therefore, optimal parameters for preparation of aluminium sulphate from Pugu kaolin were selected from existing theories. Furthermore, combination tanning, as explored in this study, was limited to assessing the effect of aluminium sulphate concentration and the order of adding tanning agents. Further investigation on why order of adding tanning agents affect the tanning ability was beyond the present scope.

CHAPTER TWO

LITERATURE REVIEW

2.1 History of Leather Tanning

Leather is one of the precious commodity traded worldwide since prehistoric times (Kuria, 2015). It is a natural fiber manufactured from animal hides/skins (Adem, 2019; Bianchi *et al*., 2015). The term hide refers to the outer covering of mature animals of the larger type such as cattle and buffalo, while skin refers to outer covering derived from mature animals of the smaller type such as sheep, goats, pigs and reptiles (Wayua & Kagunyu, 2012). Leather is one of the man's earliest and most useful discoveries, which were used by ancestors to protect themselves from cold as cloth, protect their foot as footwear and also as material for shelter through building of tents (Heth, 2015). Leather was also used to make shields (Bastian *et al*., 2018).

The process of converting raw hides and skin into leather is termed "tanning". The term originated from the discovery of the ability of tannins, plant extractable polyphenols, to react with hides/skins protein rendering it stable against heat and microbial, including enzymatic, attack that could affect the physical condition of the hides/skins (Elgailani & Ishak, 2014). Following such a discovery, in 1796, French Chemist, Armand Séguin, termed the process of converting hides/skins to leather using tannins as vegetable tanning (Falcão & Araújo, 2018).

Vegetable tanned leather becomes durable and thus stay for many years without decomposing, provided the leather is stored away from light, at the room temperature and low humidity (Carsote *et al*., 2014). Durability of leather is caused by permanent stabilization of the collagen protein of hides/skins by the action of crosslinking bonds formed with tanning agents. The ancient Egyptians made durable leather that after over 3000 years, the specimens were discovered in almost perfect condition (Nicholson, 2000; Veldmeijer, 2013). The early Greeks and Romans also made contributions to the science of leather making. Some of their methods such as oil tanning and alum tawing are still in use today (Russell, 2000). Apart from vegetable tannins, the use of other tanning agents, such as, fish oil (Hualong *et al*., 2011), animal's brain (Richter & Dettloff, 2002) and alum (Covington, 2009), were common in ancient times. Collagen stabilization using alum as a tanning agent was considered as tawing rather than tanning because the resultant leather was unstable, reverting to rawhide when alum is washed out (Covington, 2009; Nicholson, 2000).

Until the 18th century, tanning was not considered as a scientific process, but only a method of preserving hides/skins from rotting and making them pliable (Schnitzer, 1935). During the industrial revolution (19th century), leather industry marked its transformation following discovery of chrome tanning (Yeager, 1990). Chrome tanning was invented by the German technologist Friedrich Knapp and Hylten Cavalin from Sweden in 1858, and the technology was later patented by American chemist, Augustus Schultz (Covington, 2009; Yeager, 1990). Since then, chrome tanning became the most common and dominant form of tanning worldwide.

2.2 Steps Involved in Leather Manufacturing

Leather making is a labor-intensive process involving a number of steps to arrive at a finished product. It comprises the mixture of chemical and mechanical processes to impart desired properties. Leather manufacturing is divided into three major steps; pre-tanning, tanning and post tanning (Sarkar, 1981). Each step is independently important to define the quality of finished leather. No step can compensate the mistake overlooked in previous step. Therefore, all steps deserve the same weight of importance (Covington, 2009).

2.2.1 Pre-Tanning of Hides/Skins

Before tanning some components of hides/skins must be removed because their presence hinders uniform interaction of collagen with tanning agents and other chemicals used in subsequent steps. The skin components that must be removed include keratins, elastin, reticulin, glyco-proteins, albumins and globulins. Only collagen protein is retained because it is the one that, due to its fibrous nature, can be transformed to useful material named leather (Covington, 2009; Reed, 2016; Sah, 2013). The processes involved in removing these unwanted components in hides/skins before vegetable tanning include soaking, fleshing, unhairing/ liming, deliming, bating and pickling (Sah, 2013).

Soaking is the first step in the tannery, whereby the cured hides/skins are treated with water and sometimes in combination with detergents to rehydrate the collagen fibres (Black *et al*., 2013). Hides/skins must be soaked to restore the collagen fibres' original moisture that was lost during preservation. Soaking also serves to remove salt used during preservation and get rid of unwanted wastes adhered on the surface of the hide/skin such as dung, blood and soil (Kite & Thomson, 2006). The duration of soaking depends on the condition of preserved hides/skins. Usually, dried hides/skins takes longer processing time than wet salted hides/skins (Covington, 2009).

Soaking is followed by the removal of hairs and other components from the hides/skins. During this process, the hair is removed by subjecting the hides/skins to a depilating agent, which destroys the hair by attacking the hair root so that it can easily be removed (Sarkar, 1981; Zekeya *et al*., 2019). Epidermis and soluble skin proteins such as albumins, globulins and glycoproteins are loosened and removed as well. Although enzymatic unhairing is widely known nowadays (Jian *et al*., 2011; Ramesh *et al*., 2018; Zekeya *et al*., 2019), most tanneries apply lime and sodium sulphide, which are deemed cheaper and easier to control than enzymes (De Souza & Gutterres, 2012). Lime raises the pH of the liquor to alkaline, which is suitable for the action of sodium sulphide to break disulphide bonds in hair that characterize keratin; a protein that makes hair (Yapici *et al*., 2008). Apart from this, pH around 12 brought by lime induces osmotic swelling of the hide/skin that leads to the splitting of the fiber bundles into smaller units, which opens the fiber structure for effective penetration of tannins during tanning (Ramasami & Prasad, 1991; Sarkar, 1981). After liming and unhairing, excess flesh and fats on the side of hide/skin becomes lose and is mechanically removed in the process called fleshing. If not removed, these components would inhibit the penetration of tanning chemicals in subsequent processes. At this stage, hide/skin is referred to as a pelt (Covington, 2009).

Liming is followed by deliming, which is the process of adjusting the pH to 8. The latter reduction in pH is necessary for the subsequent bating stage that involves enzymatic solubilization of non-collagenous proteins present in the hides/skins (Choudhury *et al*., 2006). As collagen protein is the primary constituent that makes leather, all other proteins have to be removed during the bating stage (Dutta, 1999). Deliming also assists in reducing the swelling/plumping of the pelt resulting into a softer, stretchable and flexible leather. This process makes the grain surface of the finished leather clean, smooth and fine (Santos & Gutterres, 2007). Salts of ammonia, particularly ammonium sulphate and ammonium chloride, are commonly used as deliming agents (Sivakumar *et al*., 2015; SLTC, 1999). Before tanning, the pelt is pickled to a pH desirable for reacting with agents in a process termed pickling, with sulphuric acid and formic acid being commonly used to lower the pH (Dutta, 1999; Sarkar, 1981).

2.2.2 Post-Tanning of Hides/Skins

During post-tanning, tanned leather undergoes further chemical treatments to improve the appearance of the finished leather and thus makes it suitable for end uses (Rosu *et al*., 2018). Neutralization, re-tanning, dyeing, fatliquoring and fixing are other essential processes taking place during post-tanning (Zhou *et al*., 2012). Neuralization is for regulating the pH of the tanned leather for effective interaction with chemicals in subsequent processes. Re-tanning involves tanning leather to modify the handling properties. Dyeing intends to give leather the desired colour, while fatliquoring refers to the application of oil to the re-tanned leather for lubrication and preventing fibres from sticking upon drying. After all these processes, fixation is done to ensure all chemicals applied are well fixed to the collagen fibres. Thereafter, formic acid is used during fixation to lower the pH. Lastly, leather is dried, ready for finishing. At this stage, the material is called crust leather (Covington, 2009).

2.2.3 Tanning of Hides/Skins

Tanned leather changes its physical and mechanical properties such as shrinkage temperature, tensile strength, tearing strength and elongation to suit the needs of various end users. Organoleptic properties such as softness also get improved significantly (Nalyanya *et al*., 2018). Overall, tanning is achieved by several methods. Historically, alum tanning, smoke tanning, animal brain tanning and oil tanning were popular (Sarkar, 1981). Until the advent of chrome tanning toward the end of 19th century, options available to the tanner were limited to these methods (Covington, 2009). Currently, the dominant methods are chrome tanning and vegetable tanning that make use of chrome salts and vegetable tannins, respectively, with chrome tanning being the most preferred method (Mahdi *et al*., 2009).

2.3 Chrome Tanning and its Environmental Effects

Chrome tanning has been the most preferred method due to its versatility in processing leather. Approximately 90% of global leather is made by chrome tanning (Jian *et al*., 2012). However, chromium is known to be among hazardous chemicals. In nature, two stable oxidation states (III and VI) of chromium exist with contrasting toxicities, motilities and bioavailability (Patra *et al*., 2019). Chromium (VI) is motile, highly toxic, soluble in water and it is a potent oxidizing agent that causes severe damage to cell membranes. The damage to the cells can cause various cancers, gene mutation and teratogenic effects (Ahmed *et al*., 2017; Nigam *et al*., 2014; Nigam *et al*., 2015).

A study to investigate the sources of high-risk exposures to Cr and related health effects among tannery workers was reported in Kenya. The sample study comprised of workers working in various sections of the tannery. It was found that general workers (perform various tasks including general dusting of the floor, unblocking the drainage systems, collecting, handling and disposal of wastes, general maintenance of the machineries and keeping inventories of processed leather in place) have higher mean concentrations of Cr level (66.8 μg m^{-3}) than workers in other sections because they encounter intense and prolonged exposure to leather dust from multiple point sources, also breathing in air with a high level of Cr. Analysis of the urinary chromium level in the urine of these workers showed that the have an average of 31.1 µg Cr g^{-1} creatinine. This level exceeded the American Conference of Governmental Industrial Hygienists biological exposure index for chromium (30 µg Cr g^{-1} creatinine). Overall, 78% of chromium urinary levels of these general workers exceeded this limit (Were *et al*., 2014).

Moreover, the assessment of the occupational health risks among tannery workers in India revealed a similar trend with a high level of chromium in the urine and blood samples. These findings reflect a chromium burden in the bodies of exposed workers as a result of a high concentration of environmental chromium at the workplace (Rastogi *et al*., 2008).

Analysis of poultry feeds prepared from protein-rich tannery wastes, (trimmings, wet blue shaving dust and low chrome wet-blue scraps), have shown chromium levels far above the recommended daily intake limits (0.2 to 30 µg day^{-1}). Concentrations of chromium as high as 29 854 mg Cr Kg^{-1} were detected in animal feeds while the chromium levels in poultry's meat fed with those feeds were in the range of 0.4 to 0.8 mg Cr Kg^{-1} (Ahmed *et al*., 2017), being above the WHO permissible level of 0.1 mg Kg^{-1} (FAO/WHO, 2000). The high concentrations above the WHO limits implies that consumers of poultry products fed with these kinds of feeds are at a high risk of chromium poisoning.

2.4 Efforts to Minimize Chrome Tanning Environmental Effects

Abandoning chromium usage has been a challenging issue in leather tanning. There are several techniques innovated to improve the conventional chrome tanning so that its environmental effect is abated. Among them are chrome recovering and recycling (Cao *et al*., 2018; Sundar *et al*., 2002) and high exhaustion chrome tanning (Qiang *et al*., 2015; Zhang *et al*., 2016). Both techniques aim at reducing chromium discharged in the effluent of tanneries. With recovering and recycling techniques, chromium in spent tanning liquor is reused instead of being discharged as in conventional chrome tanning. Consequently, chrome discharged in the effluent is significantly reduced (Cao *et al*., 2018). High exhaustion chrome tanning is an improved system in which either auxiliaries (Liu *et al*., 2016; Zhang *et al*., 2017) or alternative solvents other than water (Prokein *et al*., 2017; Sathish *et al*., 2016) are used with chrome, thereby, enhancing the uptake and fixation of chromium in leather fibres. The exhaustion efficiency reported to rise to 90-99% from 60-70% of conventional chrome tanning (Liu *et al*., 2016; Prokein *et al*., 2017; Sathish *et al*., 2016; Zhang *et al*., 2017). By so doing, chrome discharged is largely reduced.

However, these techniques are unable to address the solid waste pollution caused by chrome tanned leather. It has been reported that only 20% of rawhides or skins are converted to leather, while the rest (80%) is generated as solid wastes. The respective proportional of solid wastes generated from tanneries include 56-60% fleshing, 35-40% chrome shavings, chrome splits and buffing dust, 5-7% chrome trimmings and 2-5% hairs (Puvanakrishnan *et al*., 2019). Chrome shavings, chrome splits, buffing dust and trimmings contain chromium, which can easily be deposited in the environment by rain runoff and other natural means (Rahaman, 2017). In light of these facts, chrome-free tanning methods are inevitable (Rao *et al*., 2002). One of the chrome-free tanning methods known for many years is vegetable tanning (Plavan *et al*., 2009).

2.5 Vegetable Tanning

Vegetable tanning involves the use of tannins derived from plants, which are water-soluble polyphenolic compounds having molecular weights of 500 to 20 000 Da (Khanbabaee & Van-Ree, 2001). Besides giving the usual phenolic reactions, vegetable tannins have unique properties such as the ability to precipitate alkaloids and proteins (Haslam, 1979). Vegetable tannins are distributed in many species throughout the plant kingdom. Both dicotyledonous and monocotyledonous plants contain such tannins (Ogiwara, 1980).

Vegetable tanning is among the oldest known leather tanning methods. It was done by treating the hides/skins with leaves and barks containing tannins. Ancients tanned their leather by placing layers of bark, leaves, and fruit over the hides and adding water. This process was sluggish, taking months for thin skin and even years for thick skins to be processed (Kuria, 2015). Vegetable tanning is an eco-friendly method of tanning compared to others, as it discharges minimum pollutants to the environment (Jianzhong *et al*., 2011; Oruko *et al*., 2019). Initially, the use of vegetable tannins was solely related to sole leather production (Reed, 2016). With today's technological advancements, it is feasible to obtain high quality environmentally friendly vegetable tanned leathers with excellent softness, sponginess, tightness and embossing retention properties that can be refined in many ways to adapt to different uses (Ogiwara, 1980). Vegetable-tanned leather has excellent fullness, moldering features, wear-resistance and air permeability. Thus, vegetable tanning is highly crucial in the reduction of chrome pollution in the leather tanning (Faxing *et al*., 2005).

Worldwide, researchers are paying particular attention to the use of vegetable tannins to replace chrome, and some progress has already been achieved. Modifications of the tanning recipe and the improvement of the method of preparing tanning materials has made the vegetable tanning process to be achieved within a day, as penetration and fixation processes have become efficient (Auad *et al*., 2019; Subramani *et al*., 2010; Vitolo *et al*., 2003). The result is a superior product, combining excellent technical characteristics, and aesthetic unique elements, that last and improve over the leather's lifetime (Fig. 1; Koloka & Moreki, 2011). Vegetable tannins are also used in the re-tanning stage and are applied to different kinds of chrome prepared leathers.

Figure 1: Handbag made from oak vegetable tanned leather (Jakobsen, 2016)

2.5.1 Extraction of Vegetable Tannins

Conventionally, production of vegetable tannins is done by countercurrent extraction in vats or stainless-steel vessels. During the process, boiling freshwater is introduced in the most exhausted barks. This water is then fed, vessel by vessel, over a series of barks that are increasingly fresher. As the solution continues, the resultant broth becomes more enriched with vegetable tannins (Sharphouse, 1989). Other extraction methods recently reported include maceration, decoction, microwave-assisted extraction, Soxhlet extraction, superficial fluid extraction, infrared assisted extraction (Cuong *et al*., 2019), to mention a few. The efficiency of each of these methods varies; however, their application in the production of tannins for the leather industry is limited by the required investment and operational costs.

For vegetable tannins source to be economically attractive, it must contain more than a 10% tannin content (Mahdi *et al*., 2006). To achieve this concentration, in a conventional extraction method, the extract solution is concentrated by evaporation. The concentrated extract can either be left to solidify by cooling or spray-dried to obtain powder (Hussein, 2009). However, during concentration by evaporation, high levels of heat energy (high temperature) is applied, which leads to the tannin darkening; hence, affecting its quality, with the heating requirements increasing operational costs (Sharphouse, 1989).

2.5.2 Factors Affecting the Extraction of Vegetable Tannins

The extraction efficiency of vegetable tannins is determined by the type of solvent, temperature, time and solvent extraction cycles, pH, the volume of solvent and particle size in the sample (Mokhtarpour *et al*., 2006). Since the tannins are polar, they are well extracted with polar solvents. Water and organic solvents such as acetone, methanol, ethanol, ethyl acetate and an aqueous solution of the same organic compounds are ideal for the extraction of tannins (Santos-Buelga & Williamson, 2003). Organic solvents are more efficient than water in extracting tannins, but they are more expensive (De Hoyos-Martinez *et al.*, 2019; Waksmundzka-Hajnos & Sherma, 2010). Therefore, for economic reasons, the extraction of tannins for application in the leather industry is done by using water.

Temperature is also an essential parameter in the extraction of tannins because heat renders the cell wall permeable, increase solubility and diffusivity of the compound of interest to be extracted and decrease the viscosity of the solvents thus facilitating its passage through lignin structure of the bark and subsequent separation process (Ogiwara, 1980). However, boiling temperature promotes co-extraction of non-tannins with other large molecular weights constituents such as gums, which affect the quality of the leather. The gums can interact with the amino groups on the hide/skin surface and reduce the penetration of tannins to the inside of the hide/skin structure for uniform tanning. The resultant leather becomes stiff and not fully tanned (Didato *et al*., 1999).

Time taken in exposing barks to the heated solvent also plays a significant role in extract yield. Prolonged exposure of the sample in the warm solvent, allows sufficient time for the desired compounds to migrate into the solvent (Naczk & Shahidi, 2004). However, extended extraction at a temperature above 80 °C decreases the extraction yield because the high heat causes the oxidation and degradation of the desired compounds (Sulaiman *et al*., 2017). Therefore, Sulaiman *et al*. (2017) proposed the minimum temperature to be 60 °C and 120 min for maximum extraction time to produce the highest extract yields of tannins from barks.

The number of extraction cycles also increases extraction efficiency. Thus, apportioning the solvent used and maximizing extraction cycles with virgin solvent in batches is efficient than using the whole solvent in a single extraction cycle (Kuria, 2015). Additionally, the pH of the extraction media determines the degree of solubility for soluble compounds and also influences the possible solubilization of the tannins (Bickley, 1992).

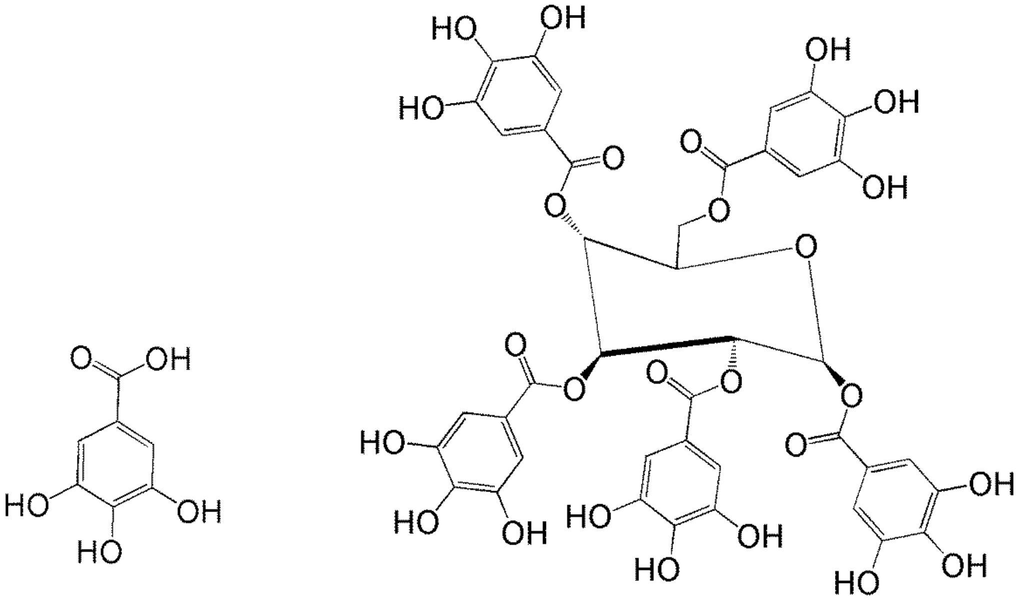
2.5.3 Chemistry of Vegetable Tannins

The chemistry of vegetable tannins differs invariably depending on the biosynthesis pathways (Ossipov *et al*., 2003; Salminen *et al*., 2001). Based on their chemical structures, tannins were previously classified into hydrolysable tannins or pyrogallol and condensed tannins or catechol (Schröpfer & Meyer, 2016). Pyrogallol is the ester of gallic acid. On the other hand, catechol is the polymers formed by the condensation of flavan (Falcão & Araújo, 2018; Covington, 2009; Dutta, 1985). Recently, a new category of tannins has been reported. The tannins in this new category are iridoid compounds (Schröpfer & Meyer, 2016; Schröpfer & Meyer, 2019). Some examples of iridoids are Oleuropein and Ligustrosid, which are found in privet lives (Schröpfer & Meyer, 2019). The nature of their properties makes them different from both pyrogallol and catechol; however, they share similar properties of converting rawhides/skins to leather.

Some components of vegetable tannins are reported to be toxic. For instance, studies have revealed that the uptake of catechol above 800 mg day^{-1} is associated with liver injury (Younes *et al*., 2018; Sergi *et al*, 2020). However, the concentration of catechin in vegetable tannin is sufficiently low to cause liver damage as compared to the effect imposed by chrome. Furthermore, being of organic nature, catechin constituents are biodegradable; hence it is easier to be destroyed in effluent treatment system than the chrome (He *et al*., 2007; Spier & Gutterres, 2018).

(i) Hydrolysable Tannins

Hydrolysable tannins are gallic acid esterified with glucose, having a molecular weight of 500-3 000 Da (Ali *et al*., 2013). They tend to hydrolyse and form blooms. Depending on the hydrolysis products, hydrolysable tannins are divided into gallotannins and ellagitannins (Grasser, 1992). Gallotannins can be hydrolysed to yield gallic acid and glucose, while ellagitannins hydrolyse to ellagic acid and glucose. They produce leather with a yellow or greenish cast; albeit, with good light fastness (Haslam, 1979). The colour darkens thereafter but does not acquire the redness so typically associated with the condensed tannins. Generally, hydrolysable tannins can be extracted from different plants, such as chestnut wood (*Castanea sativa),* oak wood (*Quercus robur*), tara (*Caesalpinia spinosa*) pod (*Terminalia chebula*) and aleppo gall (*Quercus infectoria*) (Haslam, 1989). Figure 2 shows the structure of gallic acid and hydrolysable tannins (Krause *et al*., 2005).



Gallic acid

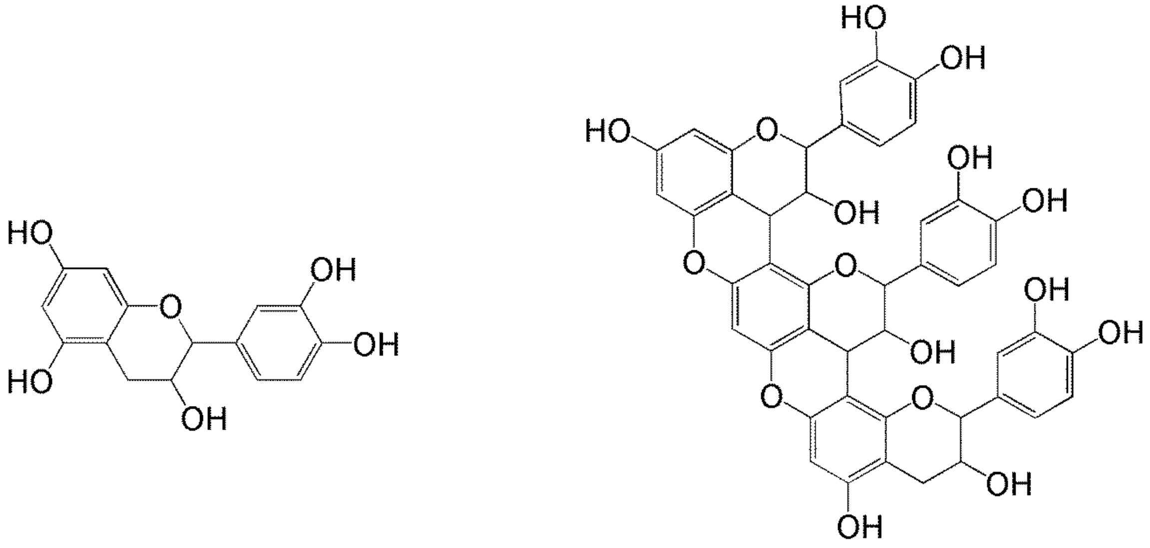
Hydrolysable tannin

Figure 2: Structure of gallic acid and hydrolysable tannins

(ii) Condensed Tannins

Condensed tannins are flavonoid units with a molecular weight ranging from 1 000 to 20 000 Da (Dey & De, 2014). Often, condensed tannins can be found as oligomers of procyanidins (PC) and prodelphinidins (PD) composed mainly of catechin and gallocatechin units, respectively (Ali *et al.*, 2013; Bianchi *et al.*, 2015). The condensed tannins are unsusceptible to hydrolysis, but they are easily oxidized and polymerized to form insoluble substances called phlobaphenes (Smeriglio *et al.*, 2017). They tend to be red (particularly on exposure to air), low in acidity, sugar and salt. Their solution is highly sensitive to pH change; hence, readily precipitate when the pH is lowered. The liquors of condensed tannins deposit less sludge, ferment less and are less liable to mold growth than those of hydrolysable tanning (Sarkar, 1981). Thus, liquors of condensed tannins lose tannin by decomposition only (Kuria, 2015).

Condensed tannins are the most abundant tannins and are found nearly in almost all families of plants (Kuria, 2015). In most cases, tropical woods contain condensed tannins, whereas, temperate woods contain hydrolysable tannins (Krause *et al.*, 2005). The most crucial commercial tanning materials such as Avaram (*Cassia auriculata*), Babul (*Vachellia nilotica*), Hemlock (*Tsuga canadensis*), Mangrove (*Rhizophora mangle*), Mimosa (*Acacia mearnsii*) and Quebracho (*Schinopsis balansae*) belong to this group i.e., the condensed tannins group (Reed, 2016). Figure 3 shows the structure of catechin and condensed tannins.



Catechin

Condensed tannin

Figure 3: Structure of catechin and condensed tannins (proathocyanidins)

(iii) Iridoids

Iridoids are relater structurally to iridodial. The latter can undergo a ring-opening after enzymatic deglycosylation to form two aldehyde groups. Thus, are applied as natural cross-linkers in various applications (Alves, 2017; Li & Zhang, 2015; Schröpfer & Meyer, 2016). However, their use on an industrial-scale for leather processing, is not yet reported.

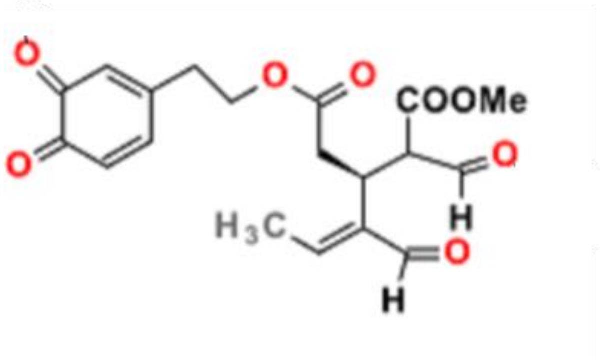


Figure 4: Structure of the iridoid

2.5.4 Mechanism of Vegetable Tanning

Application of vegetable tanning to produce leather involves the interactions between vegetable tannins and collagen of the hide/skin, forming bonds that accounts for the leather stability (Falcão & Araújo, 2018; Schröpfer & Meyer, 2016). The availability of the reactive groups to interact individually, depends on the pH of the media (Adamczyk *et al*., 2017; Kuria, 2015).

Vegetable tannins primarily interact with the side chains amino groups and peptide oxygen of the skin collagen. Depending on the pH of the medium, amino groups can be protonated or deprotonated. The presence of such an interaction has been proven in various studies (Russo *et al*., 2007; Gustavson, 1949; Schröpfer & Meyer, 2016; Velmurugan *et al*., 2014).

Vegetable tannins interact with collagen in four different ways, which are hydrogen bonding, covalent bonding, ionic interactions and hydrophobic interactions (Lu *et al*., 2003; Schröpfer & Meyer, 2016). Hydrogen bonding occurs when phenolic hydroxyl interacts with protonated amino groups or peptide oxygen of the collagen. Simultaneously, covalent bonding happens between the quinone or aldehyde group of tannins and deprotonated amino groups of the collagen (Kasmudjiastuti *et al*., 2019). On the other hand, hydrophobic interaction occurs between the aromatic ring of the phenolic compounds and the hydrophobic region of the collagen (Tang *et al*., 2003b). All these interactions can participate in the tanning of leather; however, the most meaningful interactions that contribute remarkably to the stability of collagen fibres are hydrogen and covalent bonding mechanisms (Kumar & Singh, 1984; Schröpfer & Meyer, 2016).

Furthermore, tannins hydrolysis via hydrogen bonding, occurs between the polyphenolic hydroxyl group with protonated amino groups of the skin collagen (Fig. 4). This reaction is stable at pH 3.0 - 4.5 because above this pH range, the protonated amino groups become deprotonated, thus unavailable for reactions with the phenolic hydroxyl groups (McManus *et al*., 1985; Schröpfer & Meyer, 2016).

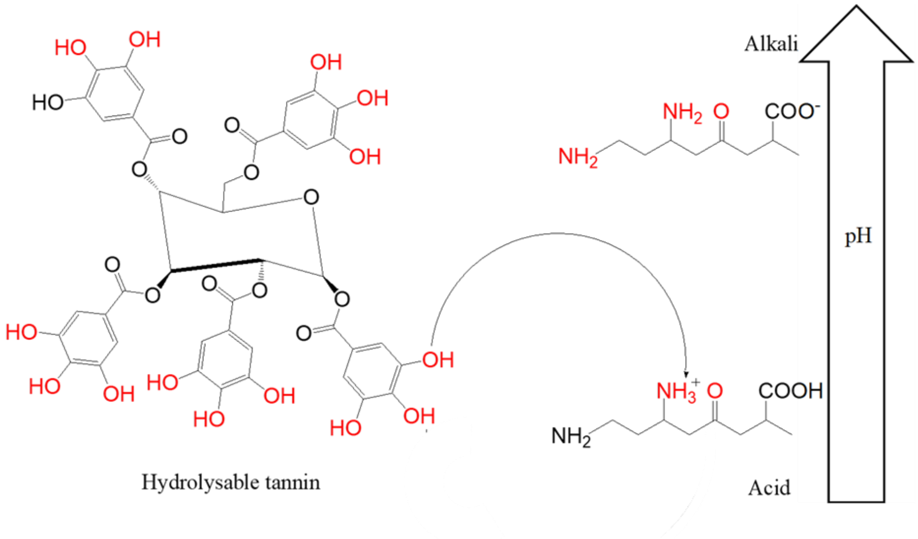


Figure 5: The interaction mechanism between hydrolysable tannins and the skin collagen

The reactions between condensed tannins and skin collagen can proceed via both hydrogen and covalent bonding. At the pH range 3.0 - 4.5, the interaction is similar as in hydrolysable tannins. But at the pH 5.0 – 9.0, the interaction is through covalent bonding between quinones and deprotonated amino groups (Fig. 5). Availability of quinones at the neutral to alkali pH is due to the tendency of phenolic hydroxyl groups to oxidize to quinones enzymatically. However, the covalent bond formed is susceptible to cleavage by acid hydrolysis (Schröpfer & Meyer, 2016; Yang *et al*., 2016).

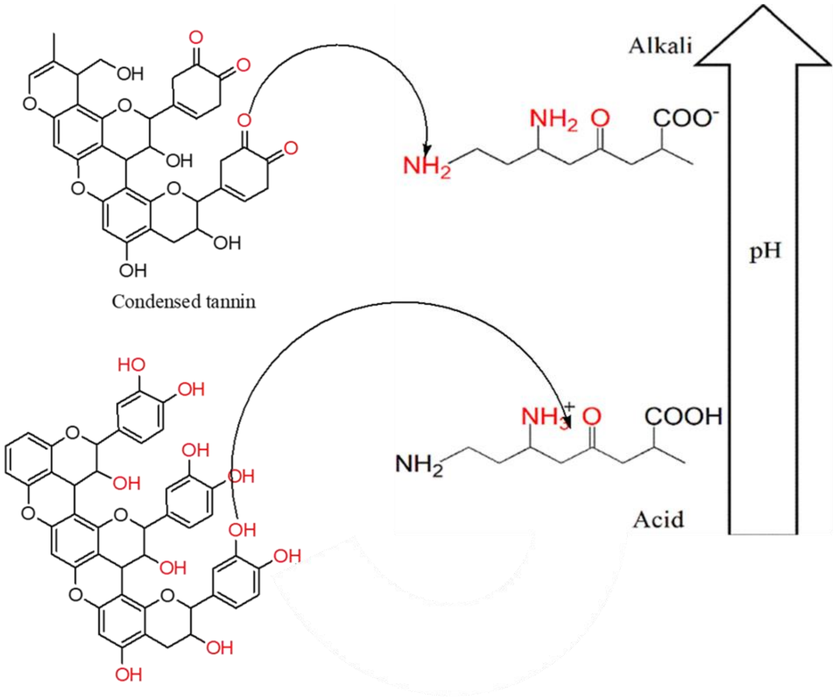


Figure 6: The interaction mechanism between condensed tannins and the skin collagen

Iridoids react in a similar way as condensed tannins, except, iridoids contain an aldehyde group that forms after deglycosylation and ring-opening (Fig. 6). The aldehyde group interacts covalently with the basic amino group of skin collagen to form acid hydrolysis resistant bonds, as opposed to those formed by quinone groups (Schröpfer & Meyer, 2016).

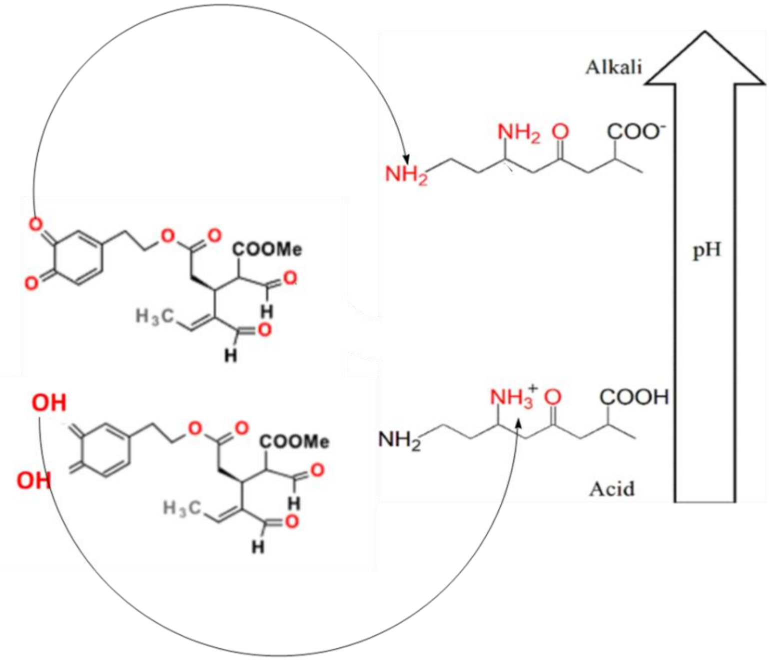


Figure 7: The interaction mechanism between iridoids and the skin collagen

2.5.5 Methods of Studying the Mechanism of the Interaction between Vegetable Tannins and Collagen of Skin

Conventionally, the reaction between vegetable tannins with the collagen has been studied by precipitation of soluble proteins and the calorimetric determination of binding constants (McManus *et al*., 1985), light scattering (Siebert *et al*., 1996), Sodium Dodecyl Sulfate (SDS) polyacrylamide electrophoresis (Konno *et al*., 1999) and turbidity (Siebert, 2006). However, these techniques do not elucidate reaction mechanisms under identical experimental conditions. Moreover, comparing the interaction of vegetable tannins and soluble protein with that of insoluble protein (collagen of skin) would lead to a significant error since insoluble and soluble proteins possess different properties (Schröpfer & Meyer, 2016).

As an alternative, Schröpfer and Meyer (2016) developed a method that compares the interactions of tannins with collagen under identical conditions. The method yields reliable information about the interaction mechanism when vegetable tannins react with the collagen of hides/skins. The method involves reacting the collagen hide powder with the tannins at the pH range from 2.5 to 9.0, followed by Differential Scanning Calorimetry (DSC) analysis, 2,4,6-Trinitrobenzene sulfonic acid (TNBS) assay and Amino Acid Analysis (ASA) on the cross linked hide powder. The DSC analysis gives an overview of the bonds type formed. Subsequently, the TNBS assay confirms the covalent bonds based on the interaction between basic amino groups and quinones. Lastly, the ASA analysis checks the stability of the covalent bonds against acid hydrolysis.

2.5.6 Non-Tannins

Non-tannins are compounds that somewhat have similar chemical nature with tannins, but in practice do not react or attach to hides/skins collagen. They are co-extracted with tannins during the extraction process, and they may be acids, salts or polyphenols (Heidemann, 1993). Although, they lack tanning power, their presence in the tanning liquor is essential and crucial to control the rate of tanning through peptizing real tannins; thereby, increasing their solubility (Ali *et al*., 2013). Moreover, they impart fulness and softness to the tanned leather (Sarkar, 1985; Dutta, 1999). For instance, leather tanned with pure gallotanin is flat, thin and lacks fullness; however, the presence of non-tannins in reasonable quantities gives a soft leather, which feels full, as oppose to an empty leather (Reed, 2013).

Additionally, non-tannins reduce the astringency of tannins; thereby, preventing fixation of tannins on the hide/skin surface. For this reason, the tanners initiate vegetable tanning process with old, mellowed liquors. The latter have high non-tannin content since most of the tannins were bound to hides/skins on the previous tanning process. Thereafter, virgin tannin liquor is gradually increased, using a high liquor strength which is freshly concentrated and thus has astringent tannins (Heidemann, 1993).

2.5.7 Limitations of Vegetable Tanning

(i) Sensitivity to Photooxidation

Vegetable tannins are prone to photooxidation. The prolonged exposure of the leather to UV light results in colour change. Changing in colour is principally due to photooxidation and photodegradation reactions of leather embedded constituents. Photooxidation results in darkening of the leather while the photodegradation causes leather-lightening (Fraga-Corral *et al*., 2020). According to Pizzi *et al*. (2004), leather darkening and lightening can occur consecutively if the tannins in the leather undergo both photooxidation and photodegradation. Photooxidation is the first phase that involves oxidation of phenol hydroxyl groups to quinones and the formation of phenoxyl radicals, which results in the darkening of the leather. The second phase is the degradation caused by phenoxyl radical decay reactions and leads to the partial discolouration of the leather. Some leathers undergo only darkening without a lightening response because the phenoxyl radical formed during photooxidation phase, become resistant to photo decay.

Nevertheless, when photooxidation represents a problem, it can be abated by the condensation of tannins with sulfonated synthetic aminoplastic resins. Melamine-urea-formaldehyde (MUF) is one of the synthetic resins, which provides softness and flexibility to leather while preventing photooxidation. It has low tanning capacity due to its low astringency, which can be counteracted with the use of polyphenols with no need for chromium salts (Pizzi, 2008).

(ii) Low Shrinkage Temperature

Although vegetable tanning plays a significant role in avoiding chromium pollution from the leather industry, replacing chromium tanning with vegetable tanning is being challenged due to the low shrinkage temperature of vegetable-tanned leather. Leather tanned with vegetable tannins has the maximum shrinkage temperature of 85 °C (Covington, 2009). Moreover, the best leather is expected to have a shrinkage temperature above 100 °C because in some stages of making some products such as footwear, leather is subjected to hot steam exceeding 100 °C. At this temperature, vegetable-tanned leather shrinks, which affects the quality of the final product. Due to this weakness, vegetable-tanned leather exhibits limitation in its uses for some products. Such a deficiency can be eliminated by combination tanning.

2.6 Combination Tanning

Combination tanning is a technique whereby two tanning agents, which individually cannot impart the required leather properties, particularly shrinkage temperature, are blended in tanning for efficient tanning. The effect is synergistic rather than additive in which each component work synergistically to give the leather a shrinkage temperature similar to that of chrome-tanned leather (Covington, 1997). Combination tanning is not only used to address shrinkage temperature limitations but also other properties such as dyeability, fulness, softness, colour fastness, tensile strength, tearing strength are improved (Madhan *et al*., 2007).

The combination of vegetable tannins with tanning agents such as Zirconium, Aluminium, Iron and Titanium salts have previously been reported (Bo *et al*., 2013; Covington, 2009). Studies revealed that combination tanning, whereby vegetable tannins are coupled with aluminium sulphate [$Al_2(SO_4)_3$] performs better in enhancing shrinkage temperature of leather than others. Such combination tanning yields leather with shrinkage temperature similar to that of chrome-tanned leather, a mechanistic phenomenon of which is well established (Musa & Gasmelseed, 2013; Covington, 2009; Madhan *et al*., 2007; Brown & Dudley, 2005). Moreover, $Al_2(SO_4)_3$ has a strong capacity of adsorbing pigments and gives the leather cationic properties making it the best mordant for dyeing. Furthermore, $Al_2(SO_4)_3$ is advantageous for being a safe and less-toxic chemical as compared to Chromium salts (Mozaffari, 2018).

2.6.1 Mechanism of Combination Tanning Between Vegetable Tannins and $Al_2(SO_4)_3$

The interaction between vegetable tannins and $Al_2(SO_4)_3$ was postulated in the Link-Lock theory. According to the Link-Lock theory, phenolic hydroxyl group of the tannin, first react with the amino group of collagens, followed by aluminium oxide (generated from $Al_2(SO_4)_3$) cross-linking the polyphenols already bound to the collagen. Figure 7 shows the interaction of vegetable tannins with collagen in the presence of $Al_2(SO_4)_3$ to form a stable matrix that determines the stability. The formed strong and complex matrix accounts for improved physical properties of the leather, notably shrinkage temperature (Covington *et al*., 2008), and consequently others.

Previous studies on combination tanning based on $Al_2(SO_4)_3$ and vegetable tanning deduced that the formation of a stable tanning matrix depends on the concentration of aluminium oxide (Al_2O_3) derived from $Al_2(SO_4)_3$ based on the stoichiometric relationship and the order of addition (Covington, 2009; Slabbert, 1981). Furthermore, it was established that vegetable tannins from some plants work better when they are added first followed by $Al_2(SO_4)_3$ (Abdella *et al*., 2018; Musa & Gasmelseed, 2012). Others determined that these agents work better in the reverse order (Fig. 8; Covington, 1997). The reason for this contradicting order has not been yet established, and thus needs further exploration.

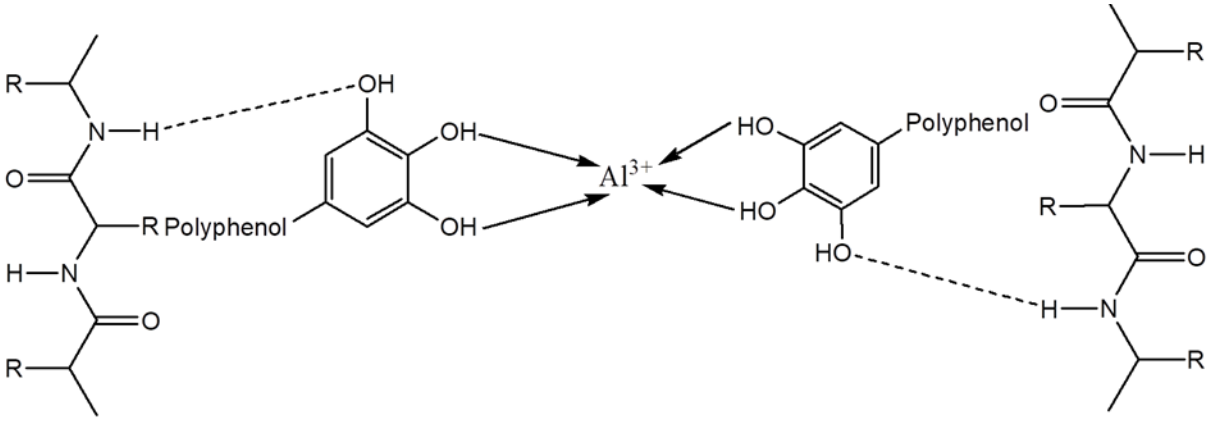


Figure 8: Interaction of skin collagen with vegetable tanning in combination with aluminium (Covington, 2009)

2.6.2 Sources of $Al_2(SO4)_3$ for Combination Tanning

Aluminium being the most abundant metal on the earth's crust (Krebs, 2006; Wood *et al*., 2004), the combination of vegetable tannins and $Al_2(SO_4)_3$ is more likely to be sustainable than that of vegetable tannins with other metal salts such as Titanium and Zirconium. The $Al_2(SO_4)_3$ is available commercially and is currently produced from bauxite (Etuaful, 2013). However, relying on bauxite has some limitations because it is diminishing globally and scarcely present in commercial quantities in most of the developing countries (Aderemi *et al*., 2009). Hence, an alternative source of $Al_2(SO_4)_3$ is an immediate need for sustainability of the leather industry.

Kaolin, an aluminosilicate clay with the molecular formula of $Al_2Si_2O_5(OH)_4$ containing 10-40% aluminium (Al Bakain *et al*., 2014; Granizo *et al*., 2000), is regarded as a potential substitute of bauxite in the production of $Al_2(SO_4)_3$ (Chigondo *et al*., 2015). Structurally, kaolin consists of repeated units of $Al(O_2OH)$ in an octahedral sheet coupled to a silica (SiO_4) tetrahedral sheet. One tetrahedral sheet of SiO_4 is linked through oxygen atoms to one octahedral sheet of $Al(O_2OH)$ (Kloprogge, 2017; Honjo *et al*., 1954). Within this structure two types of OH groups (n=2) are present, with one group extending and forming hydrogen bonds to adjacent layers (surface OH group), while the other OH group is situated within the empty spaces of the octahedral sheets (inner OH group) (Kloprogge, 2017). The structure of the kaolin is held together by hydrogen bonds; hence, in its raw form it is insoluble.

To dissolve aluminium from kaolin, the hydrogen bonds should be thermally decomposed. Thus, during the preparation of $Al_2(SO_4)_3$ from kaolin, the latter is calcined at a high temperature between 750-850 °C. Upon calcination, the kaolin undergoes dehydroxylation and transforms to metakaolin, which is consequently prone to acid dissolution because the bonds holding the structure are broken. The aluminium is exposed; hence, it can be easily dissolved to react with sulphuric acid forming $Al_2(SO_4)_3$ (Al Bakain *et al*., 2014).

About 2.3 billion metric tons of kaolin deposit of high a standard, similar to Georgia kaolin, is located at Pugu Hills, 35 km from Dar es Salaam City, Tanzania (Akwilapo & Wiik, 2003; Kimati, 2012; Schwaighofer & Muller, 1987). The potential of Pugu kaolin for industrial use is still untapped (Akwilapo & Wiik, 2003; Kimati, 2012). Thus, its utilization is limited and the ceramic industry seems to be the sole industry interested in this resource indicating underutilization (Kimambo *et al*., 2014).

2.6.3 Applications of $Al_2(SO4)_3$ from Kaolin

The use of kaolin as the source of aluminium for the preparation of $Al_2(SO_4)_3$ has recently gained attention, especially in the application as a flocculant in water treatment due to both environmental concerns and an economic viewpoint (Chigondo *et al*., 2015; Kuranga *et al*., 2018). However, there is limited information on the use of kaolin based $Al_2(SO_4)_3$ in combination with vegetable tannins in leather tanning. Therefore, this study investigated combination tanning based on $Al_2(SO_4)_3$ prepared from kaolin and vegetable tannins extracted from plant barks plenty available in Tanzania to develop eco-friendly and sustainable leather tanning technologies using local resources.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

Plant barks used for extraction of tannins were collected from various parts of Northern Tanzania. The stem barks of *A. xanthophloea* were collected from NM-AIST campus (Arusha, Tanzania), whereas that of *E. divinorum* were collected from Loliondo (Manyara, Tanzania). The stem barks of *A. mearnsii* and the root barks of *E. racemosa* were collected from Usangi (Kilimanjaro, Tanzania) (Fig. 9). The four plants were chosen based on indigenous knowledge. The communities that engage in traditional leather making employ at least one of these plants. Thus, it was worth exploring the best way to use them to enrich the traditional knowledge.

Kaolin used in this work was collected from Pugu hills, Pwani Region, Tanzania (Fig. 10). Hide powder and hide pelt samples were donated by Forschungsinstitut für Leder und Kunststoffbahnen (FILK), Research Institute of Leather and Plastic Sheeting in Germany. The skins pelts were generously donated by the Central Leather Research Institute (CLRI) pilot tannery in India. The tail of the albino mice was provided by the CLRI CHORD department. All chemicals (sodium carbonate, hydrochloric acid, citric acid, disodium hydrogen phosphate, monosodium phosphate, disodium phosphate, sodium hydrogen carbonate, lithiumcitrate buffer, Folin-Ciocalteu's phenol reagent, gallic acid, aluminium chloride, sodium hydroxide, catechin, sodium nitrite, aluminium sulphate, sodium citrate, ninhydrin, sulphuric acid, sodium carbonate, TNBS and trisodium citrate) used were of analytical grade. For tanning trials, commercial-grade chemicals were used.

Figure 9: The plants used in the study and their respective chopped and milled barks

Figure 10: Images showing the location of Pugu Hills and kaolin deposits

3.2 Extraction and Characterization of Vegetable Tannins from Investigated Plant Barks

3.2.1 Extraction of Tannins

Collected plant barks were dried under a shed for five days and cut into small chips. The chipped pieces were ground in a milling machine (Pulverisette 19, Fritsch GmbH Idar-Oberstein, Germany) and sieved by a 1 mm size mesh. The choice of particle size was based on the previous studies (Schröpfer & Meyer, 2016), which emphasize the use of small bark particle size enough to give a large surface area for mass transfer and large enough to prevent particles compactness (Baldosano *et al*., 2015). Therefore, 1 mm barks particle size was chosen in this study.

The maceration extraction method was employed with minor modifications. About 20 g of the milled barks were soaked in 200 mL of distilled water in a glass beaker covered with aluminium foil to prevent water evaporation. The mixture was placed in a water bath maintained at a chosen temperature (30, 50 and 80 ºC). The stirring of the sample mixture was maintained using an overhead stirrer connected to the beaker's opening through a small hole made on the aluminium foil (Fig. 11a). Extraction process continued for 4 h, then the filtrates were collected (Fig. 11b). Time for extraction was extended for 4 h to give the barks and water a longer time of contact.

The residues were subjected to the second extraction cycle using 200 mL distilled water for 4 h. First and second filtrates were mixed and concentrated at 40% under vacuum using a rotary evaporator (Büchi, Labortechnik AG, Essen Germany) (Fig. 11c) and then lyophilized and dried in the freeze dryer (Martin Christ Gefriertrocknungsanlagen GmbH, Osterode, Germany). Resultant plant extract powders (Fig. 12) were analysed for plant extract yield, tannin content (TC), total phenolic content (TPC) and total flavonoid content (TFC).

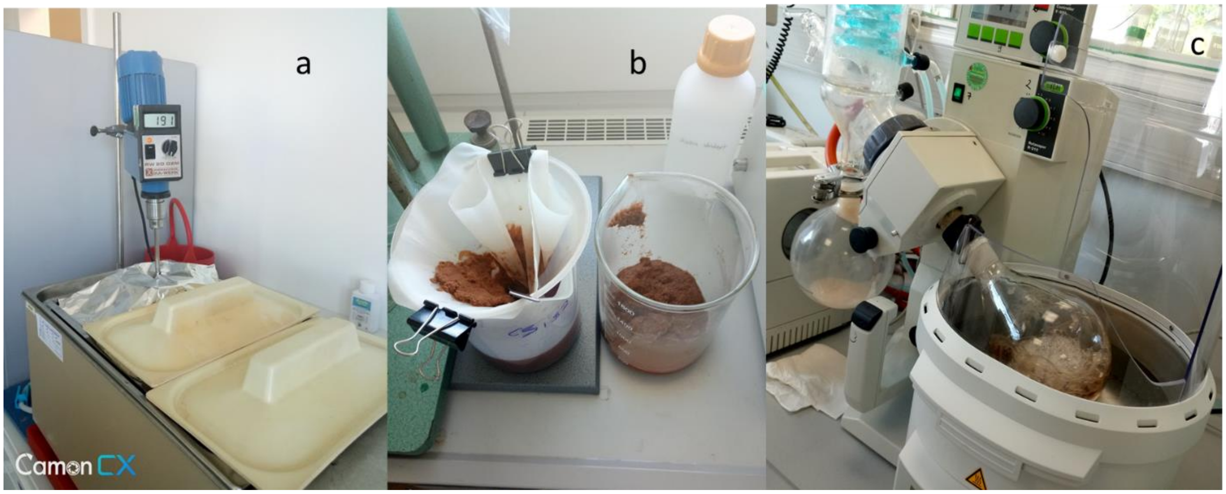


Figure 11: Recovery of vegetable tannins from plant barks (a) extraction process (b) filtering (c) concentration

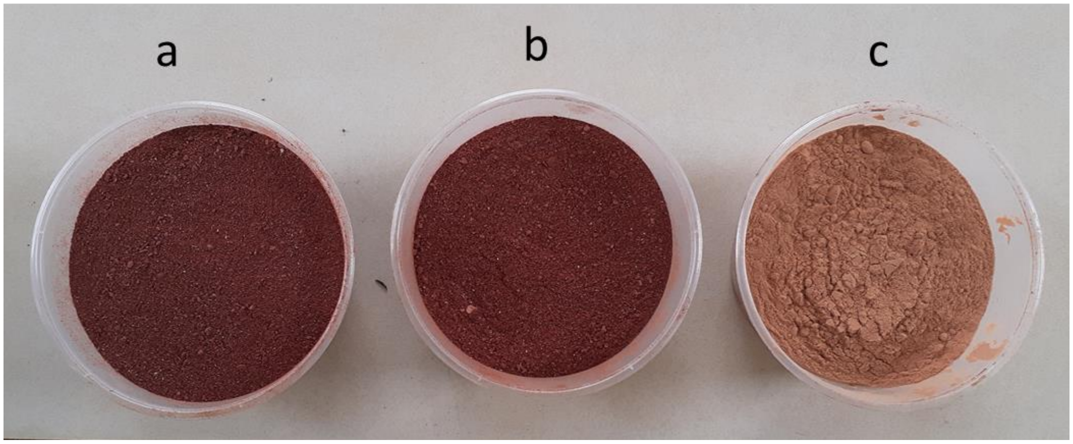


Figure 12: Plant Extracts powder after freeze drying (a) *E. divinorum* (b) *A. xanthophloea* (c) *A. mearnsii*

3.2.2 Determination of the Plant Extract Yield

The extract yield was determined based on the dry plant extract weight and the weight of dry barks by using equation 1

$$\% \, Extract \, yield = \frac{Plant \, Extract \, obtained \, (g)}{Amount \, of \, moisture \, free \, barks \, used \, (g)} \times 100 \qquad 1$$

3.2.3 Determination of the Tannin Content

Tannin content was determined by a filter bell method as described by Atkin and Thompson (1937). Unfiltered tannin solution was detanned by lightly chromed Freiberg Hide Powder batch number ‘VK 383’. Dry cotton-wool was placed in the upper part of the bell to prevent hide powder from passing through the capillary. The neck was fixed with a rubber stopper carrying a capillary glass tube bent twice at a right angle. Subsequently, the bell was filled with 7 g of hide powder and pressed outward onto the bell’s wall to block channels that may allow tannin solution to pass through undetanned.

The filter bell so prepared was placed in a 200 mL beaker, and the latter was filled with a tannin solution and placed in the water bath maintained at 18 °C. After the tannin solution having been absorbed by the hide powder up to the neck, gentle suction was applied to the capillary limb until the liquid flowed out slowly at the rate of 8-10 drops per minute (Fig. 13 and 14). The first 30 mL of the detanned solution was discarded; however, few drops were retained for the gelatin test. Exactly 50 mL of the next 60 mL was evaporated (Fig. 16) and dried to a constant weight to determine non-tannin content. Tannin content was obtained as follows (Equation 2).

$$\text{Tannin content} = \text{Soluble substances} - \text{non tannins} \qquad 2$$

A gelatin test was carried out to the detanned solution to check the completeness of the detanning process. A volume (5 mL) of the detanned solution was placed in to test tubes, and a few drops of the aqueous solution of gelatin and sodium chloride were added. The formation of precipitate was monitored (Fig. 15). Water and the tannin solution were tested as negative and positive controls, respectively.

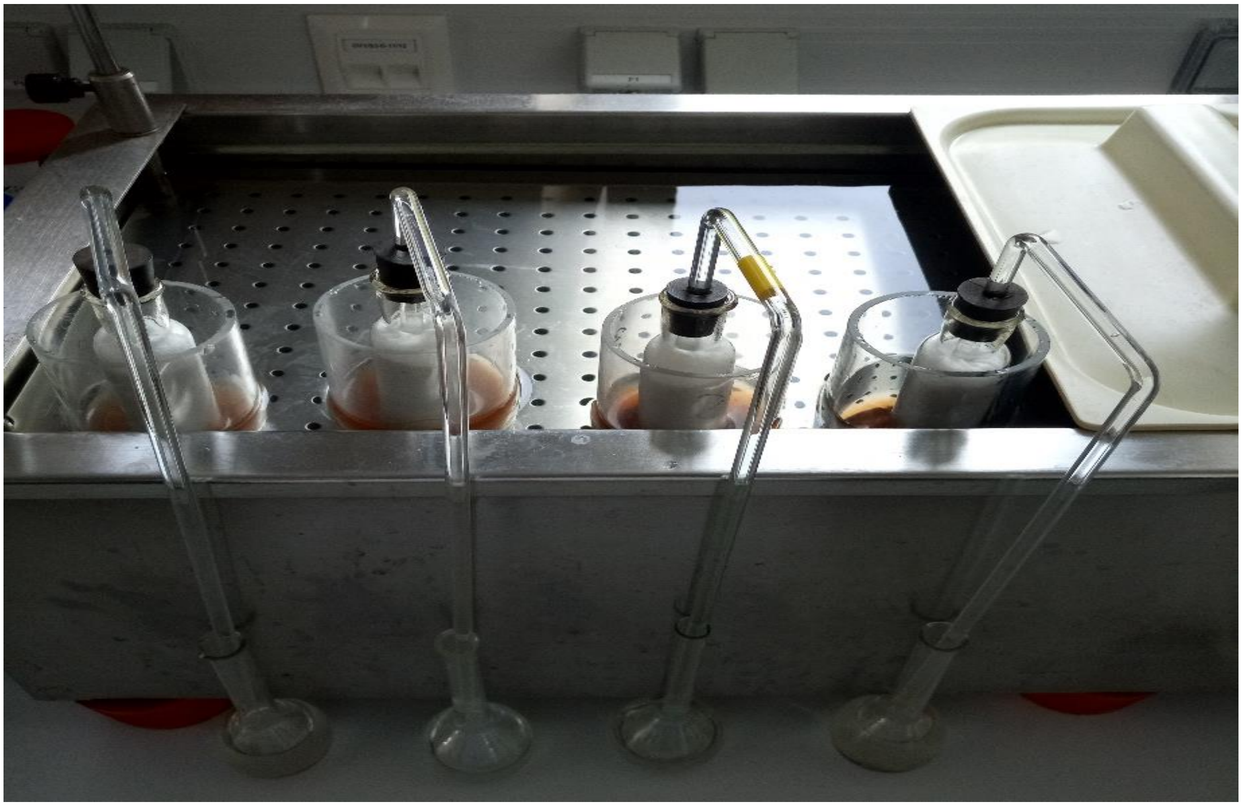


Figure 13: Experimental setup for the determination of tannin content

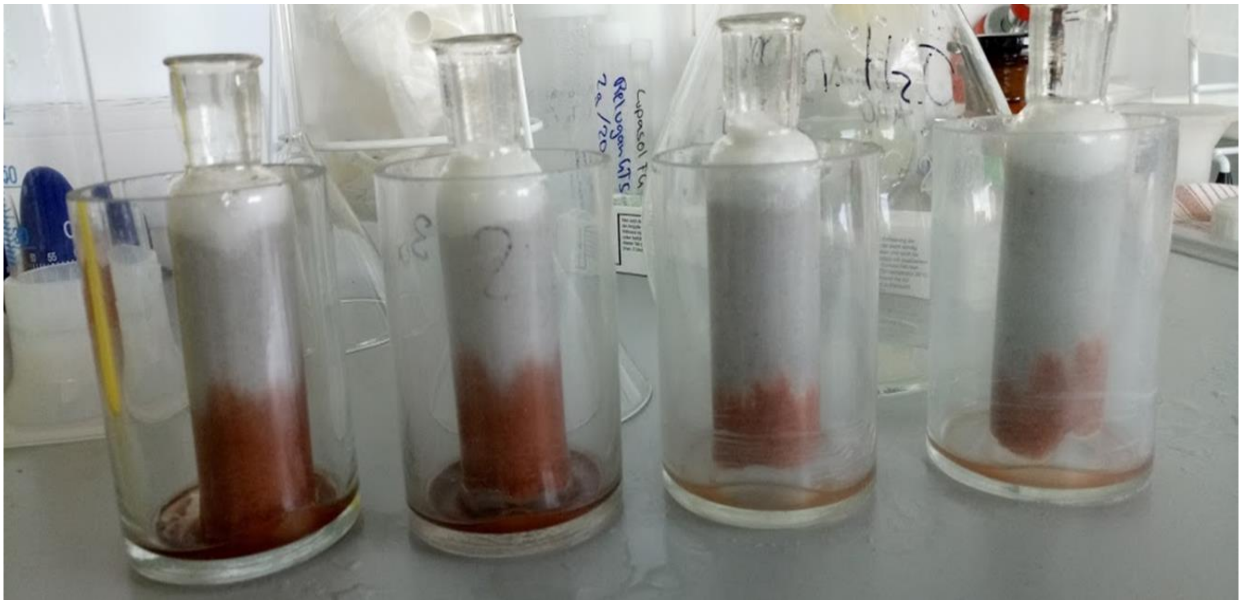


Figure 14: Tannins trapped by the hide powder inside a filter bell

Figure 15: Gelatin test tubes. (a) water (b, c and d) detanned solutions of *E. divinorum*, *A. mearnsii* and *A. xanthophloea*, respectively (e) tannin solution (f) detanned solution of *E. racemosa*

Figure 16: Evaporation of the detanned solution

3.2.4 Determination of the Total Phenolic Content

Determination of the Total Phenolic Content (TPC) was carried out as previously described (Blainski *et al*., 2013). A volume (5 mL) of 10% Folin-Ciocalteu's phenol reagent was added in to 0.2 mL of the plant extract solution and mixed well. After 6 minutes, 4 mL of 7.5% sodium carbonate was added. The mixture was diluted to 25 mL with deionized water and incubated for 90 minutes (Fig. 17). Absorbance was recorded at 760 nm using UV-VIS spectroscopy (Photometer Jasco V630, Jasco-GmbH, Groß Umstadt, Germany). Gallic acid was used to obtain a calibration curve, and the concentrations used were 50, 75, 100, 125, 200 mg mL^{-1}. The TPC was expressed as mg gallic acid equivalent per g dry weight of the barks and then presented as a percentage based on dry bark weight.

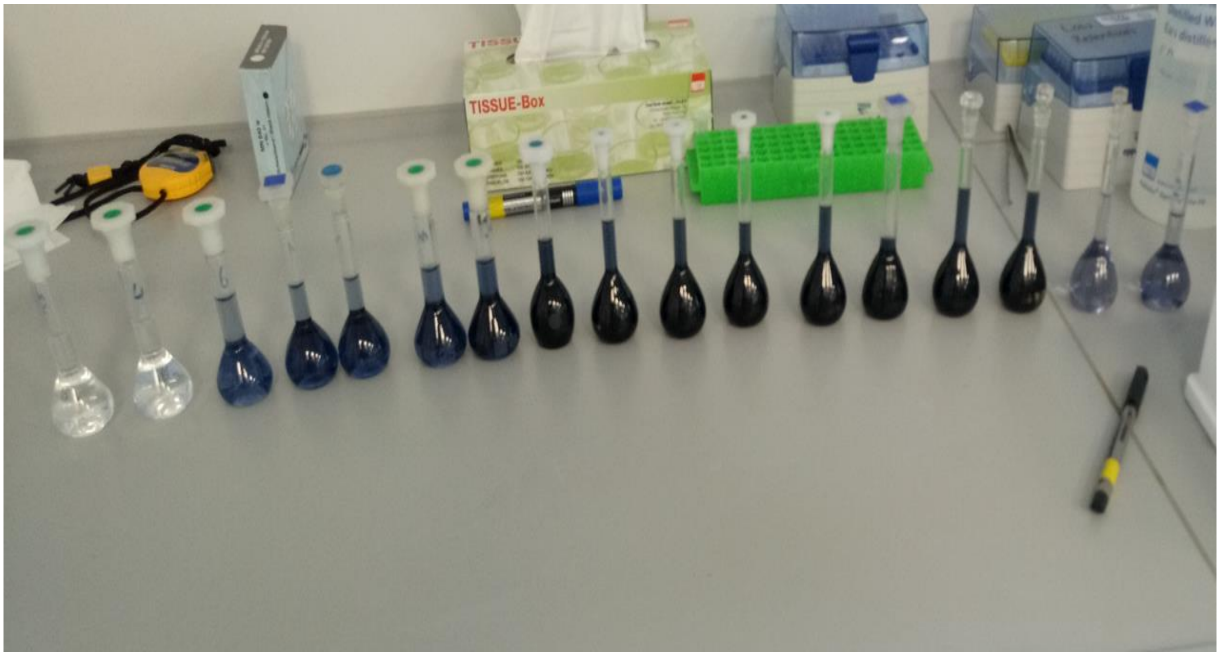


Figure 17: Samples for the Folin-Ciocalteu's assay to determine the Total Phenolic Content

3.2.5 Determination of Total Flavonoid Content

Determination of the Total Flavonoid Content (TFC) was performed as described previously (Kamtekar *et al*., 2014). Deionized water (4 mL) was added in 0.5 mL of the plant extract solution followed by 0.3 mL of a 5% $NaNO_2$ solution. After 5 min, 0.3 mL of 10% $AlCl_3$ solution was added. The solution was allowed to stand for 6 min, then 2 mL of a 1 M NaOH solution was added. Finally, the volume was made up to 10 mL with deionized water and allowed to stand for 15 min before reading absorbance at 510 nm using UV-VIS-spectroscopy (Photometer Jasco V630, Jasco-GmbH, Groß Umstadt, Germany) (Fig. 18). Catechin was used to obtain the calibration curve, and the concentrations used were 20, 40, 60, 80 and 100 mg mL^{-1}. The TFC was expressed as mg catechin equivalent per g dry weight of the barks and then presented as a percentage based on dry bark weight.

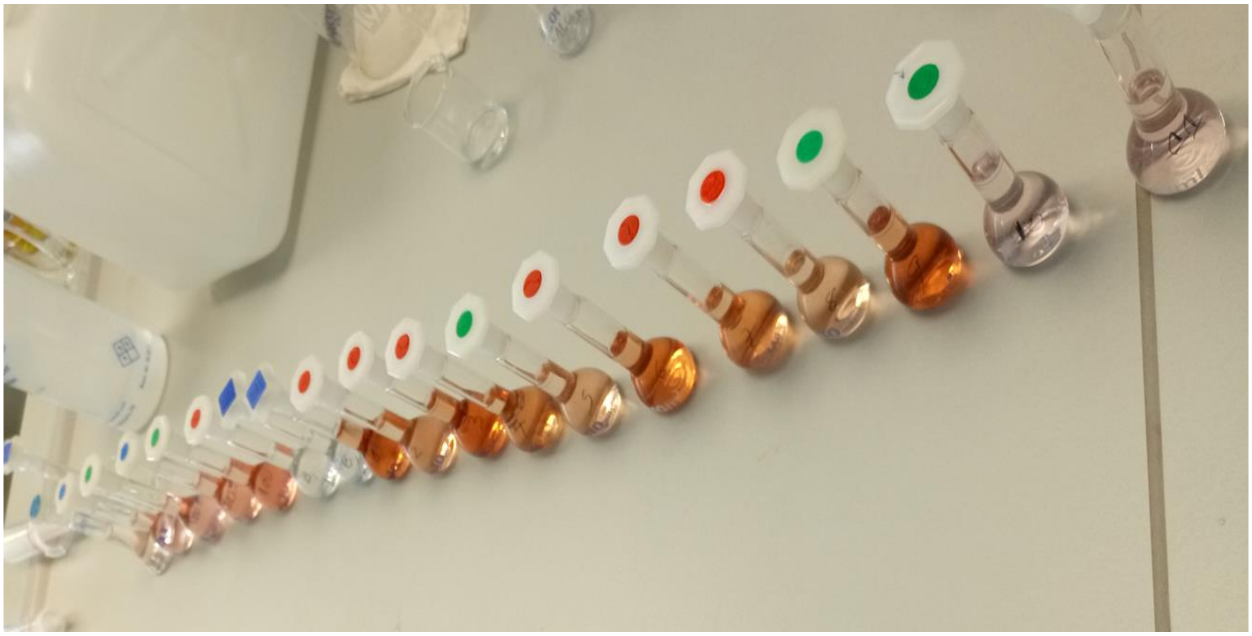


Figure 18: Samples for the determination of Total Phenolic Content

3.2.6 Preparation of Hide Powder Cross-Linked with the Extract from Investigated Plants

To evaluate the cross-linking capacity of the extracts, hide powder was treated with extract solutions by using an already established method (Schröpfer & Meyer, 2016). About 1 g of hide powder was soaked in 20 mL 0.4 M McIlvain buffer at pH 5 for 1 h. 5% (w/v) of plant extracts were added, and the solution was shaken in a mechanical shaker (Type SW 20 C, Julabo GmbH, Seelbach, Germany) at 35 °C for 5 h (Fig. 19). Then, the solution was filtered using a vacuum pump (Type N 726.3 FT.18, KNF Neuberger GmbH Freiburg im Breisgau, Germany) (Fig. 20). Filtrates were discarded and the treated hide powder was reserved for further analysis. A mass (few mg) of the crosslinked hide powder was taken for denaturation temperature analysis using a DSC device (DSC 1, Mettler-Toledo, Gießen Germany).

The effect of combining vegetable tanning with $Al_2(SO_4)_3$ on improving the crosslinking ability of the tannins was investigated. The extract of *E. racemose* showed poor crosslinking ability; hence, not considered for the subsequent experiments. In the first trial, the effect of adding vegetable tannin first was assessed. About 0.5 g of hide powder was placed in each of the 15 tubes (50 mL). Phosphate buffer saline (PBS) (pH 5) was added in each tube to soak the hide powder for 1 h at ambient temperature. The tubes containing soaked hide powder were separated into three groups of five tubes each. 5% (based on hide powder weight) of *A. xanthophloea, A.*

mearnsii and *E. divinorum* extracts' powder were added in the first, second and third group of tubes (n=15), respectively. The mixture was shaken in a water bath at 35 °C for 5 h.

Then the mixture was vacuum filtered, washed with deionized water until the supernatant was clear. Varying concentrations of basified $Al_2(SO_4)_3$ ranging from 1, 2, 3, 4 and 5% Al_2O_3 (based on hide powder weight) at pH 3.2 (masked with 8:1 of ratio Al^{3+} and sodium citrate) were added serially in 1 to 5 tubes in each group and placed in a shaking bath at 35 °C. After 3 h, the pH was adjusted to 4.5, and then the shaking was continued for an additional 3 h. Then the mixture was vacuum filtered, and the tanned hide powder samples were washed (3 times) with 10 mL of deionized water. About 20 mg of the damp filter cake was reserved for DSC analysis, while the rest was dried in ambient condition.

In the second trial, the reverse order was checked. About 0.5 g of hide powder was placed in each of the 15 tubes (50 mL) then the latter were separated in to three groups of five tubes each. Basified $Al_2(SO_4)_3$ at pH 3.2 (1, 2, 3, 4 and 5% Al_2O_3 based on hide powder weight) was added serially in 1 to 5 tubes in each group and placed in a shaking bath at 35 °C. After 3 h, the pH was adjusted to 4.8-5.0 with continued shaking for 3 more hours. Then, 5% of *A. xanthophloea, A. mearnsii* and *E. divinorum* extracts were added in the first, second and third group of tubes, respectively. The mixture was shaken in a water bath at 35 °C for 5 h. Then the mixture was vacuum filtered, washed with deionized water until the effluent was clear. About 20 mg of the damp hide powder sample was reserved for DSC analysis, while the rest was dried in air. Control samples of hide powder were prepared by tanning with 5% plant extracts only.

The cross-linking ability of the hide powder was determined on a DSC device (DSC 1, Mettler-Toledo, Gießen Germany) as reported earlier (Schröpfer & Meyer, 2016). Approximately 6 mg (calculated on dry weight) of the wet cross-linked hide powder was placed in an aluminium pan and hermetically closed. Temperature scans were run from 10-125 °C with a rate of 5 °C min^{-1}. The endotherm's onset temperature (T_{peak}) and peak temperature (T_{onset}) were calculated (Fig. 21). The remaining treated hide powder was made into tablets and dried under ambient temperature for 2 days. The thickness and softness of the hide powder were determined using thickness a gauge and softometer (KWS Basic-Wolf Meßtechnik GmbH, Freiberg), respectively.

Figure 19: Preparation of crosslinked hide powder

Figure 20: A vacuum pump filtering cross linked hide powder

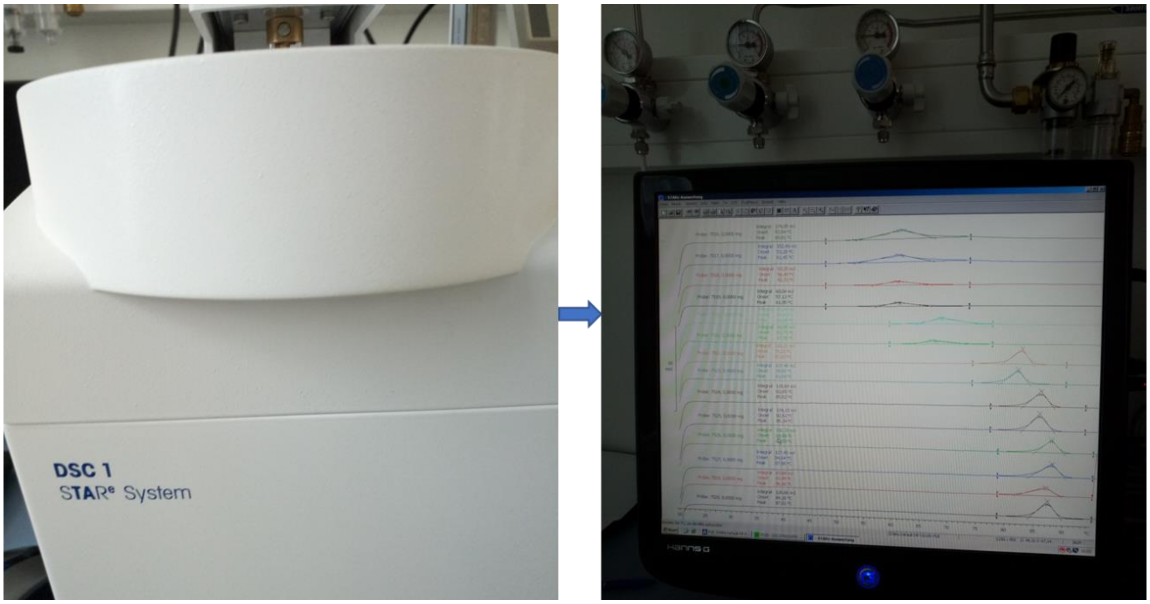


Figure 21: Differential scanning calorimetry and a thermograph generated during the analysis of cross-linked hide powders

3.2.7 Preparation of Leather Samples Tanned with Vegetable Tannins from Investigated Plants

The limed pelts were tanned with 22% of each extract, except the extract of *E. racemose*, using a conventional tanning method (without post-tanning) (Fig. 22) to assess its performance in shrinkage temperature, mechanical and chemical properties including surface modifications. Table 1 shows the tanning recipe used to tan the leather samples. The hydrothermal stability of the leather was assessed by measuring shrinkage temperature and denaturation temperature by using conventional shrinkage temperature (CST) test and the DSC method, respectively.

Table 1: The tanning recipe used to tan leather samples

Process	Dose (%)	Product	Running time (min)	Remark
Wet back	100	Water		
Pickling	10	NaCl	10	
	0.5	Formic acid	10	
	0.2	Sulphuric acid	30	pH=3.8
			Overnight	
			Drain, wash	
Tanning	150	Water		
	5.5	Plant extract	15	
	5.5	Plant extract		
	0.1	ERHA GM 3034	15	
	5.5	Plant extract		
	1	Ensul AM 90 (Fatliquor)	90	
Fill up	250	Water		
	5.5	Plant extract	90	
			Drain	
			16 hs	
3x wash	150	Water	10	
			Drain	
Preservation	150	Water		
	0.1	Mortanol (Antifungal)	20	
			Drain	
			Hang overnight	
			DSC, CST tests before drying	

Figure 22: Tanning process in the experimental drums

3.2.8 Determination of the Properties of Leather Samples Tanned with the Tannins from Investigated Plants

For DSC analysis, to assess denaturation temperature, approximately 6 mg of wet leather sample was placed in an aluminium pan and hermetically closed. Temperature scans were run from 10-125 °C with a rate of 5 °C min^{-1}. The endotherm's onset temperature (T_{onset}) and peak temperature (T_{peak}) were calculated. For conventional shrinkage temperature test (CST) to measure the shrinkage temperature, wet samples with dimensions of 2 × 4 cm were clamped and immersed in water, which in turn was stirred vigorously using a magnetic stirrer. The temperature of the solution was gradually increased. The temperature at which the sample shrunk by one-third of its original length was recorded. Testing was repeated twice per each sample (Fig. 23e). Mechanical properties were analysed as per EN ISO 17235:2015 method. SEM images of tanned leather and control sample were captured on both grain surface and cross-sectional using a SEM machine ((Fei)-Thermo-Fisher Scientific- Eindhoven, NL).

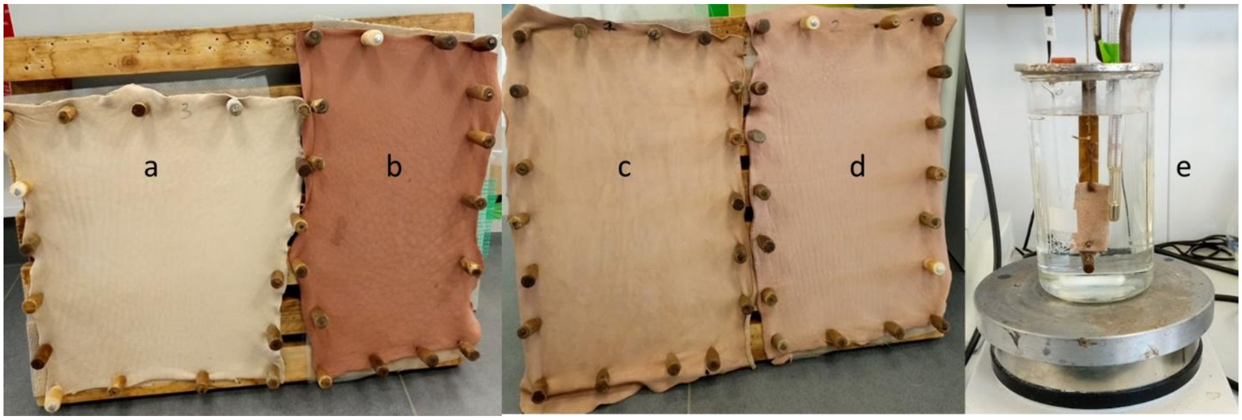


Figure 23: Determination of shrinkage temperature (CST) of the leather samples (a) control (b) *E. divinorum* tanned leather (c) *A. mearnsii* tanned leather (d) *A. xanthophloea* tanned leather and (e) shrinkage temperature testing (CST)

3.3 Preparation and Analysis of Crosslinked Hide Powder Samples for Studying the Interaction Mechanism

Combined analyses were performed to understand the interaction mechanism between tannins and collagen of hide powder as well as to identify the classes to which the tannins in the plants' extracts belong.

3.3.1 Preparation of the Hide Powder Cross-linked at Various pH

Cross-linked hide powder was prepared by mixing with tannin extracts at different pH ranging between 2.5 and 9.0. Hide powder was soaked in 20 mL of 0.4 M McIlvain buffer at varying pH

(2.5, 3, 4, 5, 7 and 9) for 1 h. 5% (w/v) of the plant extracts was added, and the solution was shaken in a mechanical shaker at 35 ºC for 5 h. The solution then was filtered using a vacuum pump. The filtrate was discarded and the cross-linked hide powder taken for analysis. The samples were either washed 3 times with excess water and finally soaked in phosphate buffer at pH 7 or remained unwashed, to assess the reversibility of any imparted (cross-link) effects.

3.3.2 Differential Scanning Calorimetry (DSC) Analysis to Determine Interaction Trend

The DSC analysis to the hide powder samples crosslinked at different pH was carried out as described in section 3.2.6.

3.3.3 2, 4, 6-Trinitrobenzenesulfonic Acid assay to Determine Cross-linked Basic Amino Groups

A TNBS assay was carried out as per the method developed by Schröpfer and Meyer (2016). About 5 mg of the cross-linked hide powder (pH 7) was incubated in 200 mL 0.5 M sodium hydrogen carbonate buffer at pH 8. A volume (200 mL) of 0.5% 2,4,6-Trinitrobenzenesulfonic acid (TNBS) was added into that mixture. The samples were incubated at 60 °C for 4 h to allow binding of the TNBS on the free primary amines in the hide powder collagen. Thereafter, the mixture was hydrolyzed with 6 N HCl at 80 °C for 1.5 h, then diluted with 1 ml distilled water and centrifuged at 14000 rpm. The supernatants were taken for measuring the absorption photometrically at 400 nm (Fig. 24). Quantification was performed by calibration with an alanine standard. The number of primary amines bound by the tannins was calculated based on the number of free primary amines of cross-linked and non-crosslinked hide powder samples (Equation 3).

$$\%\ \text{of crosslinked amino groups} = \frac{100 - \text{free amines }(\mu\text{mol per g dry sample})}{\text{mean value free amines }(\mu\text{mol per g dry hide powder})} \times 100 \qquad 3$$

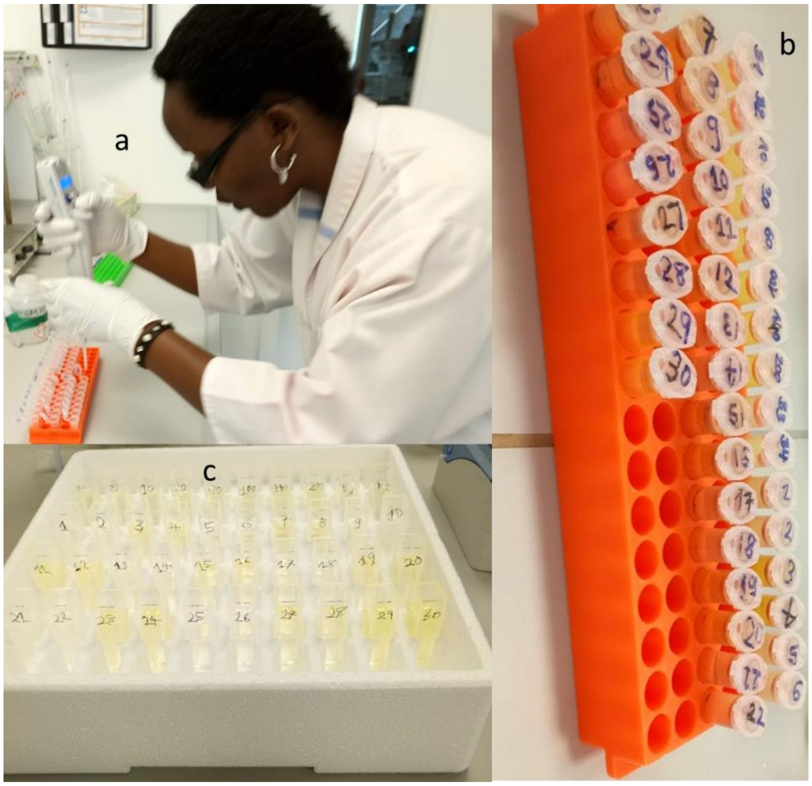


Figure 24: 2,4,6-Trinitrobenzenesulfonic acid assay (a) sample preparation (b) sample incubation (c) samples for measuring absorption

3.3.4 Amino acid Analysis to Assess the Resistance of Cross-linked amino Group on Acid Hydrolysis

The amino acid analysis was performed as per Schröpfer and Meyer (2016). Cross-linked hide powder samples were hydrolyzed with 6 N HCl at 110 °C for 20 h, then dried and dissolved in a lithiumcitrate buffer. The amino acid composition was determined from the cross-linked and non-cross-linked samples by an amino acid analyser (Biochrom 30+, Biochrom Ltd, cambridge UK) using pre-column derivatization with ninhydrin according to standard protocols (Breck *et al.*, 2005). The percentage of primary amines that formed an acid-stable bond was calculated from the area under the lysine, hydroxylysine or arginine peaks and standardized to the area under the peaks from alanine and valine (these did not involve cross-linking). The resulting factor was related to a similar factor calculated from non-cross-linked samples.

3.4 Preparation and Application of Aluminium Sulphate from Kaolin in Combination Tanning

3.4.1 Characterization of Kaolin

Three different techniques were used to analyse clay to ensure that the 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). The 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.

3.4.2 Preparation and Characterization of $Al_2(SO4)_3$ from Pugu Kaolin

Preparation of $Al_2(SO_4)_3$ from Pugu kaolin was carried out as previously described (Chigondo *et al*., 2015) with minor modifications. Figure 25 illustrate the whole process of preparing $Al_2(SO_4)_3$ from the Pugu kaolin. The kaolin sample was screened through a 250 µm sieve and was calcined in a marble furnace at 750 °C for 120 min. A leaching experiment was done by contacting the same sample with an aqueous solution of 3 M Sulphuric acid (H_2SO_4) in 500 mL reaction flask. During the leaching experiment, 300 mL of the Sulphuric acid solution was transferred into the reaction flask and heated under reflux conditions until the temperature reached 90 °C. Then, 30 g of the clay was added into the reactor and the formed slurry was stirred at 150 rpm. After 120 min, the mixture was cooled and centrifuged at 4 000 rpm for 5 min. The supernatant was concentrated in a water bath until a white slurry was formed. About 3 mg of the formed slurry was analysed using FTIR and XRD. The rest was basified using a 10% Na_2CO_3 solution and masked with $Na_3C_6H_5O_7$ at a ratio of 1:8, subsequent for use in combination tanning experiments with the *A. mearnsii* extract.

Figure 25: Preparation of $Al_2(SO_4)_3$ from kaolin (a) sieving (b) calcination (c) extraction of Aluminium from calcined kaolin and (d) preparation of the $Al_2(SO_4)_3$

3.4.3 Testing the Cross-linking Ability of $Al_2(SO4)_3$ Prepared from Kaolin

The cross-linking ability of $Al_2(SO_4)_3$ made from kaolin was verified by interacting it with the albino rat tendons (RTT) (Fig. 26). The latter was chosen because it contains collagen type one (collagen I) (Rittié, 2017), which is similar to collagens of the hide/skin used. For that reason, RTT is mostly used as an alternative source of collagen to hides/skin to study the cross-linking ability of the tanning materials (Collighan *et al*., 2004; Skopinska-Wisniewska *et al*., 2016). The RTT was incubated in a 10% $Al_2(SO_4)_3$ solution. The pH of the solution was varied from 3.0 to 5.0. The solution pH was varied because it determines the reactivity of both the collagen and $Al_2(SO_4)_3$. Thereafter, the shrinkage temperature of the treated RTT was determined using a micro-shrinkage tester. The control sample of RTT was prepared by incubating RTT in a deionized water of the same volume as the 10% $Al_2(SO_4)_3$ solution.

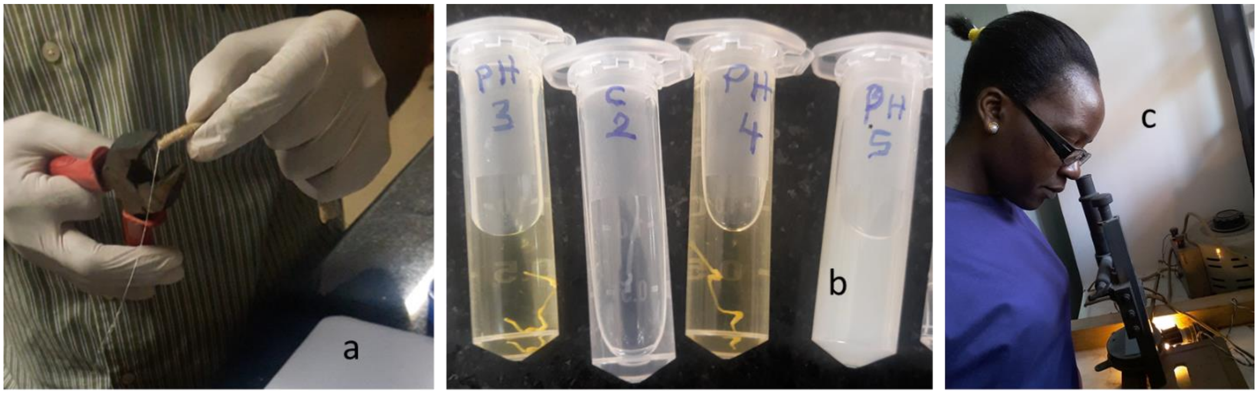


Figure 26: Analysis of the cross-linking ability of $Al_2(SO_4)_3$ prepared from kaolin (a) removal of RTT from the tail (b) incubation of RTT in $Al_2(SO_4)_3$ solution (c) measuring shrinkage temperature of the RTT

3.4.4 Preparation of leather Sample Tanned with Vegetable Tannins and $Al_2(SO4)_3$ Prepared from Kaolin

Samples of goat skins were treated with *A. mearnsii* extracts in combination the with basified $Al_2(SO_4)_3$ from kaolin. The recipe for the tanning process was adopted from a CLRI pilot tannery in India (Table 2, 3 and 4). In summary, 15% of the *A. mearnsii* extract 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 crosslinks with the collagen (Dutta, 1999; Sarkar, 2005). A control trial was carried out by tanning goatskins with 15% *A. mearnsii* extract alone.

Table 2: The tanning recipe used in combination tanning (Experiment)

Process	Dose	Product	Runing time (min)	Remarks
pH Adjustment	100	Water		
	0.75	sodium bicarbonate	3´ 15	pH 4.5 -4.7
Pre-tanning	2	Basyntan P (phenolic syntan)	30	
Tanning	10	*A. mearnsii*	120	
	5	*A. mearnsii*	120	
	2	Al_2O_3	90	
Basification	0.75	sodium bicarbonate	3´ 15	pH 4

Drain the bath and pile overnight—next day: Sammying and shaving to 1.2 mm.
Repeat the whole process with Al_2O_3 concentrations of 5% and 10%

Table 3: The tanning recipe used in combination tanning (Control)

Process	Dose	Product	Runing time (min)	Remarks
pH Adjustment	100	Water		
	0.75	sodium bicarbonate	3×15	pH 4.5 -4.7
Pre-tanning	2	Basyntan P (phenolic syntan)	30	
Tanning	10	*A. mearnsii*	120	
	5	*A. mearnsii*	120	
Fixing	0.25	Formic acid	3×10+30	
Washing	300	Water	10	pH 3.5

Drain the bath and pile overnight—next day: Sammying and shaving to 1.2 mm

Table 4: Re-tanning, dyeing and fat-liquoring of the leather samples (experiment and control)

Process	Dose	Product	Runing time (min)	Remarks
Washing	200	Water	10	
Neutralization	0.75	sodium bicarbonate	3×15	pH 5 -5.5
Pre-retannag	100	Water		
	2	Acrylic syntan	40	
Pre-fatliqour	2	Synthetic fatliquor	40	
	2	Basyntan DI	30	
Dyeing	3	Acid dye brown	30	
Fatliqouring	5	Synthetic fatliquor	40	
Retanning	3	Basyntan DI		
	2	Melamin		
	4	Phenolic syntan	40	
Fixing	1	Formic acid	3× 10 + 30	pH 3.5

Drain the bath and pile overnight—next day: toggle drying, staking and buffing

3.4.5 Analysis of the Properties of Leather Tanned with Vegetable Tannins in Combination with $Al_2(SO4)_3$ Prepared from Kaolin

Resultant leather samples were tested for denaturation temperature using a DSC technique (Perkin Elmer DCS Q200 V23) and CST. About 3 mg of the sample was heated from 10 – 125 °C at 10 min^{-1} heating rate under a 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 × 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 the leather shrunk to one-third of its original length was recorded as a shrinkage temperature, which connotes shrinkage temperature. 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 the leather. Tear strength and water vapour permeability tests were carried out using SATRA TM 162:1992. Test samples were conditioned at 20% and 65% relative humidity. Control samples were tested in similar manner. All analyses were done in duplicate. Characterization of the microstructure of the leather samples was performed using SEM. The samples were cut into predefined sampling position and shaped into a uniform thickness. Thereafter, the samples were coated with gold using Edwards E306 sputter coater followed by the scanning process.

3.5 Data Analysis

Each analysis was repeated twice, and the average values with their respective standard deviations was reported. The MS Excel (2019 version) was used to analyse the data, and the graphs were plotted using SigmaPlot 14.0 and OriginPro 9.0 64Bit.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Optimization of Extraction Temperature for Recovery of Tannins from Local Plant Barks

Vegetable tannins from investigated plant barks extracted at different temperatures (30, 50, 80 °C) were evaluated for their quality before assessing their suitability as tanning agents. After that, the temperature that yielded high-quality tannins was employed to extract vegetable tannins and subsequently used to tan leather to determining the plant extracts' suitability in tanning. The extract from *A. mearnsii* barks was included as a reference because the plant is known commercially as a commercial vegetable tanning source. Furthermore, it was used to represent other investigated plants in combination tanning with the $Al_2(SO_4)_3$ from Pugu kaolin to improve the shrinkage temperature of the vegetable-tanned leather. The results obtained are presented in the subsequent sections.

4.1.1 The Quality of the Vegetable Tannins Extracted at Different Temperatures

Heat applied during the extraction of tannins from plant material is an important parameter to consider, because it determines extract yield as well as the quality of extracts in terms of tannin, phenolics, flavonoids and non-tannins contents (Zalacain *et al*., 2003). It has been reported that a high temperature improves extraction efficiency because it increases the permeability of the cell wall and solubility of extractable matter while reducing the viscosity of the solvent (Ogiwara, 1980). On the other hand, studies have revealed that extraction at high temperatures leaches undesirable compounds such as gums that affect the quality of the leather (Didato *et al*., 1999; Kuria, 2015). In the present study, the influence of temperature on extract yield and tannin content observed was low, except for extract from barks of *E. racemosa* that has shown a slight increment with raise in temperature as shown in Fig. 27 a and b. Total phenolic content (Fig. 27 c) and flavonoid contents (Fig. 27 d) were almost constant throughout the studied extraction temperature range, except for total flavonoid content of extracts from *A. mearnsii* that were observed to be high at 50 ºC (Fig. 27 d). However, the variations between extracts from plant species studied in this work were significant.

Variations in the extract properties between plant species are reasonable because the extracts from different species have different chemical compositions and molecular structures (Laura *et al*., 2010; Würger *et al*., 2014). It was found that barks of *A. xanthophloea* and *E. racemosa* yielded extract comparable to that of *A. mearnsii,* a commercial tannin source used as a reference in the present work. A similar observation was previously reported for the bark extract of *A. xanthophloea* grown in Kenya (Mugedo & Waterman, 1992). On the other hand, *E. divinorum* barks gave far less extract yield than that of *A. mearnsii* (Fig. 27 a).

Tannin content, total phenolic content and total flavonoid content of extract from *A. xanthophloea* barks were comparable to those of *A. mearnsii*. However, those of *E. divinorum* and *E. racemosa* were very low, with *E. racemosa* recording the lowest (Fig. 27 b, c and d).

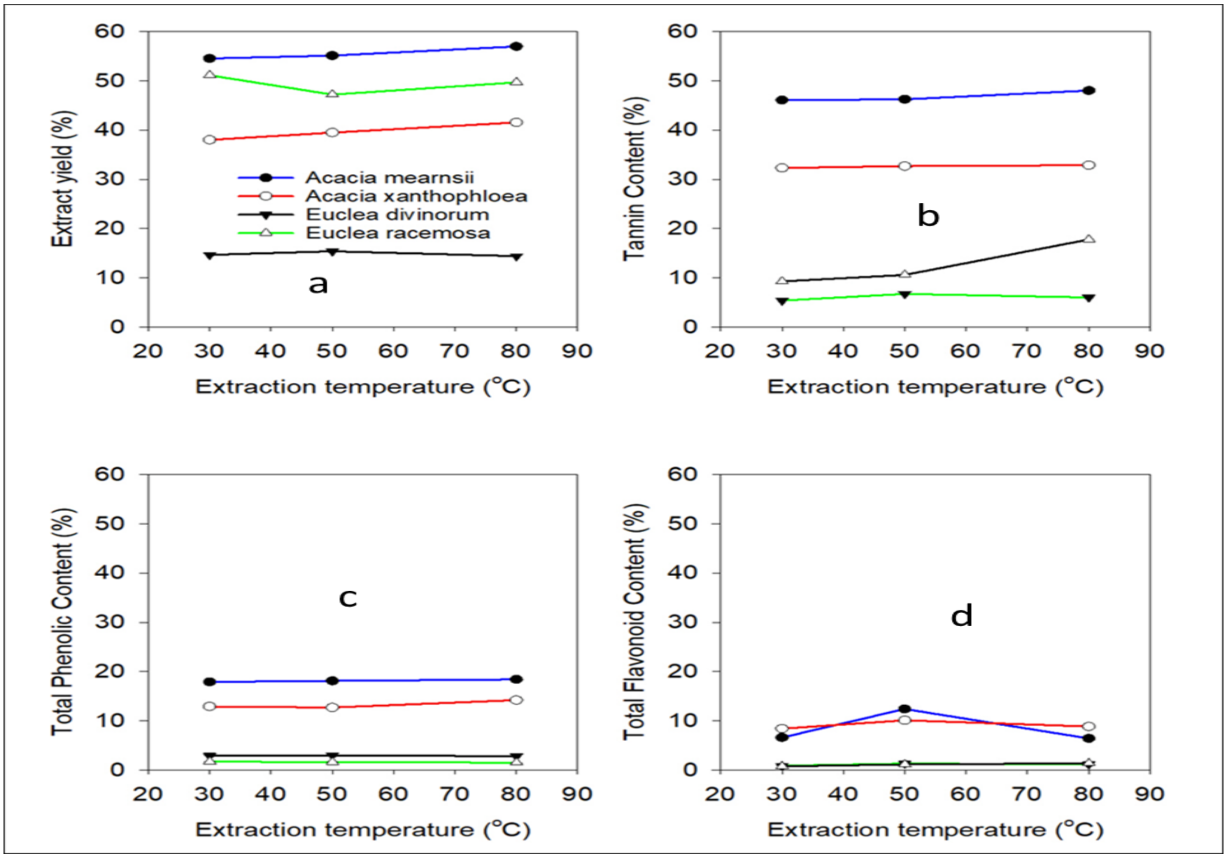


Figure 27: Effect of extraction temperature on plant extracts yield (a), tannin content of plant extracts (b), total phenolic content of plant extracts (c) and total flavonoid content of plant extracts (d)

For the plant to be of commercial interest as a tannin source, the extract must show tannin: non-tanning ratio (T/N) above 2 among extractable phenolics (Howes, 1953). The T/N for the extract from *A. xanthophloea* was lower than that *A. mearnsii* but higher than the recommended ratio values, similar to previous findings (Howes, 1953; Mugedo & Waterman, 1992) indicating that the extract is suitable for vegetable tanning (Table 5). On the other hand, T/N for extracts from *E. divinorum* and *E. racemosa* barks were lower than that of *A. mearnsii* and far below recommended values (Table 5). In light of the importance of T/N as criterion for defining the suitability of vegetable tannins, the extracts from *Euclea* species studied in this work were unsuitable for vegetable tanning. However, other parameters were analysed further to ascertain their suitability.

Table 5: Tannin/non-tannin (T/N) ratios in the extracts

Plant	*A. xanthophloea*	*A. mearnsii*	*E. divinorum*	*E. racemosa*	Recommended T/N ratio
Temperature (°C)	T/N				More than 1 and preferably over 2
30	6.7	7.9	0.9	0.3	
50	6.6	7.7	0.9	0.3	
80	6.8	8.0	0.8	0.6	

4.1.2 The Cross-Linking Ability of Vegetable Tannins from Investigated Plants Extracted at Different Temperatures

Cross-linking ability measures the capacity of a plant extract to stabilize collagen of hide against heat as the result of the formation of extra crosslinking bonds within the collagen fibre matrix (Covington, 2009). In most cases, it is assessed by measuring the denaturation temperature of treated hide powder using a DSC instrument. The latter generates thermograph showing the onset temperature at which denaturation of skin collagen starts (T_{onset}) and peak temperature indicating maximum denaturation (T_{peak}). The interval between T_{onset} and T_{peak} is an indication of the sharpness of the denaturation process, of which large interval indicates a broader distribution of collagen molecules having a different thermal stability (Choudhury *et al*., 2007; Larsen *et al*., 1993; Tang *et al*., 2003a).

The influence of extraction temperature on crosslinking ability was insignificant, except for the extract from *E. divinorum* that showed the lowest crosslinking ability for the extract obtained at 50°C (Fig. 28 c). Extracts from *A. xanthophloea* barks expressed a higher crosslinking ability than that of *A. mearnsii* (Fig. 28 a and b), consistency with earlier findings (Kuria *et al*., 2016; Kuria, 2015; Mugedo & Waterman, 1992). Extract from barks of *E. racemosa* did not show significant crosslinking ability (Fig. 28 d) when compared to others due to the low tannin, total phenolic and flavonoid content, as stated earlier. This performance was expected because the phenols and flavonoids are the one's carrying functional groups to react with the skin collagen (Covington, 2009; Dutta, 1999; Sarkar, 1985). Having poor crosslinking ability, *E. racemose* extracts were judged as an unsuitable vegetable tannin source; hence, not considered for the subsequent experiments.

Despite having less tannin content, the cross-linking ability of extract from barks of *E. divinorum* was found to be similar to that of *A. mearnsii*, except that the interval between T_{onset} and T_{peak} observed under DSC analysis was abnormally large (Fig. 28 c). The peaks in thermograph were found to be broad and resolved into multiple small peaks. This might be due to low tannin, phenolic and flavonoid contents in the extract of *E. divinorum* as shown in Fig. 27 b, c and d. As a result, few collagen molecules were cross-linked; hence, more than one population of collagen molecules with different thermal stability might be present (Choudhury *et al*., 2007; Tang *et al*., 2003a). A similar observation was made in another work on tanning that involved mimosa and oxazolidine (Choudhury *et al*., 2007).

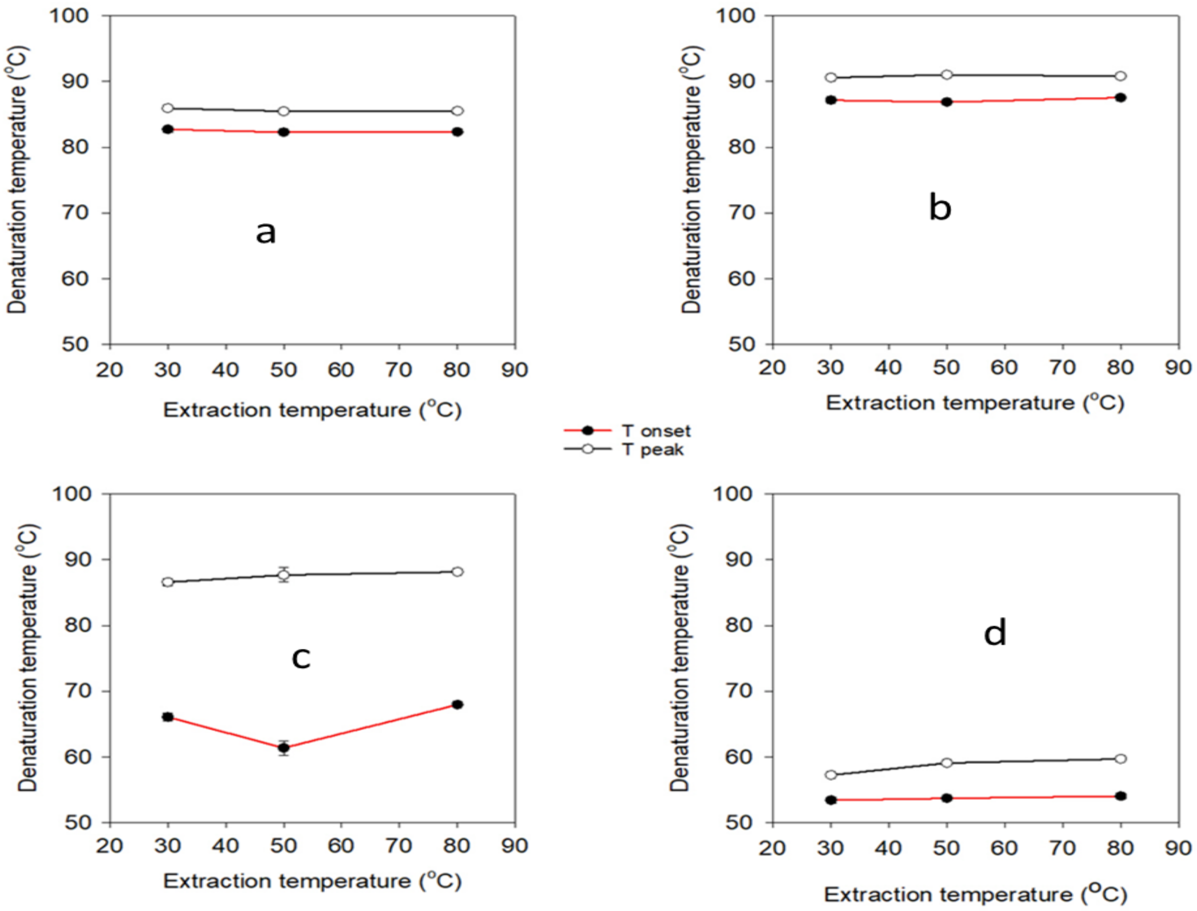


Figure 28: Effect of extraction temperature on the crosslinking ability of vegetable tannins from investigated plants (a=*A. mearnsii*, b=*A. xanthophloea*, c=*E. divinorum*, d= *E. racemosa*)

The cross-linking ability of extracts was further confirmed by assessing the thickness and softness of the hide powder tablets (Fig. 29). Hide powder tablets treated with *A. mearnsii*, *A. xanthophloea* and *E. divinorum* extracts have shown increased thickness and softness, suggesting the formation of crosslinks that brought about the separation of fibre structures and flexibility of fibres to slide over one another (Covington, 1997; Covington, 2009). Hide powder tablet treated with an *E. racemosa* extract was very stiff and thin like un-crosslinked hide powder. This was observed because *E. racemosa* extract has gluing properties that upon interaction with hide powder, resulted in compacting together of the fibres. Consequently, the hide powder tablet shrunk and its thickness became less than other tablets. Besides, the colour of the hide powder tablet treated with *E. racemosa* extract was different from others because the extract's colour (deep green) was passed on to the hide powder.

Figure 29: Hide powder tablets treated by the vegetable tannins from investigated plant barks

4.1.3 Improvement of the Cross-linking Ability of Extract by Combination Tanning

It was well acknowledged that the cross-linking ability of vegetable tannins to give leather the denaturation temperature (also referred as hydrothermal stability or shrinkage temperature) similar to that of chromium tanned leather is achieved by combination tanning technique (Covington & Suparno, 2007; Covington, 2009; Madhan *et al.*, 2007; Musa *et al.*, 2009). Using different tanning agents with weaker tanning power than chromium salt, the interaction of vegetable tannins with collagen of the hide powder is enhanced leading to an improved denaturation temperature (Covington, 2009). Among many tanning agents, $Al_2(SO_4)_3$ is mostly preferred because it has been widely studied and its mechanism is well established (Brown & Dudley, 2005; Covington, 2009; Musa & Gasmelseed, 2013; Madhan *et al.*, 2007). In addition, $Al_2(SO_4)_3$ has good capacity of adsorbing pigments and gives the leather cationic properties making it the best mordant for excellent dyeing. Furthermore, $Al_2(SO_4)_3$ is safe and a non-toxic chemical (Mozaffari, 2018).

Therefore, in the present work, extracts were applied together with $Al_2(SO_4)_3$ to study the effect of $Al_2(SO_4)_3$-blended vegetable tannins in improving cross-linking ability of extracts under investigations. Thermal denaturation of hide powder collagen treated with 5% extract and 0-5% Al_2O_3 while alternating the order of applying tanning agents was studied using DSC instrument. Figure 29a and b shows the denaturation temperature of treated hide powder as the function of Al_2O_3 concentration. As previously reported (Choudhury *et al.*, 2007; Covington, 2009), the order in which tanning agents are applied during combination tanning has shown a profound effect on denaturation temperature of treated hide powder. The effect varies depending on vegetable tannin sources. Hide powder treated with *A. mearnsii* extract first before $Al_2(SO_4)_3$ is added, gave a higher denaturation temperature (Fig. 30 a) compared to when these agents were applied in reverse order (Fig. 30 b). Similar trends have been reported in other works (Choudhury *et al*., 2007; Covington, 1997; Covington, 2009; Slabbert, 1981). It must be noted that the denaturation temperature values didn't reach 100 °C as expected based on the literature reviewed because only 5% vegetable tannins were used compared to 20-30% normally used in combination tanning.

For extract from *A. xanthophloea*, both orders of addition resulted into increased cross-linking ability, but adding $Al_2(SO_4)_3$ first before extracts, seemed to be the best way to tanning as it also reduced the interval between T_{onset} and T_{peak} (Fig. 30 a and b), suggesting uniform stabilization of collagen molecules. Unlike *A. mearnsii*, extract from *E. divinorum* worked better when $Al_2(SO_4)_3$ was added first compared to when a reverse application order was used (Fig. 30 b). Not only cross-linking ability increases, but also the gap between T_{onset} and T_{peak} were tremendously reduced (Fig. 30 b).

The effect of aluminium concentration on cross-linking ability of extracts was significant. As concentration of aluminium increased, the hydrothermal stability decreased, which was consistent with findings in another work (Haroun *et al*., 2009). As for extract from *A. mearnsii*, the maximum hydrothermal stability for *A. xanthophloea* was 1% Al_2O_3, while for extract from *E. divinorum* was 2% Al_2O_3.

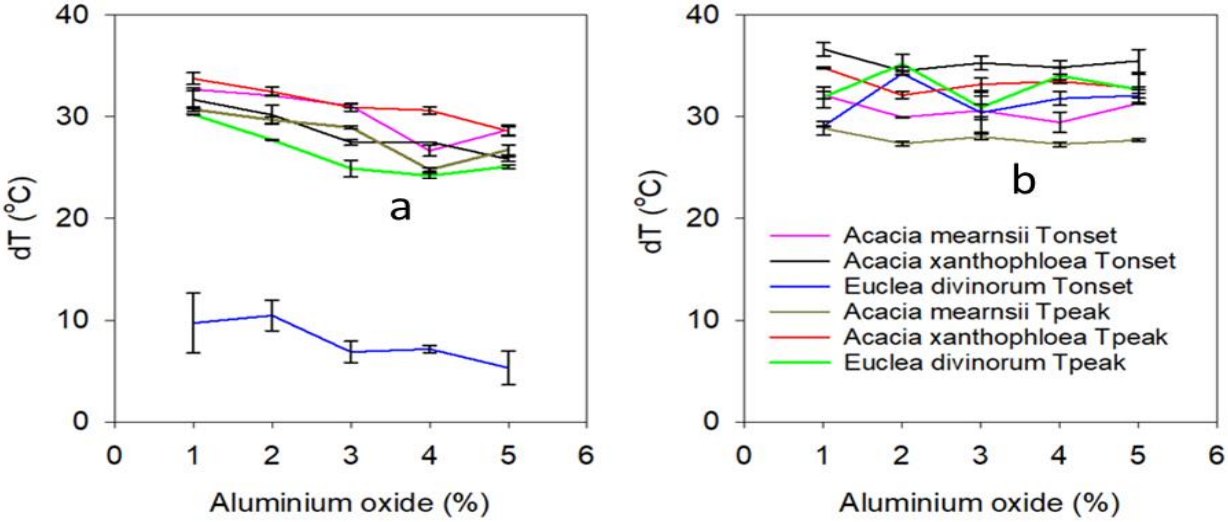


Figure 30: Effect of $Al_2(SO_4)_3$ concentration cross-linking ability of extract when extract is added first (a) and when $Al_2(SO_4)_3$ is added first (b)

4.1.4 Physical and Mechanical Properties of the Leather Tanned with the Vegetable Tannins from Investigated Plants

The shrinkage temperature of the leather samples tanned with extract from plant species under consideration was examined, and the findings are reported in Fig. 31. The shrinkage temperature was measured by DSC and CST techniques. The results revealed that extracts of *A. xanthophloea* bark performed better in terms of shrinkage temperature than that of *A. mearnsii* further corroborating previous reports (Kuria *et al.*, 2016; Kuria, 2015). The shrinkage temperature of leather tanned with extract from *E. divinorum* was comparable to that of leather tanned with *A. mearnsii*, except that the T_{onset} and T_{peak} gap was broader than that of extracts from latter species. These findings correlate with the observation made on analysis of cross-linking ability of the extracts. Despite less tannin, total phenolic and flavonoid content, *E. divinorum* was able to give the leather a shrinkage temperature similar to that of other investigated plants extracts. This might be due to highly tanning strength (it contains 7 Bé) that suggests fewer tannin, phenolic and flavonoid contents are sufficient to cause significant cross-linking, as reported by Cardon (2005).

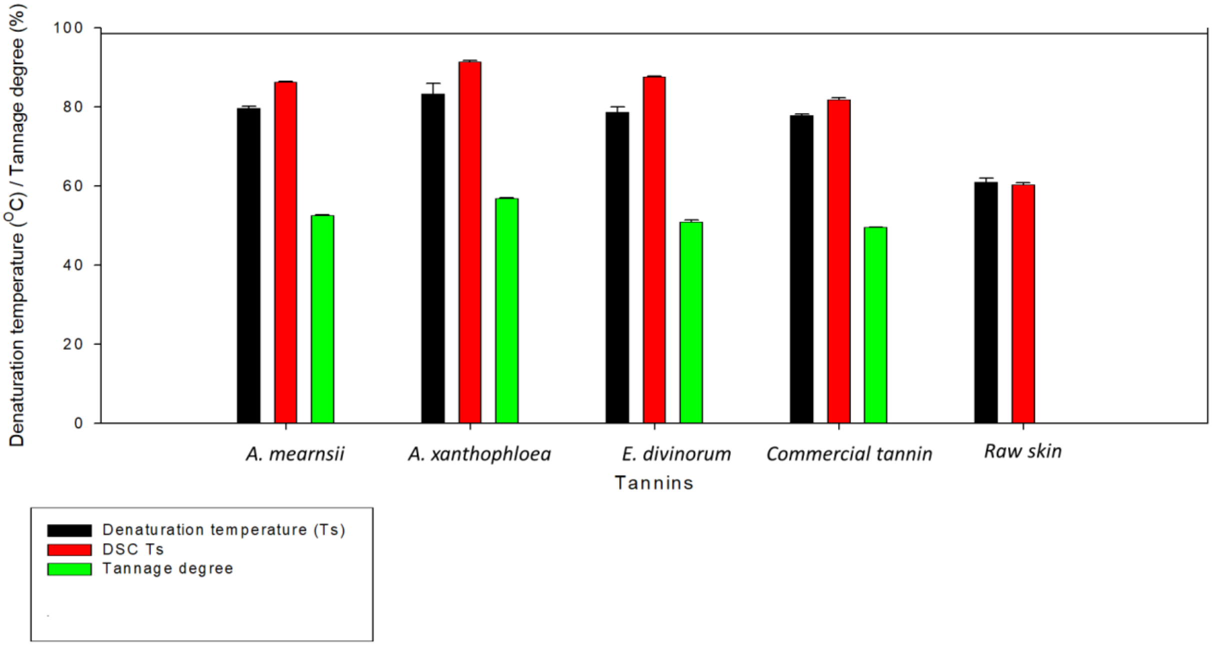


Figure 31: The Shrinkage Temperature of Leather Tanned with the Extracts from Investigated Plants

The mechanical properties of leather samples are presented in Table 6. The tensile strength of the leather tanned with *A. xanthophloea* was more or less the same as the tensile strength of the leather tanned with *A. mearnsii* extract. Still, the elongation for *A. xanthophloea* tanned leather was marginally higher than that of *A. mearnsii*, in agreement with shrinkage temperature results. For the case of softness, *A. xanthophloea* displayed lower softness value than *A. mearnsii*, although, the difference is insignificant. Leather tanned with *E. divinorum* extracts gave lower values in all parameters assessed compared to *A. mearnsii*. These results support the findings reported in present work, which confirmed the low ability of *E. divinorum* extract to cross-link all collagen molecules due to less tanning content as well as total phenolic and flavonoid content; hence, affecting the mechanical properties of the leather as well.

Table 6: Mechanical properties of leather tanned with extracts from plants under investigation

Property	*Acacia xanthophloea*	*Acacia mearnsii*	*Euclea divinorum*
Tensile strength (Nmm^{-2})	5.7±0.3	6.1±0.6	4.7±1.0
Elongation at break (%)	36.8±1.9	33.4±2.0	26.3±1.4
Softness (N)	1.9±0.4	2.4±0.3	1.7±0.4

Scanning Electron Microscopy images of leather were taken for the grain surface and cross-sectional view. The smooth grain surface is an indication that interaction between vegetable tannins from selected plants and collagen of hides modified the grain surface without causing damage (Fig. 32). It is equally important to note that vegetable tannins from each plant gave different grain surface appearance, suggesting variations in molecular interactions of vegetable tannins from various plant sources with the leather thus imparted different appearances to the leather (Brown & Dudley, 2005). Cross-sectional images of the leather samples showed the satisfying extent of fibre opening due to excellent penetration and distribution of tannins within the skin matrix (Fig. 33).

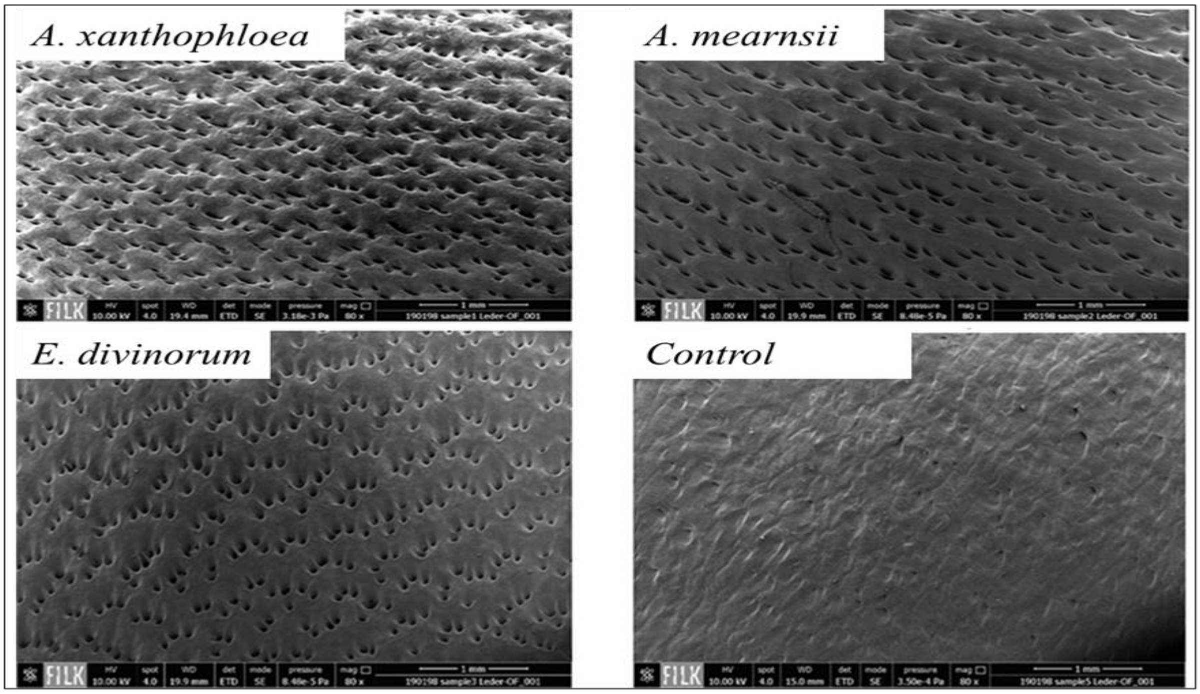


Figure 32: Scanning electron microscopy images of leather samples (Grain surface) (Magnification is ×80)

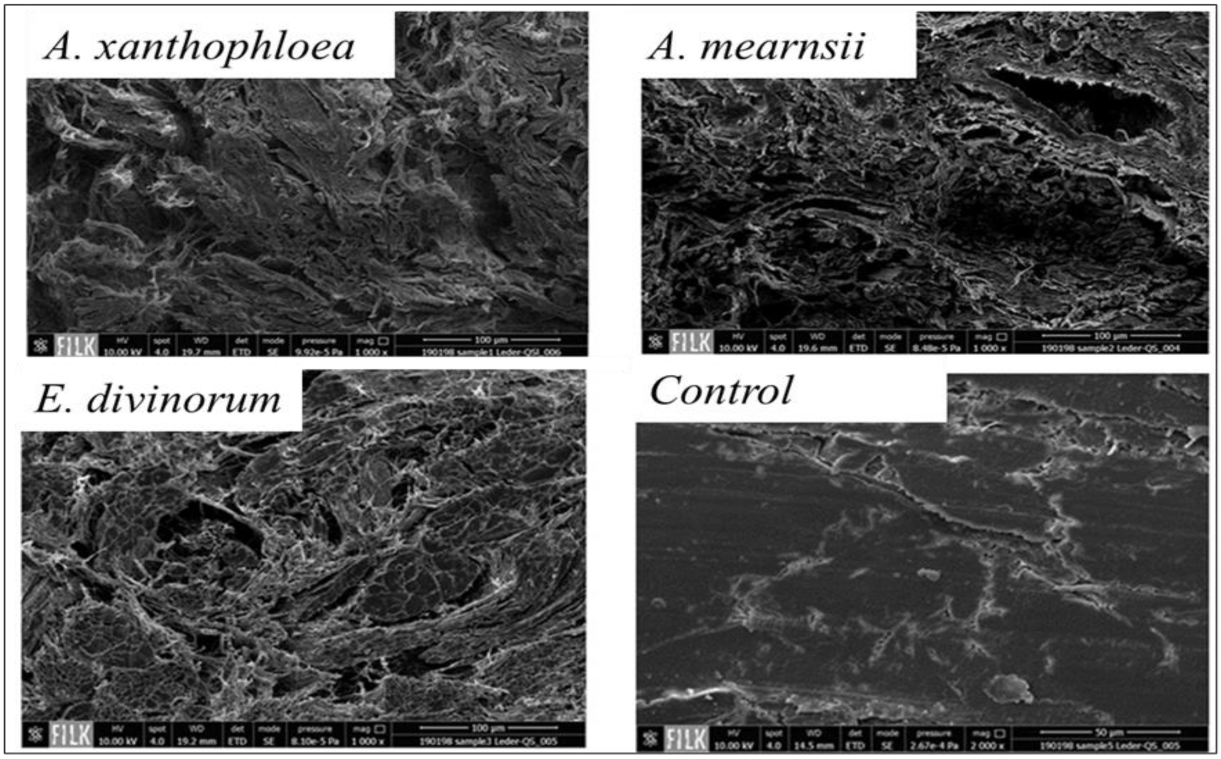


Figure 33: Scanning electron microscopy images of leather samples (Cross-sectional) (Magnification is ×80)

4.2 The Binding Mechanisms between Vegetable Tannins from Local Plants Barks and the Skin Collagen

The interaction mechanism between the extracts from each plant and collagen of hide powder was carefully investigated by three different methods to understand the underlying chemistry and confirm the classification of tannins. Hide powder samples were treated with extracts from selected plants under the same conditions and analysed using different methods. Results from the DSC analysis (Fig. 34 a) showed that there was significant interaction throughout pH range studied, indicating the presence of hydroxyl groups at an acidic pH and ketonic carbonyl groups (quinone) at neutral to alkali pH to interact with protonated and unprotonated amino groups via hydrogen and covalent bond formation, respectively. By washing treated hides, the dT (difference in denaturation temperature between uncross-linked hide powder and cross-linked one) decreased slightly, except for *E. divinorum* extracts hide powder treated at pH 3.5, indicating that the bonds formed are irreversible (Fig. 34 b).

The results from TNBS assay (Fig. 34 c) have confirmed the existence of an interaction between unprotonated amino group of collagens and ketonic carbonyl group of tannins, which resulted into crosslinks through covalent bonding as observed in the DSC analysis. Amino acid analysis (Fig. 34 d) revealed that the crosslinks formed are not resistant against acid hydrolysis.

According to Schröpfer and Meyer (2016), the interaction mechanism of this kind is typical for condensed tannins of which tannins from *A. mearnsii*, a reference plant used in the present study, belongs. Therefore, it can be concluded that the extracts from *A. xanthophloea, E. divinorum* and *E. racemosa* contain condensed tannins and the maximum interactions occurs at a pH range between 3.5-4.5. It is important to note that extracts from *E. racemosa* contained low amount of tannins as indicated in the results (Fig. 34 a, b and c).

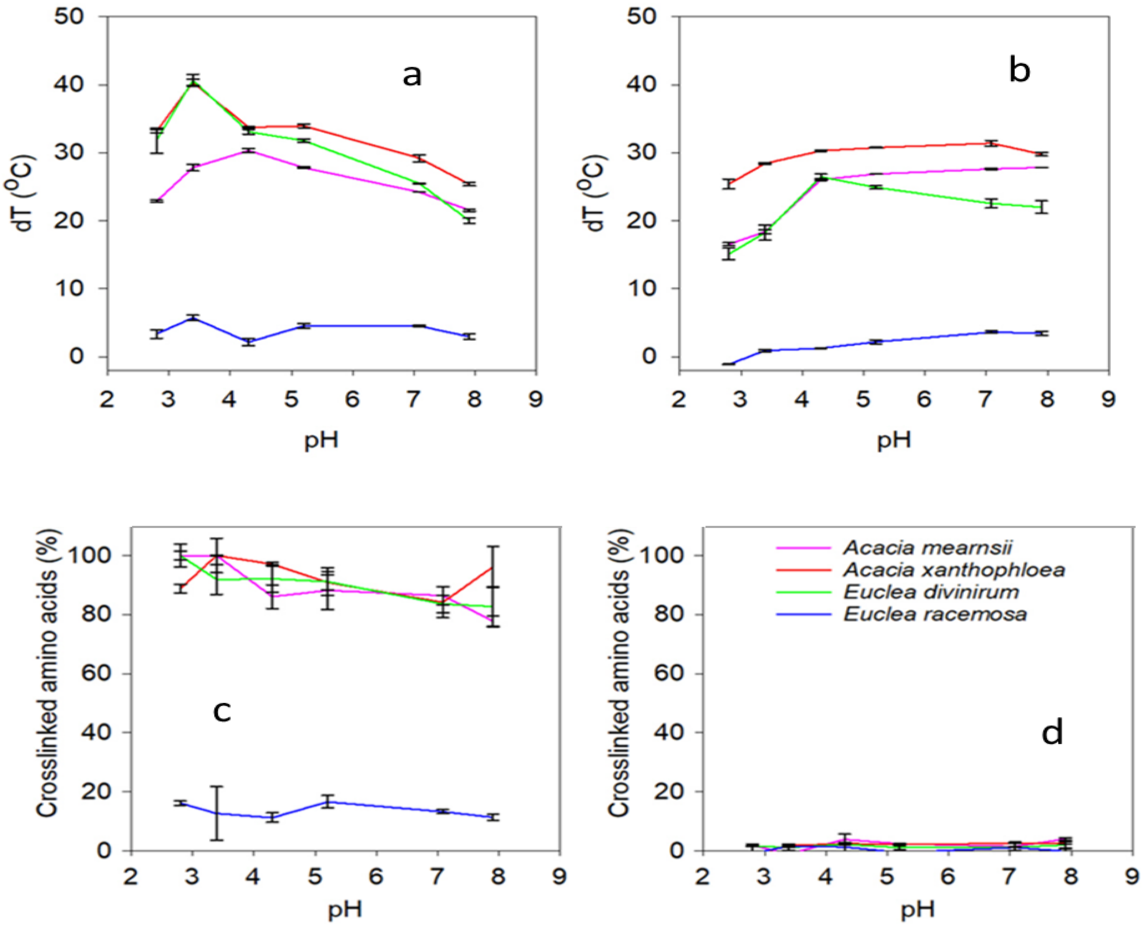


Figure 34: Effect of pH on denaturation temperature of hide powder cross-linked with vegetable tannins relative to non-cross-linked control (dT) (a= unwashed samples, b= washed samples), as well as percentage of crosslinked amino groups (c= before acid hydrolysis, d= after acid hydrolysis)

4.3 Combination Tanning Based on Vegetable Tannins from Local Plants Barks and Aluminium Sulphate Prepared from Pugu Kaolin

4.3.1 Characterization of Pugu Kaolin

To ensure that the clay under investigation was kaolin, several analyses were carried out and results are presented here in. The XRD spectrum of the Pugu kaolin is shown in Fig. 35. Significant peaks of kaolinite was observed, similar to the previous work (Al Bakain *et al*., 2014). Results from XRF analysis of kaolin in Table 7 shows that the major content of kaolin are the oxides of aluminium (25.8%) and silicate (63.4%), which is the characteristic feature of the 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 (Sempeho *et al*., 2012).

Table 7: Chemical composition of Pugu kaolin

		Chemical composition of kaolin sample (% weight)					
Oxide		Al_2O_3	TiO_2	CaO	Fe_2O_3	SiO_2	K_2O
Quantity	Pugu kaolin	25.80	2.88	0.39	2.89	63.4	3.19
	Commercial kaolin	30.70	0.27	0.05	0.89	59.84	1.53

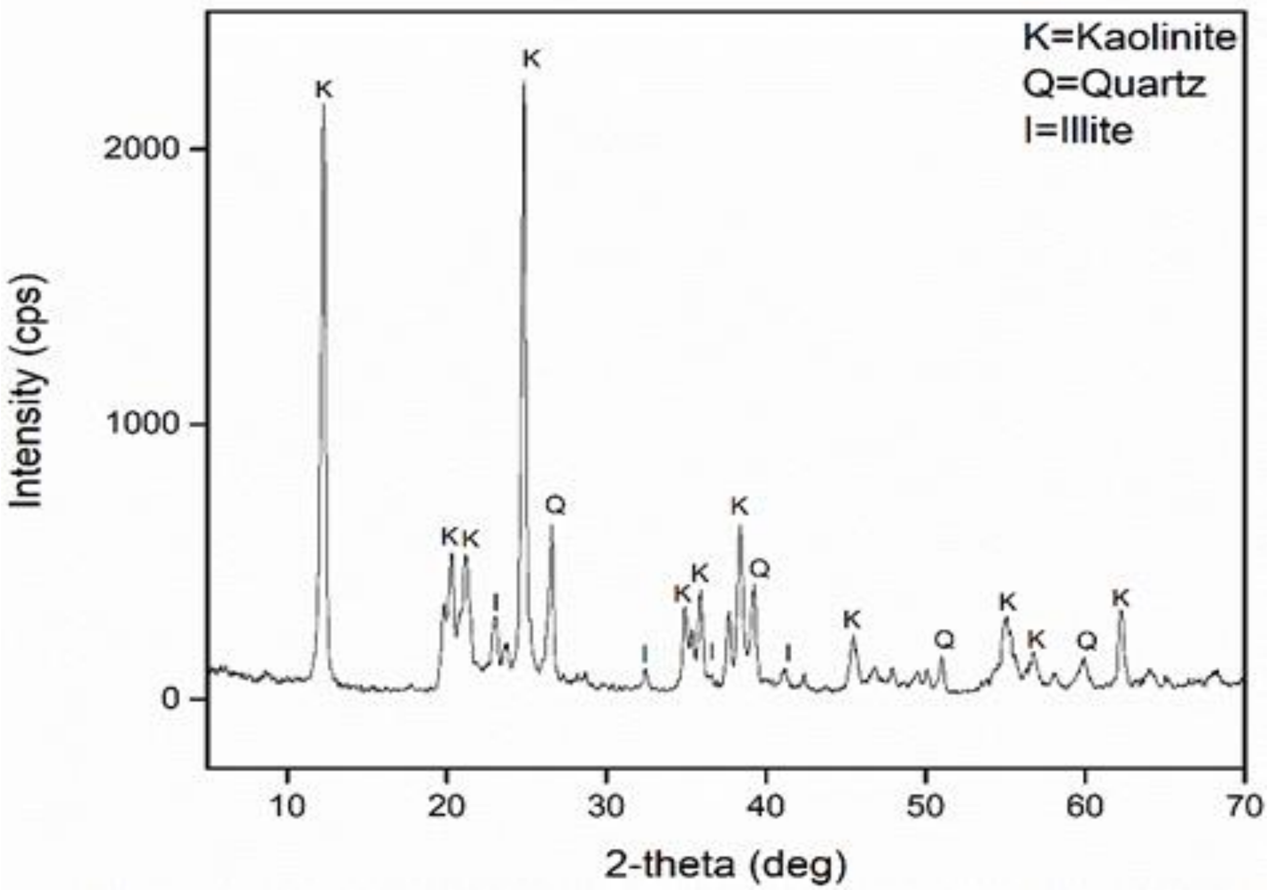


Figure 35: X-ray diffraction pattern of Pugu kaolin

An FTIR spectrum of Pugu Kaolin in Fig. 36 presents multiple absorptions related to Si–O bonds at 1005, 1026 and 1118 cm^{-1}. Absorption bands at 907 cm^{-1} correspond to inner Al-OH. Presence of absorption bands at 3690 cm^{-1} corresponds to outer OH group while that at 3620 cm^{-1} is due to bonded molecular water. The absorption bands observed correlated well with the once previous reported for the kaolin (Tironi *et al*., 2012).

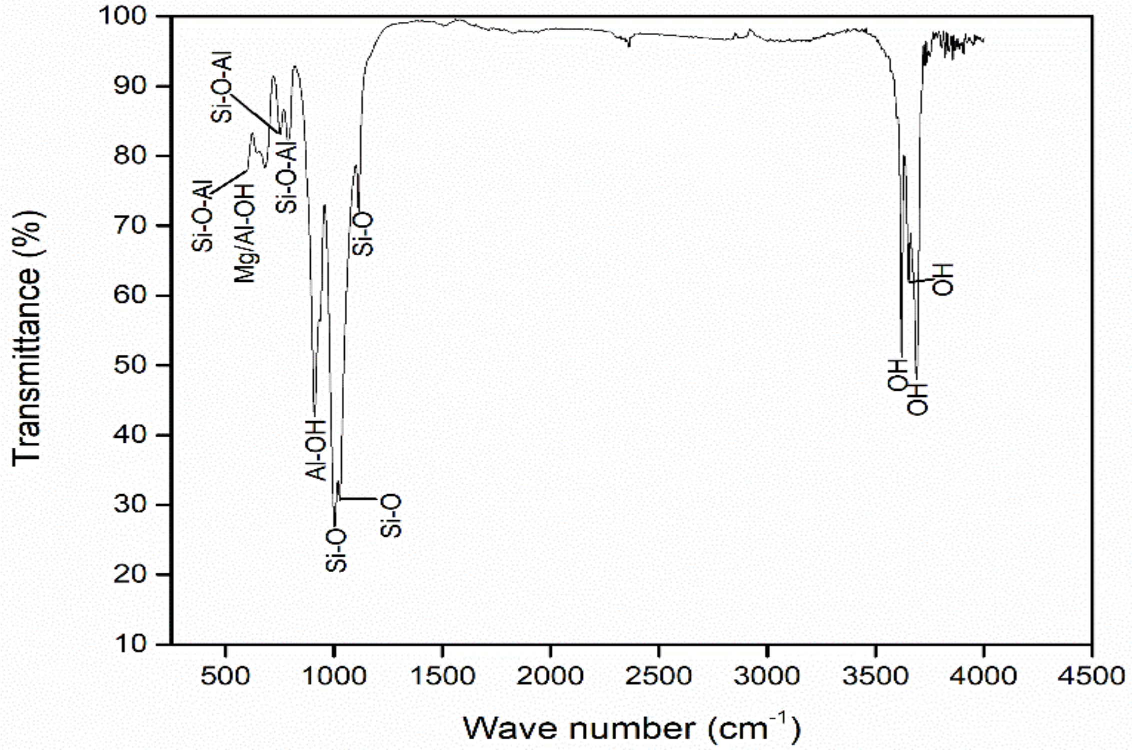


Figure 36: Fourier transmission infra-red spectrum of Pugu kaolin

The SEM images for the kaolin in Fig. 37 showed plate-like layers stacked over one another, confirming morphological characteristic of kaolin clay as earlier reported (Michot *et al*., 2008). The assemblage of plate-like hexagonal structures or book-like kaolinite stacks is a common feature of kaolin clay observed under SEM (Ariffin *et al*., 2008).

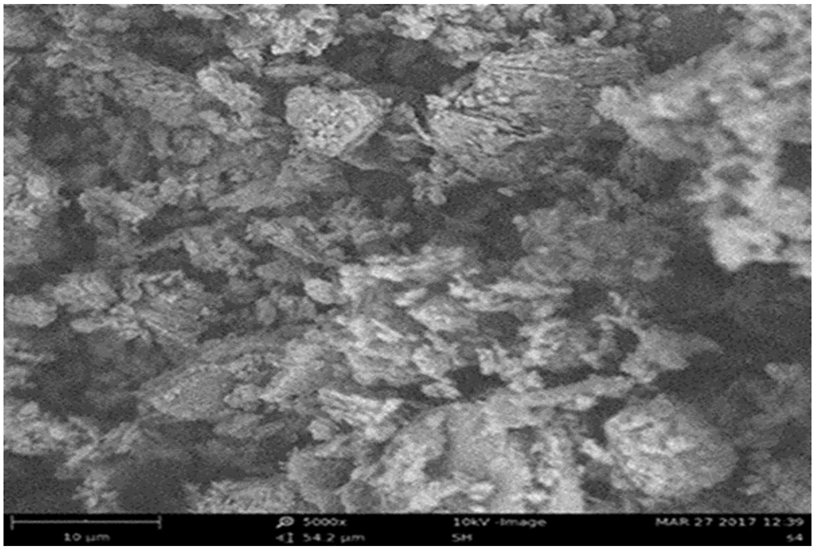


Figure 37: Scanning electron microscopy image of Pugu kaolin

For easy leaching of aluminium from kaolin aluminosilicate structure, the bonds holding structure must be decomposed. This is achieved by calcinating kaolin, transforming its structure to an amorphous metakaolin structure, which is a more reactive form of kaolin towards dissolution agents than raw kaolin (Lima *et al*., 2018; Pinna *et al*., 2018). Upon heating, the kaolin structure breaks down into small pieces resulting into an increased surface area for dissolution agents to react with aluminium oxide efficiently, as in bauxite rock (Arıkan *et al*., 2019). In the temperature of 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 (Miller, 1961). Therefore, the main changes are related to the loss of OH groups that result in diminishing of the band corresponding to OH and Al-OH in calcined clay FTIR spectrum (Tironi *et al*., 2012). It is further elaborated that vanishing of Al-OH and immerging of Si-O band at 1 047 cm^{-1} indicates the destruction of the octahedral sheet (Freund, 1974). Similar observations were seen in the present work signifying the dehydroxylation and dehydration during calcination process was successful (Fig. 38).

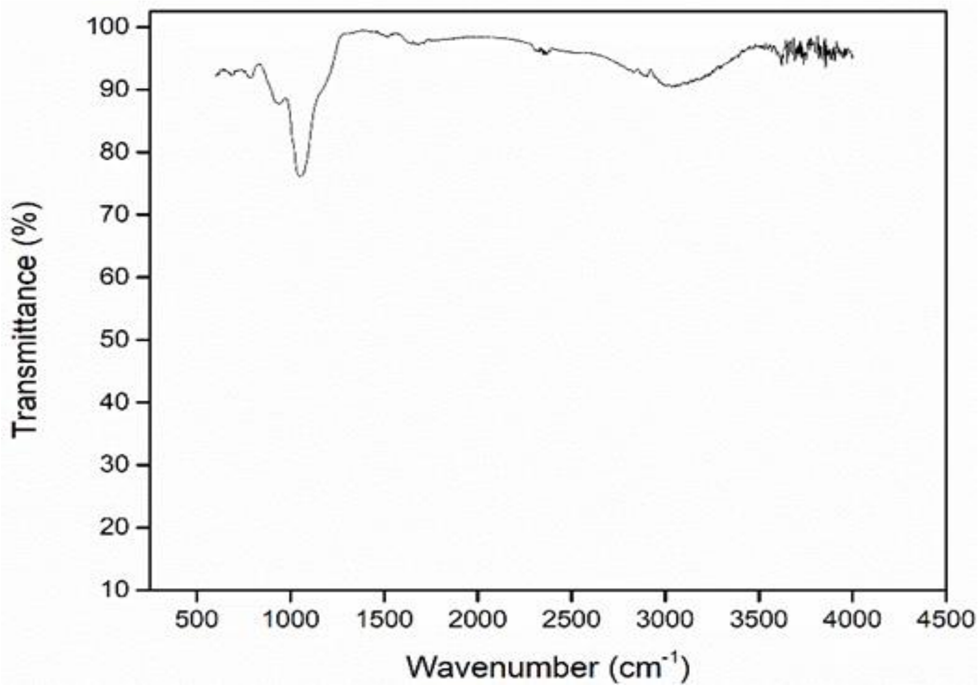


Figure 38: Fourier transmission infra-red spectrum of calcined kaolin

4.3.2 Characterization of $Al_2(SO4)_3$ Prepared from Kaolin

During the 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 (Equation 2). The XRD spectrum of the prepared $Al_2(SO_4)_3$ is shown in Fig. 39. Most characteristic peaks for $Al_2(SO_4)_3$ (El Ouatib *et al*.,

2005) are reflected in the synthesized product from kaolin, suggesting that $Al_2(SO_4)_3$ was formed during the extraction process.

$$Al_2O_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2O \qquad 2$$

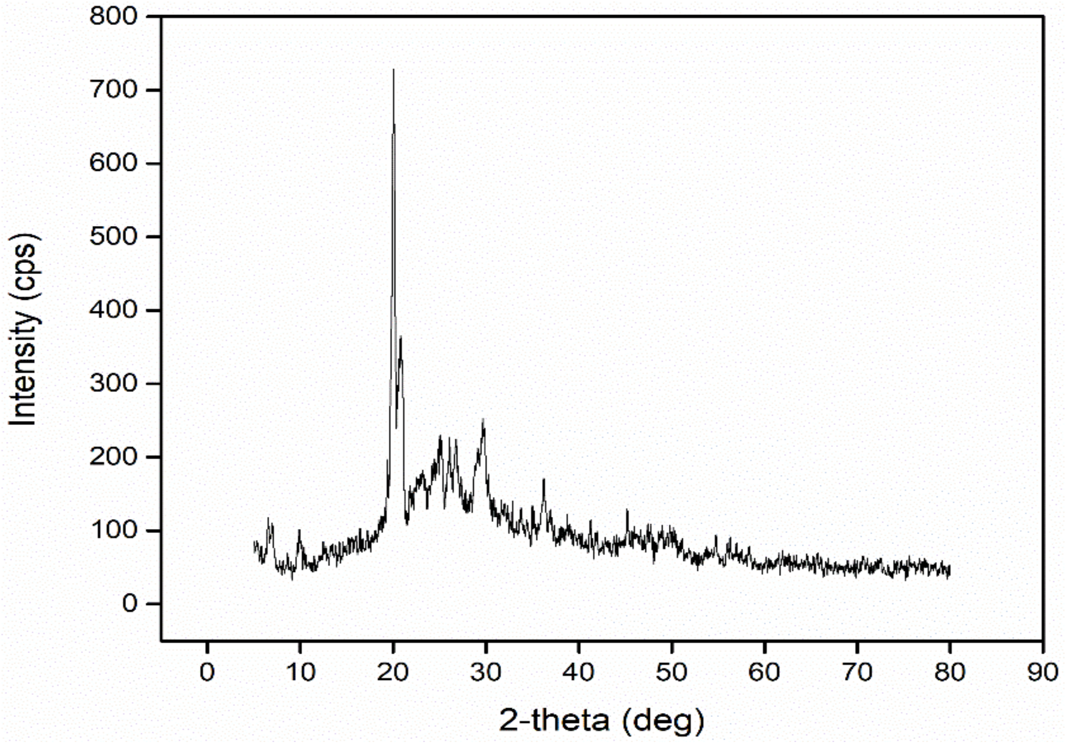


Figure 39: X-ray diffraction patterns of $Al_2(SO_4)_3$ prepared from Pugu kaolin

From the FTIR spectrum of $Al_2(SO_4)_3$ was shown in Fig. 40, 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 findings corroborated with the absorption bands of commercial $Al_2(SO_4)_3$ previously reported (Contreras *et al*., 2006; Jafar-Tafreshi *et al*., 2012).

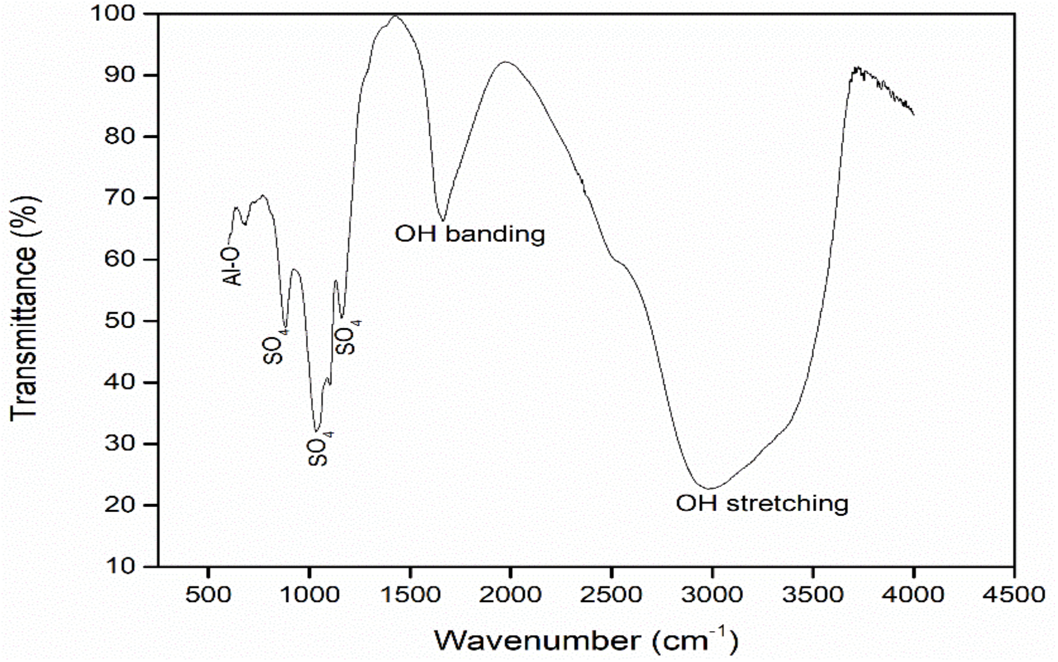


Figure 40: Fourier transmission infra-red spectrum of $Al_2(SO_4)_3$ prepared from Pugu kaolin

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 the presence of sulphuric acid, it reacted to form $Al_2(SO_4)_3$.

4.3.3 Cross-linking Ability of $Al_2(SO4)_3$ Prepared from Pugu Kaolin

The cross-linking ability of prepared aluminium sulphate was assessed by measuring the shrinkage temperature of the rat tail tendons (RTT) treated with $Al_2(SO_4)_3$ solution at varying pH. The shrinkage temperature values are given in Fig. 41. It was observed that the shrinkage temperature increased the pH to 4.0, above which a gentle increase was observed. White precipitates were formed in the sample at pH 5.0 due to the precipitation of Al(OH) at high pH as reported by Bond and Hughes (2019). The formation of white precipitates as pH increases is another evidence that the product made from kaolin in this study is $Al_2(SO_4)_3$ because this is how it behaves at raised pH.

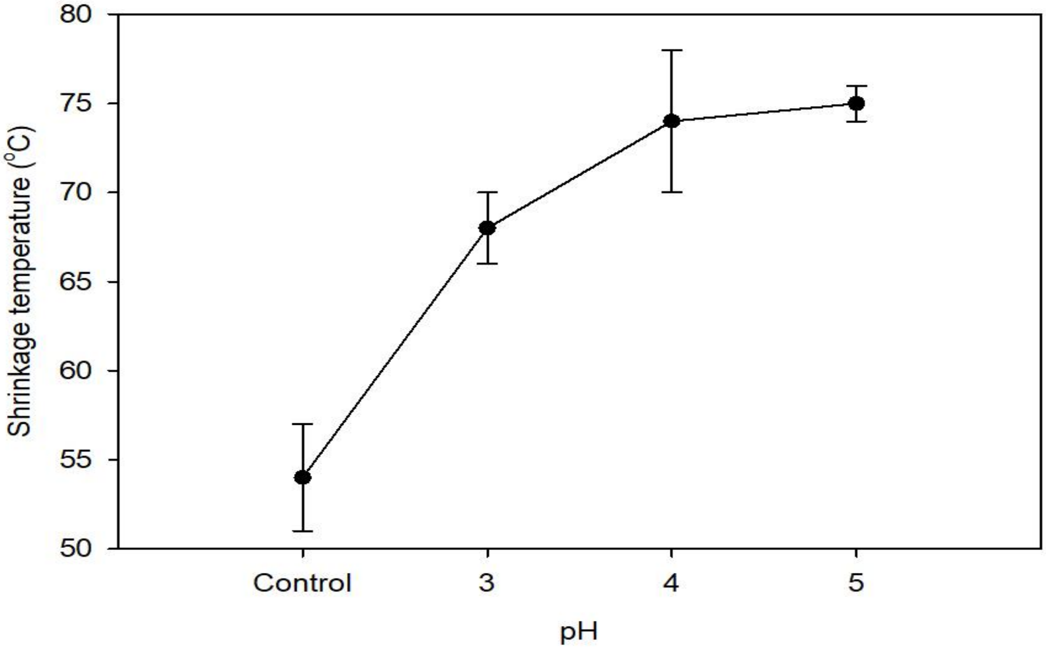


Figure 41: The cross-linking ability of $Al_2(SO_4)_3$ extracted from kaolin as the function of pH

4.3.4 Performance of $Al_2(SO4)_3$ from Pugu Kaolin on Combination Tanning

The increase in denaturation temperature brought by combination tanning using $Al_2(SO_4)_3$ and vegetable tannins was previous elaborated using various assumptions (Covington, 2009; Covington *et al*., 2008; Covington, 1997). The most common and accepted hypothesis is that of a link-lock (Covington *et al*., 2008). According to the link-lock theory, increased denaturation temperature of treated collagen is due to the creation of a matrix that becomes securely bound to the collagen molecule.

Leather tanned with the combination of *A. mearnsii* extract and $Al_2(SO_4)_3$ from kaolin demonstrated improved denaturation temperature as compared to the control sample (Fig. 42). It was observed that the addition of $Al_2(SO_4)_3$ resulted in a significant increase in the denaturation temperature. On addition of $Al_2(SO_4)_3$ (2% Al_2O_3 equivalent), a sharp increase in denaturation temperature was observed, but a further increase of $Al_2(SO_4)_3$ resulted only in a slight rise. This corroborates previous reports (Covington, 2009; Covington, 1997; Leaf-nosed, 2009; Madhan *et al*., 2007; Slabbert, 1981). The findings ascertained that Al_2O_3 from Pugu kaolin triggered chemical modification in the collagen structure and raised the denaturation temperature of vegetable tanned leather.

The values of denaturation temperature measured by DSC method are generally higher than those measured by CST (Fig. 42). This observation is due to the presence of other higher energy structures associated with the side chain of collagen that are not observed on measuring denaturation/shrinkage temperature by using the CST method as previously noted (Covington, 2009).

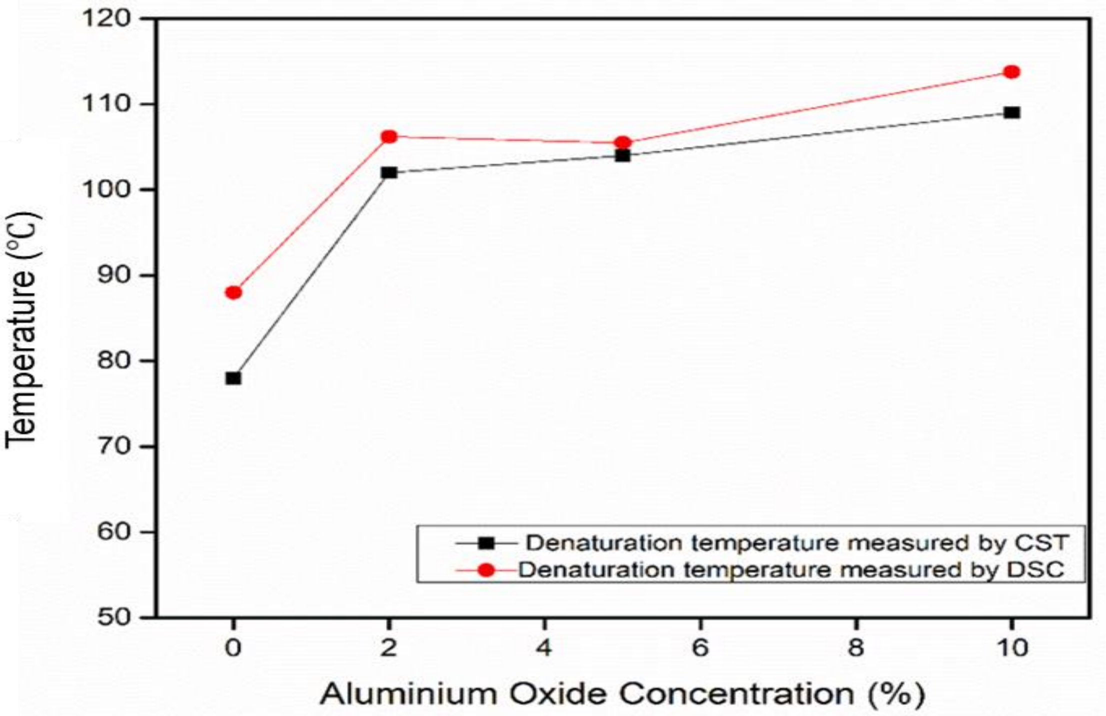


Figure 42: Shrinkage temperature of leather tanned with *A. mearnsii* extract in combination with aluminium sulphate from kaolin

It was earlier reported that the penetration of tanning agent across the skin matrix results into good fibre separation and hence desired leather properties (Kanth *et al*., 2008). As the impact of strong bonds formed inside the leather fibre matrix, the mechanical properties have been significantly improved. All samples have shown tearing strength and water vapour permeability better than recommended values (Table 8).

Microstructure studies of collagen fibres have proven that the combination tanning with $Al_2(SO_4)_3$ from kaolin can lead to higher fibre dispersion and clear spacing among collagen fibres, as it does commercial $Al_2(SO_4)_3$. The SEM images of control and leather tanned with 0% and 2% Al_2O_3 showed clear grain surface without damage, but that tanned with 5% and 10% Al_2O_3 displayed grain swelling and damage, respectively (Fig. 43). This might be due to acid burn caused by a high concentration of $Al_2(SO_4)_3$ in the tanning solution as it is known to be acidic (Bond & Hughes, 2019). Compared to the leather tanned with *A. mearnsii* extract alone, combination tanned leather has shown better fibre dispersion. The former displayed a compact and tight fibre pattern (Fig. 44), which signifies that $Al_2(SO_4)_3$ is vital to bring about excellent fibre separation that leads to the strength and softness of the leather. 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.

Therefore, a combination tanning with 2% Al_2O_3 is appropriate to give the leather desired properties without damage on the grain surface. Other studies have recommended the same concentration of Al_2O_3 for effective combination tanning (Musa & Gasmelseed, 2013; Musa & Gasmelseed, 2012).

Table 8: Physical properties of leather tanned with the combination of *A. mearnsii* extract and Al_2O_3

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

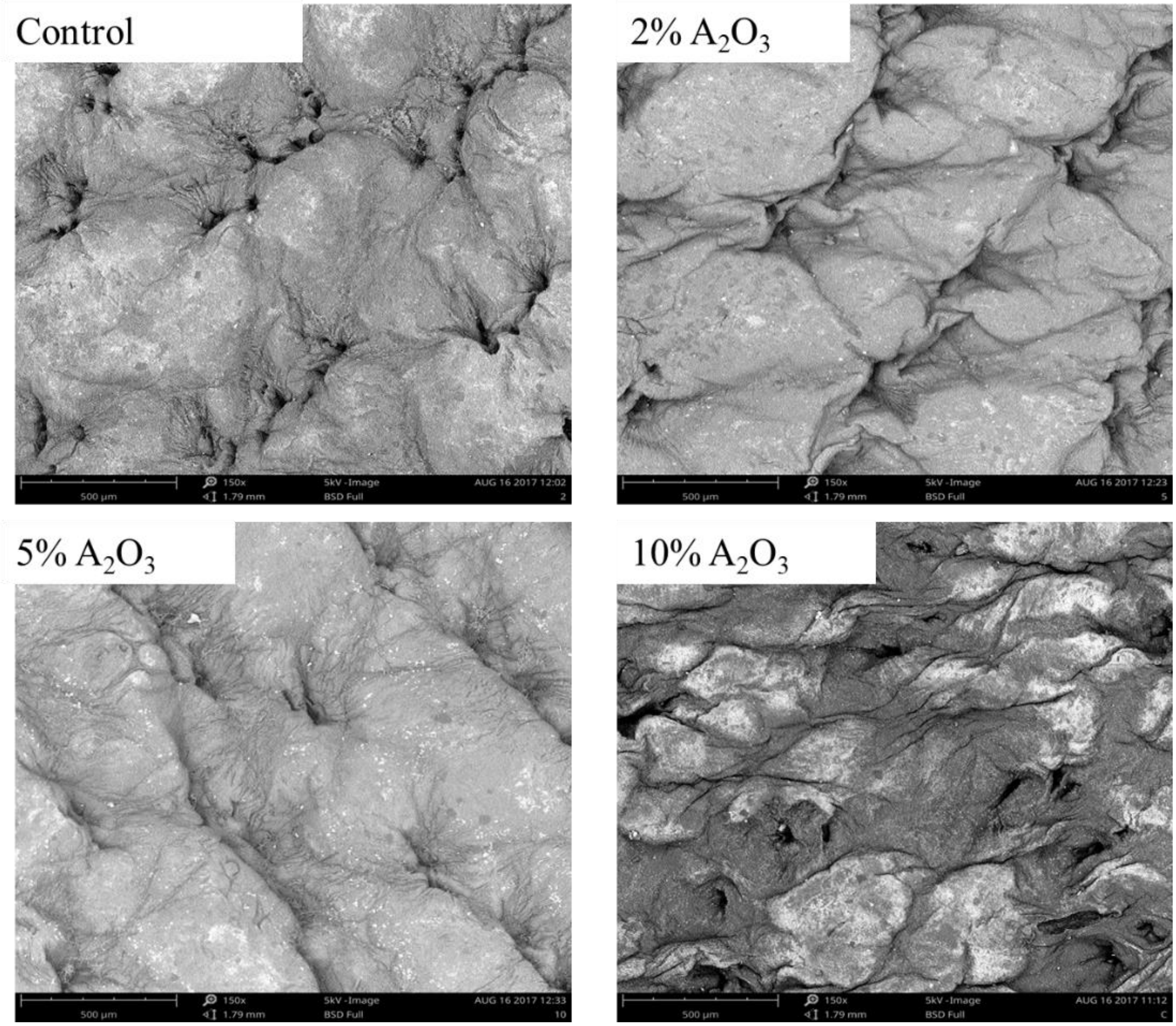


Figure 43: SEM images of leather samples tanned with 15% *A. mearnsii* extract and different concentration of Al_2O_3 (grain surface) (Magnification is ×150)

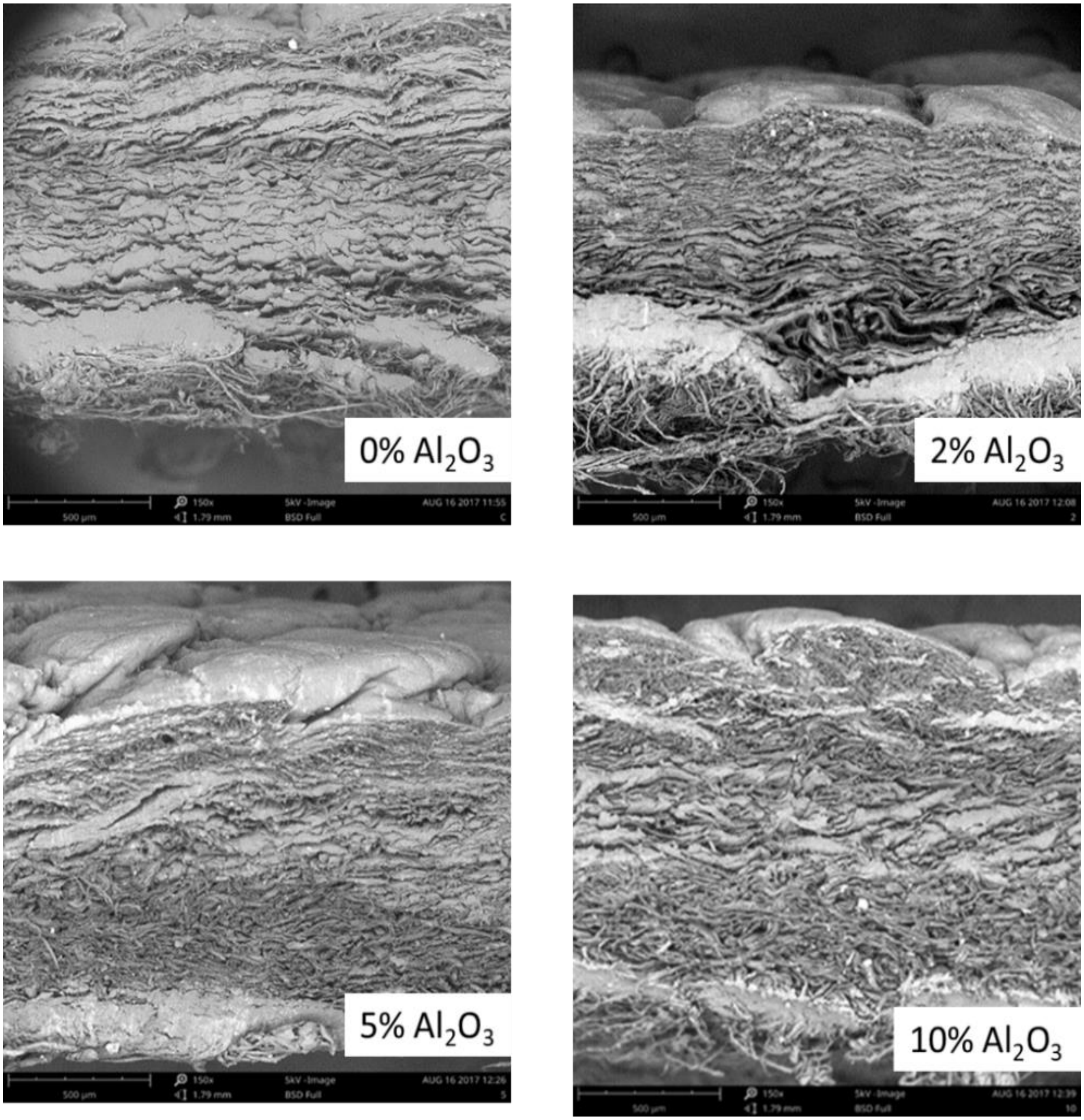


Figure 44: SEM images of leather samples tanned with 15% *A. mearnsii* extract and different concentration of Al_2O_3 (cross-sectional) (Magnification is ×150)

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The present investigation aimed to develop an ecofriendly tanning technology using local Tanzanian resources to sustain the leather industry. Extraction of vegetable tannins from selected plant barks (*A. mearnsii, A. xanthophloea, E. divinorum* and *E. racemosa*) under the influence of temperature was optimized. Extracted tannins at different temperatures were characterized for the percent yield, tannin, phenolic, flavonoid, and non-tannin content. Interaction mechanisms between tannins from selected plants and collagen of the hide were investigated. The possibility of improving tanning efficiency of the tannins from selected plants by using $Al_2(SO_4)_3$ via combination tanning was also examined. Subsequently, the study of kaolin as a source of $Al_2(SO_4)_3$ to be used in combination tanning was carried out.

The study has ascertained that the temperature of extracting tannins from studied plants has little effect on the quality of the extracts. That means, even at a low-temperature high-quality vegetable tanning agent can be recovered and produce good quality vegetable-tanned leather. Good quality leather tanned with the extracts from *A. xanthophloea, A. mearnsii* and *E. divinorum* barks recovered at 50 °C validated the claim. Extraction at lower heat is beneficial because the cost for heat supply is reduced while co-extraction of undesirable compounds is avoided.

Furthermore, the barks of *A. xanthophloea* grown in Tanzania can produce a commercially acceptable extract in terms of extract yield, tannin, total phenolic and flavonoid contents, and have a crosslinking ability almost comparable to that of extract from *A. mearnsii* barks, which is globally known to be among reliable commercial tannin sources. Hence, *A. xanthophloea* abundantly available in Tanzania with its scarce use can potentially be cultivated for the production of vegetable tannins. The *E. divinorum* barks, on the other hand, are a good tannin source only when used in combination with 2% Al_2O_3, particularly when the latter is added first. *E. racemosa* has been proven to be poor tannin source. Thus, it should be discouraged to be used in the tanning process among cottage tanneries in Tanzania.

Based on the interaction mechanism studies, it was deduced that the extracts from *A. xanthophloea, E. divinorum* and *E. racemosa* contain condensed tannins. The interactions with collagen of the skin/ hide occurred throughout the studied pH range, but high interactions are preferably high at pH between 3.5 and 4.5. Therefore, this pH range should be considered for effective tanning when using the extracts from these plants for vegetable tanning. As the four plants investigated in this work are deployed by communities engaging in traditional leather processing, the findings reported here have significantly enriched the traditional knowledge of processing leather in Tanzania and elsewhere were applicable.

Since the sources of $Al_2(SO_4)_3$ in the world are diminishing (Aderemi *et al.*, 2009), and this is worse in developing countries such as Tanzania, the investigation of local materials as sources of $Al_2(SO_4)_3$ for combination tanning was a worthy idea. It was confirmed in the present study that $Al_2(SO_4)_3$ can be prepared from kaolin using sulphuric acid as a dissolution agent and thus can be applied in combination tanning to yield leathers with the shrinkage temperature beyond 100 °C and other leather properties preferred by tanners.

Therefore, it can be concluded that vegetable tannins from the barks *A. xanthophloea* and *E. divinorum* abundantly grown in Tanzania and aluminium sulphate from Pugu kaolin are suitable for the development of an eco-friendly tanning method. In this way, both local plants (*A. xanthophloea* and *E. divinorum*) and kaolin deposits can catalyse the application of green chemistry leather tanning through avoiding the use of toxic chemicals such as chromium salts in the leather industry, thereby bringing about sustainable leather production practices.

5.2 Recommendations

Based on the findings in this study, the following are recommended as the follow-up studies to enrich what has been reported here:

(i) Preparation of $Al_2(SO_4)_3$ from kaolin is influenced by several parameters such as particle size, the temperature of calcination, the temperature of extraction, solid to liquid ratio during extraction, time of extraction and calcination. These parameters need to be optimized for an effective process. Due to time constraints, parameter optimization was beyond the scope of this work. Therefore, the optimization of these parameters for preparing $Al_2(SO_4)_3$ from Pugu kaolin is hereby recommended.

(ii) The crosslinking ability of the extract from *E. divinorum* was of doubt due to observed broad peaks between T_{onset} and T_{peak}, but the reason for this observation was uncertain. Therefore, the study on the molecular structure of the tannins extracted from *E. divinorum* is crucial to understand their chemistry for explaining such abnormality. In addition to the determination of tannin, phenolic and flavonoid content covered in this work, the determination of composition of extracts from barks using high tech equipments such as HPLC/MC is recommended.

(iii) The order of adding tanning agents in combination tanning gave different results among the studied plants. The reasons for having differences have not been yet established, and thus needs further exploration.

(iv) The analysis of cost effectiveness of proposed method was not covered in this study. It is important to carry out the study to establish the cost effectiveness of the proposed method as compared to the conventional chrome tanning method.

(v) Last but not least, the survey on the economic importance of growing *A. xanthophloea* and *E. divinorum* for commercial production of tannins is essential. The focus should be on their agronomy to establish how long they take to obtain the tannins that are commercially profitable. If profitable, the community must be sensitized to grow these plants commercially.

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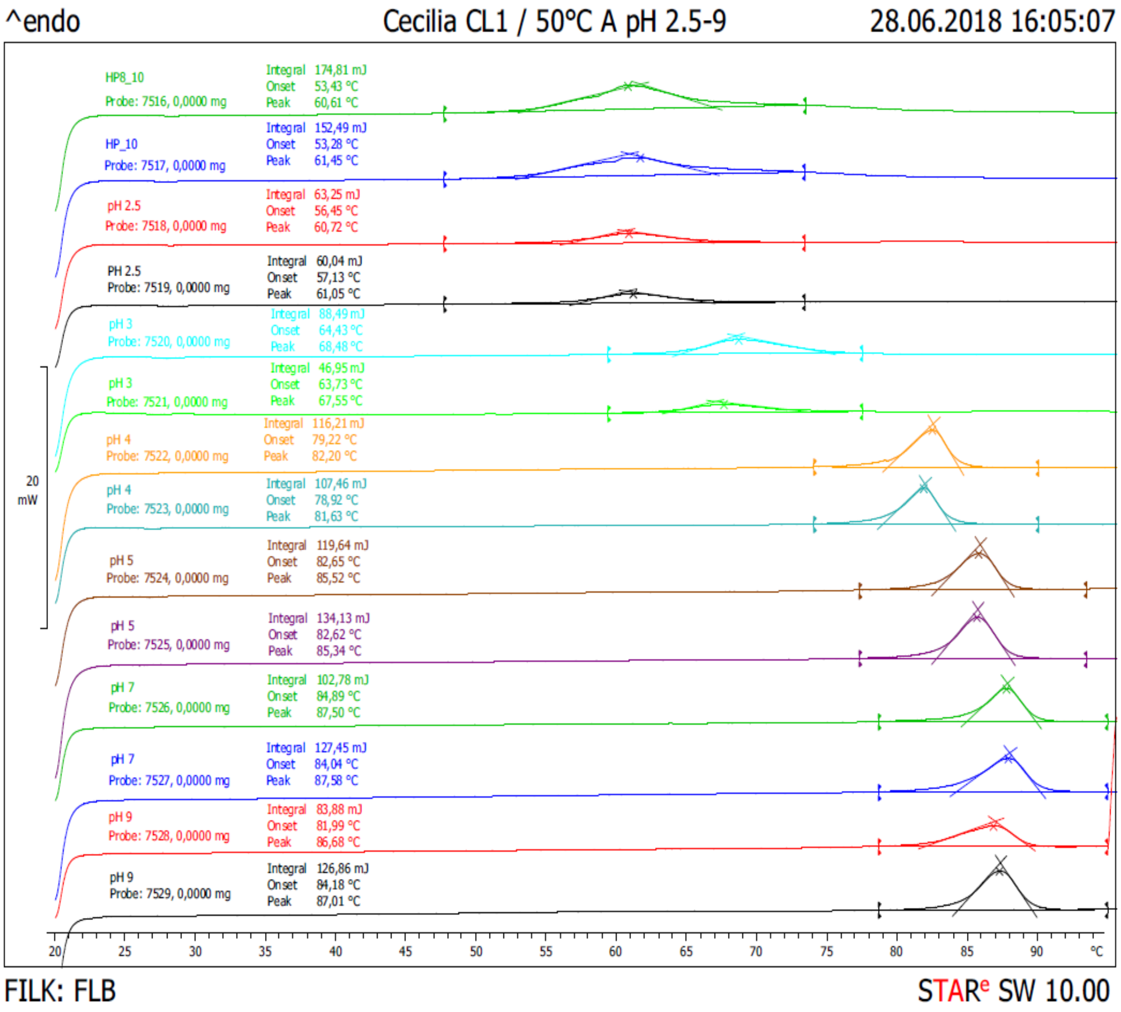
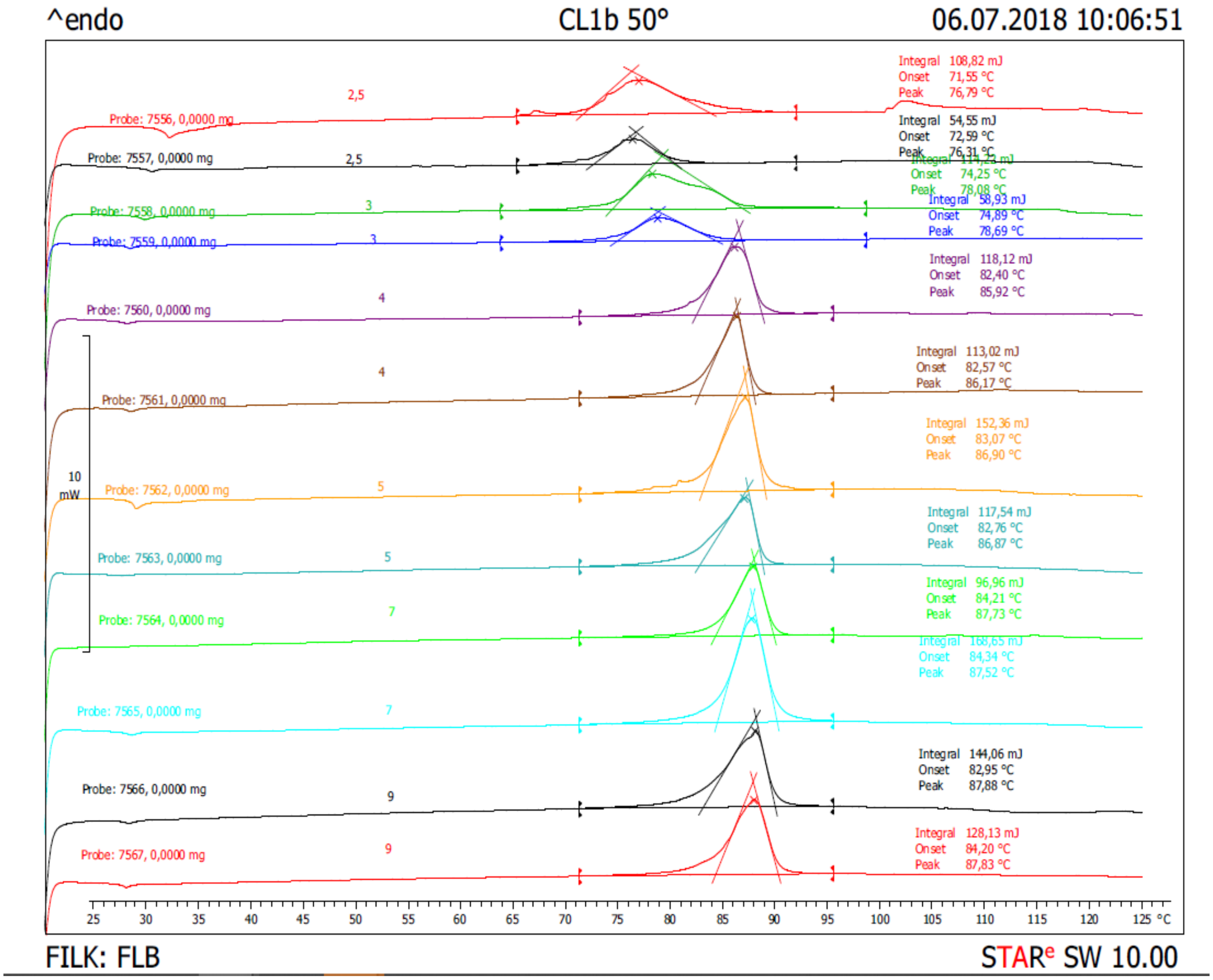
APPENDICIES

Appendix 1: Community Outreach

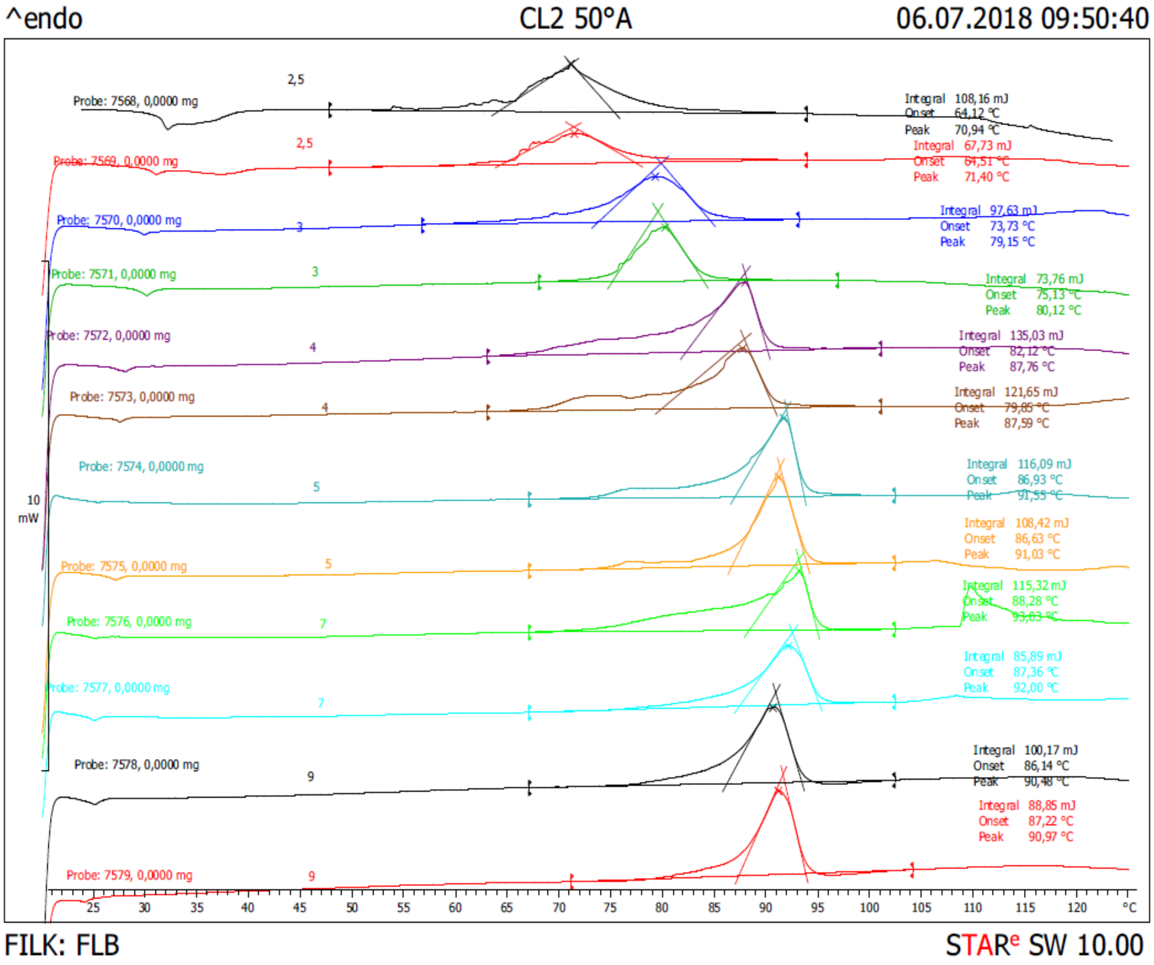
Explaining to the visitors about this work and its advantage to the community during 15th Exhibitions on Higher Education, Science, Technology and Innovation (TCU exhibitions 2019) and Nane nane exhibitions

Appendix 2: Thermographs for the Samples





^endo
CL1b 50°
06.07.2018 10:06:51
Integral 108,82 mJ
Onset 71,55 °C
Peak 76,79 °C
2,5
Probe: 7556, 0,0000 mg
Integral 54,55 mJ
Onset 72,59 °C
Peak 76,31 °C
Probe: 7557, 0,0000 mg
2,5
Integral 114,22 mJ
Onset 74,25 °C
Peak 78,08 °C
Probe: 7558, 0,0000 mg
3
Integral 58,93 mJ
Onset 74,89 °C
Peak 78,69 °C
Probe: 7559, 0,0000 mg
3
Integral 118,12 mJ
Onset 82,40 °C
Peak 85,92 °C
4
Probe: 7560, 0,0000 mg
Integral 113,02 mJ
Onset 82,57 °C
Peak 86,17 °C
4
Probe: 7561, 0,0000 mg
Integral 152,36 mJ
Onset 83,07 °C
Peak 86,90 °C
10
mW
Probe: 7562, 0,0000 mg
5
Integral 117,54 mJ
Onset 82,76 °C
Peak 86,87 °C
Probe: 7563, 0,0000 mg
5
Integral 96,96 mJ
Onset 84,21 °C
Peak 87,73 °C
7
Probe: 7564, 0,0000 mg
Integral 168,65 mJ
Onset 84,34 °C
Peak 87,52 °C
Probe: 7565, 0,0000 mg
7
Integral 144,06 mJ
Onset 82,95 °C
Peak 87,88 °C
Probe: 7566, 0,0000 mg
9
Integral 128,13 mJ
Onset 84,20 °C
Peak 87,83 °C
Probe: 7567, 0,0000 mg
9
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
105
110
115
120
125 °C
FILK: FLB
STAR^e SW 10.00


^endo
CL2 50°A
06.07.2018 09:50:40
Probe: 7568, 0,0000 mg
2,5
Integral 108,16 mJ
Onset 64,12 °C
Peak 70,94 °C
Probe: 7569, 0,0000 mg
2,5
Integral 67,73 mJ
Onset 64,51 °C
Peak 71,40 °C
Probe: 7570, 0,0000 mg
3
Integral 97,63 mJ
Onset 73,73 °C
Peak 79,15 °C
Probe: 7571, 0,0000 mg
3
Integral 73,76 mJ
Onset 75,13 °C
Peak 80,12 °C
Probe: 7572, 0,0000 mg
4
Integral 135,03 mJ
Onset 82,12 °C
Peak 87,76 °C
Probe: 7573, 0,0000 mg
4
Integral 121,65 mJ
Onset 79,85 °C
Peak 87,59 °C
Probe: 7574, 0,0000 mg
5
Integral 116,09 mJ
Onset 86,93 °C
Peak 91,55 °C
10
mW
Integral 108,42 mJ
Onset 86,63 °C
Peak 91,03 °C
Probe: 7575, 0,0000 mg
5
Integral 115,32 mJ
Onset 88,28 °C
Peak 93,03 °C
Probe: 7576, 0,0000 mg
7
Integral 85,89 mJ
Onset 87,36 °C
Peak 92,00 °C
Probe: 7577, 0,0000 mg
7
Integral 100,17 mJ
Onset 86,14 °C
Peak 90,48 °C
Probe: 7578, 0,0000 mg
9
Integral 88,85 mJ
Onset 87,22 °C
Peak 90,97 °C
Probe: 7579, 0,0000 mg
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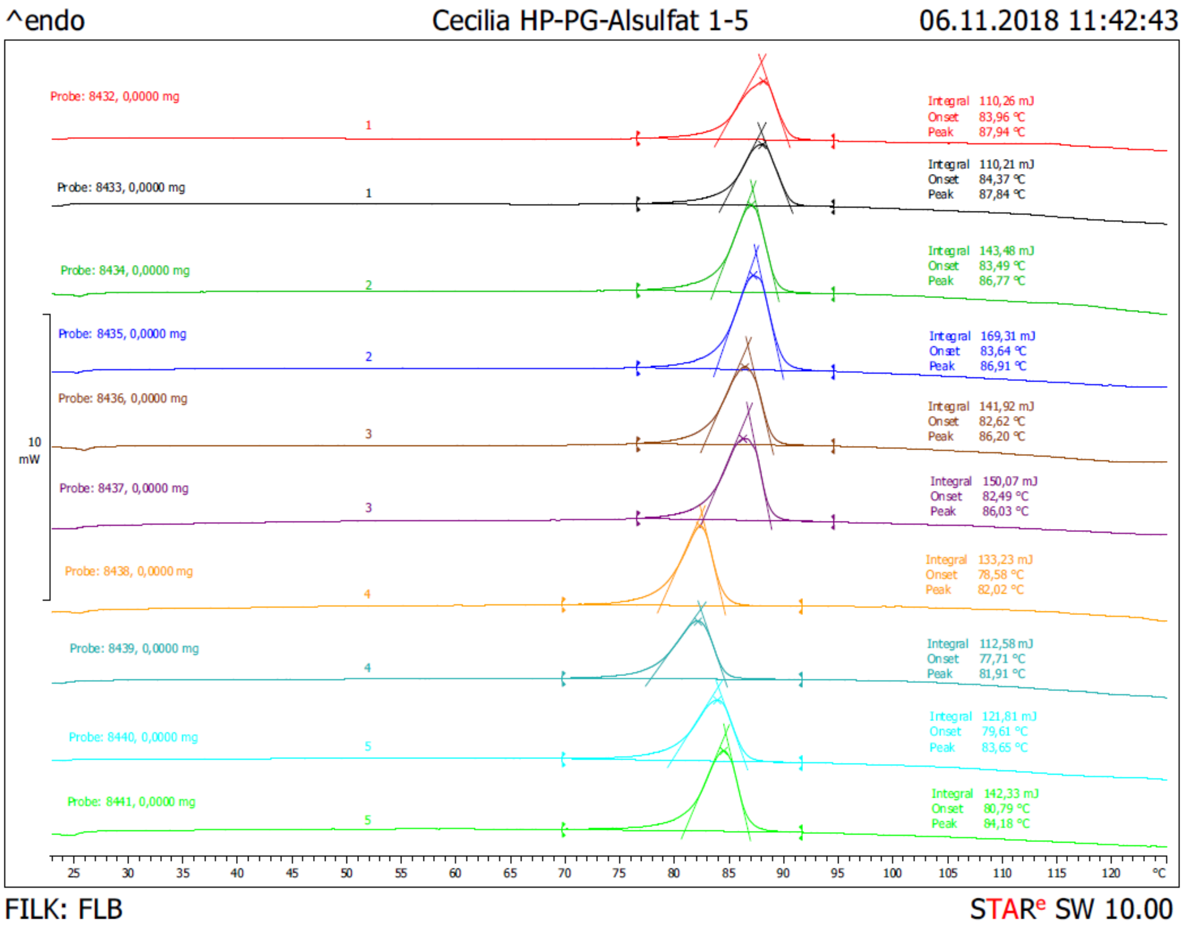
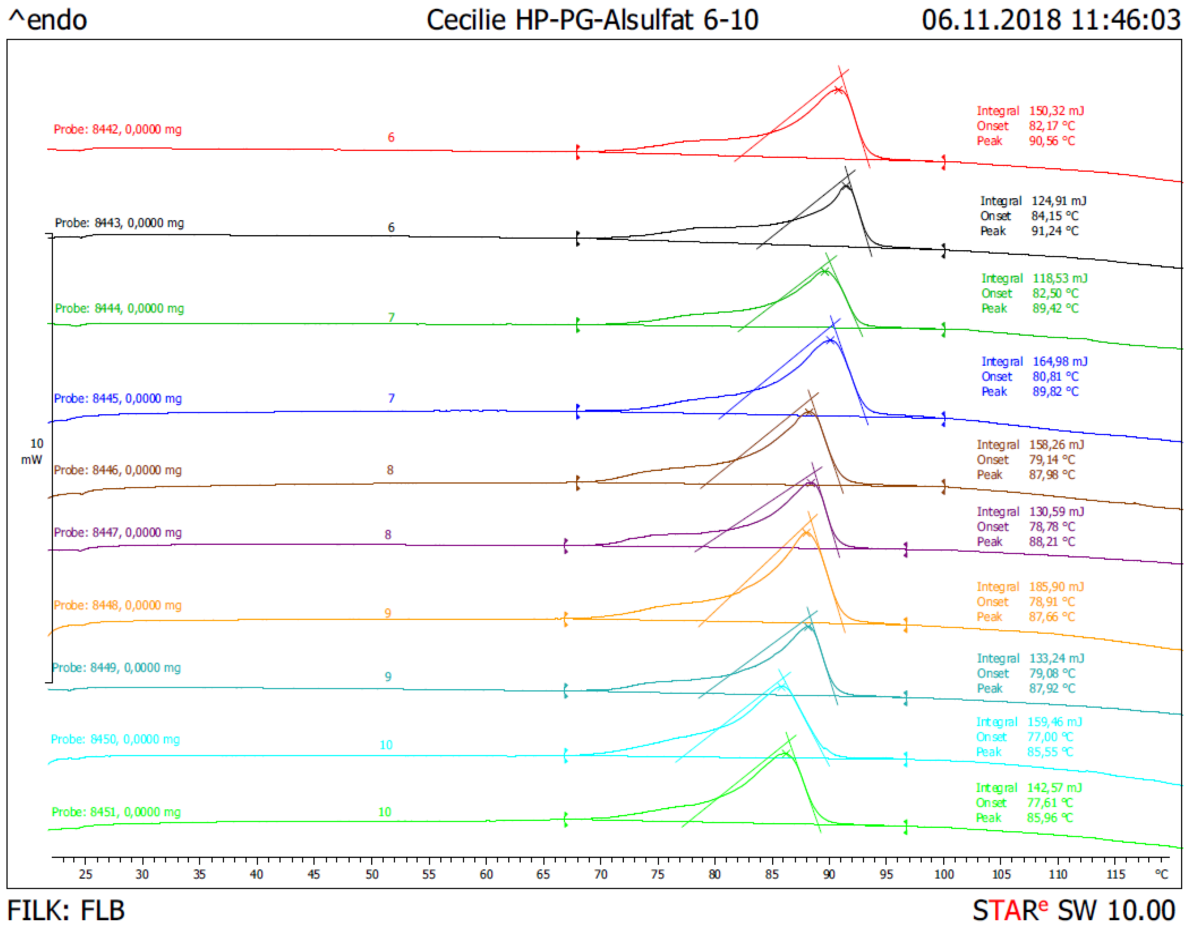
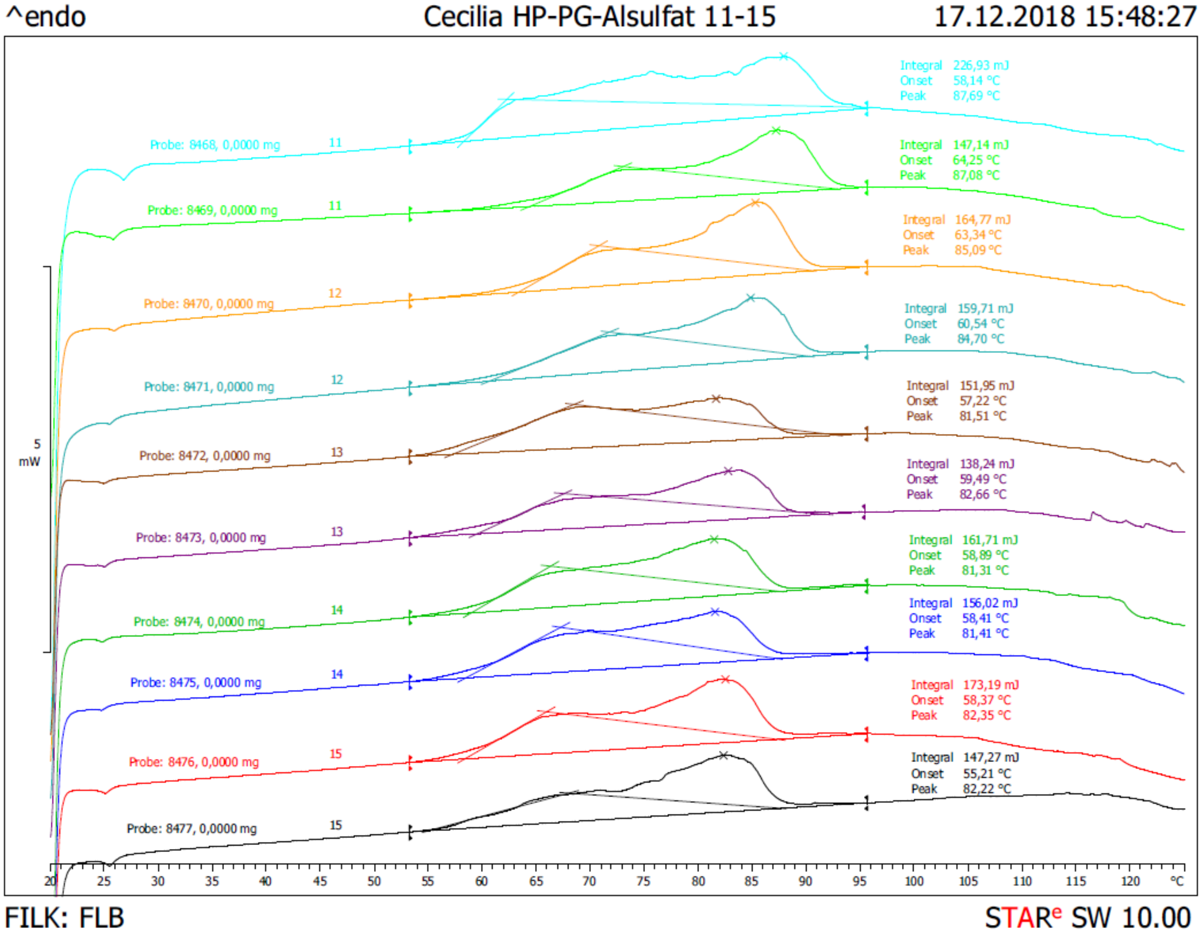
FILK: FLB
STARe SW 10.00


^endo
Cecilia HP-PG-Alsulfat 1-5
06.11.2018 11:42:43
Probe: 8432, 0,0000 mg
1
Integral 110,26 mJ
Onset 83,96 °C
Peak 87,94 °C
Probe: 8433, 0,0000 mg
1
Integral 110,21 mJ
Onset 84,37 °C
Peak 87,84 °C
Probe: 8434, 0,0000 mg
2
Integral 143,48 mJ
Onset 83,49 °C
Peak 86,77 °C
Probe: 8435, 0,0000 mg
2
Integral 169,31 mJ
Onset 83,64 °C
Peak 86,91 °C
Probe: 8436, 0,0000 mg
3
Integral 141,92 mJ
Onset 82,62 °C
Peak 86,20 °C
10 mW
Probe: 8437, 0,0000 mg
3
Integral 150,07 mJ
Onset 82,49 °C
Peak 86,03 °C
Probe: 8438, 0,0000 mg
4
Integral 133,23 mJ
Onset 78,58 °C
Peak 82,02 °C
Probe: 8439, 0,0000 mg
4
Integral 112,58 mJ
Onset 77,71 °C
Peak 81,91 °C
Probe: 8440, 0,0000 mg
5
Integral 121,81 mJ
Onset 79,61 °C
Peak 83,65 °C
Probe: 8441, 0,0000 mg
5
Integral 142,33 mJ
Onset 80,79 °C
Peak 84,18 °C
25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 °C
FILK: FLB
STARe SW 10.00


^endo
Cecilie HP-PG-Alsulfat 6-10
06.11.2018 11:46:03
Probe: 8442, 0,0000 mg
6
Integral 150,32 mJ
Onset 82,17 °C
Peak 90,56 °C
Probe: 8443, 0,0000 mg
6
Integral 124,91 mJ
Onset 84,15 °C
Peak 91,24 °C
Probe: 8444, 0,0000 mg
7
Integral 118,53 mJ
Onset 82,50 °C
Peak 89,42 °C
Probe: 8445, 0,0000 mg
7
Integral 164,98 mJ
Onset 80,81 °C
Peak 89,82 °C
10 mW
Probe: 8446, 0,0000 mg
8
Integral 158,26 mJ
Onset 79,14 °C
Peak 87,98 °C
Probe: 8447, 0,0000 mg
8
Integral 130,59 mJ
Onset 78,78 °C
Peak 88,21 °C
Probe: 8448, 0,0000 mg
9
Integral 185,90 mJ
Onset 78,91 °C
Peak 87,66 °C
Probe: 8449, 0,0000 mg
9
Integral 133,24 mJ
Onset 79,08 °C
Peak 87,92 °C
Probe: 8450, 0,0000 mg
10
Integral 159,46 mJ
Onset 77,00 °C
Peak 85,55 °C
Probe: 8451, 0,0000 mg
10
Integral 142,57 mJ
Onset 77,61 °C
Peak 85,96 °C
25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 °C
FILK: FLB
STARe SW 10.00

^endo
Cecilia HP-PG-Alsulfat 11-15
17.12.2018 15:48:27
Integral 226,93 mJ
Onset 58,14 °C
Peak 87,69 °C
Probe: 8468, 0,0000 mg
11
Integral 147,14 mJ
Onset 64,25 °C
Peak 87,08 °C
Probe: 8469, 0,0000 mg
11
Integral 164,77 mJ
Onset 63,34 °C
Peak 85,09 °C
Probe: 8470, 0,0000 mg
12
Integral 159,71 mJ
Onset 60,54 °C
Peak 84,70 °C
Probe: 8471, 0,0000 mg
12
Integral 151,95 mJ
Onset 57,22 °C
Peak 81,51 °C
Probe: 8472, 0,0000 mg
13
5
mW
Integral 138,24 mJ
Onset 59,49 °C
Peak 82,66 °C
Probe: 8473, 0,0000 mg
13
Integral 161,71 mJ
Onset 58,89 °C
Peak 81,31 °C
Probe: 8474, 0,0000 mg
14
Integral 156,02 mJ
Onset 58,41 °C
Peak 81,41 °C
Probe: 8475, 0,0000 mg
14
Integral 173,19 mJ
Onset 58,37 °C
Peak 82,35 °C
Probe: 8476, 0,0000 mg
15
Integral 147,27 mJ
Onset 55,21 °C
Peak 82,22 °C
Probe: 8477, 0,0000 mg
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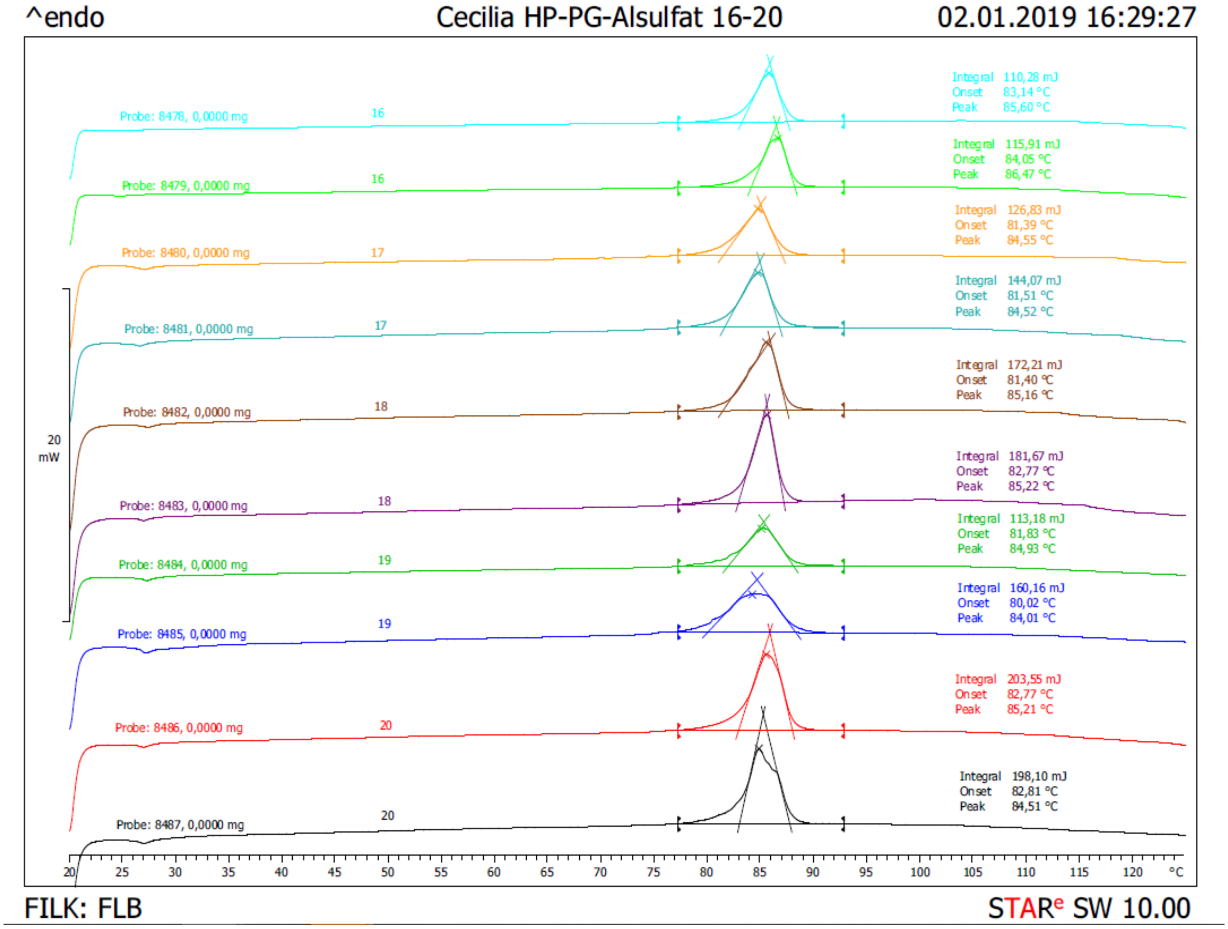
°C
FILK: FLB
STARe SW 10.00


^endo
Cecilia HP-PG-Alsulfat 16-20
02.01.2019 16:29:27
Probe: 8478, 0,0000 mg
16
Integral 110,28 mJ
Onset 83,14 °C
Peak 85,60 °C
Probe: 8479, 0,0000 mg
16
Integral 115,91 mJ
Onset 84,05 °C
Peak 86,47 °C
Probe: 8480, 0,0000 mg
17
Integral 126,83 mJ
Onset 81,39 °C
Peak 84,55 °C
Probe: 8481, 0,0000 mg
17
Integral 144,07 mJ
Onset 81,51 °C
Peak 84,52 °C
Probe: 8482, 0,0000 mg
18
Integral 172,21 mJ
Onset 81,40 °C
Peak 85,16 °C
20
mW
Probe: 8483, 0,0000 mg
18
Integral 181,67 mJ
Onset 82,77 °C
Peak 85,22 °C
Probe: 8484, 0,0000 mg
19
Integral 113,18 mJ
Onset 81,83 °C
Peak 84,93 °C
Probe: 8485, 0,0000 mg
19
Integral 160,16 mJ
Onset 80,02 °C
Peak 84,01 °C
Probe: 8486, 0,0000 mg
20
Integral 203,55 mJ
Onset 82,77 °C
Peak 85,21 °C
Probe: 8487, 0,0000 mg
20
Integral 198,10 mJ
Onset 82,81 °C
Peak 84,51 °C
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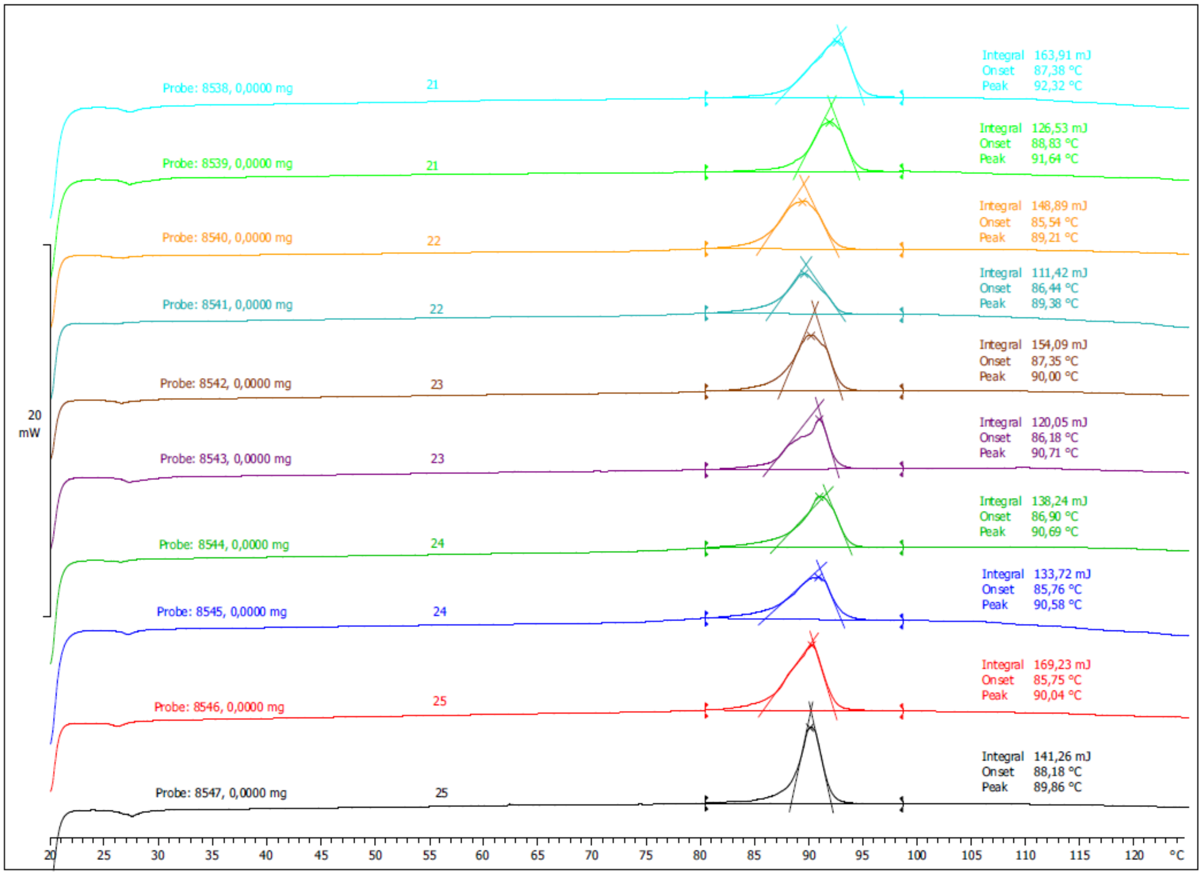
°C
FILK: FLB
STARe SW 10.00

^endo Cecilia HP-PG-Alsulfat 21-25 02.01.2019 16:40:34



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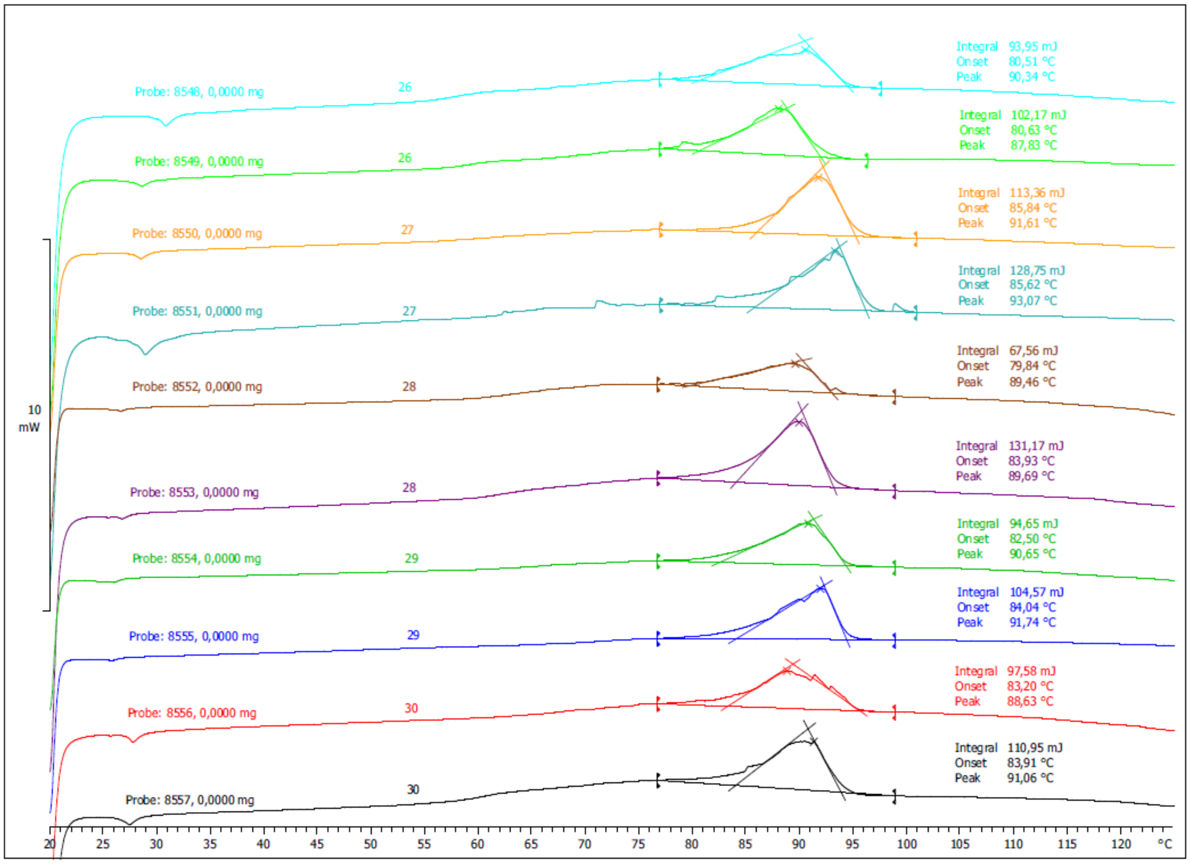

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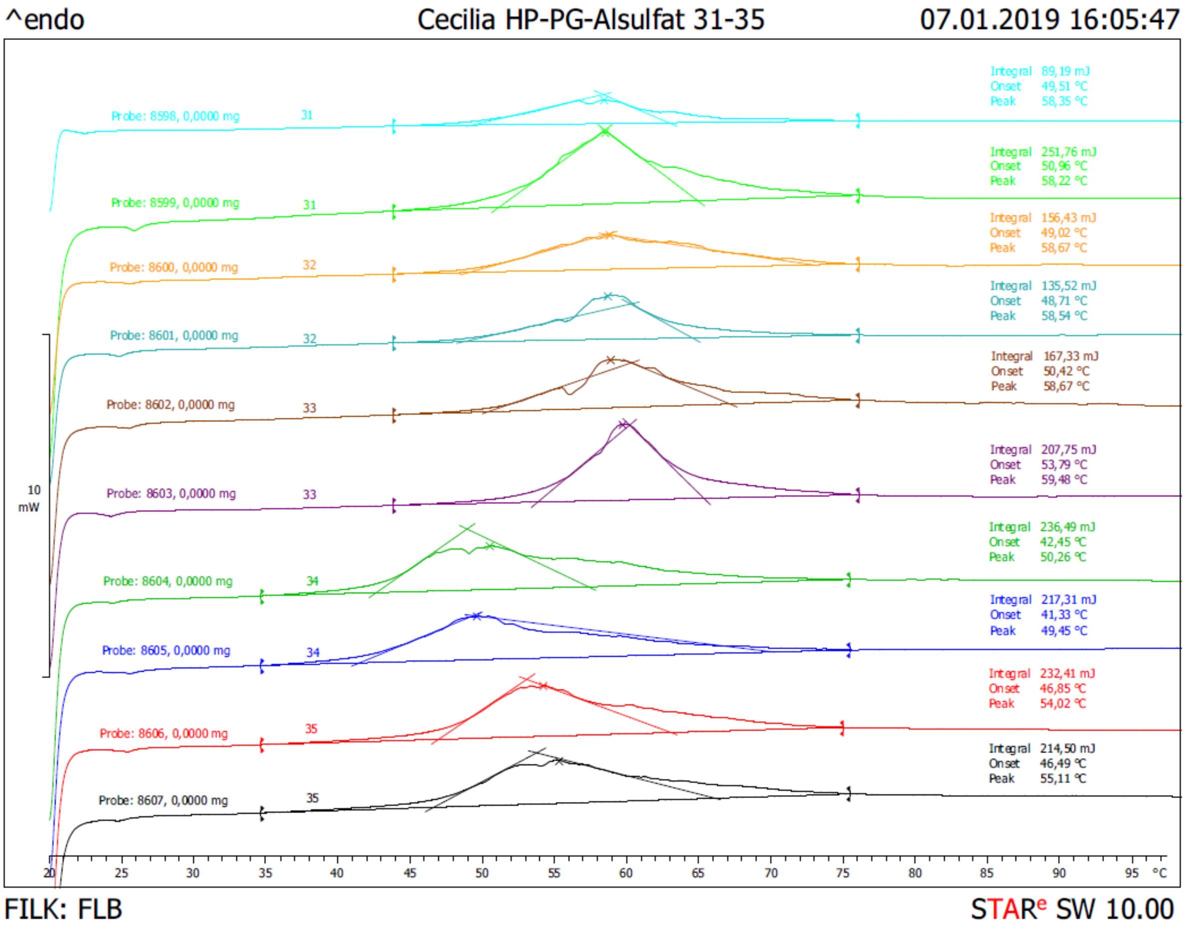
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Cecilia HP-PG-Alsulfat 31-35
07.01.2019 16:05:47
Probe: 8598, 0,0000 mg
31
Integral 89,19 mJ
Onset 49,51 °C
Peak 58,35 °C
Probe: 8599, 0,0000 mg
31
Integral 251,76 mJ
Onset 50,96 °C
Peak 58,22 °C
Probe: 8600, 0,0000 mg
32
Integral 156,43 mJ
Onset 49,02 °C
Peak 58,67 °C
Probe: 8601, 0,0000 mg
32
Integral 135,52 mJ
Onset 48,71 °C
Peak 58,54 °C
Probe: 8602, 0,0000 mg
33
Integral 167,33 mJ
Onset 50,42 °C
Peak 58,67 °C
Probe: 8603, 0,0000 mg
33
Integral 207,75 mJ
Onset 53,79 °C
Peak 59,48 °C
10
mW
Probe: 8604, 0,0000 mg
34
Integral 236,49 mJ
Onset 42,45 °C
Peak 50,26 °C
Probe: 8605, 0,0000 mg
34
Integral 217,31 mJ
Onset 41,33 °C
Peak 49,45 °C
Probe: 8606, 0,0000 mg
35
Integral 232,41 mJ
Onset 46,85 °C
Peak 54,02 °C
Probe: 8607, 0,0000 mg
35
Integral 214,50 mJ
Onset 46,49 °C
Peak 55,11 °C
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80
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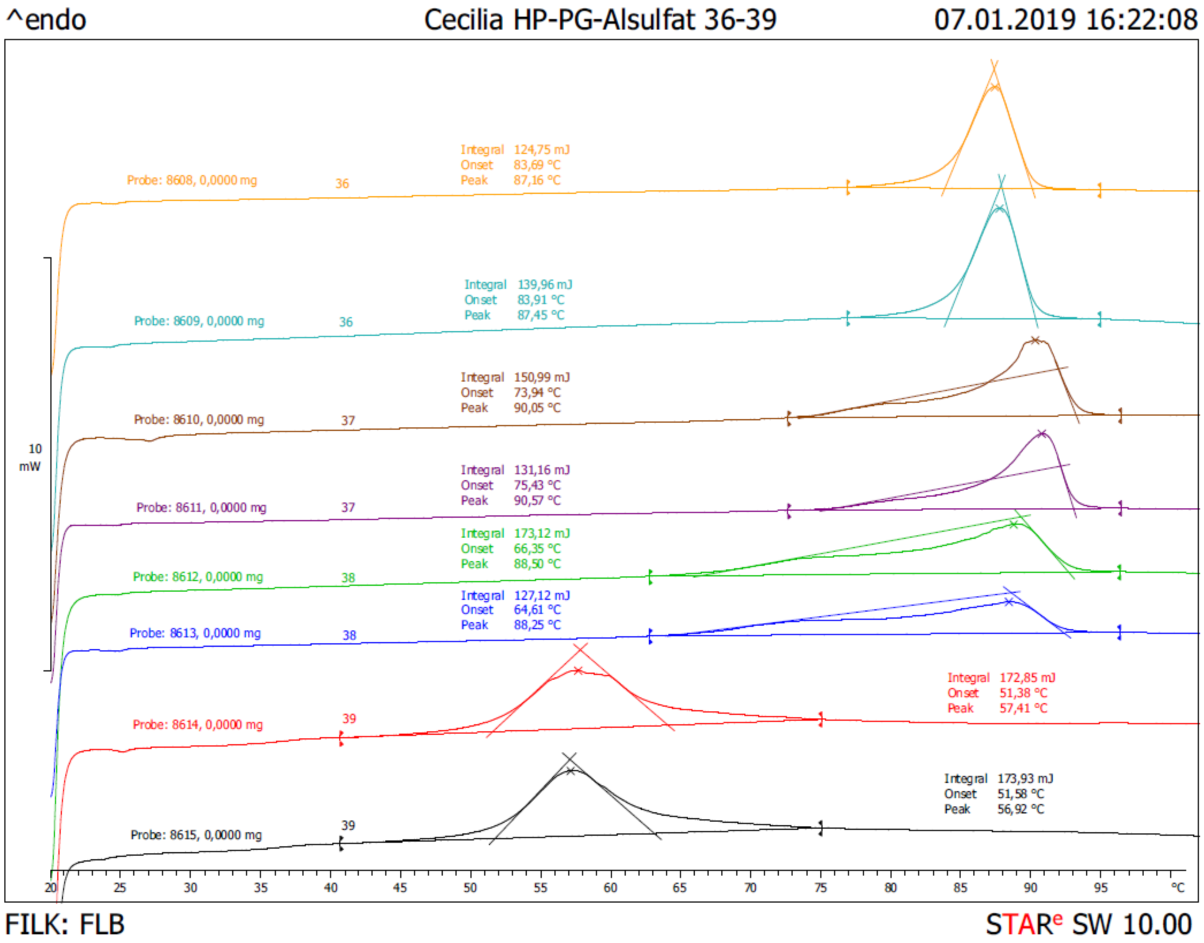
90
95
°C
FILK: FLB
STARe SW 10.00


^endo
Cecilia HP-PG-Alsulfat 36-39
07.01.2019 16:22:08
Integral 124,75 mJ
Onset 83,69 °C
Peak 87,16 °C
Probe: 8608, 0,0000 mg
36
Integral 139,96 mJ
Onset 83,91 °C
Peak 87,45 °C
Probe: 8609, 0,0000 mg
36
Integral 150,99 mJ
Onset 73,94 °C
Peak 90,05 °C
Probe: 8610, 0,0000 mg
37
10
mW
Integral 131,16 mJ
Onset 75,43 °C
Peak 90,57 °C
Probe: 8611, 0,0000 mg
37
Integral 173,12 mJ
Onset 66,35 °C
Peak 88,50 °C
Probe: 8612, 0,0000 mg
38
Integral 127,12 mJ
Onset 64,61 °C
Peak 88,25 °C
Probe: 8613, 0,0000 mg
38
Integral 172,85 mJ
Onset 51,38 °C
Peak 57,41 °C
Probe: 8614, 0,0000 mg
39
Integral 173,93 mJ
Onset 51,58 °C
Peak 56,92 °C
Probe: 8615, 0,0000 mg
39
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75
80
85
90
95
°C
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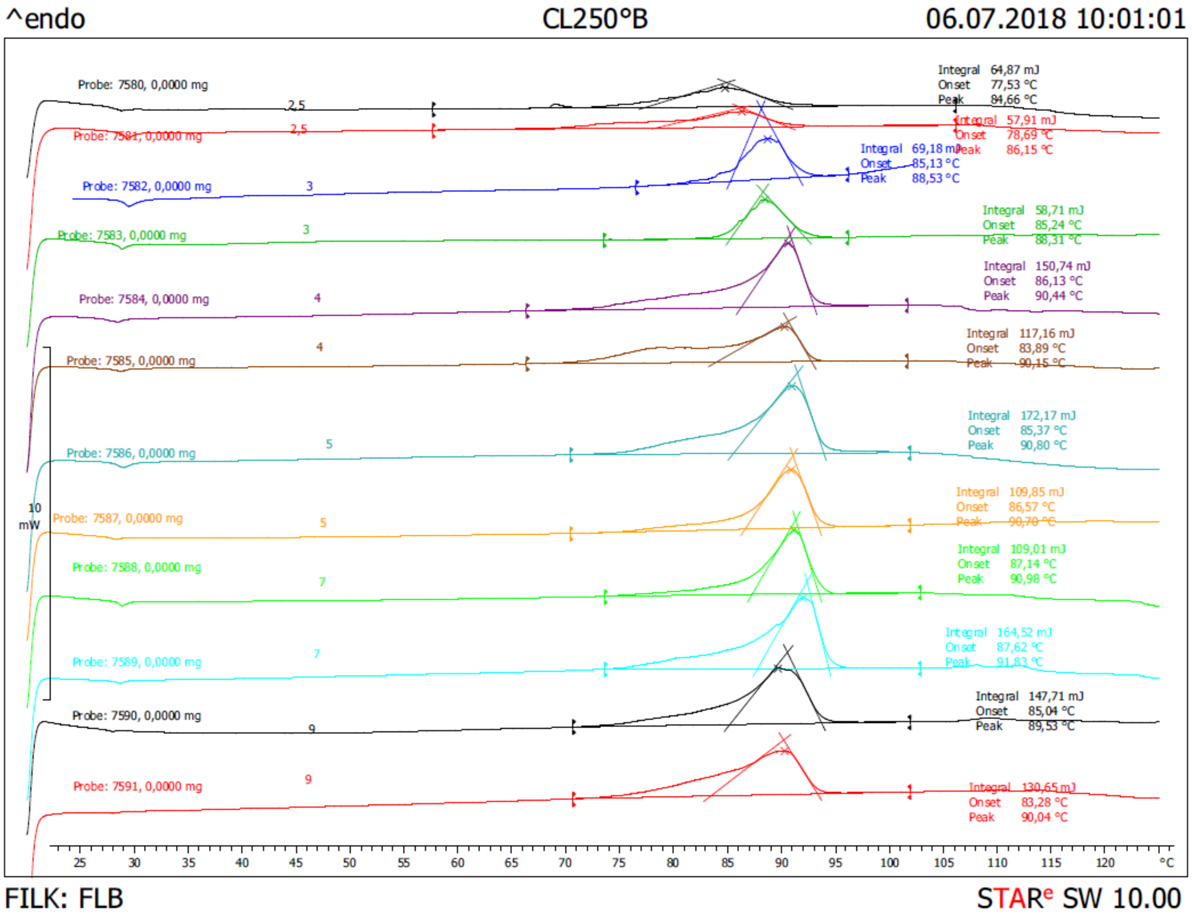
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RESEARCH OUTPUTS

(1) Research articles

(2) Conference Paper

(3) Poster Presentation

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Review

Alternative tanning technologies and their suitability in curbing environmental pollution from the leather industry: A comprehensive review

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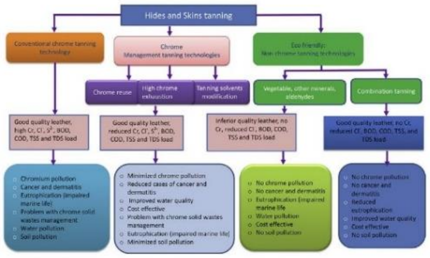
HIGHLIGHTS

- Chrome tanning's effluent contains Cr and other pollutants above permissible limits.
- Wastes from chrome tanning pose a global environmental management challenge.
- Proxies for chrome tanning are vital to protect the environment and human health.
- Vegetable and $Al_2(SO_4)_3$ blend is a pledging eco-friendly leather tanning technology.
- Optimization of combination tanning technologies for industrial use is decisive .

GRAPHICAL ABSTRACT



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ABSTRACT

Chrome tanning remains the most favourite technology in the leather industry worldwide due to its ability to produce leather with attributes desirable for high-quality leather such as excellent hydrothermal stability, better dyeing characteristics and softness. Nevertheless, the technology has been censured globally for its severe environmental detriments and adverse effects on human health and other organisms. Developing alternative eco-friendly tanning technologies capable of producing leather of high quality has remained a challenging scientific inquiry. This review article provides an assessment of various eco-friendly tanning attempts geared towards improving or replacing the chrome technology without compromising the quality of the produced leather. The reviewed publications have ascertained that, these attempts have been centred on recycling of spent liquors; chromium exhaustion enhancement and total replacement of chromium salts. The research gaps and levels of key environmental pollutants from the reviewed technologies are presented, and the qualities of the leather produced from these technologies are highlighted. Of all the examined alternative technologies, total replacement of

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Environmental pollution
Human health

chromium salts sounds ideal to elude adverse effects associated with chrome tanning. Combination tanning, which implies blending two tanning agents that individually cannot impart desired properties to the leather, is anticipated to be an alternative technology to chrome tanning. Apart from being an eco-friendly technology, combination tanning produces leather with similar features to those produced by chrome tanning. In this regard, blending vegetable tannins with aluminium sulphate provides a promising chrome-free tanning technology. However, further studies to optimize combination tanning technologies to suit industrial applications are highly recommended.

Contents

1. Introduction

Leather is a flexible and durable material obtained from livestock by-products through various processes in which different chemicals are employed (Leafe, 1999; Covington, 2009). It remains to be the consumers' first choice due to its flexibility, durability and uniqueness. The uniqueness and beauty of leather as a natural product are unmatched with similar man-made synthetic products (Ferreira et al., 2010). It takes time with the application of technical expertise and passion for coming up with finished leather ready for production of various leather items. Leather making involves four steps namely; pre-tanning, tanning, post-tanning and finishing (Fig. 1) (Dutta, 1999; Marik et al., 2003; Covington, 2009). Pre-tanning processes aim at preparing raw hides and skins for proper interaction with tanning agents while post-tanning enhances physical and organoleptic properties of tanned leather (Beghetto et al., 2013; Duraisamy et al., 2016).

The tanning process is the most crucial step because it brings actual conversion of raw hides/skins to leather through stabilizing collagen against heat and enzymatic attack (Zeiner et al., 2011; Beghetto et al., 2013). After tanning, raw hides and skins change their physical and chemical properties. They become flexible, non-putrescible and mechanically more durable than in their raw forms (Dutta, 1985; Sarkar, 1997; Covington, 2009). Although many tanning methods are well known since ancient time (Grantz, 1969; Churchill, 1983), the most deployed method is chrome tanning (Guertin et al., 2016). Chrome tanning involves the application of basic chromium sulphate containing 33% basicity and 23% chromium (III) oxide (Cr_2O_3) that forms a complex with collagen molecules via covalent bonds to stabilize collagen against heat and enzymatic attack, rendering it flexible and non-degradable (Covington, 2009; Crudu et al., 2010).

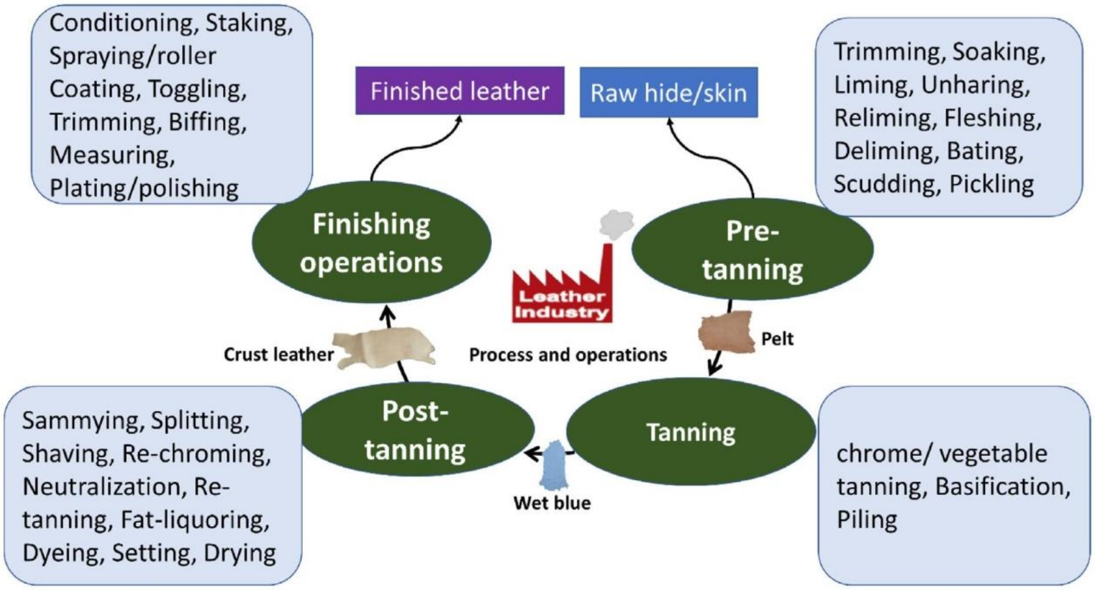


Fig. 1. Steps involved in leather production (Dixit et al., 2015).

Chromium tanned leather is known for its versatility, excellent hydrothermal stability, better dyeability and softness (Kanagaraj et al., 2008). However, chrome tanning has been condemned worldwide as the most polluting unit process since it releases trivalent chromium ions [Cr(III)] in water bodies. At micro-levels, Cr(III) is an essential trace element required in the human body for its physiological functions. Chromium (III) plays a role in glucose, fat, and protein metabolism by potentiating the action of insulin (Anderson, 1981). The chromium (III) content in the range of 8.4–23.7 μg 1,000 kcal^{-1} with a mean of 13.4 μg 1,000 kcal^{-1} has been proved by nutritionists to be optimal for daily diets (Oruko et al., 2019), but its excess is harmful to human health (Jin et al., 2017). According to Snow (1994), excess Cr(III) can lead to mutagenic effect. Even though it is not easy for Cr(III) complexes to pass through the cell membranes, their accumulation around cells in the body induces cell-surface morphological alteration (Wang et al., 2017). The latter results into cell-membrane lipid injuries via disruption of cellular functions and integrity and finally causes DNA damage (Wang et al., 2017).

In the effluent Cr(III) can easily be converted to Cr(VI) due to the presence of oxidizing agents such as dissolved oxygen and MnO_2. Furthermore, pH fluctuations in an effluent treatment plant can accelerate the oxidation of Cr(III) to Cr(VI) (Fendorf and Zasoski, 1992; Kumar, 2005; Apte et al., 2006; Başaran et al., 2008; da Silva et al., 2011). Also it has been established that, stored leather and other leather products do degrade with time due to humidity, temperature, and UV lights effects (Bayramoglu et al., 2012). During this process, the fatliquoring agents, tanning agents and auxiliary agents replace molecules of the leather structure and free radicals are subsequently formed. Consequently, these radicals become the potential drivers of Cr(III) oxidation to Cr(VI) (Yılmaz et al., 2016; Bayramoglu et al., 2012). Leather products have been proved to contain Cr(VI) content over time, which makes it challenging to guarantee that Cr(III) used in the leather tanning process is harmless to leather products consumers (Fontaine et al., 2019). Hexavalent chromium [Cr(VI)] threatens terrestrial and marine life due to its high toxicity nature (Belay, 2010). Furthermore, Cr(VI) is carcinogenic, mutagenic and allergic to human and causes death to organisms (Kotaś and Stasicka, 2000; Patra et al., 2019; da Silva et al., 2011).

Of all chromium salt entering the tanning liquor during tanning, only 55–70% is fixed in the leather, and the rest gets its way to the effluent (Saravanabhavan et al., 2003; Belay, 2010; Mandal et al., 2011). The main portion of chrome effluent comes from the tanning float with a significant amount of the same also being discharged from sammying and re-tanning processes. Chromium concentrations in the spent liquor is in the range of 2000 mg L^{-1} - 5000 mg L^{-1} (Ahamed and Kashif, 2014) while environmental regulation agencies worldwide allow as less as 20 mg L^{-1} total chromium for the discharge of effluent into public sewers (Table 1) (UNIDO, 2000). Practically, the reduction of chromium concentrations to permissible levels in the tannery waste stream is possible, but it is highly capital intensive which presents operational costs burden to the tanneries. This challenge calls for appropriate technologies to minimize or eliminate chrome in the effluent for the sustainability of the leather industry.

Moreover, chrome tanning produces a considerable amount of solid wastes in the form of chrome-tanned leather shavings, trimmings and buffing powder that are generated during corresponding processes. Chrome-tanned leather shavings alone contribute around 75% of solid wastes generated from leather manufacturing (Erdem and Özverdi, 2008; da Silva et al., 2011). Since they are non-degradable due to strong crosslinking bonds formed between chromium and collagen of hides and skins during the tanning process (Sreeram and Ramasami, 2003; Dixit et al., 2015), in landfills chrome-tanned leather shavings introduce challenges similar to those posed by plastic wastes (Sreeram and Ramasami, 2003; Pathak, 2018; Rahaman et al., 2018). This problem is intense in developing countries where the technologies to recover chromium from this kind of waste are not easily afforded (Xiaoli et al., 2007; Yılmaz et al., 2007; Ferreira et al., 2010; Oruko et al., 2019). Following the high contribution of the tanning process in environmental pollution by chromium, the World Bank has ranked the leather industry in the 9th position for the negative environmental impacts (Crudu et al., 2010).

Despite a substantial ecological deterioration posed by the

Table 1
Permissible limits for discharge of effluents into water bodies and sewers from various countries.

Country	Parameter (mg L^{-1})											
	BOD		COD		S^2		Cr^{+6}		Total Chromium		Oil and grease	
	Water body	Sewer	Water body	Sewer	Water body	Sewer	Water body	Sewer	Water body	Sewer	Water body	Sewer
Argentina	50	200	250	700	–	1	–	–	0.5	2	100	100
Australia	40	–	–	–	0.1	1–5	0.1	–	1	1–20	20	100–1000
Austria	25	–	200	–	0.1	2	0.1	0.1	1	3	20	100
China	20–100	600	100–300	500	1	10	0.5	0.5	1.5	1.5	10–15	100
Denmark	–	–	–	–	2	–	–	–	0.2	2	5	–
France	30	800	125	2000	2	–	0.1	0.1	–	–	–	–
Germany	25	–	250	–	2	2	–	–	1	1	–	–
Greece	15–40	500	45–150	1000	1	1–2	0.02–0.5	0.5	2.5	2.5	5–20	40
Holland	5	–	–	–	–	–	–	–	0.05	2	–	–
Hungary	–	–	50–150	–	0.01–5	1	0.5–1	1	–	5	8–50	60
India	30	500	250	250	2	2	–	–	2	2	30–100	300–100
Italy	40	250	160	500	1	2	0.2	0.2	2	4	20	40
Japan	160	160	160	160	2	2	–	–	2	2	30	30–50
Spain	40–300	750–1000	160–500	1500–2500	1–2	1–20	0.2–0.5	0.5	–	3–5	20–40	150
Switzerland	20	–	–	–	0.1	1	0.1	0.5	2	2	20	–
Turkey	100	250	200	800	1	2	0.3	–	2	5	20	100
United Kingdom	20–30	–	–	2000–6000	1.0	2–5	0.1	0.1	1–2	1–20	–	50–500
USA	40	–	–	–	–	24	–	–	1.0	8–19	–	–

Data source (UNIDO, 2000):

leather industry, it remains to be one of the crucial sectors in the world since it contributes large shares in the economy of many countries especially in Asia (Shahab and Mahmood, 2013; Islam and Siddique, 2014; Al-Muti, 2018). On the other hand, Africa is also expecting to benefit economically from the leather sector because of a huge livestock potential (Abtew, 2015; Banga et al., 2015). Since chromium offers effective and efficient tanning process, the demand for chromium sulphate is expected to increase in the future. The anticipated increase in the application of chromium sulphate signifies massive environmental pollution due to Cr(VI) toxicity and its associated ecological deterioration.

Currently, about 90% of global leather is produced through chromium tanning (Covington et al., 2008; Covington, 2009; Fei and Liu, 2016), because other tanning agents such as vegetable tannins, aluminium sulphate, zinc sulphate, titanium sulphate, aldehydes do not produce leather with similar properties as those of chromium tanned leather (Dutta, 1999; Covington, 2009). Thus, the decision to abandon chromium sulphate from use in the leather industry remains to be debatable. Some researches encourage replacement of chromium with chrome-free tanning systems (Wang et al., 2009; Tunay et al., 2010; Roig et al., 2012) such as combination tanning (China et al., 2019), while others are emphasizing its use to be coupled with management measures to reduce its adverse effects on the environment (Morera et al., 2011; Mwinyihija, 2012; Hashem et al., 2015). In this article, the recently reported environmentally friendly tanning approaches are covered with the main focus being on exploring their effectiveness in producing good quality leather while keeping environmental parameters on a check.

2. Methodology

The publications reviewed in this article were selected from various literature sources, including GoogleScholar, ScienceDirect, Researchgate, PubMed and Scopus databases. Specifically, information was extracted from books, journal papers, reports and PhD and Master Degree theses by referring to the main focus of the review. The following topics guided the selection of documents; the type of the technology, the efficiency of the technology in terms of quality of the produced leather and its environmental and human health implications. Phrases used for literature search included "chrome-less tanning technologies", "chrome-free tanning technologies", "combination tanning", "minimization of chromium pollution in leather industries", "chrome solid wastes", "environmental effects of chrome tanning", "effects of chromium to human health", "chromium poisoning in chrome tanning industries", "effects of chromium to soil" and "global leather production". Suitability of articles for inclusion in the review was examined, and those found to be pertinent to this review's objective were studied. Articles on epidemiology studies on the toxicity of tannery waste were also included.

3. Problem statement

Chrome tanning technology is the most popular and a first choice of the leather industry in the world owing to the fact that, the technology produces high quality leather with all the desired features. Nevertheless, this technology is controversial due to its adverse effects on the environment, human health and other organisms. Studies have confirmed that 30%–45% of chromium used in the conventional chrome tanning process is discharged as waste thereby leading to critical environment pollution (Oliveira, 2012; Saravanabhavan et al., 2003; Belay, 2010; Mandal et al., 2011). Disposal of solid wastes generated from tanneries and chromium contaminated sludge remains to be a global environmental challenge (Macchi et al., 1991). Under favourable conditions, Cr(III) contained in tannery effluent, sludge and chromium tanned leather wastes oxidizes to Cr(VI) (Ahamed and Kashif, 2014; Bacardit et al., 2008; Başaran et al., 2008; Fontaine et al., 2019). Chromium (VI) is associated with many human's health problems and ecological adverse effects (International Agency for Research on Cancer, 1990; Nigam et al., 2015). Various types of cancer associated with chromium (VI) exposure have been documented (Yan et al., 2020; Wang et al., 2019; da Silva et al., 2011; Kotaś and Stasicka, 2000). In the environment, Cr(VI) has been reported to pollute both water and soil deeming them unsuitable for human consumption and agricultural activities, respectively (Oliveira, 2012; Muhammad et al., 2020). Studies show that Cr(VI) can lead to the shifts in the composition of soil microbial populations due to harmful effects on metabolism of microbial cell at high concentrations (Huang et al., 2009). Other pollutants linked to chrome tanning technology are chlorides, sodium sulfides as well as a high load of total dissolved solids (TDS), biological oxygen demand (BOD) and chemical oxygen demand (COD) in effluents (Suresh et al., 2001). For ecological reasons cum sustainability of the leather industry, minimization of chromium inputs or phasing out chromium use in the leather tanning process has become an immediate need.

Various studies have been carried out around the globe to seek for solutions to combat chromium pollution created by the leather industry. Most of them focus on minimization of chromium input and subsequent enhancement of its exhaustion vis-à-vis conventional chromium tanning. At the same time, some have reported alternative technologies to chromium tanning such as vegetable tanning and combination tanning. A comprehensive assessment of these articulated technologies intended to combat environmental pollution caused by chrome tanning is scarcely available. Thus, this review article has been designed to cater for this. The article provides a detailed analysis of alternative tanning technologies on their suitability in industrial applications as well as in curbing environmental pollution from the leather industry.

4. Future perspective of the leather industry in connection to chromium pollution

Leather is ranked among the top 25 most traded commodities in the world (Abtew, 2015; UNIDO, 2010). The total estimate of annual global leather production is 23 billion square feet where the leather footwear sub-sector embraces 65%, and the remaining 35% goes to the manufacturing of a diversity of other types of leather products (Mwinyihija, 2018).

In the year 2017, the market size of global leather goods was USD 414 billion, and it was anticipated to progress at a Compound Annual Growth Rate (CAGR) of 5.4% from 2018 to 2025 (Grand View Research, 2019). The main drivers of market growth include; growing disposable income, improved living standards, changing fashion trends and growing domestic and international tourism (Grand View Research, 2019). Furthermore, increasing demand for comfortable, trendy and fancy footwear along with raising brand awareness among the leather products users has been determined to have a positive impact on the footwear market (Malani, 2015). The projected increase in leather products market denotes increased chromium pollution in future if proper mitigation measures are not put in place.

5. Environmental impacts of leather industries

Despite significant economic influence of leather industries, careless disposal of tannery solid wastes, gaseous emissions and discharge of tannery wastewater containing hazardous chemicals such as Cr(VI) compounds, synthetic tannins, oil and grease, resins, biocides and detergents creates a negative image of the leather industry (Meriç et al., 2005; Dixit et al., 2015; Taghipour and Jalali, 2016; Hu et al., 2011; Kanagaraj and Elango, 2019). Furthermore, high levels of BOD, COD and PO_4^{3-} from the leather industries have been blamed for causing eutrophication in the aquatic environment (Juel et al., 2016). To rescue the image of the leather industry, holistic approaches to propel the reduction of pollutants emissions while recycling solid waste are of paramount importance. Fig. 2 illustrates pollution control holistic approaches and the effects on the environment if no control measures are taken to manage the wastes generated.

Countries around the globe have different permissible limits for various water pollutants resulting from tanneries as presented in Table 1 below.

6. Routes of human exposure to chromium

Chromium (VI) is a major ecological and public health concern due to its toxic and hazardous nature (Sawalha et al., 2019). It is a strong oxidizing agent causing severe damage to cell membranes (Yan et al., 2020; Ahmed et al., 2017). Exposure to high levels of chromium via inhalation, ingestion, or dermal contact may cause some adverse health effects (Nordberg et al., 2014) in which ingestion has been reported as the main route of exposure to chromium (Rowbotham et al., 2000; Nigam et al., 2015). These exposure routes are divided into two categories namely;

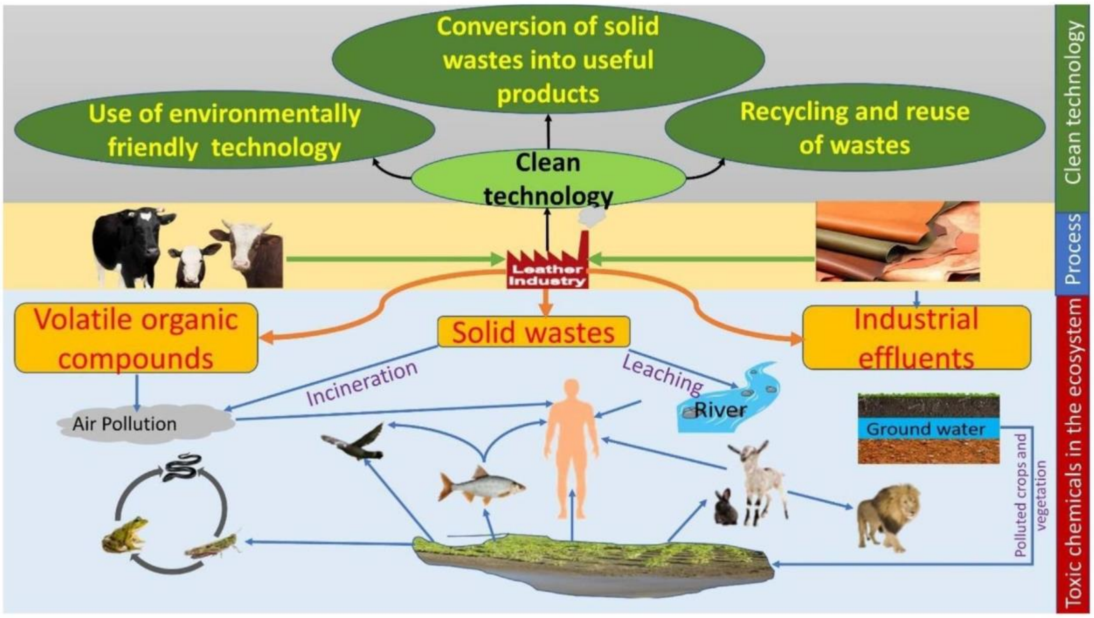


Fig. 2. Environmental impact of the leather industry and technologies to combat the threat (Dixit et al., 2015).

occupational and non-occupational.

6.1. Occupational exposure

Occupational exposure to chromium is common to tannery workers, and it is the leading cause of health problems which they experience. The study by Rahman et al. (2019) revealed severe health threats to the tannery workers in Hazaribagh, Bangladesh. This study reported complaints which were raised by tannery workers about dermatological problems, infections on body surfaces, and respiratory ailments. Analysis of these tannery workers' haematological and biochemical parameters proved liver damage and haematological disorders (Rahman et al., 2019). A similar case based on the dermatological effect of chromium to tannery workers in Bangladesh was recently documented (Al Hossain et al., 2019). Occupational exposure to chromium has been reported to cause death to tannery workers (Oruko et al., 2019; Stern et al., 1987). Oruko et al. (2019) reported the death incidence occurred in 2014, whereby two tannery workers died during the cleaning process of chromium blocked tunnel in one of the tanneries in Kenya.

Assessment of chromium exposure and associated health consequences amongst workers in the tannery in Kenya revealed higher airborne levels of chromium at a concentration of 63 $\mu g\ m^{-3}$ (Were et al., 2014). Workers at the tanning line had urine level of chromium of 66.8 $\mu g\ m^{-3}$. The mean urinary chromium level exceeded the American Conference of Governmental Industrial Hygienists biological exposure index for chromium of 30 $\mu g\ g^{-1}$ creatinine, and 78% of chromium levels of the general workers exceeded this limit (Were et al., 2014). The study conducted to assess the occupational health risks among the workers employed in leather tanneries at Kanpur, India, reported significant levels of chromium in urine and blood samples collected from the exposed groups. This was attributed to high concentration of environmental chromium at the workplace (Rastogi et al., 2008).

6.2. Non-occupational exposure

Non-occupational exposure to chromium occurs through ingestion, inhalation and dermal contact. Ingestion occurs mostly due to eating and drinking chromium-contaminated foods and water, respectively (Langård, 2013). Most foods such as wheat get contaminated with chromium mainly due to bioaccumulation when irrigated with contaminated water. Subsequently, eating such contaminated food puts the consumers at a risk of chromium poisoning (Muhammad et al., 2020). Meat contaminated with chromium also plays a significant role in exposing human being to chromium. Analysis of poultry feeds in Bangladesh which were prepared from protein-rich tannery wastes, namely raw skin trimmings (RST), wet blue shaving dust (WSD), and low chrome wet-blue scraps (LCWS) detected chromium levels far above the recommended limits in all the products. Concentrations of chromium as high as 29,854 mg kg^{-1} were detected in the poultry feeds while the chromium levels in poultry's meat fed with those feeds were in the range of 0.42–0.84 mg kg^{-1} (Ahmed et al., 2017), above the World Health Organization permissible level of 0.1 mg kg^{-1} (FAO/WHO, 2000). This implies that consumers of poultry fed with these kinds of feeds are vulnerable to chromium poisoning. Exposure through inhalation occurs mainly through airborne particles (Sun et al., 2015), and this is the primary cause of cancer cases (Hu et al., 2012).

Though not commonly reported in the literature, the skin can be an excellent route of chromium exposure. Acute chromium poisoning related to dermal involvement has been published by Lin et al. (2009). The absorption of Cr(VI) through the skin is rapid, reaching peak blood level within 5 h after skin exposure (Lin et al., 2009). Hexavalent chromium is a more effective skin penetrant than the trivalent form (Mäkinen and Linnainmaa, 2004). According to Hu et al. (2012), among the studied heavy metals, chromium is leading in posing carcinogenic risks in mankind, suggesting that, it is vital to avoid release of chromium in the environment.

7. Current trends in chromium management technologies

Following the discovery of chromium salts as tanning agents in the 19th century, various efforts have been made to manage its effect in the environment. These environmental management efforts kept evolving with the development of innovative ideas on the management of chromium wastes. Recently, a number of techniques to manage chromium pollution from tanning industries have been reported. These techniques can generally be categorized as recycling of spent chrome liquors, high chromium exhaustion tanning technologies that make use of auxiliaries or other solvents than water to enhance chrome uptake and total replacement of chrome salts through use of alternative tanning agents. Each category of these technologies is reviewed in this article.

7.1. Recycling of spent chromium contained in spent tanning liquor

The techniques under this category involve reutilisation of spent chrome salt. After the first tanning, spent chromium salt present in tanning liquor is not wasted. Instead, it is recycled in the subsequent tanning process either with the addition of a small quantity of fresh chromium salt to compensate the deficit or without (Rajamani, 1998). Spent chromium can be effectively reused for tanning without compromising the leather quality while bringing economic benefits to tanners (Tunay et al., 2010).

Two main options for recycling spent chromium, namely; direct recycling and indirect recycling have been adopted so far (Buljan and Kral, 2015; Badar et al., 2016). Acceptance of each option depends on local conditions such as space/infrastructure available, type and quality of leather to be produced, the cost of chemicals, skilled labour and chromium discharge limits (Buljan and Kral, 2015).

7.1.1. Direct chrome tanning float recycling

Direct chrome tanning float recycling involves reusing spent liquor back into the process without chrome recovering. Direct recycling of chrome spent liquor is the cheapest and the most straightforward method because no chrome precipitating agents are needed, and investment in new infrastructure is minimal as compared to indirect chrome recycling (Tunay et al., 2010; Thakur, 2013). In the pilot-scale study carried out in Bangladesh, it was demonstrated that, direct chromium recycling can save about USD 6,319.05 per annum at the leather production capacity of 30,000 kg per day whereas the capital investment of chrome recycling system is approximately USD 9,055.07 with a payback period of 1.5 months (Badar et al., 2016). Furthermore, direct recycling leads to water savings of up to 90% since it is possible to recycle tanning liquor up to five (5) times (Morera et al., 2011), thereby saving cost associated with water uses (Leafe, 1999). Similar findings were reported in the closed-loop system, where significant savings in processing chemicals including lime, sodium sulfide/hydrosulfide, salts, acids, chromium tanning agents and water were observed (Daniels et al., 2018).

However, direct recycling method has some disadvantages. Since chromium salt of 33% basicity is commonly used in tanning, raising pH (basification) to fix chromium in hide/skin in each recycling phase is necessary. Basification is essential to increase the number of free hydroxyl groups for a higher proportion of multicore chromium complexes for enhancing interaction of chrome and the hide/skin collagen to achieve the desired tanning effect (Morera et al., 2011). Basification is carried out by adding alkali to the tanning float resulting in a high amount of neutral salts and high pH that would complicate its reusability potential. Morera et al. (2011) proposed the use of highly basified chrome (66% basicity) and highly masked tanning liquor system to obtain tanning liquor with the right pH for subsequent recycling. But this alternative has cost implication since extra chemicals are required for basification and masking.

7.1.2. Indirect chromium recycling

Indirect recycling of chromium refers to the process of recovering chromium from spent liquor and reuse it in tanning after mixing with fresh chromium sulphate in a ratio of 30%:70%, respectively (Kanagaraj et al., 2008; Patwardhan, 2008). Recovery is achieved mostly by using either MgO, NaOH or wattle extract as a precipitating agent (Esmaeili and Vazirinejad, 2005; Kanagaraj et al., 2008; Patwardhan, 2008). Although MgO ensures high recovery capacity of chromium from spent liquor (Minas et al., 2017), uptake and fixation of chromium recovered by MgO and NaOH are lower compared to chrome recovered through wattle extract (Table 2) (Minas et al., 2017). This observation can be ascribed to the capacity of wattle extract to form a strong complex with chromium ions accelerated by the presence of phenolic compounds that have multi hydroxyl groups to chelate chromium ions hence increasing its uptake (Chrysochoou and Reeves, 2017). However, the latter is associated with the generation of higher biological oxygen demand (BOD) and chemical oxygen demand (COD) than the former (Table 2) (Kanagaraj et al., 2008). Therefore, the choice of using wattle extract to attain high recovery of chromium should take into consideration on how BOD and COD will be handled.

A comparison of economic aspect between the two recycling options (direct and indirect) suggests that direct recycling is economical as it requires minimal equipment, and no chrome precipitating chemicals are required for chromium recycling. Unlike direct recycling, indirect recycling necessitates investment in a new separate unit for recovery of chromium. Since it involves the use of chemicals, operational costs are increased, and it adds to the BOD, COD, TDS and TSS challenge in wastewater. Moreover, recovered chromium salt from indirect recycling has been reported to contain impurities that occur as the result of chromium interaction with organics present in the tanning liquor (Zong et al., 2016). Organic pollutants incorporated with chromium could increase the molecular weight of recovered chromium salt making it hard to penetrate inside skin matrix, leading to the poor effect of tanning (Zong et al., 2016). Removal of those organic pollutants has not been considered in the recovery methods by precipitation using MgO, NaOH and wattle extract.

Recent innovative research conducted by Zong et al. (2016) has indicated a simultaneous recovery and purification of chromium from chrome wastewater. The method involves pre-treatment of chromium effluent before recovery through degrading organic impurities. Degradation experiments using Fenton oxidation, acid enzyme and flocculants have been carried out and yielded optimum degradation efficiencies of 71.15%, 65.26%, and 22.05% respectively (Zong et al., 2016). Based on these degradation rates, it was concluded that the organic content of chrome tanning wastewater could be significantly reduced through pre-treatment of tannery waste (chrome liquor) with Fenton oxidation (Zong et al., 2016).

Table 2
Effluent parameters for spent liquor from chromium reuse system.

Parameter	Precipitating agent		
	Wattle extract	MgO	NaOH
BOD (mg L^{-1})	432.52	185.00	339.14
COD (mg L^{-1})	761.36	287.96	491.87
TDS (mg L^{-1})	613.99	327.61	638.67
Cr in spent liquor (mg L^{-1})	1350	2180	2655
% Cr exhaustion	85	76	74

Data Source (Minas et al., 2017):

7.2. High chromium exhaustion tanning technologies by using auxiliaries

Conventional chromium tanning suffers less efficiency chrome uptake that contributes significantly to water pollution and loss of tanning agent (chromium sulphate). Enhancing chromium uptake reduces chromium content in the effluent, serves chrome sulphate that would otherwise be wasted and cuts operational costs of treating wastewater (Rao et al., 2004; Renner et al., 2013; Zhang et al., 2017). According to various studies, chromium uptake can be enhanced when auxiliary chemicals are used in combination with chromium sulphate or by using other solvents than water in the tanning process (Legesse et al., 2002; Rao et al., 2004; Renner et al., 2009; Manfred et al., 2012; Ibrahim et al., 2013; Silambarasan et al., 2015; Liu et al., 2016; Prokein et al., 2017). From these studies, the effectiveness of various auxiliaries and solvents in enhancing chromium uptake has been established. Some of the recently researched auxiliaries used in high exhaustion chromium tanning systems are discussed in the following sections.

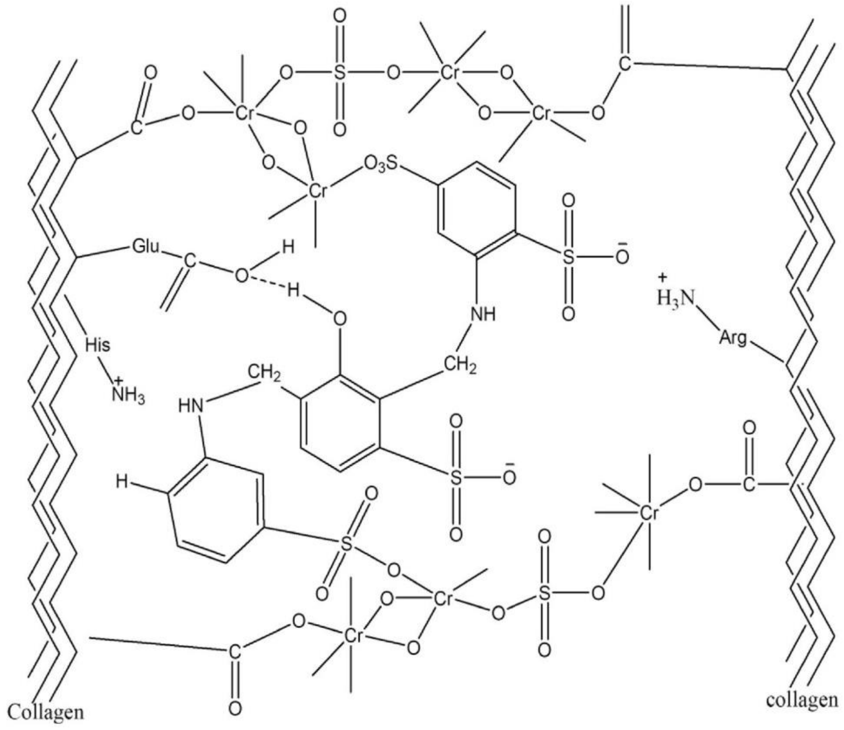
7.2.1. Sulphonic aromatic acid

In conventional chrome tanning, formic and sulphuric acids are employed to acidify the collagen of the hide/skin to the pH 2.8. Acidification serves to protonate side-chain carboxylic groups that will react with chromium during tanning. Protonated carboxyl group becomes less reactive towards chrome ion to allow penetration and distribution of chromium into the inner layer of hide/skin (Sarkar, 1981). Acidification of collagen gives rise to the net increase in electrolyte within the pelt, compared to outside the pelt.

Consequently, the hide/skin surface becomes a semi-permeable membrane, across which electrolyte and water can pass inside hides/skins osmotically leading to swelling (Covington, 2009). To prevent acid swelling, about 6–8% sodium chloride is added before the addition of acid to balance electrolyte concentration within hide/skin and in the external solution (Zhang et al., 2017). All Sodium chloride added in the process ends in effluent since it does not react with collagen of the hide/skin. Removal of sodium chloride from the effluent is highly capital intensive.

Furthermore, high solubility and stable nature of chloride make it unaffected by effluent treatment, thus remaining as a burden to the environment (Vaishnavi et al., 2019). Studies have divulged that high chloride levels can lead to the breakdown of cell structure and inhibit the growth of plants, bacteria and fish in surface waters (Bosnic et al., 2000). Thus, the existing challenges associated with chloride use in the tanning process raises the need for salt-free pickling systems (Boopathy et al., 2013; Zouboulis et al., 2019).

Sulphonic aromatic acid is a non-swelling acid that can substitute use of formic acid, sulphuric acid and sodium chloride in the pickling process (Bacardit et al., 2008). The suitability of sulphonic acid is due to its bipolar properties that lead to collagen acidification while inhibiting swelling of the skin. Swelling inhibition is induced by the binding of sulphonic acid to collagen through electrovalent bonding between the amino groups of collagen's side chain and sulphonic groups in acidic condition to reduce electrolyte within a pelt, hence preventing uncontrolled water absorption (Li et al., 2009). Subsequently, the rest of sulphonic groups crosslink



Scheme 1. Interaction of sulphonic acid with collagen and chromium complex in skin matrix (Zhang et al., 2017).

chromium as depicted in Scheme 1 (Zhang et al., 2017), which results into enhanced chrome fixation, hence less chrome is discharged in the effluent while sodium chloride is avoided.

Bacardit et al. (2008) informed that use of sulphonic aromatic acid reduces chloride and chrome discharge in effluent by 94% and 99%, respectively. In addition to that, tanning with sulphonic acid can be carried out without float, hence, considerable savings in water consumption. According to Bacardit et al. (2008), about 42% cost reduction can be achieved compared to traditional tanning method. Moreover, physical and mechanical properties of resultant leather, except for grain, are as per proposed standards (Bacardit et al., 2008). However, reported failure in grain stress observed need to be improved to ensure leather produced meets all required properties.

Similar findings were reported by Zhang et al. (2017). The latter studied four different sulphonic aromatic acid derivatives in salt-free pickling chromium tanning, and one of the four derivatives exhibited the best performance at optimized conditions. Sodium chloride usage was reduced by 80%, while 98.6% chromium exhaustion and 46.9% cost reduction were attained (Zhang et al., 2017).

However, the use of sulphonic acid as an auxiliary in chrome tanning is associated with some challenges. It was reported that high-molecular-weight of aromatic sulphonic acid condensates might impede penetration of chromium in the skin structures (Jia et al., 2020). Furthermore, Jia et al. (2020) have cautioned that there is the possibility of leather properties alteration when sulphonic acid is applied in leather processing. For these reasons, sulphonic acid is not yet accepted as a commercial tanning auxiliary (Morera et al., 2007).

7.2.2. *Polymeric syntans*

Polymeric syntans are soluble chemicals most recommended for re-tanning in the leather making process due to their filling property on leather's empty spaces (Lesko et al., 1998; Nashy et al., 2010; Jaisankar et al., 2013). Although most of them have been reported to possess no tanning features due to weak linkages with skin collagen, some of them have shown the ability to enhance chromium uptake (Rao et al., 2004).

Most polymeric syntans are condemned of being synthesized using formaldehyde that entails toxicity due to slow release of formaldehyde into the environment (Suresh et al., 2001). According to animal studies, inhalation of formaldehyde can damage the lining of the nose and throat while high concentrations can affect the lungs. Consequently, the International Agency for Research on Cancer (IARC) has categorized formaldehyde as a human carcinogen (ATSDR, 2008). Furthermore, formaldehyde is a restricted substance, and thus, it may lead to residues of restricted substances in the leather product itself (Sivaram and Barik, 2019). Nevertheless, Rao et al. (2004) have reported a novel polymeric syntan that is free from formaldehyde with high capacity of enhancing chromium uptake while reducing the environmental challenge (Rao et al., 2004). The salient feature of this new polymeric syntan is that, it can prevent chromium from hydrolysing at pH above 4, which is unsuitable for chrome penetration due to rapid surface deposition.

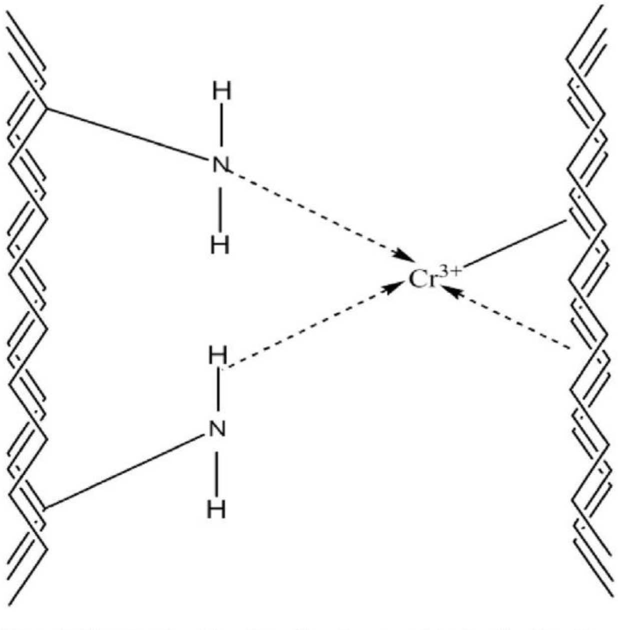
Provided that the use of polymeric syntans ensures penetration and fixation of chromium at pH 4, no pickling is required before tanning to lower the pH. Therefore, the use of sodium chlorides is avoided leading to discharge of tannery effluents which is free of chlorides. The chromium uptake achieved by this novel polymeric syntan is 95%. The shrinkage temperature of produced leather and other physical properties are similar to that of conventionally made leather.

7.2.3. *Hyperbranched polymers*

Hyperbranched polymers are becoming popular in chromium tanning researches due to their unique properties such as lower viscosity, higher solubility and higher amount of reactive terminal groups. These kind of polymers can interact with reactive groups in the collagen of the hide/skin and chrome complex for desired tanning outcome (Ibrahim et al., 2013; Prokein et al., 2017; Yao et al., 2019).

Hyperbranched polymers are mostly applied as pre-tanning agents to enhance chromium uptake and fixation. Ibrahim et al. (2013) reacted methyl acrylate and ethyldiamine in a single pot reaction to synthesize a hyperbranched poly(amidoamine) (HPAM). Its performance as a pre-tanning agent was investigated and it was confirmed that amino groups present in HPAM provide multiple binding sites for binding and fixing more chromium in collagen (Ibrahim et al., 2013). Since the reactive groups inside the triple-helix structure of the collagen are limited, a substantial amount of chromium is not fixed in the skin, resulting in 30%–40% release of chromium in the tanning effluent in conventional chrome tanning (Ibrahim et al., 2013; Prokein et al., 2017).

Reacting skin with HPAM before tanning increases the number of amino groups that can interact with more chromium, as shown in Scheme 2. By so doing, the release of chrome to the effluent is significantly reduced, which accounts for the environmental and economic benefits of applying HPAM. Chromium exhaustion efficiency upon using HPAM is 99.8% leaving 2.15 mg L^{-1} of total chromium in effluent (Ibrahim et al., 2013), which is acceptable for effluent discharge in sewers but slightly above the permissible levels for effluent discharge in water bodies in many countries (Table 1). Apart from that, the resultant leather's physical and organoleptic properties such as shrinkage temperature, softness and fullness meet the standard for high-quality leather. But it was not investigated if the use of HPAM would lead to a reduction in COD, BOD, TSS and TDS. Additionally, mechanical properties of produced leather such as tearing and tensile strength were not investigated in that work. For the comprehension of this method, investigation on the effects of HPAM on pollutants levels and mechanical properties of the produced leather is of paramount importance.



Scheme 2. Chromium ions interacting with amino groups introduced in skin collagen after reacting HPAM with the skin before tanning (Ibrahim et al., 2013).

Apart from HPAM, Qiang et al. (2015) prepared a hyperbranched polymer based on aluminium ion (HPC–Al) by reacting the hydroxy-hyperbranched polymer with maleic acid and aluminium sulphate, then applied it as an auxiliary in chrome tanning. The process resulted in increased uptake of chromium up to 87% compared to the control sample. Moreover, BOD, TDS and TSS were reduced by 22.5%, 21.5% and 8.3%, respectively compared to the conventional chrome tanning technique. However, the compound didn't bring a reduction in COD; rather it increased it by 11.5% compared to traditional chrome tanning method.

7.2.4. *Epoxy resin*

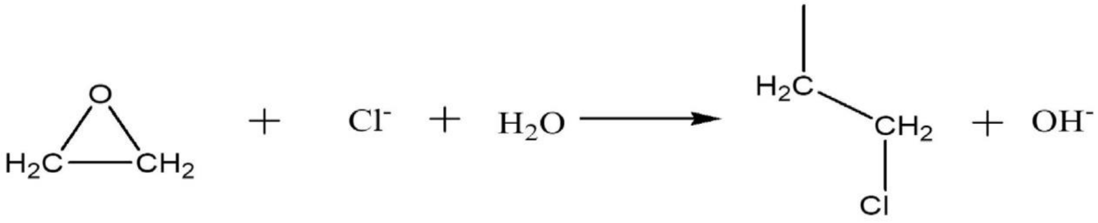
Epoxy resins are critical industrial polymers that are widely used in many major industries in the world such as coating, adhesive, civil engineering, leather industry and casting due to the high reactivity of epoxy group (Langmaier et al., 2007). In the leather industry, epoxy resins are commonly employed in the retanning process to ensure strong fixation of the filler in the structure of the skin and prevent its migration to the surface of the leather (Chursin, 2014). Epoxy resins are also suitable tanning agents that impart the leather with hydrothermal stability similar to that conferred by oxazolidine and glutaraldehyde (Heath et al., 2005). Crosslinking ability of epoxy resin is attributed to the presence of multifunctional groups on epoxy resin structure that provide multiple binding sites to bind the hide/skin collagen (Alferiev et al., 2001). Furthermore, the low molecular mass of epoxy resin makes it easy to penetrate in the skin (Heath et al., 2005). However, the use of epoxy resin as a sole tanning agent is limited by low shrinkage temperature (85 °C) and a lower reaction rate (Di and Heath, 2009).

Heath et al. (2005) reported enhanced reactivity of epoxy resin when combined with sodium chloride. Chloride ions collectively act as a nucleophilic reagent that attacks and breaks the epoxide ring releasing –OH- groups (Scheme 3), which in turn increase the pH to 10 in 2 h, hence promoting the epoxide-collagen reaction and stabilization of the collagen structure. However, the use of sodium chloride is associated with severe environmental concerns that necessitate its avoidance in the leather industry.

Alternatively, Lyu et al. (2018b) have recently studied the application of modified epoxy resin as an auxiliary to enhance chrome exhaustion. In their investigation, epoxy resin was functionalized with a carboxyl group to increase multiple sites for fixing more chromium. The outcome was highly promising as 3% chromium sulphate, instead of the commonly used 8%, was enough to produce leather of standard quality. Shrinkage temperature, organoleptic and mechanical properties of leather tanned under this process are comparable to those of the conventionally tanned leather. These results are due to stable inter and intra-molecular crosslinks formed between polar groups in carbon functionalized epoxy resin and collagen of the hide/skin. Since less chrome is used, and most of it is fixed in the collagen, chromium released in the effluent is far lower than in conventional chrome tanning (Lyu et al., 2018b).

Similar findings were recently reported by Jia et al. (2020) who investigated the application of polyoxyethylene diepoxy (PODEE) ether and urotropine as auxiliaries in chrome tanning. Following low reactivity of epoxy compounds, combination with urotropine was necessary to accelerate the reactivity. It was revealed that combined application of PODEE and urotropine can lead to 96% chromium uptake, decrease in chromium content in effluent up to 77.1 mg L^{-1} and reduced COD and TDS by 15% and 42% respectively, without compromising the integral performance of leather. Furthermore, the use of NaCl is wholly avoided.

Despite its potential in stabilizing collagen of hides and skins, epoxy resin is reported to cause allergic dermatitis or acts as a skin



Scheme 3. Reaction of epoxy with chloride ions (Heath et al., 2005).

sensitizer (Greenberg, 2003). But the effect of carbon functionalized epoxy resin has not yet been investigated. Therefore, for the safety of leather consumers, the health risks associated with carbon functionalized epoxy resin has to be investigated and reported accordingly (Chursin, 2014).

7.2.5. Nanocomposite assisted chromium tanning

Nanomaterials have been extensively investigated on their suitability in leather processing to aid in achieving higher performance of leather (Lu et al., 2013; Chen et al., 2011). Studies have publicized application of Montmorillonite (MMT) (Bao et al., 2011), SiO_2 (Lu et al., 2013) and other nanomaterials to enhance leather performance that includes toughness, good feel and handle and hydrothermal stability. Owing to small molecular size and possession of carboxyl or hydroxy groups, nanomaterials especially nanocomposites, can link with active groups of collagen in the hides/skins with that of the inorganic complex such as chromium complex at the molecular level to form crosslinked networks for achieving the tanning purpose (Liu et al., 2016).

Recently, two different studies have reported the performance of nanocomposites, namely vinyl polymer/MMT and Polymer/ZnO in which a chromium exhaustion efficiency of 92% was attained. This efficiency indicates high potential of these nanocomposites in enhancing chromium exhaustion in the tanning process (Liu et al., 2016; Lyu et al., 2018a). High chromium exhaustion under this technology is ascribed to the amphoteric nature of nanocomposites that enables an increase in the number of multi-ligand cross-linking between chrome tanning agent and collagen of the hide/skin (Ma et al., 2014). Significant decrease in BOD, COD and TSS was also observed, but without explanations on how this was achieved. Application of nanocomposite as a pre-tanning agent ensures reduction of the chromium salt dose from 8% of conventional chrome tanning to 3%–4%. Physical and mechanical properties of the resultant leather are comparable to those of conventionally tanned leather (Liu et al., 2016; Lyu et al., 2018a). However, nanocomposites are challenged with a limited capacity to ensure uniform penetration and distribution of chrome tanning agents (Li et al., 2019).

Li et al. (2019) modified the application of nano-materials to ensure uniform distribution of chromium tanning agents. They synthesized a pH-sensitive and chromium loaded mineralized nanoparticles by self-assembly of poly (poly (ethylene glycol) methyl ether acrylate-co-acrylic acid ((poly(PEG-co-AA)) copolymers templated $Cr(OH)_3$ mineralization. Such core-shell structured chromium (III) loaded (Cr-PPA) nanoparticles contain PEG on the surface which has high density, hydrophilic surface and antifouling properties hence repel the interaction with the skin collagen during penetration process to achieve uniform distribution. Because of its pH sensitivity nature, upon successful penetration inside skin structure, lowering pH to 2.5 induces release of Cr(III) that was encapsulated inside the nanoparticles. Upon its release, Cr(III) reacts with collagen uniformly during the tanning process. Delivering chromium using nanoparticles is an effective way to avoid reaction of chromium with collagen during penetration that inhibits uniform distribution of chromium throughout the skin structure. The efficiency of this method is verified by high chromium exhaustion attained and chromium reduction in the tannery effluent. Chromium exhaustion efficiency achieved under this technique was higher than 90%, leaving 126 mg L^{-1} chromium content in the effluent as compared to 895 mg L^{-1} of the conventional process (Li et al., 2019).

Application of this technique should take into consideration the handling of chloride introduced during pH lowering (pickling). Sodium chloride is used for pickling as in conventional chromium tanning to prevent acid swelling of skin collagen. Environmental effects of chloride are well known and have been briefly explained elsewhere in this article. Therefore, it is crucial to consider alternative ways of lowering pH without using sodium chloride. Use of sulphonic acids as demonstrated by Li et al. (2009) and Zhang et al. (2017) can be a best option.

7.2.6. High chromium exhaustion tanning by using alternative solvents

Usually, chrome tanning is mediated by water that facilitates dissolution and distribution of chromium throughout the hide/skin structure (Silvestre et al., 1994; Clark et al., 2017). It is acknowledged that water is safe, non-toxic, abundantly available and a cheap resource (Jungnickel, 2011; Manahan, 2013; Zuorro et al., 2019). But, because of water pollution caused by the discharge of voluminous amount of wastewater rich in chemicals and less uptake of chrome in water media (Nur-E-Alam et al., 2018), several attempts have been made to find alternative solvents to replace or reduce the use of water for enhanced chromium uptake and reduced water pollution. Compressed carbon dioxide and organic solvents such as ethanol and their derivatives have been investigated, and their feasibilities have been documented (Silambarasan et al., 2015; Muralidharan, 2016). The summary of each option is explained in the following sub-sections.

7.2.6.1. High chromium exhaustion tanning mediated with compressed carbon dioxide. Application of compressed carbon dioxide gas (CO_2) in chromium tanning is associated with an increased rate of chromium uptake (Renner et al., 2009; Manfred et al., 2012; Ibrahim et al., 2013; Prokein et al., 2017). The increased rate of chrome uptake is due to increased dissolution of CO_2 that forms carbonic acid, which lowers the pH of the system and facilitates the penetration of the chromium into skin fibres for uniform distribution (Renner et al., 2009). On top of that, carbonic acid causes skins fibres to swell slightly leading to the widening of pores in the skin which allows fast penetration of chromium polynucleated complex that would have been difficult due to size limitations (Fig. 3). The application of high-pressure carbon dioxide as a tanning media facilitates mass transfer, reduces processing time and lowers processing costs (Onem et al., 2015).

Unlike conventional chromium tanning, use of compressed CO_2 requires no basification because lowering pressure results into the

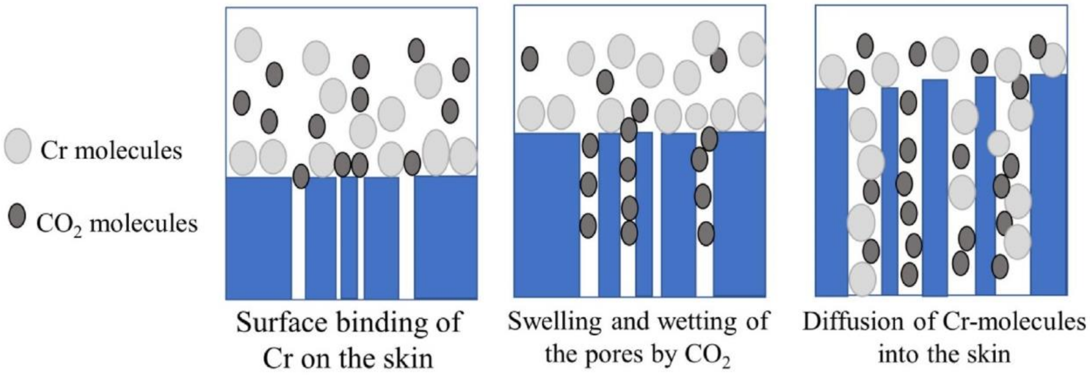


Fig. 3. Mechanism on enhanced chromium uptake by compressed CO_2 (Renner et al., 2009).

release of CO_2 to the atmosphere. Escape of CO_2 causes pH in the tanning system to raise to 4.0, which is optimal for chromium fixation without adding alkali chemicals, hence saving costs for chemicals and reduce TDS in the effluent (Manfred et al., 2012; Prokein et al., 2017).

In comparison with the conventional tanning, chrome tanning coupled with compressed CO_2 reduces tanning time from 12 h to 4 h (Renner et al., 2009; Prokein et al., 2017), water consumption is reduced by 90% while 50% chromium sulphate is saved and no alkali chemicals are applied (Manfred et al., 2012). Leather tanned with compressed CO_2 is of high quality comparable to conventionally tanned leather (Renner et al., 2013). However, the studies didn't consider recycling of CO_2 instead of releasing it to the atmosphere where it can contribute to the global warming effect.

A recent study by Onem (2018) which employed vegetable tannins as tanning agents under supercritical fluid system using CO_2 as a supercritical fluid has demonstrated the possibility of recycling CO_2 to overcome its wastage. The recycled CO_2 was efficient in improving vegetable tannins diffusion on the skin surface that resulted in high-quality leather. Based on these findings, it is worth to insist on recycling of CO_2, whereby released CO_2 gas can be tapped and reused in the subsequent tanning process to reduce the cost of purchasing new CO_2 gas. This act demonstrates a sustainable way of curbing CO_2 environmental consequences.

7.2.6.2. Ethanol-based high chromium exhaustion tanning. Ethanol is an organic solvent that has shown promising results in enhancing the chromium exhaustion rate to reduce chromium pollution and substitute water in tanning (Silambarasan et al., 2015). The effectiveness of ethanol in chrome uptake is due to less solubility of chromium in ethanol medium, the situation that drives more chromium inside the skin where there is free internal water (Legesse et al., 2002; Silambarasan et al., 2015). Since green chemistry principles have grouped ethanol as a greener and renewable solvent for sustainable utilization (Alfonsi et al., 2008), its usage in tanning is as safe as water. Ethanol mediated chromium tanning ensures 95% chromium exhaustion with 100% reduced water consumption without generating tanning effluent hence achieving greener tanning (Silambarasan et al., 2015). Leather produced from this procedure is of good quality comparable to that of conventional chrome tanning. The drawback of this process is the high cost of ethanol as compared to water.

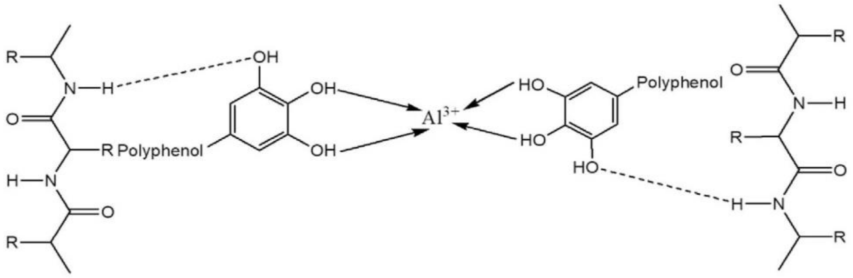
7.2.7. Advantages and disadvantages of high exhaustion chromium tanning technologies

The main benefits of high exhaustion chrome tanning technologies as compared to conventional chrome tanning include; reduced environmental impacts especially those associated with wastes containing chromium; considerable reduction in TDS, TSS, BOD and COD which makes effluent handling exercise much easier and high per cent of Cr_2O_3 is fixed to the hide fibres which leads to production of durable leather. Other advantages are; extremely light wet-blue leather colour is achieved, uniform and excellent fullness of the leather, chrome-less sludge, versatile wet-blue leather with more performing dyeing characteristics as well as reduced chances of Cr(VI) formation. Reduction in processing cost is another benefit emanating from high exhaustion chromium tanning technologies. This cost reduction is due to the fact that more than 90% of applied chromium is fixed in leather (Rao et al., 2004); less amount of chromium salt (3–4%) compared to conventional tanning (6–8%) (Liu et al., 2016) is required in high exhaustion technologies thus rendering them more cost-effective.

However, chrome tanning technology has a strong impact on the environment due to the pollution associated with chrome solid wastes such as chrome-tanned leather shavings, trimmings and buffing powder. It is challenging to get rid of the solid waste containing chrome because their degradability rate is very low (Dhayalan et al., 2007; Constantinescu et al., 2014), causing environmental challenge like that of plastic wastes. Additionally, chrome solid wastes deposited in the soil contaminate the soil and water. The expensive disposal of leather scraps such as chrome-tanned leather shavings, splitting, trimmings and buffing dust by dumping process also discredit the high exhaustion chrome tanning methods (Hu et al., 2012). Above all, some of the proposed methods under this category such as salt-free pickling chromium tanning that uses sulphonic acid, polyoxyethylene diepoxy ether and urotropine as auxiliaries in chrome tanning are impractical for large-scale leather production due to the need of expensive equipment and chemicals (Yao et al., 2019). Though chromium fixation is high with high exhaustion tanning technologies, lots of chromium are eluted in the subsequent process of wet-finishing such as re-tanning, dyeing, greasing and so on, resulting in water pollution (Liu et al., 2016). Therefore, the disadvantages of high exhaustion chrome tanning technologies justify a need for chrome-free technologies to sustain the leather industry.

7.3. Total replacement of chromium salts (chrome-free technologies)

Chrome-free technologies are the ones that completely abandon the use of chromium sulphate in the tanning and re-tanning processes (Liu et al., 2016). Tanning techniques such as aluminium tanning, vegetable tanning, zirconium tanning, iron tanning, titanium tanning and aldehyde tanning have been known for many



Scheme 4. Interaction of skin collagen with vegetable tannins in combination with aluminium (Covington, 2009).

years as chrome-free tanning methods designed to replace the high polluting chrome tanning technique (Covington, 2009; Crudu et al., 2010; Duki et al., 2013; Onem et al., 2014; Qiang et al., 2015). Unfortunately, none of them can individually bestow the leather with the properties similar to those of chrome-tanned leather, especially in terms of shrinkage temperature. Possible maximum shrinkage temperature of leather tanned by these chrome-free tanning methods is 85 °C, while for chrome tanned leather it goes beyond 100 °C which conforms to the international standards (Covington, 2009). Shrinkage temperature is a crucial parameter, especially for leather intended for use in footwear manufacturing because, during footwear making, leather is subjected to above 100 °C temperatures. If leather's shrinkage temperature is below 100 °C, shrinking occurs and adversely affects the quality of produced footwear. To overcome this challenge, a combination of two chrome-free tanning agents was proposed to improve the shrinkage temperature, and the process is termed as combination tanning (Choudhury et al., 2007; Ding et al., 2007; Musa et al., 2009; Musa and Gasmelseed, 2013a). Combination tanning has been proved to confer leather with the shrinkage temperature comparable to that of chrome tanning (China et al., 2019).

7.3.1. Mechanism of combination tanning

Several combination tanning systems have been reported so far, and the most important ones are oxazolidine combined with either henna (*Lawsonia inermis*) or garad (*Acacia nilotica*) (Musa et al., 2009; Musa and Gasmelseed, 2013a); combination of aluminium sulphate with *Euclea divinorum* (China et al., 2020); combination of tetrakis(hydroxymethyl)phosphonium sulphate (THPS) with either sodium metasilicate and aluminium oxide or iron oxide (Fathima et al., 2005); combination of aluminium sulphate with either garad or mimosa (*Acacia mearnsii*) (Slabbert, 1981; China et al., 2019) or genipin (*Gardenia jasmoides*) (Musa et al., 2011).

In most cases, combination tanning involves vegetable tannins blended with either aldehyde bearing tanning agents, such as oxazolidine, or inorganic salts, such as aluminium sulphate. Vegetable tannin-oxazolidine combination tanning system involves the interaction of oxazolidine bearing aldehydic group with side chain amino groups of lysine and arginine, whereas polyphenolic constituents of vegetable tannin participate in non-specific interactions with collagen via hydrogen bonding, electrostatic and hydrophobic, thereby leading to the synergistic effect to enhance the physical properties of skin collagen (Musa et al., 2011). On the other hand, the interaction between vegetable tannins and aluminium sulphate, as postulated in Link-Lock theory, involves hydroxyl groups of polyphenols in vegetable tannins to first react with amino group of collagen, followed by aluminium crosslinking polyphenols already bound to the collagen (Scheme 4). By so doing, a strong complex matrix that accounts for improved physical properties of leather is formed (Covington et al., 2008). The mechanism for silica-aluminium-THPS (Si-al-THPS) combination tanning has not been established. Still, its results have revealed high performance suggesting synergistic effect during combination tanning (Fathima et al., 2005).

7.3.2. Performance of different combination tanning systems

Analysis of leather performance is meant to ascertain its toughness when in use for everyday life. It is not worth to purchase an expensive leather product that won't last long due to performance failure. All leather processing steps have a contribution in defining the performance of leather. Of all the processes involved in leather making, the tanning process bears a significant influence on the leather performance because the strength of leather fibres and their ability to withstand external stresses depends on the crosslinks formed between collagen and the tanning agent (Nasr et al., 2013), i.e. the stronger the crosslinks, the more durable are the leather fibres. Each tanning method influences leather performance differently depending on the crosslinks formed with skin collagen (Kuria et al., 2016). Therefore, it is vital to understand the performance of various combination tanning blends for a better selection of suitable combinations.

Physical properties of different combination tanning blends are presented in Fig. 4. It can be observed that Genipin-aluminium (Gen-Al) combination can give the highest elongation at break but low values of tensile strength and hydrothermal stability. This trend is also depicted by the blend of silica-aluminium-THPS (Si-al-THPS). Other combination tanning systems give a relatively equal amount of elongation (percentage extension) at break, which is also above the international acceptable standard value of 30% according to ISO 3376:2011(E): IULTCS/IUP 6:2011(E). Garad-aluminium (Gar-Al) combination tanning produces leather with the best tensile strength (39 N/cm^2) and shrinkage temperature (128 °C), followed by the blend of Garad and oxazolidine (Gar-Ox). Therefore, there is an impression that the blend of Garad with either oxazolidine or aluminium is likely to produce good quality leather while avoiding chromium pollution. The BOD/COD for both Gar-Al and Gar-Ox ratio is far lower than that of chromium tanning and other combination tanning blends. Highly reduced BOD/COD ratio is the evidence of high exhaustion of tanning agents to the extent that less organic load is released into the effluent (Plavan et al., 2017), signifying improved biodegradability nature of effluent waste resulting from this technology (Krishnamoorthy et al., 2012).

Since chromium is not applied in Gar-Al and Gar-Oxazolidine blends, the effluent from these combination tanning systems is free from chromium ions. The approach eliminates not only chromium from effluents but also has an advantage of avoiding other pollutants such as sulphates, thereby gaining environmental acceptability.

7.3.3. Oxazolidine or aluminium sulphate?

As observed in the previous section (7.3.2), a combination of vegetable tannins with either oxazolidine or aluminium sulphate

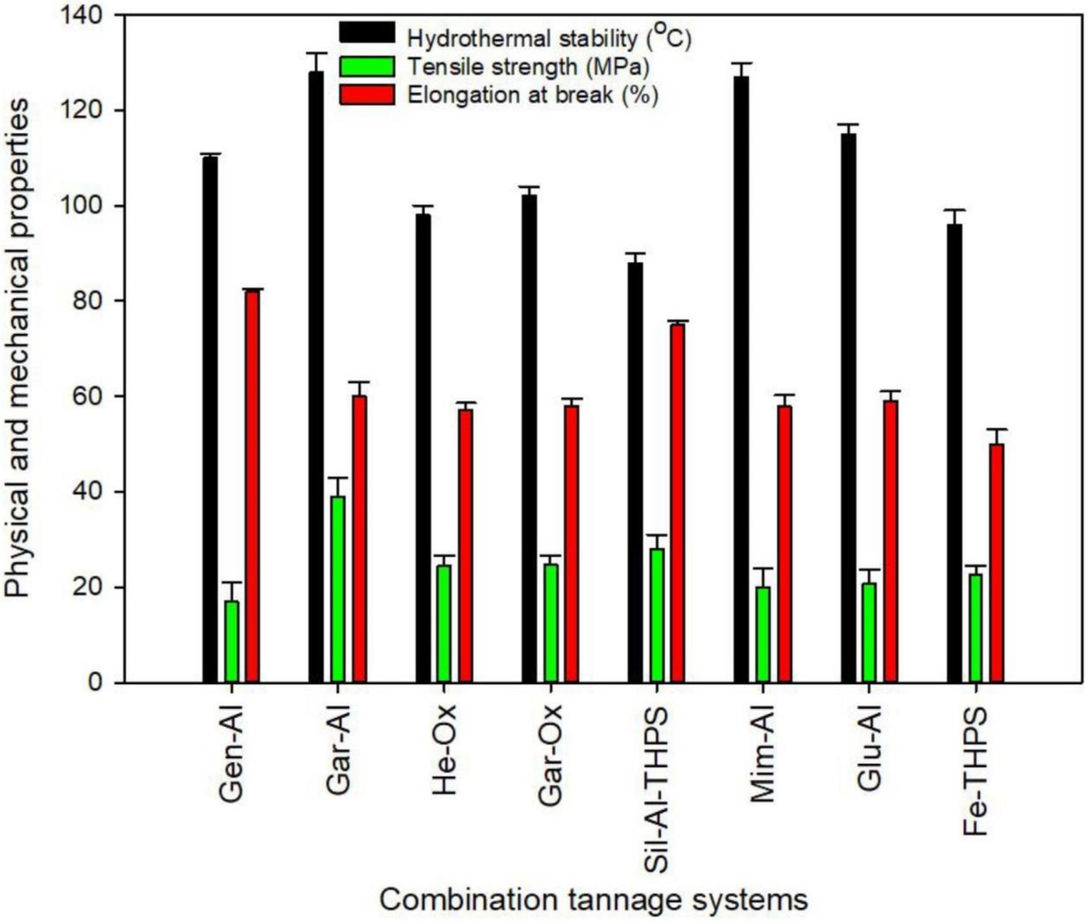


Fig. 4. Physical and mechanical properties of various combination tannages (Covington et al., 2008; Musa et al., 2011; Musa et al., 2009; Musa and A Gasmelseed, 2013a; Fathima et al., 2005).

produces leather of desired properties and reduced environmental effects. Since aluminium is the most abundant metal on the earth's crust (Wood et al., 2004; Krebs, 2006), the combination of vegetable tannins and aluminium sulphate is more likely to be sustainable than that of vegetable tannins and oxazolidine. Aluminium sulphate is available commercially and can be easily produced from bauxite (Etuaful, 2013) and kaolin (China et al., 2019). Recently reported studies also have recommended the same (Covington, 2009; Covington and Wise, 2019).

Moreover, despite the excellent performance of resultant leather, application of oxazolidine in leather tanning exhibits various challenges. The chemical reaction between collagen and oxazolidine is so reactive that it can result in an excessive combination of oxazolidine on the surface of the skin, causing wrinkles on the grain layer. Apart from that, the strong unpleasant smell from oxazolidine is very harmful to human health and can cause sickening among tannery workers (Krishnamoorthy et al., 2013; Jia et al., 2020).

8. Quality of produced leather from different alternative tanning technologies

The qualities of produced leather from various techniques described above are summarized in Table 3. The technology that produces leather with the highest quality is high exhaustion chrome tanning using alternative solvent followed by high exhaustion chrome tanning using auxiliaries namely chrome syntans, sulphonic aromatic acid, polymeric syntans, hyperbranched polymers, modified epoxy resin, glucose and nanocomposites. In the latter technology, use of syntans produces the highest quality leather followed by hyperbranched polymers and polymeric syntans.

9. Levels of environmental pollutants produced from different alternative tanning technologies

Table 4 recaps the levels of environmental contaminants from different tanning technologies discussed in this review. Indirect chrome recycling has shown the highest reduction in Cr, BOD, COD and TDS, followed by high exhaustion chrome tanning using auxiliaries. This reduction of the effluent parameters in primary effluent is associated with reduced costs of investing and treating effluent in effluent treatment plants. In high exhaustion chrome tanning using ethanol as a solvent and in combination tanning based on vegetable tannins, pollutants such as BOD and COD are far beyond the recommended values. These findings can be accounted to the fact that ethanol and vegetable tannins are organic compounds, and organic compounds are well known for their

Table 3
Qualities of produced leather from different alternative tanning technologies.

Technology	Auxiliaries/ solvent used	Reference	Physical parameters of tanned leather				
			Tensile strength (Nmm^{-2})	Tearing strength (Nmm^{-1})	Elongation at break (%)	Tearing load (N)	Grain distension (mm)
Indirect chrome recycling	–	Cao et al. (2018)	13.7	–	–	–	–
Direct chrome recycling	–	Faki et al. (2018)	27.5	34.4	65	–	–
High exhaustion chromium tanning using auxiliaries	Chrome syntans	Suresh et al. (2001)	33	84.3	78	–	–
	Sulphonic aromatic acid	Zhang et al. (2017)	17	85	71	–	–
	Polymeric syntans	Rao et al. (2004)	24	66.7	62	–	12
	Hyperbranched polymers	Qiang et al. (2015)	21	25	90		
	Epoxy resins	Lyu et al. (2018b)	15	58	63	–	–
	Glucose	Puccini and Castiello (2014)	–	–	–	81	87
	Nanocomposite	Liu et al. (2016)	16	51	78	–	–
High exhaustion chromium tanning using alternative solvent	Compressed CO_2	Ma et al. (2014)	34	145.2	80	–	–
	Ethanol	Silambarasan et al. (2015)	21.9	30.2	47.7		7
Total replacement of chromium salts (Combination tanning based on vegetable tannins)	Aluminium sulphate	Musa and Gasmelseed (2013b)	24.5	44.9	56	–	11
UNIDO requirement		**UNIDO (1996)**	**≥20 (IUP6)**	**≥65 (DIN 53333)**	**≥40 (ISO 3376 - IUP 6)**	**≥20**	**≥7 (IS0/3379-IUP 9**

Table 4
Levels of environmental pollutants produced from different tanning technologies.

Technology	Auxiliary/solvent used	Reference	Levels of pollutants generated in wastewater (mg L^{-1})					
			Cr	BOD	COD	TDS	TSS	Cl
Indirect chrome recycling	–	Minas et al. (2017)	720	185	287	337	–	–
Direct chrome recycling	–		–	–	–	–	–	–
High chrome exhaustion system	Chrome syntans	Suresh et al. (2001)	216	–	2120	28,036		715
	Sulphonic aromatic acids	Zhang et al. (2017)	45	–	–	–	–	–
	Polymeric syntans	Rao et al. (2004)	954	–	2,640	21,540	–	750
	Hyperbranched polymers	Qiang et al. (2015)		373	182	7231	161	–
	Epoxy resins	Lyu et al. (2018b)	683	–	–	–	–	–
	Glucose	Puccini and Castiello (2014)	1021	–	–	–	–	–
	Nanocomposite assisted chrome tanning	Liu et al. (2016)	811	386	685	–	377	–
High exhaustion chromium tanning using alternative solvent	Compressed CO_2		–	–	–	–	–	–
	Ethanol	Silambarasan et al. (2015)	250	4,580	17,855		8622	
Total replacement of chromium salts (Combination tanning based on vegetable tannins)	Aluminium Sulphate	Abdella et al. (2018)	0	12,500	43,600	19,200	–	–
	Conventional chrome tanning		**2000 –5000**	**350 –800**	**1000 –3500**	**29,000 –67,500**	**30,000 –70,000**	**15,000 –30,000**
	UNIDO required standards		**2**	**200**	**500**	**1000**	**1500**	**50**

significant contribution to high BOD and COD loads in effluents. Therefore, when using these technologies to minimize chromium pollution, increased investment cost in effluent treatment to reduce COD and BOD to required levels should be seriously considered.

10. Identified gaps

The gaps identified in the existing studies create avenues for subsequent inquiries to address a particular issue (Rasmussen et al., 2018). In reviewing various publications reported in this article, it has been discerned that, there are several issues which need further investigation to establish comprehensive information which will clear out all the pending doubts about the reviewed eco-friendly tanning technologies. Concerning high chromium exhaustion technologies, it was observed that the effect of sodium chloride on the reactivity of carboxy functionalized epoxy resin has not been investigated. Furthermore, the allergic effect of epoxy resin when used as a pre-tanning agent was not considered either.

Additionally, analysis of the mechanical properties of leather and levels of BOD, COD and TSS in effluent when HPAM is used as a pre-tanning agent have not been reported. More importantly, there is a need to investigate the tearing strength and tensile strength of leather when the hyperbranched polymer is used to enhance chromium uptake. For the case of chromium recycling technologies, mainly when MgO, NaOH and Wattle extract are used as precipitating agents, removal of organic pollutants to reduce BOD and COD load in the effluent was not considered. For high chromium exhaustion using alternative solvents, possible recycling of CO_2 in subsequent tanning after the first tanning to overcome emission of CO_2 to the atmosphere has not yet been investigated. Therefore, these gaps provide new avenues for further researches.

11. Conclusion and recommendations

11.1. Conclusion

Chrome tanning technology remains an environmental issue of concern entailing for global attention. Thus, for the sustainability and attaining green leather industry, chromium pollution should be minimized or avoided to enable tanneries to adhere to environmental norms. Studies have clearly indicated that effective minimization of chromium pollution can be attained by employing chromium management techniques, but chrome-tanned leather shavings and trimmings generated pose serious solid waste challenge similar to that of plastic wastes. Hence, the application of chromium-free technologies is a desirable permanent solution to chromium pollution from the leather industry. Based on the observations cited in this review, it is worth concluding that, combination tanning using vegetable tannins and aluminium sulphate is considered an appropriate chromium-free tanning method because vegetable tannins are renewable resource while aluminium is abundantly available on earth's crust and both of them are nontoxic. Moreover, vegetable-aluminium combination tanning produces leather of high quality with nearly similar properties to that produced from chrome tanning.

11.2. Recommendations

More investigations need to be conducted to perfect combination tanning based on vegetable tannins and aluminium sulphate for cleaner production of leather to avoid chromium pollution. The studies should focus on optimizing their performance in order to suit for industrial applications, cost-benefit analysis and possible reduction of other pollutants emanating from this process particularly BOD and COD.

Declaration of competing interest

None.

CRediT authorship contribution statement

Cecilia Rolence China: Conceptualization, Writing - original draft, Methodology. **Mihayo Musabila Maguta:** Conceptualization, Methodology, Writing - review & editing. **Stephen Samwel Nyandoro:** Writing - review & editing. **Askwar Hilonga:** Writing - review & editing, Supervision. **Swarna V. Kanth:** Conceptualization, Writing - review & editing. **Karoli N. Njau:** Conceptualization, Writing - review & editing, Supervision.

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Suitability of selected vegetable tannins traditionally used in leather making in Tanzania

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ABSTRACT

The use of chromium salt has dominated in tanning industry worldwide due to its high versatility in quality leather production. However, Environmental concerns of chromium have shifted the interest of current research to chrome-free and greener chemical processing options. Vegetable tannins, especially when used in combination with some benign metals, have been proven to be environmentally safe and manageable, while producing good quality leather with similar shrinkage temperature as that of chromium tanned. As such, shortage of vegetable tannin supply necessitates characterization of non-commercialized sources locally available to feed cottage tanneries. In the present work, extracts from *Acacia mearnsii*, *Acacia xanthophloea*, *Euclea divinorum* and *Euclea racemosa*, leached by simple technique at 30–80 °C temperature range were characterized for extract yield, tannin, total flavonoid and phenolic contents, crosslinking ability as well as properties of tanned leather. Results indicate that at 50 °C extraction temperature, *A. xanthophloea* bark gave extract with properties similar to that of *A. mearnsii* (commercialized source of tannin). Extract from *E. divinorum* bark contain fairly less extract yield, tannin, total flavonoid and phenolic contents than that of *A. mearnsii*, but had good crosslinking ability and tanning performance similar to that of *A. mearnsii* when used in combination with Aluminium Sulphate [$Al_2(SO_4)_3$]. The 2% Aluminium Oxide (Al_2O_3) equivalent was established to be optimal dose of $Al_2(SO_4)_3$ for extract pre-treatment. *E. racemosa* barks have high extract yield, but very low crosslinking ability, making it not suitable as a tannin source. This work provides useful information on the potential source of tannins for cottage leather industries in Tanzanian and beyond.

1. Introduction

Leather industry is among the oldest technologies in human history involving production of leather and varieties of products from animal skins (Brown and Dudley, 2005; Sarkar, 1981). About 90% of world leather is processed by acid salt of trivalent chromium as sole tanning agent (Pizzi, 2008). However, negative environmental impacts associated with its tanning derivative, hexavalent chromium, have brought a major concern about the sustainability of leather industry as they are known to be carcinogenic, mutagenic and allergic agents affecting the health of human being and other organisms (Fathima et al., 2004). Having less and manageable environmental effects, vegetable tannins are highly recommended (Madhan et al., 2006). Vegetable tannins generally contain no hazardous substances, hence perceived environmentally benign if produced under green chemical processes. Moreover, cultivating tannin rich tree neither needs pesticides nor other agrochemicals, and assist in carbon sequestration (TANAC, 2016).

Vegetable tannins are plant polyphenols with molecular weight between 500 and 30,000 Da, capable of interacting with skin collagen and stabilize the skin matrix against heat and

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degradation (Covington, 2009; Laura et al., 2009). They are also applied in other industries such as wine, pharmaceutical, and adhesive industries with high performance and economic advantages (TANAC, 2016). Vegetable tannins are classified based on their chemical structures as hydrolysable tannins consisting with esters of gallic acid and glucose moieties, condensed tannins which are mainly catechinoid polymerized flavonoids, and tannins with iridoid or secoiridoid structures (Dutta, 1985; Schropfer and Meyer, 2016). Interaction of vegetable tannins with collagen in leather making varies depending on such classes due to structural differences (Schropfer and Meyer, 2016; Suparno, 2005). Thus, different plant species can produce particular class or combination of classes of vegetable tannin categories, hence the need for their characterization and extraction efficiency optimization.

With today's modern technology vegetable tannins can produce leathers with good softness, sponginess, tightness and embossing retention properties that can be refined in many ways in order to adapt to different uses (Kuria, 2015). However, hydrothermal stability, measured as denaturation temperature, is limited to 85 °C (Covington, 2009). Studies have revealed that combination tanning, whereby vegetable tannins are coupled with Aluminium Sulphate [$Al_2(SO_4)_3$] synergistically improve hydrothermal stability, hence the promising approach to produce highly stable vegetable tanned leather (Choudhury et al., 2007; Covington, 1997; E Musa and A Gasmelseed, 2013; Hassan and Ibrahim, 2014; Mahdi et al., 2008; Musa and Gasmelseed, 2012, 2013a, b; Musa et al., 2009). It has been established that improvement by combination tanning depends on the order of adding ingredients and concentration of Aluminium Oxide (Al_2O_3) calculated from $Al_2(SO_4)_3$ using stoichiometric relationship (Covington, 2009; R. Slabbert, 1981), the idea that has been adopted in the present work.

Global vegetable tannin market is dominated by commercial tannins from *Schinopsis balansae* (quebracho), *Castanea vesca* (Chestnut), *Acacia mearnsii* (wattle), *Rhus coriaria* (sumac), *Terminalia chebula* (myrobalan) and *Caesalpinia spinosa* (tara) (Dutta, 1985; Pizzi, 2008). In Africa commercially available vegetable tannins have not been widely used due to their shortage and high cost. In Tanzania, only mimosa extract derived from *A. mearnsii* is available commercially. However, it is too expensive to cottage tanners. Alternatively, they utilize barks from *A. xanthophloea, E. divinorum* and *E. racemosa* among others to make leather by traditional methods. Thus, the three plant species were chosen for investigations based on their indigenous use by the cottage tanners and availability in the localities. The quality of leather is poor compared to leather made of commercial extract of *A. mearnsii*. (Mahdi et al., 2006). Most of the locally used vegetable tannins have been scantly characterized to provide valuable scientific information to identify and commercialize plants with potentials of being tannin source for the purpose of increasing supply of vegetable tannins (Kuria et al., 2016a; Mahdi et al., 2006). Further still, very little has been done to improve their extraction methods and possible blending approaches to enhance their application in leather industry. Therefore, in the work hereby reported vegetable tannins from *A. xanthophloea, E. divinorum* and *E. racemosa* richly available in Tanzania extracted at different temperature and characterized to understand their suitability as vegetable tannins sources. Vegetable tannins extracted from *A. mearnsii* were also characterized as reference since its extract has already been commercialized as vegetable tannin for leather making. In addition, the work reports possibility of improving the performance of extract on leather by combining with $Al_2(SO_4)_3$.

2. Methodology

2.1. Materials

Barks used for extraction of tannins were from various parts of Northern Tanzania. *Acacia xanthophloea* were collected from Arusha town, whereas that of *Euclea divinorum* were collected from, Loliondo, Ngorongoro. Barks of *Acacia mearnsii* and *Euclea racemosa* where collected from Mwanga district, Kilimanjaro. Hide powder and pelt samples were donated by FILK - Forschungsinstitut für Leder und Kunststoffbahnen (Research Institute of Leather and Plastic Sheeting) in Germany. All chemicals (2,4,6-trinitrobenzenesulphonic acid, Sodium carbonate, Hydrochloric acid, citric acid, disodium hydrogen phosphate, monosodium phosphate, disodium phosphate, Sodium hydrogen carbonate, lithiumcitrate buffer, Folin-Ciocalteu's phenol reagent, Gallic acid, Aluminium Chloride, Sodium Hydroxide, Catechin, Sodium Nitrite, $Al_2(SO_4)_3$, sodium citrate and ninhydrin) used were of analytical grade and for tanning trials, commercial grade chemicals were used.

2.2. Extraction of tannins

Collected barks were dried under shed for five days and cut into small chips. The chipped pieces were ground in a milling machine (Retsch SM 2000) and sieved by 1 mm size mesh. Therefore, the barks of particle size less or equal to 1 mm were collected for extraction experiments. About 20 g of milled barks were soaked in 200 mL of distilled water in a glass beaker covered with aluminium foil to prevent water evaporation. The mixture was placed on water bath maintained at a chosen temperature (30, 50 and 80 °C). Stirring of the sample mixture was maintained using overhead stirrer connected to the beaker's opening through small hole made on the aluminium foil. Extraction process continued for 4 h, then the filtrates were collected. The residues were subjected to the second extraction using 200 mL distilled water for 4 h. First and second filtrates were mixed and concentrated at 40 °C under vacuum using rotary evaporator (Rotavapor R210) and then lyophilized. Resultant extract powder was analyzed for extract yield, tannin content (TC), total phenolic content (TPC) and total flavonoid content (TFC).

Extract yield was determined using the following equation;

$$\%\,Extract\ yield = \frac{Extract\ obtained\ (g)}{Amount\ of\ moisture\ free\ barks\ used\ (g)} \times 100$$

2.3. Determination of tannin class by interaction mechanism

Combined analyses were performed to understand the interaction mechanism between tannins and collagen of hide powder for the purpose of identifying classes to which tannins in extracts belong. Differential Scanning Calorimetry was used to examine crosslinking capacity at different pH values between 2.5 and 9. To determined crosslinked amino groups before and after acid hydrolysis 2,4,6-trinitrobenzenesulphonic acid (TNBSA) assay and Amino Acid Analysis (ASA) were applied, respectively. Crosslinked hide powder was prepared by mixing with tannin extract at different pH ranging between 2.5 and 9. Hide powder was soaked in 20 mL 0.4 M McIlvain buffer at varying pH (2.5,3,4,5,7 and 9) for 1 h. 5% (w/v) of extract was added and the solution was shaken in mechanical shaker at 35 °C for 5 h. The solution then was filtered using vacuum pump. The filtrate was discarded and crosslinked hide powder samples were either washed 3 times with excess of water and finally soaked in phosphate buffer at pH 7 or remained unwashed, with the purpose of assessing the reversibility of any effects. TNBSA assay was performed to the samples to determine bound primary amine before acid hydrolysis. About 5 mg of sample were incubated in 200 mL 0.5 M Sodium hydrogen carbonate buffer at pH 8. 200 mL of 0.5% TNBSA were added. The samples were incubated at 60 °C for 4 h for TNBSA to bind to the free primary amines. After this step, the samples were hydrolyzed with 6 N HCl at 80 °C for 1.5 h, diluted with 1 ml distilled water and centrifuged at 14000 rpm. The supernatants were taken for measuring absorption photometrically at 400 nm. Quantification was performed by calibration with an alanine standard. The number of primary amines bound by the tannins was calculated based on the number of free primary amines of cross-linked and non-cross-linked hide powder samples as follows:

$$\%\ \text{crosslinked amino groups} = \frac{100 - \text{free amines } (\mu\text{mol per g dry sample})}{\text{mean value free amines } (\mu\text{mol per g dry hide powder})} \times 100$$

Amino acid analysis was carried out to determine the stability of bound primary amino acid against acid hydrolysis. Crosslinked hide powder samples were hydrolyzed with 6 N HCl at 110 °C for 20 h, then dried and dissolved in lithiumcitrate buffer. Amino acid composition was determined from cross-linked and non-cross-linked samples by an amino acid analyser (Biochrom 30+) using pre-column derivatisation with ninhydrin according to standard protocols (Breck et al., 2005). The percentage of primary amines that formed an acid-stable bond was calculated from the area under the lysine, hydroxylysine or arginine peaks and standardized to the area under the peaks from alanine and valine (these did not involve in cross-linking). The resulting factor was related to the same factor calculated from non-cross-linked sample. All results are averages of two analyses.

2.4. Determination of tannin content

Tannin content was determined by filter bell method as described by Atkin and Thompson (1937). Unfiltered tannin solution was detanned by lightly chromed Freiberg Hide Powder batch number 'VK 383'. A little dry cotton-wool was placed in the upper part of the bell to prevent hide powder from passing through the capillary. The neck was fixed with rubber stopper carrying capillary glass tube bent twice at right angle. Subsequently the bell was filled with 7 g of hide powder and pressed outward onto the bell's wall to block channels that may allow tannin solution to pass through undetanned. The filter bell so prepared was placed in 200 ml beaker and the latter was filled with tannin solution and placed in the water bath maintained at 18 °C. After the tannin solution being absorbed by hide powder up to the neck, gentle suction was applied to the capillary limb until liquid flows out slowly at the rate of 8–10 drops per minute. The detanned solution gave no turbidity with gelatin-salt reagent. The first 30 mL of detanned solution was discarded and 50 mL of the next 60 mL was evaporated and dried to constant weight to determine non-tannin content. Tannin content was obtained as follows:

$$\text{Tannin content} = \text{Soluble substances} - \text{non tannins}$$

2.5. Determination of total phenolic content

Determination of total phenolic was carried out as previously described (Blainski et al., 2013). 5 mL of 10% Folin-Ciocalteu's phenol reagent was added in 0.2 mL of extract solution and mixed well. After 6 min, 4 mL of 7.5% sodium carbonate was added. The mixture was diluted to 25 mL with deionized water and incubated for 90 min. Absorbance was recoded at 760 nm using UV-VIS spectroscopy (Evolution 201). Gallic acid was used to obtain calibration curve and the concentrations used were 50, 75, 100, 125, 200 mgmL^{-1}. Total Phenolic Content was expressed as mg Gallic acid equivalent per g dry weight of the barks and then presented as percentage based on bark dry weight.

2.6. Determination of total flavonoid content

Determination of total flavonoid content was performed as described previously (Kamtekar et al., 2014). 4 ml of deionized water was added in 0.5 ml extract solution followed by 0.3 ml of 5% $NaNO_2$ solution. After 5 min, 0.3 mL of 10% $AlCl_3$ solution was added. The solution was left to stand for 6 min, then 2 mL of 1 M NaOH solution was added. Finally, the volume was made to 10 mL with deionized water and allowed to stand for 15 min before reading absorbance at 510 nm using UV-VIS-spectroscopy (Evolution 201). Catechin was used to obtain calibration curve and the concentrations used were 20, 40, 60, 80, 100 mgmL^{-1}. The Total Flavonoid Content was expressed as mg catechin equivalent per g dry weight of the barks and then presented as percentage based on bark dry weight.

2.7. Determination of cross-linking ability with hide powder

To evaluate the cross-linking capacity of the extracts, hide powder was treated with extract solutions following already established method (Schropfer and Meyer, 2016). About 1 g of hide powder was soaked in 20 mL 0.4 M McIlvain buffer at pH 5 for 1 h. 5% (w/v) of extracts was added and the solution was shaken in mechanical shaker at 35 °C for 5 h. Then, the solution was filtered using vacuum pump. Filtrates were discarded and treated hide powder was taken for further analysis. Few mg of crosslinked hide powder was taken for denaturation temperature analysis using DSC 1 device (Mettler-Toledo). Approximately 6 mg (calculated on dry weight) of wet cross-linked hide powder was placed in an aluminum pan and hermetically closed. Temperature scans were run from 10 to 125 °C with a rate of 5°Cmin^{-1}. From the endotherm's onset temperature (T onset) and peak temperature (T peak) were calculated. The remaining treated hide powder was made into tablets and dried under ambient temperature for 2 days. The thickness and softness of hide powder were determined using thickness gauge and softometer KWS Basic, respectively.

2.8. Determination of blending effect of $Al_2(SO_4)_3$ and vegetable tannins on crosslinking ability

Effect of combining vegetable tanning with $Al_2(SO_4)_3$ on improving the crosslinking ability of tannins was investigated. In the first trial, effect of adding vegetable tannin first was checked. About 0.5 g of hide powder was placed in each of 15 tube (50 mL). Phosphate buffer saline (PBS) (pH 5) was added in each tube to soak the hide powder for 1 h at ambient temperature. The tubes containing soaked hide powder were separated in three groups of five tubes each. 5% (based on hide powder weight) of *A. xanthophloea*, *A. mearnsii* and *E. divinorum* extracts were added in first, second and third group of tubes, respectively. The mixture was shaken in a water bath at 35 °C for 5 h. Then the mixture was vacuum filtered, washed with deionized water until the supernatant was clear. Varying concentrations of basified $Al_2(SO_4)_3$ ranging from 1, 2, 3, 4 and 5% Al_2O_3 (based on hide powder weight) at pH 3.2 (masked with 8:1 of ratio Al^{3+} and $Na_3C_6H_5O_7$) were added serially in 1–5 tubes in each group and placed in a shaking bath at 35 °C. After 3 h the pH was adjusted to 4.5 then the shaking was continued for additional 3 h. Then the mixture was vacuum filtered and the tanned hide powder was washed 3 times with 10 mL deionized water. About 20 mg of the damp filter cake was reserved for Differential Scanning Calorimetry analysis, while the rest was dried in ambient condition.

In the second trial, the reverse order was checked. About 0.5 g of hide powder was placed in each of 15 tubes (50 mL) then the latter were separated in three groups of five tubes each. Basified $Al_2(SO_4)_3$ at pH 3.2 (1, 2, 3, 4 and 5% based on hide powder weight) was added serially in 1–5 tubes in each group and placed in a shaking bath at 35 °C. After 3 h the pH was adjusted to 4.8–5.0 then continued shaking for 3 h more. 5% of *A. xanthophloea, A. mearnsii* and *E. divinorum* extracts were added in first, second and third group of tubes, respectively. The mixture was shaken in water bath at 35 °C for 5 h. Then mixture was vacuum filtered, washed with deionized water until the effluent was clear. About 20 mg of damp hide powder sample was reserved for DSC analysis, while the rest was dried in air. Control samples of hide powder were prepared by tanning with 5% plant extracts alone.

2.9. Differential Scanning Calorimetry analysis for crosslinked hides powder

Cross-linking ability of hide powder was determined on DSC 1 device (Mettler-Toledo) as reported earlier (Schropfer and Meyer, 2016). Approximately 6 mg (calculated on dry weight) of wet cross-linked hide powder was placed in an aluminum pan and hermetically closed. Temperature scans were run from 10 to 125 °C with a rate of $5°Cmin^{-1}$. From the endotherm's onset temperature (T peak) and peak temperature (T onset) were calculated.

2.10. Determination of leather properties

The limed pelts were tanned with 22% of each extract using conventional tanning method (without post-tanning) to assess its performance in hydrothermal stability, mechanical properties chemical properties and surface modification. Hydrothermal stability was assessed by measuring shrinkage temperature and denaturation temperature by using conventional shrinkage temperature (CST) test and DSC method, respectively. For DSC analysis to check denaturation temperature, approximately 6 mg of wet leather sample was placed in an aluminum pan and hermetically closed. Temperature scans were run from 10 to 125 °C with a rate of $5°Cmin^{-1}$. From the endotherm's onset temperature (T peak) and peak temperature (T onset) were calculated. For CST, wet samples with dimensions of 2 × 4 cm were clamped and immersed in water, which in turn was stirred vigorously using magnetic stirrer. The temperature of the solution was gradually increased and the temperature at which the sample shrinks by one third of its original length was recorded. Testing was repeated twice per each sample.

Mechanical properties were analyzed as per EN ISO 17235:2015 method. SEM images of leather samples and control were taken on both grains surface and cross-sectional by using SEM technique. Chemical properties, which include ash content, volatile substances, nitrogen content, water soluble organic substances and dichloromethane-soluble substances, were determined according to DIN EN ISO 4047 method, ISO 5397 method, DIN EN ISO 40482 method and DIN EN ISO 4098, respectively. Skin substance, bound tannin and the degree of tannage were determined by calculations. All experiments were repeated twice.

3. Results and discussion

3.1. Interaction mechanism between vegetable tannins from selected plants and hide powder

The interaction mechanism between extract from each plant and collagen of hide powder was carefully investigated by three different methods with the purpose of understanding the underlying chemistry and confirming the classification of tannins. Hide powder samples were treated with extracts from selected plants under the same conditions and analyzed using different methods. Results from DSC analysis (Fig. 1 A) showed that there was significant interaction throughout pH range, indicating presence of hydroxyl group at acidic pH and ketonic carbonyl groups at alkali pH to interact with protonated and unprotonated amino groups via hydrogen and covalent bond formation, respectively. By washing treated hides, the denaturation temperature (dT) that measured hydrothermal stability of the formed bonds slightly decreased, except for *E. divinorum* at pH 3.5, indicating that the bonds formed are irreversible (Fig. 1 B). The results from TNBSA assay (Fig. 1 C) have confirmed the existence of interaction between unprotonated amino group of collagens and ketonic carbonyl group of tannins, which resulted into crosslinks through covalent bonding as observed in DSC analysis. Amino Acid analysis (Fig. 1 D) revealed that the crosslinks formed are not resistant against acid hydrolysis. According to Schroepfer and Meyer (2016), the interaction mechanism of this kind is typical for condensed tannins of which tannins from *A. mearnsii*, a reference plant used in the present study, belong to. Therefore, it can be concluded that the extracts from *A. xanthophloea, E. divinorum* and *E. racemosa* contain condensed tannins. It is important to note that Extract from *E. racemosa* contain low amount of tannins as indicated in the results (Fig. 1 A, B and C).

3.2. Characterization of plant extracts

Extraction was carried out while varying temperature from 30 to 80 °C. Extract obtain at each temperature was characterized to determine extraction yield, tannin content, total phenolic and flavonoid content, as well as crosslinking ability. The temperature that gave maximum values for all characteristics was chosen to extract vegetable tannins for studying combination tanning and tanning performance.

3.3. Extraction yield, tannin content, total phenolic and flavonoid content

Temperature applied during extraction of tannins from plant material is an important parameter to consider, because it determines extract yield as well as the quality of extracts in terms of tannin, phenolics and flavonoids and non-tannins contents (Zalacain et al., 2003). It has been reported that, high temperature improves extraction efficiency because high heat increase permeability of cell wall and solubility of extractable matters, while

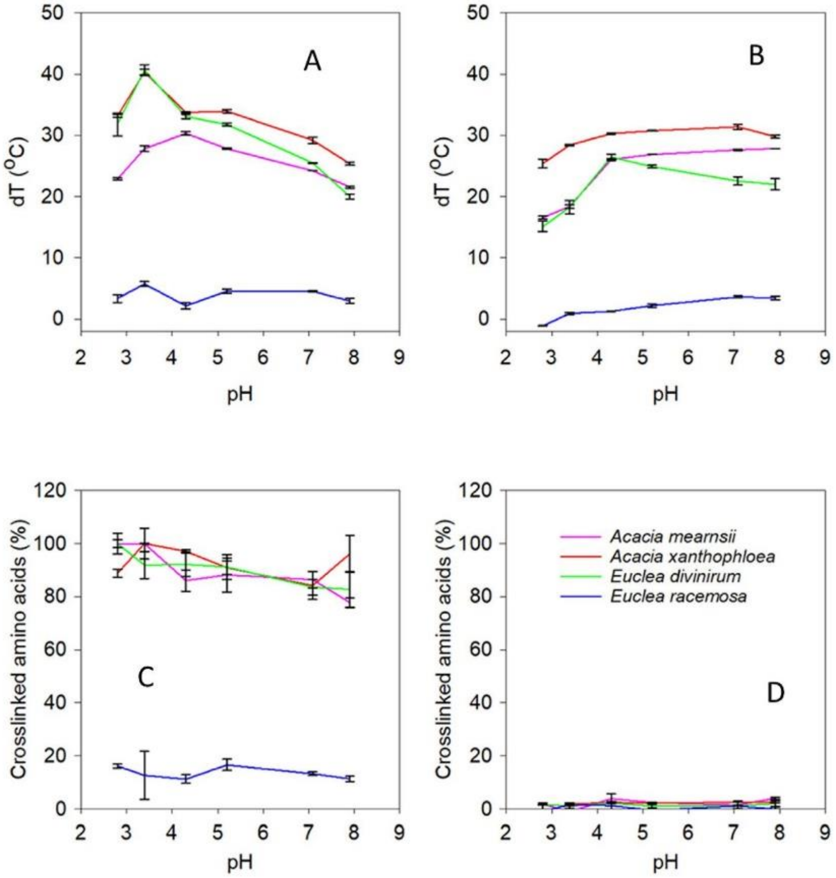

Fig. 1. Effect of pH on denaturation temperature of hide powder cross-linked with vegetable tannins relative to non-cross-linked control (dT) (A = unwashed samples, B = washed samples), as well as percentage of crosslinked amino groups (C = before acid hydrolysis, D = after acid hydrolysis).

reducing viscosity of the solvent (Ogiwara, 1980). On the other hand, studies have revealed that extraction at high temperatures leaches undesirable compounds such as gums that affect the quality of leather (Didato et al., 1999; Kuria, 2015; Syed, 2000). In the present study, the influence of temperature on extract yield and tannin content observed was low, except for extract from barks of *E. racemosa* that has shown a slight increment with raise in temperature as shown in Fig. 2 A and B. Total phenolic content (Fig. 2 C), flavonoid contents (Fig. 2 D) and non-tannins (Table 1) varied insignificantly with the increase in extraction temperature, except for total flavonoid content of extract from *A. mearnsii* that observed to be high at 50 °C (Fig. 2 D).

Variations in extract properties between extracts from plant species studied in this work were significant. This is due to the fact that extracts from different species have different chemical composition and molecular structures (Laura et al., 2010; Würger et al., 2014). It was found that barks of *A. xanthophloea* and *E. racemosa* yielded extract comparable to that of *A. mearnsii*, a commercial tannin source used as reference in the present work. Similar observation was previously reported for *A. xanthophloea* barks extract grown in Kenya (Mugedo and Waterman, 1992). On the other hand, *E. divinorum* barks gave far less extract yield than that of *A. mearnsii* (Fig. 2 A).

Tannin content, total phenolic content and total flavonoid content of extract from *A. xanthophloea* barks were comparable to those of *A. mearnsii*. However, those of *E. divinorum* and *E. racemosa* were very low, with *Euclea racemosa* recording the lowest (Fig. 2 B, C and D).

For the plant to be of commercial interest as a tannin source, extract must show high tannin: non-tanning ratio (T/N) among extractable phenolics (Howes, 1953). T/N for extract from *A. xanthophloea* is lower than *A. mearnsii* (Table 1), but higher than recommended values (Howes, 1953; Mugedo and Waterman, 1992) indicating that the extract is suitable for vegetable tanning. On the other hand, T/N for extracts from *E. divinorum* and *E. racemosa* barks are lower than that of *A. mearnsii* and far below recommended values (Table 1). In light of importance of T/N as criterion for defining the suitability of vegetable tannins, the extracts from *Euclea* species studied in this work are not suitable for vegetable tanning. However, other parameters were analyzed further to ascertain their suitability.

3.4. Crosslinking ability of extracts

Crosslinking ability measures the capacity of plant extract to stabilize collagen of hide against moist heat as the result of formation of extra crosslinking bond within collagen fiber matrix (Covington, 2009). In most cases, it is assessed by measuring denaturation temperature of threated hide powder using DSC instrument. The latter generates thermograph showing onset temperature at which denaturation of skin collagen starts (T onset) and peak temperature indicating maximum denaturation (T peak). The

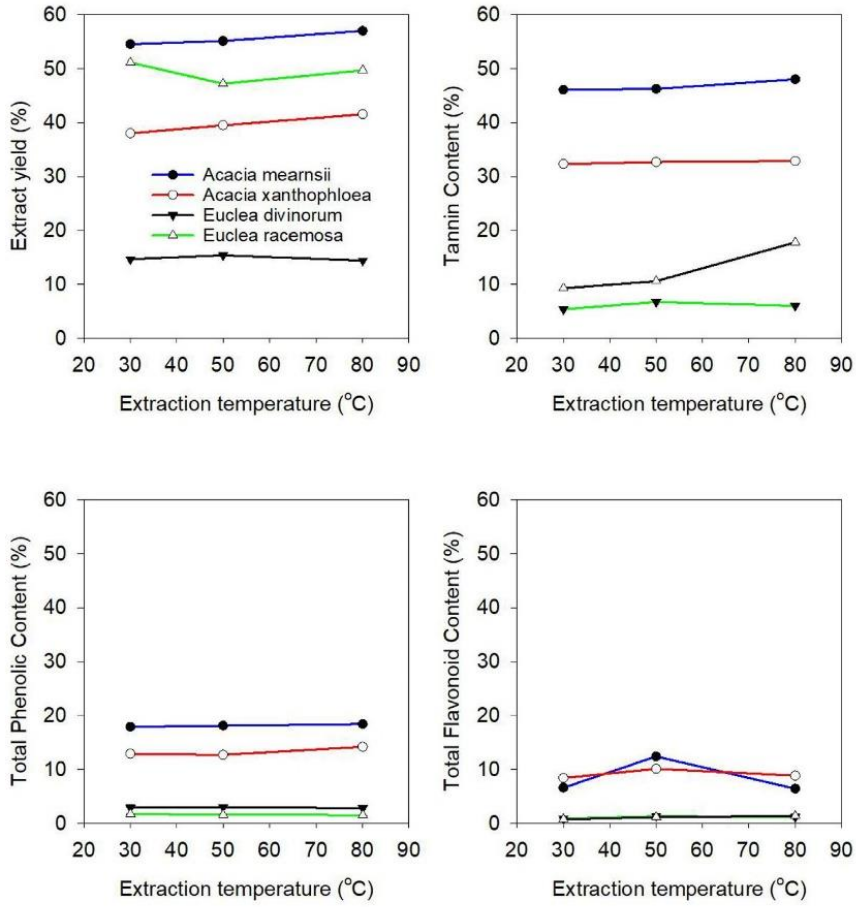

Fig. 2. Effect of extraction temperature on plant extracts yield (A), tannin content of plant extracts (B), total phenolic content of plant extracts (C) and total flavonoid content of plant extracts (D).

interval between T onset and T peak is an indication of the sharpness of the denaturation process, of which large interval indicates broader distribution of collagen molecules having a different thermal stability (Choudhury et al., 2007; Larsen et al., 1993; Tang et al., 2003).

Extract from *A. xanthophloea* barks corroboratively expressed higher crosslinking ability than that of *Acacia mearnsii* (Fig. 3), consistency with earlier findings (Kuria et al., 2016b; Kuria, 2015; Mugedo and Waterman, 1992). Extract from barks of *E. racemosa* did not show significant crosslinking ability (Fig. 3) compared to others due to low tannin content, total phenolic content and flavonoid content stated earlier in this paper. Being poor tannin source, it was judged as not suitable vegetable tannin source, hence not considered for the subsequent experiments.

Despite having less tannin content, the crosslinking ability of extract from barks of *E. divinorum* found to be similar to that of *A. mearnsii*, except that the interval between T onset and T peak observed under DSC analysis was abnormally large (Fig. 3) and peaks in thermograph were found to be wide and resolved into multiple of small peaks (thermograph not shown). This might be due to low tannin, phenolic and flavonoid contents in extract of *E. divinorum* as shown in Fig. 2 B, C and D. As the result, few collagen molecules were crosslinked, hence more than one population of collagen molecules with different thermal stability might be present (Choudhury et al., 2007; Tang et al., 2003). Similar observation was made in another work on tanning that involved mimosa and oxazolidine (Choudhury et al., 2007).

The crosslinking ability of extracts was further confirmed by assessing the thickness and bending force of the hide powder tablets, which relate to their softness and stiffness (Fig. 4). Hide

Table 1
Tannin/non-tannin (T/N) ratios.

Plant	*A. xanthophloea*	*A. mearnsii*	*E. divinorum*	*E. racemosa*	Recommended T/N ratio
Temperature (°C)	T/N				More than 1 and preferably over 2
30	6.7	7.9	0.9	0.3	
50	6.6	7.7	0.9	0.3	
80	6.8	8.0	0.8	0.6	

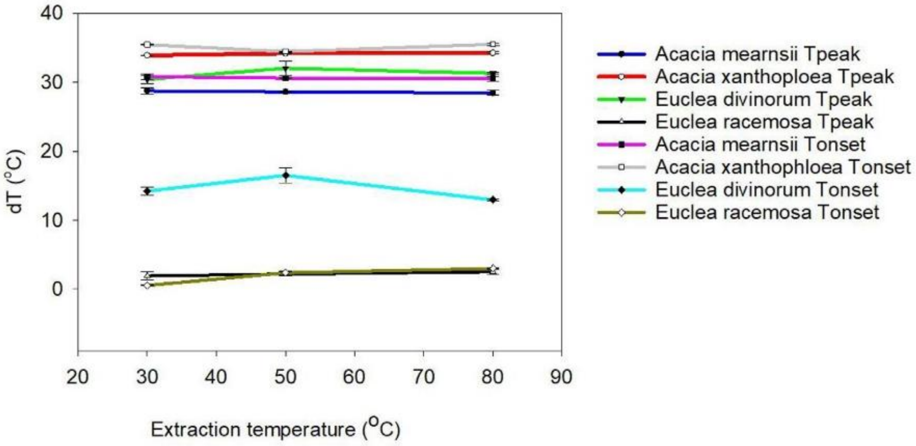

Fig. 3. Effect of extraction temperature on crosslinking ability of plant extracts.

powder tablets treated with *A. mearnsii*, *A. xanthophloea* and *E. divinorum* extracts showed an increased thickness and softness. The resistance to bending is low, suggesting the formation of crosslinks that brought about separation of fiber structures and flexibility of fibers to slide over one another. This was in agreement with previous reports (Covington, 1997, 2009). However, hide powder tablet treated with *E. racemosa* extract was stiff and thin like un-crosslinked hide powder tablet. Bending it required large

Fig. 4. Crosslinked and un-crosslinked hide powder tablets.

force (Fig. 4). This could have been attributed to gluing properties of *E. racemosa* extracts that upon interaction with hide powder resulted into compacting together of fibers. As the result, the hide powder tablet shrunken and its thickness became less than other tablets. In addition, the color of the hide powder tablet treated with *E. racemosa* extract was different from others (appeared black on image) because extract's color (deep green) was passed on to the hide powder.

3.5. Improvement of crosslinking ability of extract by combination tanning

It was well acknowledged that the crosslinking ability of vegetable tannins to give leather the hydrothermal stability similar to that of chromium tanned leather is achieved by combination tanning technique (Covington and Suparno, 2007; Covington, 2009; Madhan et al., 2007; Musa et al., 2009). Using different tanning agents with weaker tanning power than chromium salt, the interaction of vegetable tannins with collagen of the hide powder is enhanced leading to improved hydrothermal stability (Covington, 2009). Among many tanning agents, $Al_2(SO_4)_3$ is mostly preferred because it has been widely studied and its mechanism is well established (Brown and Dudley, 2005; Covington, 2009; E Musa and A Gasmelseed, 2013; Madhan et al., 2007). In addition, $Al_2(SO_4)_3$ has good capacity of adsorbing pigments and gives the leather cationic properties making it the best mordant for excellent dyeing. Furthermore, $Al_2(SO_4)_3$ is safe and non-toxic chemical (Mozaffari, 2018).

Therefore, in the present work, extracts were applied together with $Al_2(SO_4)_3$ to study the effect of $Al_2(SO_4)_3$-blended vegetable tannins in improving crosslinking ability of extracts under investigations. Thermal denaturation of hide powder collagen treated with 5% extract and 0–5% Al_2O_3 while alternating order of applying tanning agents was studied using DSC instrument. Fig. 5 A and B show the denaturation temperature of hide powder as the function of Al_2O_3 concentration. As previously reported (Choudhury et al., 2007; Covington, 2009), order in which tanning agents are applied during combination tanning has shown profound effect on hydrothermal stability of treated hide powder. The effect varies depending on vegetable tannin sources. Hide powder treated with *A. mearnsii* extract first before $Al_2(SO_4)_3$ is added gave higher hydrothermal stability (Fig. 5 A) compared to the reverse order (Fig. 5 B). Similar trends have been reported in other works (Choudhury et al., 2007; Covington, 1997; Covington, 2009; R. Slabbert, 1981). For extract from *A. xanthophloea*, both orders of addition resulted into increased crosslinking ability, but adding $Al_2(SO_4)_3$ first before extracts seem to be the best as it also reduces the interval between T onset and T peak (Fig. 5 A and B), suggesting uniform stabilization of collagen molecules. Unlike *A. mearnsii*, extract from *Euclea divinorum* works better when $Al_2(SO_4)_3$ is added first compared to reverse order (Fig. 5 B). Not only crosslinking ability increases, but also the gap between T onset and T peak are tremendously reduced (Fig. 5 B).

The effect of aluminium concentration on crosslinking ability of extracts was significant. As concentration of aluminium increases, the hydrothermal stability decreases, consistence with findings in another work (Haroun et al., 2009). As for extract from *A. mearnsii*, the maximum hydrothermal stability for *A. xanthophloea* was 1% Al_2O_3, while for extract from *E. divinorum* was 2% Al_2O_3.

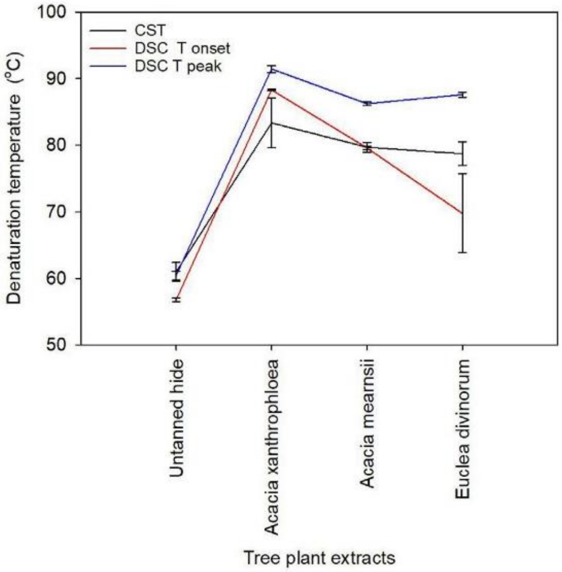

Fig. 6. Denaturation temperature of leather samples and untanned hide.

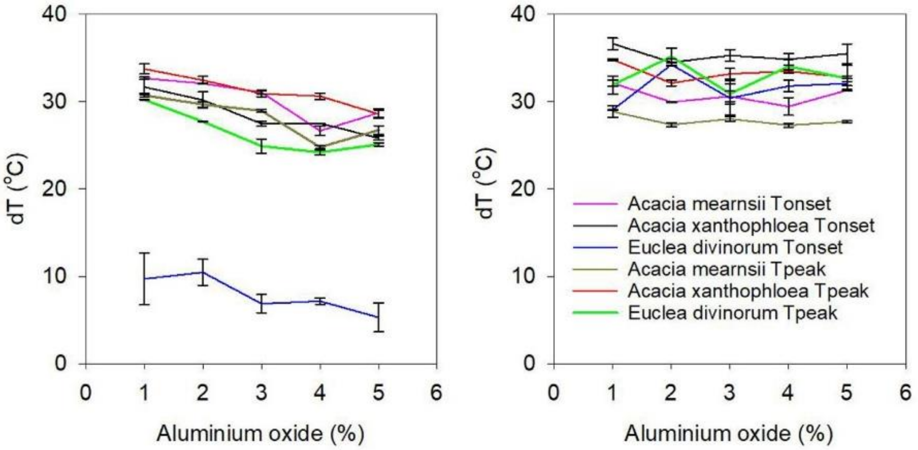

Fig. 5. Effect of $Al_2(SO_4)_3$ concentration crosslinking ability of extract when extract is added first (A) and when $Al_2(SO_4)_3$ is added first (B).

3.6. Hydrothermal stability of leather samples

Hydrothermal stability of leather samples tanned with extract from plant species under consideration was examined. Hydrothermal stability was measured by DSC and CST techniques. The findings revealed that extracts of *A. xanthophloea* bark performed better in terms of hydrothermal stability than that of *A. mearnsii* (Fig. 6) corroborating previous reports (Kuria et al., 2016b; Kuria, 2015). Hydrothermal stability of leather tanned with extract from *E. divinorum* was comparable to that of leather tanned with *A. mearnsii*, except that T onset and T peak gap was wider than that of the latter species. These findings correlate with the observation made on analysis of crosslinking ability of extracts. Therefore, as it was observed in combination tanning with hide powder, wide gap on T onset and T peak observed for leather samples tanned with extract from *E. divinorum* can be reduced by blending tanning with 2% of Al_2O_3 by adding aluminium first before the extract in the tanning liquor.

3.7. Mechanical properties of leather samples

The mechanical properties of leather samples are presented in Table 2. The tensile strength of the leather tanned with *A. xanthophloea* is more or less the same as the tensile strength of the leather tanned with *A. mearnsii* extract, but elongation at break for *A. xanthophloea* tanned leather is marginally higher than that of *A. mearnsii*, in agreement with hydrothermal stability results. For the case of softness, *A. xanthophloea* displayed lower softness value than *A. mearnsii*, though the difference is not large. Leather tanned with *E. divinorum* extracts gave the lower values in all parameters compared to *A. mearnsii*. These results support the findings reported in present work, which confirmed low ability of *E. divinorum* extract to crosslink all collagen molecules due to less tanning content as well as total phenolic and flavonoid content, hence affecting the mechanical properties as well.

3.8. Chemical properties of leather samples

For the case of chemical properties, all leather samples showed desirable results. Low water solubility observed in all sample indicates that leather tanned with tannins from studied plants have good water resistance (Table 3). Degree of tannage in both leather samples was almost similar to that of leather tanned with *A. mearnsii* (Table 3) and it falls in the recommended value for vegetable tanned leather, 50–95% (Heidemann, 1993).

3.9. SEM images for leather samples

The images of leather grain surface and cross-sectional were taken. Smooth grain surface is indication that interaction between vegetable tannins from selected plants and collagen of hides modified grain surface without causing damage (Fig. 7). It is equally important to note that vegetable tannins from each plant gave different grain surface appearance, suggesting variations in molecular characteristics of vegetable tannins from different plant sources that tend to bring different appearance (Brown and Dudley, 2005). Cross sectional images of leather samples showed satisfying extent of fiber opening due to good penetration and distribution of tannins within skin matrix (Fig. 8).

Table 3
Chemical properties of leather samples tanned with extracts from three plants under investigation.

Characteristics	*Acacia xanthophloea*	*Acacia mearnsii*	*Euclea divinorum*
Moisture content %	12.4 ± 0.05	12.6 ± 0.04	14.0 ± 0.00
Fat content %	4.4 ± 0.25	3.0 ± 0.01	3.5 ± 0.01
Hide substance %	59.7 ± 0.05	59.8 ± 0.02	62.4 ± 0.30
Tannage degree %	52.6 ± 0.16	56.9 ± 0.20	50.9 ± 0.58
Organic WSS %	4.4 ± 0.05	2.5 ± 0.10	0.8 ± 0.10

Characterization of extracts from local plants for their application is crucial activity for development of appropriate recipe and possible commercialization. For instance, Mahdi et al. (2006), characterized vegetable tannin from *A. nilotica* abundantly available in Sudan. Results helped to obtain vegetable tannin with similar quality as that of commercial mimosa. Kuria et al. (2016a), characterized vegetable tannins from the *A. nilotica*, *A. xanthophloea* and *Hagenia Abyssinica* grown and used by cottage tanners in Kenya to make leather by traditional means. The purpose was to optimize vegetable tanning using locally available materials. They concluded that vegetable tannins from *A. nilotica, A. xanthophloea* and *H. Abyssinica* can be used to replace commercial mimosa in a tanning process amongKenyan tanneries. However, characterization was based on few parameters without investigating interaction mechanism and crosslinking ability when blended with $Al_2(SO_4)_3$. Thus, characterization of extracts from local trees used by local tanners in Tanzania, reported in this work will form the basis for effective exploitation of local resources for production of good quality leather to contribute to growth of leather sector.

4. Conclusion

In the present work, investigations were made to study the suitability of tannins from Tanzania local trees used traditionally by cottage industries to make leather. Using simple extraction technique and at 50 °C temperature of extraction, barks of *A. xanthophloea* grown in Tanzania can produce commercially acceptable extract in terms of extract yield, tannin, total phenolic and flavonoid contents, and crosslinking ability almost comparable to that of extract from *A. mearnsii* barks, which is a globally known to be commercial tannin source. That means, *A. xanthophloea* abundantly available in Tanzania with scarce use can potentially be cultivated for production of tannins. The *E. divinorum* barks, on the other hand, is good tannin source only when used in combination with 2% Al_2O_3 particularly when the latter is added first. *E. racemosa* has been proven to be poor tannin source, hence it should be discouraged to be used in tanning process among cottage tanneries in Tanzania. This study provides useful information for possible commercialization of local plants used by cottage tanners as tannin source for increasing supply of tannin towards development leather sector in Tanzania and beyond.

Table 2
Mechanical properties of leather samples tanned with extracts from three plants under investigation.

Property	*Acacia xanthophloea*	*Acacia mearnsii*	*Euclea divinorum* ISO
Tensile strength (Nmm^{-2})	5.69 ± 0.3	6.06 ± 0.6	4.71 ± 1.0
Elongation at break (%)	36.80 ± 1.89	33.44 ± 1.98	26.30 ± 1.41
Softness (mm)	1.9 ± 0.4	2.4 ± 0.3	1.7 ± 0.4

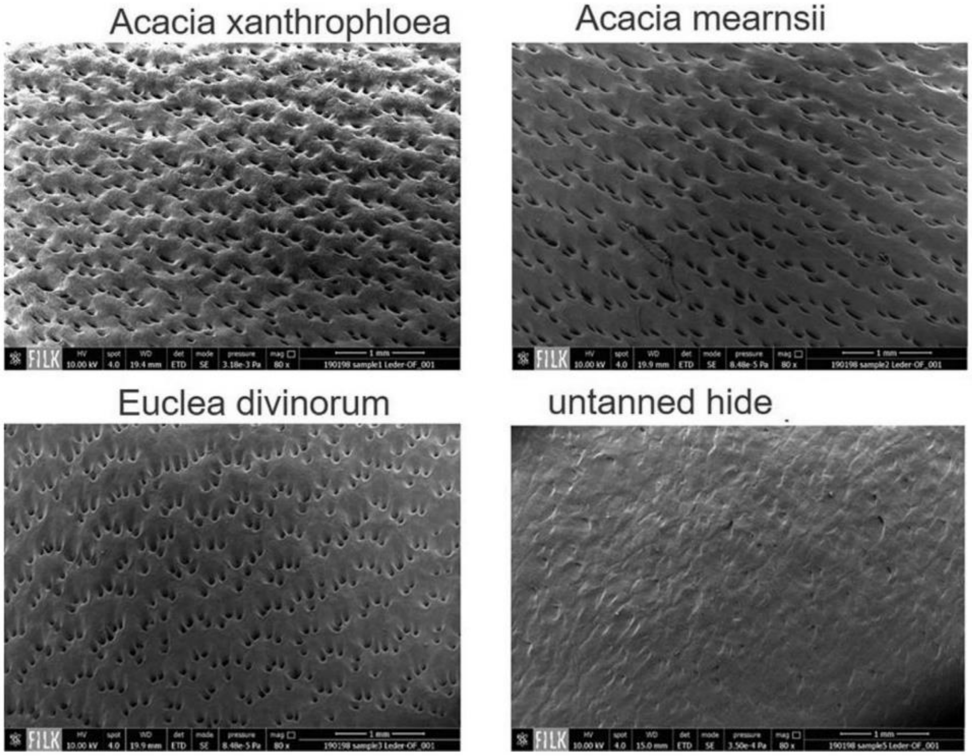

Fig. 7. SEM images of leather samples (Grain surface).

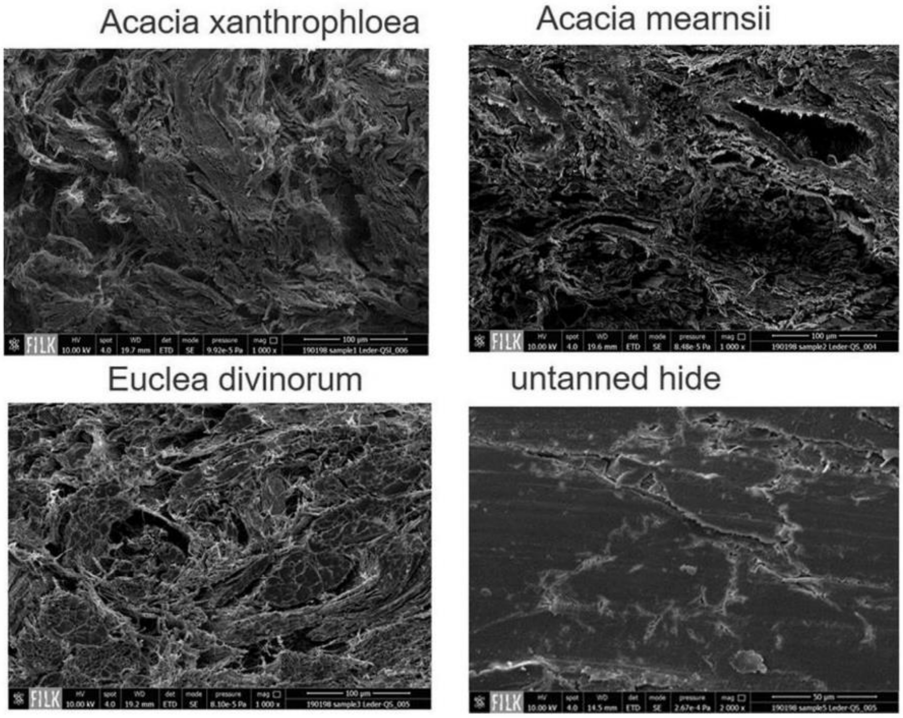

Fig. 8. SEM images of leather samples (Cross-sectional).

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Cecilia R. China: Conceptualization, Writing - original draft, Methodology. **Michaela Schroepfer**: Conceptualization, Methodology, Writing - review and editing. **Michael Meyer**: Conceptualization, Methodology, Writing - review and editing**. Steven S. Nyandoro**: Methodology, Writing - review & editing. Askwar Hilonga: Supervision, Writing - review and editing. **Swarna V. Kanth**: Supervision, Writing - review & editing. **Karoli N. Njau**: Supervision and editing.

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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}

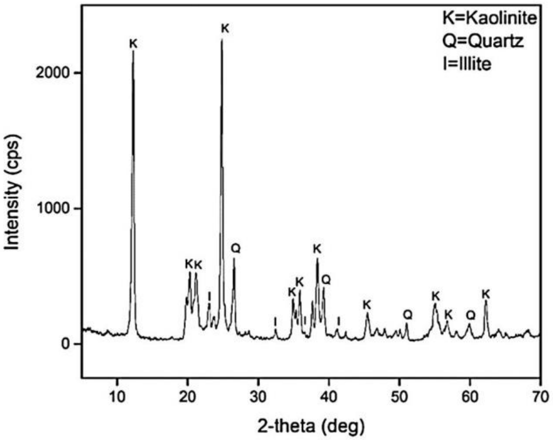

Fig. 1 XRD pattern of Pugu kaolin

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

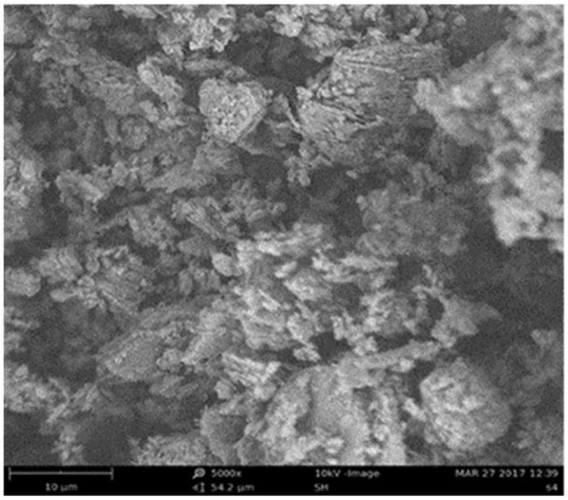

Fig. 2 Scanning Electron Microscopic image of Pugu kaolin

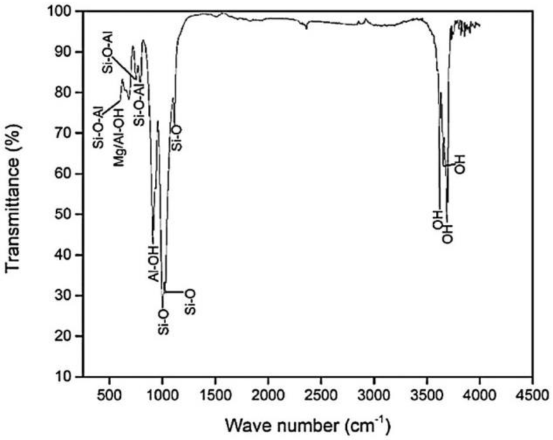

Fig. 3 FTIR spectrum of Pugu kaolin

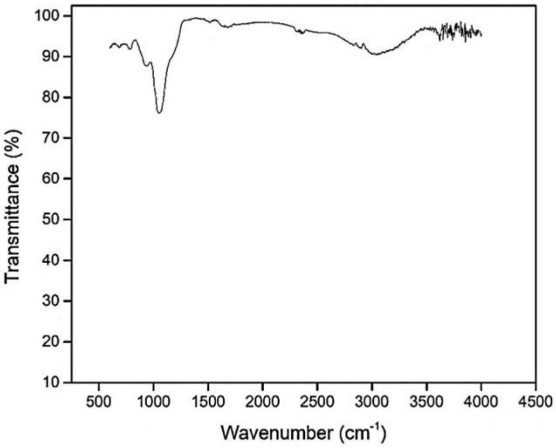

Fig. 4 FTIR spectrum of calcined kaolin

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 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.

$$Al_2O_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2O \tag{1}$$

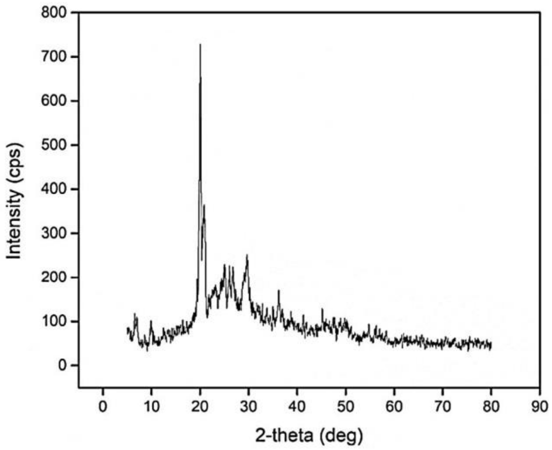

Fig. 5 XRD patterns of $Al_2(SO_4)_3$ prepared from Pugu kaolin

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 $Al_2(SO_4)_3$.

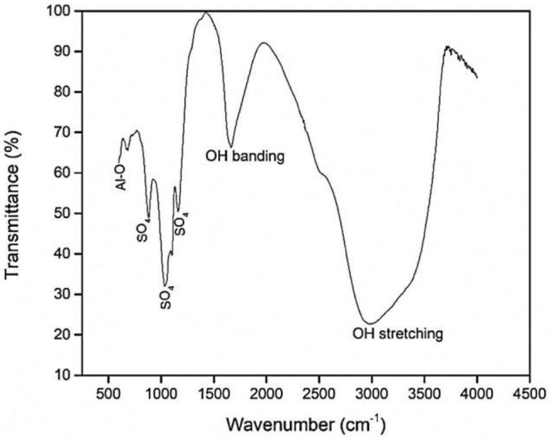

Fig. 6 FTIR spectrum of $Al_2(SO_4)_3$ prepared from Pugu kaolin

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

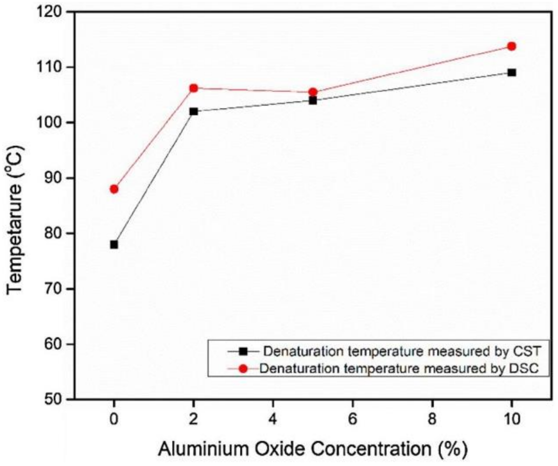

Fig. 7 Hydrothermal stability of leather samples

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 162:1992
Across	62.5	64.2	69.2	67.2	0.8 mm min. 25	
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

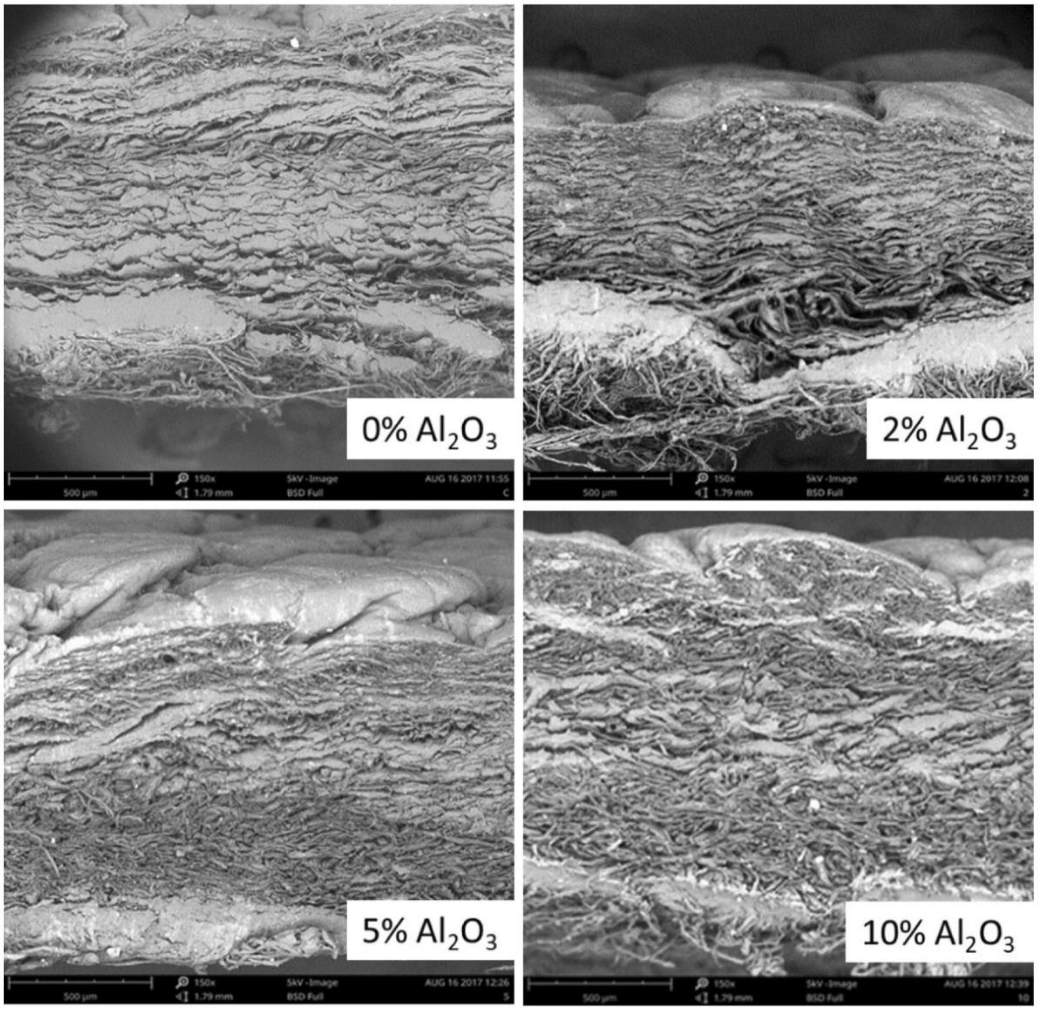

Fig. 8 SEM images of leather samples tanned with 15% mimosa and different concentration of Al_2O_3

$Al_2(SO_4)_3$ 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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STRIDING TOWARDS SELF-SUSTAINABILITY USING ALUMINIUM FROM TANZANIAN KAOLIN FOR COMBINATION TANNING SYSTEM

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Abstract. Sustainability is a key factor which controls future leather manufacture. Developing several new technologies is one of the primary agendas for sustainability. However, developing countries are facing several challenges which not only limited to best practice technologies but also finding self-sustainability in maximizing the available resources. In the present study, an attempt has been made to explore the potential resource of aluminium sulphate from kaolin of Pugu hills, Tanzania for combination tanning. Though, extraction of aluminium sulphate from several resources are available, there is limited literature pertaining to Tanzania resources. Therefore, aluminium sulphate extracted from kaolin was basified and studied for its tanning efficiency. Diffraction and vibrational spectroscopic studies were carried out to assess the confirmation of extracted aluminium. Combination tanning has been carried out with vegetable tannins, which are from natural resources. Leathers tanned with aluminium sulphate and mimosa resulted with a hydrothermal stability temperature beyond 100°C as compared to vegetable tannin alone showed 78°C. Physical strength characteristics met the standard norms. Fiber separation was good, which has been confirmed through microscopic studies. The study provides a new insight on accomplishing self-sustainability through available resources and manufacture eco-friendly system.

Key words: Pugu kaolin, Combination tanning, Aluminium sulphate, mimosa, leather manufacturing

1 Introduction

Sustainability is a key factor, which controls future leather manufacture. Today's leather industry is dominated by use of chromium salt as tanning agent. However, Chromium tanning is being debatable owing to reported toxicity of chromium (VI) and associated disposal issues [1]. A new tanning system without using chromium salt is an immediate need for sustainable leather industry. Studies revealed that combination tanning, whereby vegetable tannins are coupled with Aluminium Sulphate [Al2(SO4)3], produce good quality leather mimicking the properties of chrome-tanned leather [1-10]. Al2(SO4)3 currently used in combination tanning is industrially produced by the Bayer and Hall-Herault processes, using bauxitic rocks as raw materials, which contain between 20 and 30% of aluminium [11, 12]. However, bauxite is globally diminishing and also it is often completely absent in known commercial quantity in most developing countries [13]. Kaolin, which is richly available in most developing countries, containing between 10-20% aluminium, can be a reliable source of aluminium for production of Al2(SO4)3 for various applications [12].

Tanzania is endowed the largest kaolin deposit in Africa that entails possible production of Al2(SO4)3 for combination tanning. About 2.3 billion metric tons kaolin deposit of high standard is located in Pugu Hills, 35 km from Dar es Salaam, Tanzania [14-16]. The potentials of Pugu kaolin for industrial use is still untapped [14, 15]. In the present study, an attempt has been made to explore the potential resource of aluminium from kaolin of Pugu hills, Tanzania for combination tanning.

3 Results and discussion

In the present study, Combination tanning using mimosa and $Al_2(SO_4)_3$ extracted from kaolin was carried out with the main goal of exploring potential utilization of kaolin resource in leather industry (Fig. 1).

Figure 1. Step by step preparation of aluminium sulphate from Pugu kaolin (A=Kaolin deposit, B=Preparation and extraction, C=Aluminium sulphate)

3.2 Analysis of $Al_2(SO_4)_3$ from Pugu kaolin

During extraction process, Al_2O_3 present in kaolin is leached and react with sulphuric acid used for dissolution to form $Al_2(SO_4)_3$ and water (eq. 1). XRD and FTIR spectra of extract have displayed most characteristic peaks of $Al_2(SO_4)_3$ signifying that $Al_2(SO_4)_3$ was formed during extraction process.

$$Al_2O_3 + 3H_2\,SO_4 \rightarrow Al_2(SO_4)3 + 3H_2O \qquad \textit{Equation 1}$$

3.3 Determination of shrinkage temperature

The shrinkage temperature of the samples was determined to assess the tanning effect. It was observed that addition of $Al_2(SO_4)_3$ resulted in significant increase in shrinkage temperature in the order of 78, 115, 118, 114°C for 0, 2, 5 and 10% Al_2O_3, respectively.

3.4 Physical properties of leather samples

It is important to study the influence of the tanning system on the strength properties of leathers. Physical properties analyses carried out are tearing strength and water vapour permeability. Physical characteristic data for leather samples tanned with different concentrations of Al_2O_3 meet standard values recommended by CLRI. Micrographs of leather samples tanned with combination system show better fiber dispersion than those tanned using mimosa alone.

4 Conclusion

In the present work, investigation was made to study potential of Pugu kaolin as source of $Al_2(SO_4)_3$ for combination tanning. $Al_2(SO_4)_3$ was successful obtained from kaolin using sulphuric acid as dissolution agent. Its application in combination tanning with mimosa gave leathers with shrinkage temperature beyond 100°C that can be achieved with as low concentration as 2% Al_2O_3. Produced leather showed physical properties above recommended values and good fiber structures separation. This study provides useful information on accomplishing self-sustainability through available resources in Tanzania for eco-friendly leather manufacturing.

2 Material and Methods

2.1 Materials

Kaolin was collected from Pugu hills, Kisarawe in the coast region of Tanzania, by using quarter sampling technique as described by Sempeho [17]. All chemicals used were of analytical grades purchased from Sigma Aldrich Ltd, India. Industrial chemicals used were of commercial grade, Goatskins pelts were generously donated by CSIR-CLRI pilot tannery, pre-tanning section.

2.2 Extraction of kaolin

Raw kaolin was grounded to fine particles, activated by heating and dissolved in concentrated sulphuric acid at a definite ratio for 90 minutes. Resultant filtrate was concentrated to obtain white crystals of aluminium sulphate. The latter was analysed by XRD AND FTIR to assess the confirmation of extracted aluminium.

2.3 Combination tanning trials

Sample goatskins were treated with mimosa in combination with basified and masked $Al_2(SO_4)_3$ from kaolin. The recipe for tanning process was adopted from CSIR-CLRI pilot tannery. In summary, 15% of mimosa was used in combination with varying concentrations of $Al_2(SO_4)_3$ expressed as % Al_2O_3. Control skin sample treated with mimosa alone.

2.4 Determination of shrinkage temperature

The shrinkage temperature test was carried out as per SATRA STD 114 method. A strip of about 2 cm^2 leather were cut from tanned leather sample clamped between jaws of the clamp that in turn was suspended in a solution of water: glycerol mixture (3:1). The mixture was gradually heated and the temperature at which leather sample shrinks to one third of its original length was recorded as a shrinkage temperature. All analyses were done in duplicate.

2.5 Post tanning process

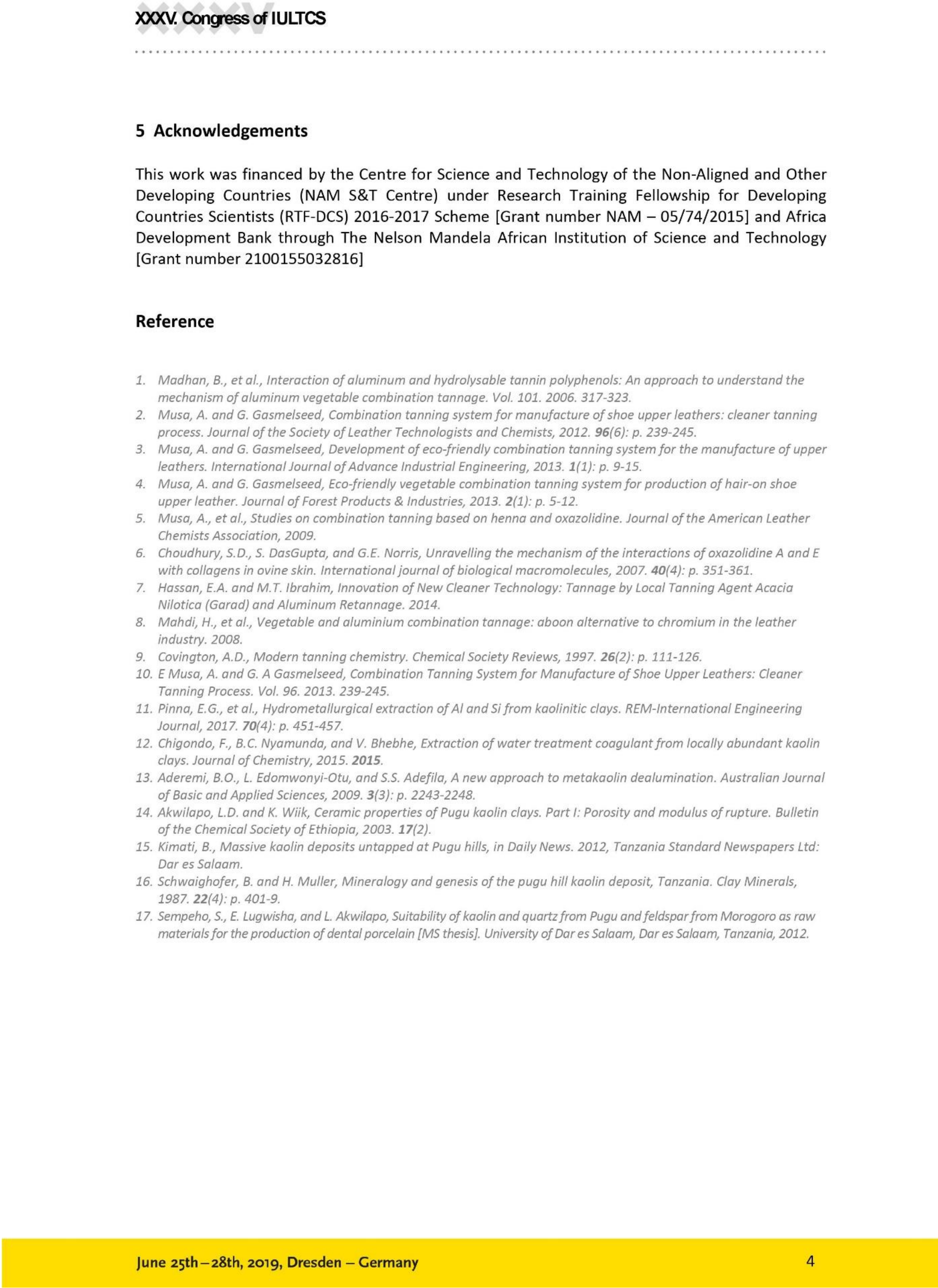
After tanning the samples were shaved to uniform thickness of 1.1 mm and conventional post tanning processes where carried out by 13% syntans and 8% fatliquor. Thereafter, leather samples were set, toggled to dry, staked and buffed.

2.6 Physical characterization of crust leather

Experiment and control crust leather samples were subjected to physical testing to determine the influence of $Al_2(SO_4)_3$ from kaolin on physical properties of leather. Tear strength water vapour permeability tests were carried out using SATRA TM 162:1992. All test samples were conditioned at 20°C and 65% relative humidity. Duplicate analyses were performed for each sample.

2.7 Scanning Electron Microscopic analysis of Leather Samples

Experiment and control crust leather samples were cut into predefined sampling position and shaped into uniform thickness, coated with gold using Edwards E306 sputter coater followed by scanning process. The micrographs for cross section were obtained by operating the SEM at an accelerating voltage of 5 KV with 150X magnification.



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PREPARATION AND APPLICATION OF ORGANIC TANNING CHEMICALS FROM PLANT BARKS IN LEATHER PROCESSING:

A benign alternative to chromium salts

Cecilia China, Askwar Hilonga, Swarna Kanth, Michaela Schroepfer, Karoli Njau

INTRODUCTION

Water is the precious resource needed to sustain life, but industrial activities limits its access due to pollutions. Following use of chromium salts, leather industry is leading in introducing chromium pollutant in water bodies. Alternative chemicals such as Oxazolidines, Aluminium, Zinc and Titanium salts are reported, but they are too expensive for most firms in developing countries. Use of organic tanning chemicals prepared from local plants can be affordable alternative. Moreover, solid wastes and wastewater generated is safe for recycling and its handling in is manageable. In this work, organic tanning chemicals from local plants in Tanzania were extracted, characterized and applied in producing leather and ultimately leather goods.

LABORATORY TRIALS

Organic tanning chemicals were innovatively extracted from plant barks of three different plant species and tested for their suitability in converting raw goat skin to leather

Figure 1: Preparation of organic tanning chemical from local plant bark and its application in leather processing

PROCESS SCALLING UP

Goat skin processing using organic tanning chemicals was scaled up to leather goods production stage

Figure 2: Scaling up of Goat skin processing using organic tanning chemicals to make leather

USABILITY OF WASTEWATER AND SOLID WASTES

Figure 3: Solid and liquid waste generated from processing hides and skin using organic chemicals

A= Extract residues (plant biomass) can be used as source of renewable energy or organic fertilizer

B= Hair and flesh can be used as organic fertilizer, animal feed or gelatin production

C= Wastewater can be used in irrigation or treated to get clean water for reuse

CONCLUSION

- Use of organic tanning chemicals in leather industry will prevent water pollution caused by chromium salt.
- Local plants abundantly available in Tanzania are suitable for production of organic tanning chemicals to replace use of chromium salts.

ACKNOWLEDGEMENT

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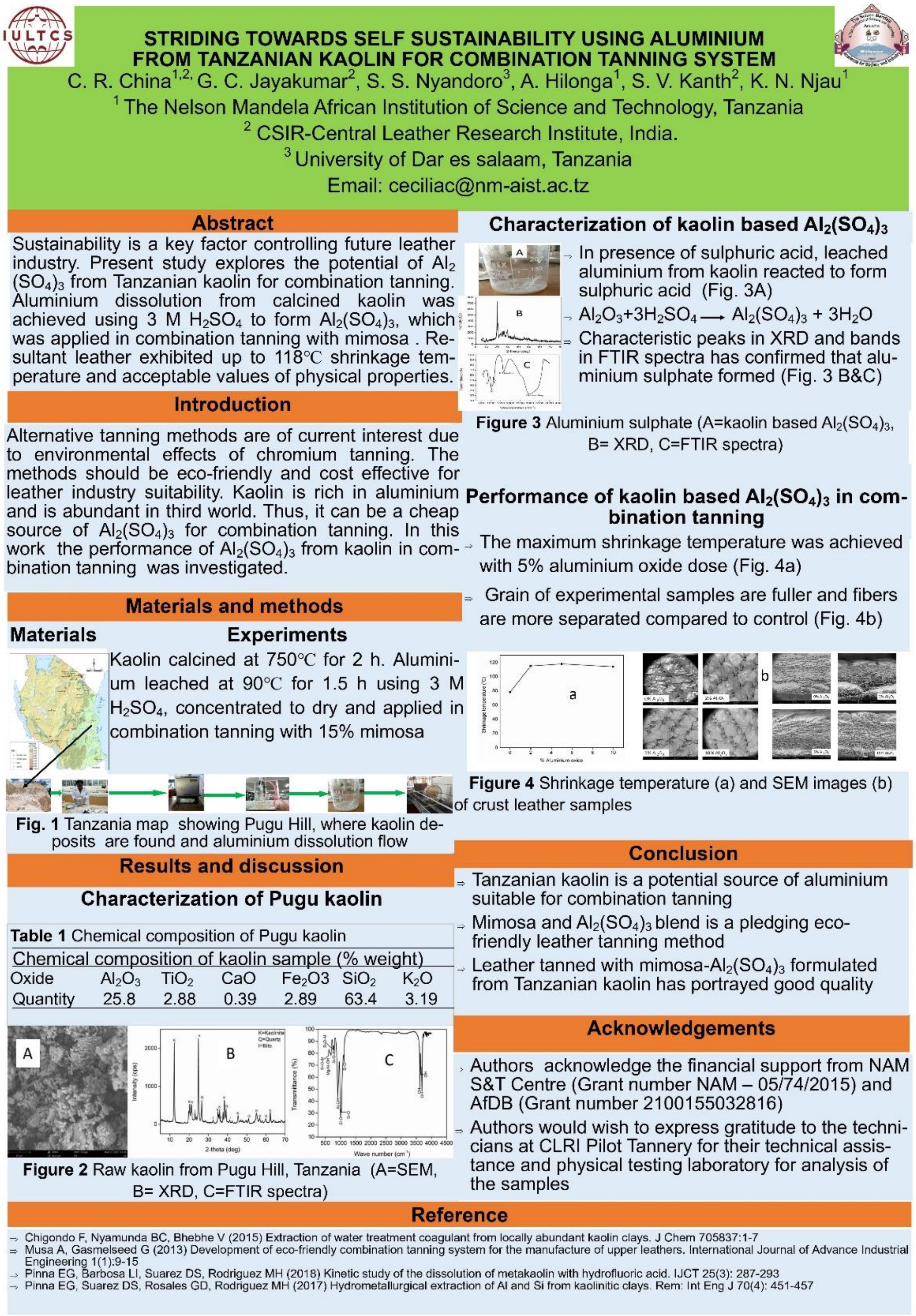

STRIDING TOWARDS SELF SUSTAINABILITY USING ALUMINIUM FROM TANZANIAN KAOLIN FOR COMBINATION TANNING SYSTEM

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Abstract

Sustainability is a key factor controlling future leather industry. Present study explores the potential of $Al_2(SO_4)_3$ from Tanzanian kaolin for combination tanning. Aluminium dissolution from calcined kaolin was achieved using 3 M H_2SO_4 to form $Al_2(SO_4)_3$, which was applied in combination tanning with mimosa . Resultant leather exhibited up to 118℃ shrinkage temperature and acceptable values of physical properties.

Introduction

Alternative tanning methods are of current interest due to environmental effects of chromium tanning. The methods should be eco-friendly and cost effective for leather industry suitability. Kaolin is rich in aluminium and is abundant in third world. Thus, it can be a cheap source of $Al_2(SO_4)_3$ for combination tanning. In this work the performance of $Al_2(SO_4)_3$ from kaolin in combination tanning was investigated.

Materials and methods

Materials **Experiments**

Kaolin calcined at 750℃ for 2 h. Aluminium leached at 90℃ for 1.5 h using 3 M H_2SO_4, concentrated to dry and applied in combination tanning with 15% mimosa

Fig. 1 Tanzania map showing Pugu Hill, where kaolin deposits are found and aluminium dissolution flow

Results and discussion

Characterization of Pugu kaolin

Table 1 Chemical composition of Pugu kaolin

Chemical composition of kaolin sample (% weight)						
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

Figure 2 Raw kaolin from Pugu Hill, Tanzania (A=SEM, B= XRD, C=FTIR spectra)

Characterization of kaolin based $Al_2(SO_4)_3$

- In presence of sulphuric acid, leached aluminium from kaolin reacted to form sulphuric acid (Fig. 3A)
- $Al_2O_3 + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2O$
- Characteristic peaks in XRD and bands in FTIR spectra has confirmed that aluminium sulphate formed (Fig. 3 B&C)

Figure 3 Aluminium sulphate (A=kaolin based $Al_2(SO_4)_3$, B= XRD, C=FTIR spectra)

Performance of kaolin based $Al_2(SO_4)_3$ in combination tanning

- The maximum shrinkage temperature was achieved with 5% aluminium oxide dose (Fig. 4a)
- Grain of experimental samples are fuller and fibers are more separated compared to control (Fig. 4b)

Figure 4 Shrinkage temperature (a) and SEM images (b) of crust leather samples

Conclusion

- Tanzanian kaolin is a potential source of aluminium suitable for combination tanning
- Mimosa and $Al_2(SO_4)_3$ blend is a pledging eco-friendly leather tanning method
- Leather tanned with mimosa-$Al_2(SO_4)_3$ formulated from Tanzanian kaolin has portrayed good quality

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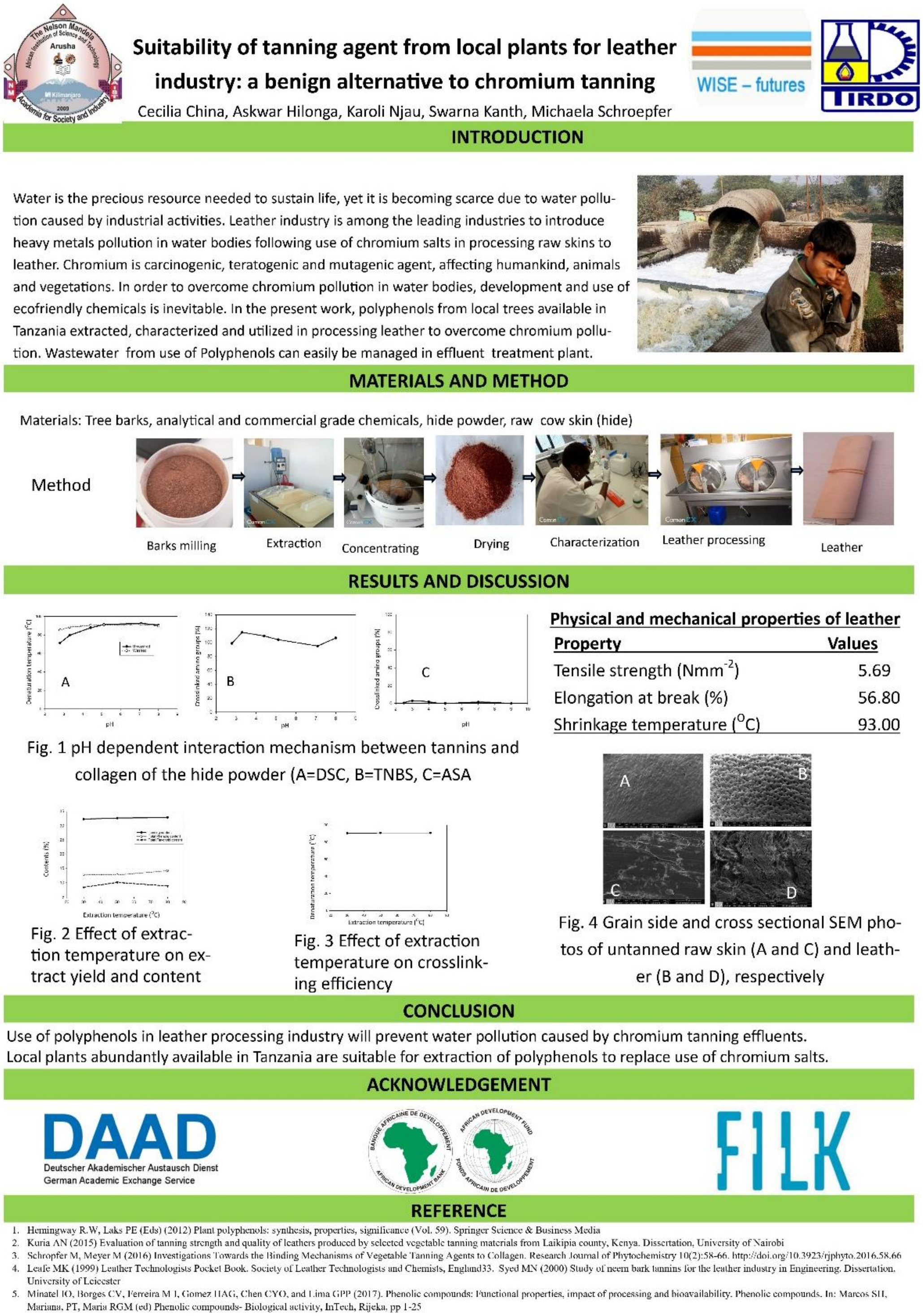

Suitability of tanning agent from local plants for leather industry: a benign alternative to chromium tanning

Cecilia China, Askwar Hilonga, Karoli Njau, Swarna Kanth, Michaela Schroepfer

INTRODUCTION

Water is the precious resource needed to sustain life, yet it is becoming scarce due to water pollution caused by industrial activities. Leather industry is among the leading industries to introduce heavy metals pollution in water bodies following use of chromium salts in processing raw skins to leather. Chromium is carcinogenic, teratogenic and mutagenic agent, affecting humankind, animals and vegetations. In order to overcome chromium pollution in water bodies, development and use of ecofriendly chemicals is inevitable. In the present work, polyphenols from local trees available in Tanzania extracted, characterized and utilized in processing leather to overcome chromium pollution. Wastewater from use of Polyphenols can easily be managed in effluent treatment plant.

MATERIALS AND METHOD

Materials: Tree barks, analytical and commercial grade chemicals, hide powder, raw cow skin (hide)

Method

RESULTS AND DISCUSSION

Fig. 1 pH dependent interaction mechanism between tannins and collagen of the hide powder (A=DSC, B=TNBS, C=ASA

Physical and mechanical properties of leather

Property	Values
Tensile strength (Nmm^{-2})	5.69
Elongation at break (%)	56.80
Shrinkage temperature (^{O}C)	93.00

Fig. 2 Effect of extraction temperature on extract yield and content

Fig. 3 Effect of extraction temperature on crosslinking efficiency

Fig. 4 Grain side and cross sectional SEM photos of untanned raw skin (A and C) and leather (B and D), respectively

CONCLUSION

Use of polyphenols in leather processing industry will prevent water pollution caused by chromium tanning effluents.
Local plants abundantly available in Tanzania are suitable for extraction of polyphenols to replace use of chromium salts.

ACKNOWLEDGEMENT

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5. Minatel IO, Borges CV, Ferreira M I, Gomez HAG, Chen CYO, and Lima GPP (2017). Phenolic compounds: Functional properties, impact of processing and bioavailability. Phenolic compounds. In: Marcos SH, Mariana, PT, Maria RGM (ed) Phenolic compounds- Biological activity, InTech, Rijeka, pp 1-25

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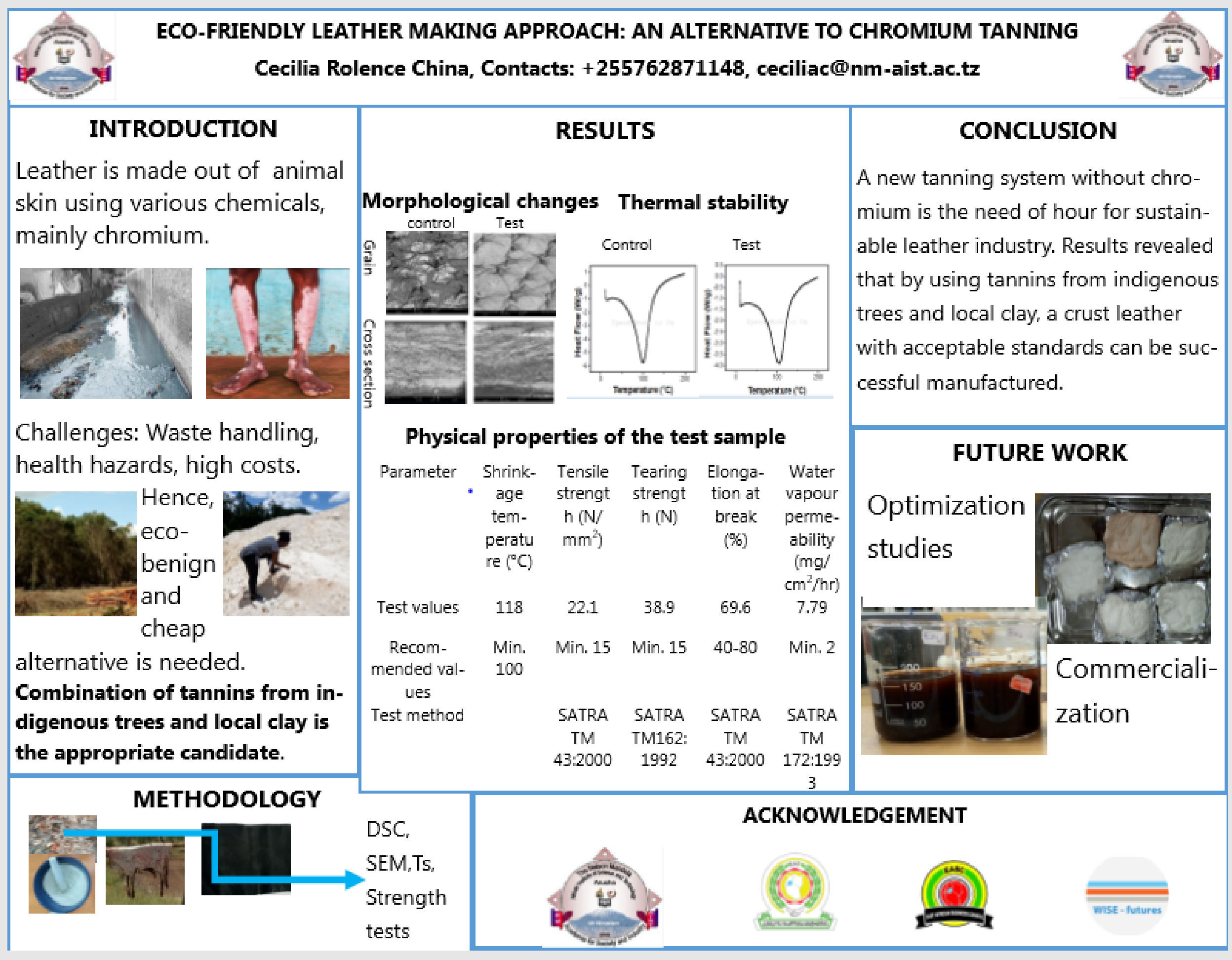

ECO-FRIENDLY LEATHER MAKING APPROACH: AN ALTERNATIVE TO CHROMIUM TANNING

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INTRODUCTION

Leather is made out of animal skin using various chemicals, mainly chromium.

Challenges: Waste handling, health hazards, high costs.

Hence, eco-benign and cheap alternative is needed.

Combination of tannins from indigenous trees and local clay is the appropriate candidate.

RESULTS

Morphological changes

control

Test

Grain

Cross section

Thermal stability

Control

Test

Heat Flow (W/g)

Temperature (°C)

Physical properties of the test sample

Parameter	Shrinkage temperature (°C)	Tensile strength (N/mm²)	Tearing strength (N)	Elongation at break (%)	Water vapour permeability (mg/cm²/hr)
Test values	118	22.1	38.9	69.6	7.79
Recommended values	Min. 100	Min. 15	Min. 15	40-80	Min. 2
Test method		SATRA TM 43:2000	SATRA TM162: 1992	SATRA TM 43:2000	SATRA TM 172:1993

CONCLUSION

A new tanning system without chromium is the need of hour for sustainable leather industry. Results revealed that by using tannins from indigenous trees and local clay, a crust leather with acceptable standards can be successful manufactured.

FUTURE WORK

Optimization studies

Commercialization

METHODOLOGY

DSC, SEM, Ts, Strength tests

ACKNOWLEDGEMENT

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NJIA RAHISI YA KUANDAA DAWA ZA ASILI ZA KUSINDIKA NGOZI KUTOKA KWENYE MITI IPATIKANAYO TANZANIA

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3: FILK - Research Institute of Leather and Plastic Sheeting, Meißner Ring 1-5, 09599 Freiberg, Germany

Utangulizi

- **Tanzania ni nchi ya Pili katika Afrika kwa uwingi wa mifugo, ikizalisha zaidi ya vipande milioni 11 kwa mwaka, lakini uchangiaji wa sekta ya ngozi kwenye pato la taifa bado ni hafifu.**
- **Ngozi zinazosindikwa ni chini ya 50% ya zinazozalishwa, huku zaidi ya 50% ya ngozi ghafi husafirishwa kwenda nje ya nchi au kutupwa majalalani au kupewa mbwa (kielelezo namba 1).**
- **Hali hii inaathiri mchango wa sekta ya ngozi katika kufikia malengo ya Tanzania ya viwanda, ajira kwa vijana na ukuaji wa pato la taifa kwa ujumla.**
- **Sababu kubwa inayochangia ufanisi mdogo wa sekta ni ukosefu wa technolojia sahihi ya kusindika ngozi.**
- **Teknolojia ya kusindika ngozi kwa kutumia chumvi ya kromiam inaathili uwezo wa viwanda vilicyopo nchini kwa sababu ni ghali, inachafua mazingira na kusababisha magonjwa kama kansa**
- **Hivyo basi, kutegemea chumvi ya kromium kutadidimiza sekta ya ngozi nchini Tanzania. Njia mbadala ni muhimu kwa usindikaji ngozi endelevu.**

Hali ya sasa

Hali inayotakiwa

Kielelezo namba 1: Ngozi ghafi zinazozalishwa Tanzania (a) zilizotelekezwa kwenye mabanda ya kukusanyia (b) zinazoliwa na mbwa (c) zinazosafirishwa nje ya nchi (d) uchafuzi wa mazingira

Suluhisho

- **Ubunifu: njia rahisi ya kuandaa dawa za asili kutokana na magome ya miti ipatikanayo Tanzania zenye uwezo wa kusindika ngozi**

Wazo la ubunifu

Utekelezaji wa wazo: kuzalisha dawa za asili kutokana na magome ya miti

Majaribio ya ufanisi wa dawa katika kusindika ngozi

Kelelezo namba 2: Hatua zilizofuatwa katika ubunifu

Faida za ubunifu

- **Kuepuka ucafuzi wa mazingira**
- **Uzalishaji wa gharama nafuu**
- **Kukidhi mahitaji ya viwanda vya ngozi hasa viwanda vidogo (SMEs).**
- **Kuchochea ongezeko la thamani la zao la ngozi**
- **Ongezeko la pesa za kigeni nchini.**
- **Ongezeko la ajira kwa vijana**

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INVIRONMENTALLY FRIENDLY LEATHER PRODUCTION TECHNIQUE USING ORGANIC CHEMICALS FROM LOCAL PLANTS

Cecilia Rolence China

Benefits

versatile leather and leather products

CHROMIUM TANNING

One of the leading chromium pollution source in the world

Environmental challenges

VEGETABLE TANNING

An environmentally responsible and economically viable method

Adherence to the Principles of Green chemistry

1. Prevention
3. Less hazard
4. Safer chemical
6. Energy efficiency
7. Renewable feed-stocks
10. degradable design

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DAAD Deutscher Akademischer Austausch Diens German Academic Exchange Service

FILK

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AMRS 2019
10TH INTERNATIONAL CONFERENCE OF THE
AFRICAN MATERIALS RESEARCH SOCIETY
ARUSHA CITY • TANZANIA

Thermo-stabilization of leather using tannins from *Euclea divinorum* blended with Aluminium sulphate

Cecilia R. China, Askwar Hilonga, Stephen S. Nyandoro, Michaela Schroepfer, Swarna V. Kanth, Michael Meyer and Karoli Njau