TENSILE AND VISCOELASTIC CHARACTERIZATION OF KENYAN INDIGENOUS BORAN COW HIDE DERMIS

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A Research Thesis Submitted to the Graduate School in Partial Fulfillment of the Requirements for the Award of the Master of Science Degree in Physics of Egerton University

EGERTON UNIVERSITY

FEBRUARY, 2016

DECLARATION AND RECOMMENDATION

DECLARATION

This is my original work and has not been submitted in part or whole for an award in any institution.

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DEDICATION

This work is dedicated to my mother, Maxmillah Nasimiyu Murunga for educating me despite her meagre resources; my uncle, Moses Nalyanya Murunga who has been like a father and a friend to me; Ruth Mwenje Lumarai; Elizabeth Sylvia Nanjala; Peter Wanjala and his family; and Mercy Naliaka who supported me in all they could and patiently prayed with me. Lastly, to my father, Nicholas Wafula Lubini, whose desire to have a son in a University, inspired me to work hard.

ABSTRACT

The wide range of applications, the industrial processing techniques and storage of collagenous materials expose them to a variety of environmental conditions such as temperature, humidity and solar ultraviolet (UV) radiations. In this study, a freshly flayed hide from a mature Boran bovine was prepared to pickling stage using conventional tanning processes. The hide was then cut into two halves along the backbone. One half was left at pickled stage while the other half was tanned using Chromium Sulphate. Suitably cut specimens from each pelt in parallel and perpendicular to the backline were then taken to determine their tensile properties using Instron Testing Machine, Model 1101. Effect of direction of sampling, pickling and chrome tanning on the tensile properties was determined. Other suitable samples were exposed to solar radiation for a duration of 0-24 hours and artificial Ultraviolet radiation for 0-30 hours to determine their effects on viscoelastic properties. The samples were conditioned in a standard atmosphere prior to Dynamic Mechanical Analysis. Effects of oscillation frequency and temperature were also determined. Results showed that chrome-tanning significantly increased tensile strength (p=0.0344*)*, storage modulus (E'), complex and dynamic viscosity (η), shear stress (σ) and thermal stability at all frequencies and temperatures. However, it decreased the percentage elongation, loss modulus, tan δ, and shear strain. Hence tanning makes molecular chains difficult to slide over each other when shearing forces are applied. Tanned hide showed stabilized trend in the changes of their viscoelastic properties. Hence, tanning stabilizes leather structure. Bovine hide showed dispersion phenomenon with frequency of 30 Hz probably its natural frequency. Solar radiation decreased storage modulus but as the duration of irradiation increased, the modulus started to increase gradually. Both tan δ and thermal stability decreased progressively with both solar and artificial radiations. Hence sun-drying during tanning can be discouraged especially for strong and stiff leather. Tensile properties showed that Boran bovine hide meets the international UN standards for leather. The study recommends rearing of Boran bovine breed.

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LIST OF ABBREVIATIONS AND ACRONYMS

ASALs	Arid and Semi-Arid Lands
ASTM	American Society of Testing Methods
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimetry
ESA	Ethiopian Standards Agency
FAO	Food and Agriculture Organization
GDP	Gross Domestic Product
GF	Geometrical Factor
ISO	International Standards Organization
IULTCS	International Union of Leather Technologists and Chemists Society
KIRDI	Kenya Industrial Research and Development Institute
RH	Relative Humidity
SATRA	Shoe and Allied Trades Research Association
UNIDO	United Nations Industrial Development Organization
UV	Ultraviolet
UVR	Ultraviolet Radiations

LIST OF SYMBOLS

E’	Storage modulus
E”	Loss modulus
ℓ	Small length
T_d	Denaturation Temperature
T_g	Glass Transition Temperature
T_m	Melting Temperature
T_s	Shrinkage Temperature
α	Significance level
Tan δ	Lag between the tensile stress and strain
ε	Shear strain
η	Dynamic viscosity
η*	Complex Viscosity
λ	Wavelength
σ	Shear stress
ω	Angular frequency
p	Probability of obtaining a result equal to or "more extreme" than what was actually observed, assuming that the null hypothesis is true

CHAPTER ONE

INTRODUCTION

1.1 Background Information

Boran cattle breed are among the predominant indigenous breeds in most African countries (Ojango *et al.*, 2006). It's estimated that 70% of the Kenyan meat production and hence leather comes from Arid and Semi-Arid Lands, whose major adapted cattle breed is indigenous Boran (DAGRIS, 2006; Ojango *et al.*, 2006; Mwinyihija, 2010; Haile *et al.*, 2011). This breed has outstanding adaptive traits that make it survive in this hostile area such as dark pigmentation and black points which protect it against sunburns of the hot Arid and Semi-Arid Lands (ASALs) (Haile-Mariam, 1994; Oklahoma State Education, 2012). Its smooth, loose but motile and shiny coat/skin is another trait associated with the ability to reflect away a high proportion of the solar radiation (Robertshaw and Finch, 1976). Their reasonably large body, thick skin and well-marbled beef with even fat cover make this breed a promising source of beef and hide for production of leather. According to research done by Food and Agricultural Organization (FAO), animal by-products such as hides, skins, leather and leather by-products have potential to generate more revenue percentage compared to the beef itself (FAO, 2010; Haile *et al*., 2011).

Importance of cattle hides to the economy is immense since it offers employment opportunities, a source of livelihood for pastoralist communities, and a raw material for various industries and contributes more than 4% of the annual national Gross Domestic Products (GDP). Furthermore, these raw materials sustain vast number of industries such as tanning, clothing, fashion, footwear, medicine, engineering, food, automotive and sports (Tuckermann *et al.*, 2001, Sturrock *et al.*, 2004). During the processing of leather, all non-collagenous components such as epidermis, fats, hairs, and flesh are discarded except dermal layer, which undergo the pickling and tanning processes (Tuckermann et al, 2001). The main component of this dermal layer is collagen, a fibrous natural biopolymer, of peptide class (Liu et al, 2006; Xing et al, 2011). Although there are several types of collagens, type I forms the major type present in bovine hide, whose diverse applications are attributed to its versatile properties such as high strength, ability to undergo chemical modification such as tanning, gelatization and chromophoric nature (Lee *et al.*, 2001; Xing *et al.*, 2011; Annumary *et al.*, 2013).

Solar and UV radiations have been shown to alter the physical, mechanical and chemical structure of collagen-based materials (Menter *et al.*, 2001; Jariashvili *et al.*, 2012). These radiations cause photopolymerization in the teleopeptide regions of the collagen molecule and some energy causes local heating (Fujimori, 1989; Afaq *et al.*, 2005; Rabotyagova *et al.*, 2008; Ninh *et al.*, 2014). The absorption of these UV radiation is enhanced by the presence of tyrosine and phenylalanine amino acids in the collagen molecule (Fathima *et al.*, 2007). This alters its structure through crosslinks and molecular chain scissions hence mechanical properties (Weadock *et al.*, 1995; Kato *et al.*, 1999; Sionkowska *et al.*, 2006; Fathima *et al.*, 2007; Jariashvili *et al.*, 2012).

Therefore the industrial tanning processes, the range application fields and storage conditions of the leather have a significant effect on the quality of this hide. The processes include solar radiations during sun drying, chrome tanning, high temperatures and accelerated ultraviolet radiations (Larsen, 2000; Thomson, 2002; Metreveli *et al.*, 2010).

Significant researches have been done on tensile properties of camel skins, kangaroo, sheep and goats (Wang and Attenburrow, 1989; Snyman and Jackson-Moss, 2000; Salehi *et al.*, 2013; Samia, 2014). Other studies have characterized collagen on the basis of their viscoelastic properties (Jeyapalina *et al.*, 2007; Chaudhry *et al.*, 2009; Ershad-Langroudi *et al.*, 2012). A number of studies have characterized the influence of UV irradiation on collagenous materials (Miles *et al.*, 2000; Metreveli *et al.*, 2010; Jariashvili *et al.*, 2012; Sionkowska *et al.*, 2013). Effects of key leather making processes on the physical and mechanical properties have been documented (Valeika et al, 2010). A documented research done on Boran Bovine involved enhancing their production (Ojango et al, 2006). However, there was no documented work done on the effect of both solar radiation and artificial UV radiation on the viscoelastic properties of indigenous bovine hides. Therefore, this study investigated the tensile properties of both pickled and tanned hide of Kenyan indigenous Boran hide, effect of solar radiation and artificial ultraviolet radiation on their viscoelastic properties and thermal stability.

1.2 Statement of the Problem

Bovine hide is an important by-product of the meat industry. It is the main raw material for the production of leather and other related diverse products in bioengineering and food processing. These applications of hide are determined by the mechanical properties of the hide such as viscoelastic and tensile properties. These properties depend on the animal breed, age, origin, living conditions, nutrition and other environmental factors. In addition, the industrial processing of hide into finished leather products and the use of the products exposes them to harsh environmental factors such as electromagnetic radiations, solar radiations, heat, humidity, and mechanical stress and strain. Manufacturers and designers of leather products need information about these properties and how they are affected by various environmental conditions in order to produce high quality products and hence meet the demands of the consumers. Although some of these properties of hide have been investigated, the tensile properties of Kenyan indigenous breeds and the effect of various environmental factors have not been investigated. This study focused on the effect of tanning, solar radiations and artificial UV radiations on the tensile and viscoelastic properties of a mature indigenous Boran bovine hide. Tensile strength, tear strength, percentage elongation, storage and loss moduli, dynamic viscosity and thermal stability of hide are critical parameters for assessing the quality of hide and by extension leather. These parameters and the effect of tanning and direction of sampling and UV and solar irradiation on them were investigated.

1.3 Objectives

1.3.1 General Objective

To investigate the effect of tanning, solar radiations and artificial UV radiations on the tensile and viscoelastic properties of Kenyan indigenous Boran bovine hide.

1.3.2 Specific Objectives

i) To determine the effect of direction of sampling and tanning on the tensile strength, tear strength and percentage elongation of bovine hide.
ii) To investigate the effect of tanning and terrestrial solar radiation on the viscoelasticity and thermal stability of bovine hide.
iii) To investigate the effect of tanning and artificial UV radiation on viscoelasticity of bovine hide.

1.4 Hypotheses (H_o)

i) Direction of sampling and tanning and have no significant effect on the tensile properties of bovine hide.

ii) Tanning and terrestrial solar radiation have no effect on the viscoelastic properties and thermal stability of bovine hide.

iii) Tanning and artificial UV radiation have no effect on the storage modulus, tan delta and dynamic viscosity of bovine hide.

1.5 Justification for the study

The leather industry offers significant employment opportunities and is a major source of livelihood to the people of Arid and Semi-Arid Lands (ASALs) in Kenya. Its foreign exchange earnings contribute approximately 4% of the annual National GDP. However, currently the performance of the sector is far below its potential due to a number of factors, which include the relatively low quality of the leather getting to the world market. Leather quality is affected by factors such as management practices of the cattle and the raw materials and the leather manufacturing processes such as sun drying and chemical-based tanning. This study sought to determine the effect of UV radiation, temperature and tanning on the tensile and viscoelastic properties of bovine hide, which are indicative of its quality. The findings of this study will inform decisions on management practices of livestock and the raw material and the leather manufacturing process for quality hides and leather.

CHAPTER TWO

LITERATURE REVIEW

2.1 Animal hides and skins

Animal hide and skin is the largest organ that forms a physical protective barrier on the living animal body comprising of 4-12% of the live weight of the animal (Ockerman and Hansen, 2000). Collagen, a polypeptide natural biopolymer, forms about 98% of the fibrous proteins of this hide and skin (Wenger *et al*., 2007). Unlike human skin that develops from cells, animal hide and skin collagen is formed from amino acids which connect together to form tropocollagen of long chains (Lewis, 1989). A typical raw hide comprises of not only collagen but also other soluble proteins, mucopolysaccharides, keratin, elastin, fats and water among others. During the initial of the leather making processes, most of the non-collagenous materials are removed from the skin, followed by the addition of tanning agents to confer stability and an aesthetic feel to the collagen fibres. The hides and skins of the majority of the indigenous breeds have international reputation for their unique natural substance of fineness, flexibility, strength, and compactness of texture (Asfaw, 1997).

The leather forming layer of the hide, dermis, is divided into two layers; corium and grain. Corium is mainly composed of fibre bundles interwoven in three-dimensions. A fibre bundle is made up of a number of elementary fibres held up by sheaths of reticular tissue and interfibrillar proteins. These fibre bundles subdivide into smaller units or elementary fibres as they approach the grain. The angle of weave of the fibre bundles is normally defined as the angle the fibres make with the limiting membrane on the flesh side. In general, the fibres are woven in such a way that the angle of weave is low near the flesh side and increases toward 90 degrees in the centre and then tends to be low again as the fibres approach the grain. However, this general pattern varies significantly between the types of animals. Similarly, variations in the environmental factors such as UV radiation and temperatures, the hide’s physical, chemical and structural characteristics change hence mechanical properties (Daniels and Landman, 2005; Liu *et al*., 2006).

2.1.1 Structure of collagen

Collagen molecule is composed of three polypeptide α chains each with a left-handed, polyproline II-type conformation (Gelse *et al*., 2003). These helices are twisted together to form a right-handed coil, triple-helix called quaternary collagen structure held together by hydrogen bonds, intramolecular van der Waals bonds and covalent bonds as shown in figure 2.1 (Brinckmann *et al.*, 2005). The structure also has right-handed microfibrils and fibrils of diameter approximately 40 nm and 100-200 nm respectively that form collagen fibres mechanical strength to the structure (Kaplan and Xu, 2004). Collagen has distinctive periodic arrangement of amino acids in each of the three chains of its subunits. Each unit is repeatedly arranged as Gly-X-Y for glycine (Gly)-proline (Pro)-X or Gly-X-hydroxyproline (Hyp), where a third of the sequence is Gly, while X and Y are other residues of amino acids. X and Y-position are almost exclusively occupied by Pro and Hyp respectively constituting a sixth of the sequence (Gorham *et al*., 1992). This periodic pattern and high content of Gly is only found in elastin but not in globular proteins. The primary sequence of this fibril assembly and conformation determines the physical properties of the entire hide and leather (Persikov *et al*., 2005). Between Gly and Pro super-coil is the hydrogen bonds from both the neighboring chains and water-network between the several carbonyl and hydroxyl peptides residues (Brinckmann *et al*., 2005). Of the 26 types of collagen types, the main structural component of leather and skin is type I, which forms the basis strong fibril (Wells *et al.*, 2013). The helical part is further positioned by the non-helical parts (9-26) amino acids called teleopeptide (amorphous collagen) that is crucial in the formation of fibril and the natural crosslinking. These native collagens triple helix are the most sensitive to UV-254nm radiation due to the presence of aromatic amino acids such as tyrosine and phenylalanine (Rabotyagova *et al.*, 2008).

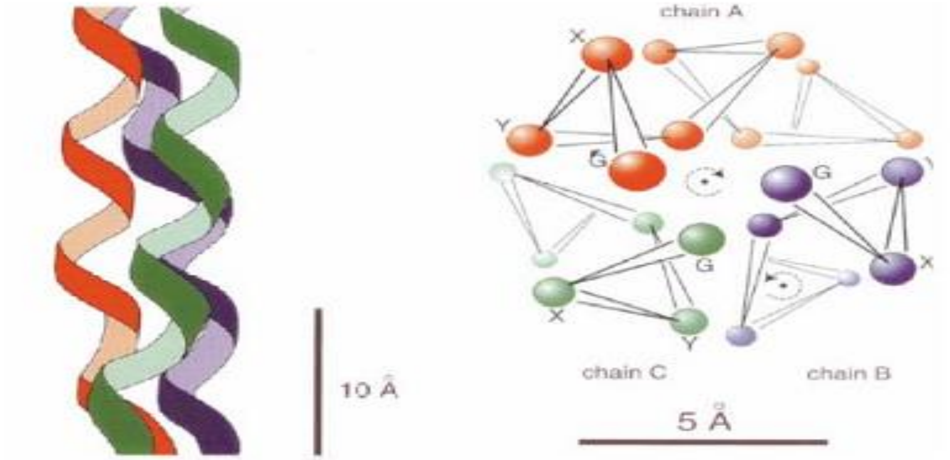

Figure 2.1: The structure of collagen triple-helix (Beck and Brodsky, 1998)

2.1.2 Dynamic Mechanical and Thermal Analysis (DMTA) of Collagen-based materials

As the temperature increases, additional molecular chain relaxations can occur, which markedly change the flexibility of the polymer and hence its viscoelastic properties (Aklonis and McKnight, 1983). The distinct temperature, at which the material's properties change profoundly, is called the viscoelastic transition temperature. The existence of these viscoelastic transitions becomes apparent when the modulus, representing the stiffness of a given material, is plotted as a function of temperature. The major viscoelastic transition of an amorphous polymer is called the glass transition (T_g) whereas the major transition of a crystalline polymer is melting (T_m). Fibrous structural collagen and keratin show structural stability that confer both mechanical and thermal stability. The strength of bonding between collagen molecules increases the structural mechanical stability by restricting the free movement of the individual collagen molecules (Miles and Burjanadze, 2001; Liu *et al.*, 2009). The strength of bonding can increase as a result of molecules crosslinking e.g. tanning introduces covalent or coordative bonds. On heating, these bonds will break or collapse due to extensive breakage of hydrogen bonds and van der Waals bonds at a certain critical temperature known as the shrinkage temperature (T_s) (Samoillan *et al.*, 1999; Miles and Burjanadze, 2001). The shrinking or denaturation results directly from melting of the crystalline triple-helix of collagen (Cucos *et al.,* 2011). The increased structural stability and thermal stability is indicated by the increased shrinkage temperature in the Dynamic Mechanical Analysis (DMA) (Haroun *et al.*, 2009). In DMA, these temperatures correspond to the peaks in tan δ (Nguyen *et al.*, 1974). In collagenous materials, three peaks have been identified and are referred to as secondary transitions (Menard, 1999). The first stage of the transition is the true melting of fibrils into dissociated/random coil collagen. The second stage could be the collapse transition of dissociated collagen into shrunken collagen. In fibrils, the dissociated collagen could be restricted from collapsing into a random coil by intermolecular crosslinking. Once the heat labile crosslinks are broken, then dissociated collagen molecules are free to collapse to the shrunken state (Pietrucha, 2005). The shrinking temperature is also referred to as the melting point of collagen. In this work, the words melting, denaturation and shrinking have been used to refer to the same phase transition of collagen. Covalent bridges increase the melting temperature and water depresses the melting temperature (Cucos and Budrugeac, 2010).

In dynamic mechanical analysis of collagen based materials, leather has shown low values of initial storage modulus (E') which slightly increases on heating up to about 180–200 °C. Above this temperature, a rapid increase is seen, which could be due to additional cross-linking of the collagen fibrils by the excess tannins. Beyond the temperatures 230-250 ^{0}C, the materials begin to decompose as indicated by sharp decrease in E' due to denaturation or melting of crystalline collagen (Cohen *et al.*, 2000; Budrugeac *et al.*, 2004). In Differential Scanning Calorimetry (DSC), collagen based materials have exhibited a phase transition or melting in the temperature range of 210-260 ^{0}C, characterized by an endothermic peak in the DSC curve and an abrupt decrease of E'. Using Dynamic Mechanical Analysis (DMA), Thermo-Mechanical Analysis (TMA) and Derivative Thermal Analysis (DTA), Nguyen *et al*. (1974) confirmed the melting temperature of dry pure collagen from bovine tendon to be around 218 ^{0}C. Budrugeac and Miu (2008) working on leather and parchments using DSC analysis pointed out that the first endothermic peak is due to dehydration at around 100 ^{0}C and the second peak is due to melting of the crystalline zone of collagen at temperature between 205 ^{0}C and 245 ^{0}C. In a study by Cucos *et al.* (2011) later using both DMA and DSC, it was observed that all the collagen-based materials exhibit a decrease in the storage modulus at temperatures above 200 ^{0}C, due to the melting of crystalline zone of collagen.

2.1.3 Collagen and Water

Under high humidity, water is absorbed and is uniformly distributed within the structure or heterogeneously located in specific clusters at polar sites and free volume locations in collagens (Nguyen *et al*., 1974). This creates water bridges that provide hydrogen bonds that hold the triple helical structure of collagen together alongside inter/intra chain hydrogen bonds (Jeyapalina *et al.*, 2007). This enhances the strength and the modulus of the polymer (Jankauskaite *et al.*, 2004). On the other hand, dehydration introduces inter-fibre sticking that affect the physical properties of collagen (Haines, 1991). As the water content falls in the internal capillaries, so the surface tension of the water begins to exert a pull on the walls of the capillaries, bringing them closer together until the fibril surfaces stick. Other experiments have observed that hardness and E' decrease remarkably with humidity (Altaf *et al.*, 2011; Hu *et al.*, 2013). A study by Li *et al.* (2009) showed that at high moisture content of around 60 % Relative Humidity, leather exhibits a non-linear stress-strain relation.

2.1.4 Collagenous biomaterials and UV radiation

When collagenous biomaterials are exposed to the solar radiation, the absorbed energy induces photochemical reactions by radical mechanisms. Firstly, chemical compounds split off and free radicals are formed. Secondly, these radicals react immediately with oxygen to form peroxide radicals. Peroxide radicals further react with the organic constituents of leather, and dyes, tanning agents and fat liquors, breaking some of the bonds between the said products and collagen (de Volder *et al.*, 2007). Breaking the bonds affects mechanical properties (Larsen, 2000; Thomson, 2002; Sionkowska *et al.*, 2006). Native collagen triple-helix absorb these radiation especially UV-254nm causing collagen structural damage (Afaq *et al.*, 2005; Rabotyagova *et al.*, 2008; Lapshin *et al.*, 2010; Metreveli *et al.*, 2010). Structural damage leads to structural scission of –OH, decarboxylation (structural scission of –C=O), hydrogen abstraction (structural scission of –N–H) and general oxidative degradation (Tyan *et al.*, 2002; Sionkowska *et al.*, 2006). Destruction of collagen triple-helix leads to rapid and extensive peptide bond scission events through the free radical reactions (Miles *et al.*, 2000). Some of the radicals originate from the aromatic amino acids found in collagen that form primary source of free electrons. The formed free radicals interact with other collagen molecules and water, and propagate impact on collagen degradation (Rabotyagova *et al.*, 2008). This process decreases the stability of fragmented triple-helices, increasing the chain scission with increasing UV-C radiation (Khan *et al.*, 2002; Herascu *et al.*, 2008; Jariashvili *et al.*, 2012). One hour of irradiation is sufficient to completely change the collagen conformational state (Metreveli *et al.*, 2010). Proline residues are more susceptible to UV damage than hydroxyproline. Thus, although the UV damage to collagen peptides is non-specific, there appears to be a high preference for the cleavage between Gly and Pro (X position) peptide bonds, which could be the most targeted site prone for UV damage in collagen (Jariashvili *et al.*, 2012).

2.2 Solar and UV radiations

UV radiation forms 6.8% of the total solar radiation reaching the earth's surface of wavelength from 10 - 400 nm with energy range 3 -30 eV (Mishra *et al.*, 2011) as shown in figure 2.2. Three bands are relevant: UV-A, also called near UV, long wave UV, or black light region; UV-B, called mid-UV, erythema band or actinic UV; and UV-C, also called far UV or germicidal radiation. The band UV-C (100 - 280 nm), medium wavelengths UV-B (280 - 320 nm), and long wavelengths UV-A (320 - 400 nm) (Afaq *et al.*, 2005; Saraf *et al.*, 2007). The spectral region below 180 nm is called vacuum UV. The band UV-C which is extremely damaging to the collagen, even for very short exposure is absorbed by molecular oxygen and ozone in the Earth's atmosphere (Afaq *et al*., 2005). The UV radiation content in the terrestrial Solar radiation comprises of 95-98% UV-A and 2-5% UV-B, all the UV-C being absorbed by stratospheric ozone (Mishra *et al.*, 2011). Solar UV-B radiation at any location, in cloudless sky conditions, depends on the solar zenith angle, column ozone content and column aerosol content as well the altitude of the observation site (McKinlay and Diffey, 1987). Among all, ultraviolet light is the most harmful to the collagen (Svobodova *et al*., 2003). The amount of ultraviolet (UV) radiation reaching the earth's surface has markedly increased in recent years due to ozone layer depletion (McKenzie *et al.*, 2003).

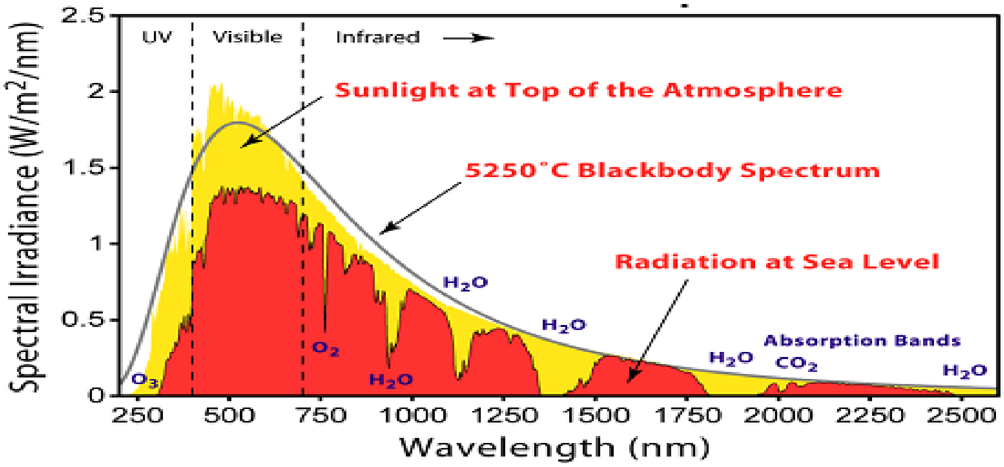

Figure 2.2: Solar Radiation Spectrum (Mishra *et al.*, 2011)

2.3 Dynamic Mechanical Analysis (DMA)

DMA is a combination of thermal and rheological analysis, which provides corresponding values of thermo-mechanical properties under dynamic loads, especially for polymers and polymer-based composites. It gives the possibility to determine the time-temperature or frequency-temperature dependence (Katumin *et al.*, 2010). During experimental runs, the DMA measures the raw signals of force, amplitude of deformation, and phase angle of the sample in response to the applied oscillating force over a range of temperatures and /or frequencies. It then uses amplitudes of deformation to compute the complex stiffness, which together with the phase angle is applied to calculate the storage stiffness and loss stiffness. The instrument then calculates the storage and loss moduli by multiplying the raw stiffness measurements by the appropriate Geometric Factor (Lee-Sullivan and Dykeman, 2000). Measurements of loss modulus (E'') and storage modulus (E') and the tan δ are obtained directly from the DMA by the help of the thermal analysis software. Typical values of dynamic moduli for polymers range from 10^6-10^{12} Pa depending on the type of polymer, temperature and frequency (Lakes, 2004). Calibration of the DMA using standard samples must precede any measurements to ensure reliability of the machines output data. The output is in graphical form over a range of temperature, time and frequencies. It can operate at the temperatures ranging from -145 ^{0}C to 600 ^{0}C with heating rate of up to 50 ^{0}C per minute and can work with samples that are bulk solid, flimsies, fiber, gel or viscous liquid form. It gives a range of clamps such as dual or single cantilever, compression, film tension or fiber film and three point bending depending on the nature and geometry of samples under study. The wide range of clamps allows measurements of properties such as modulus, damping factor, creep, stress relaxation, glass transition and softening points to be accurately made.

2.3.1 Viscoelasticity

When a viscoelastic material is subjected to a sinusoidal varying tensile strain at a frequency below resonant value, under steady state conditions, the stress, σ, sustained by the sample is also sinusoidal; but the stress is out of phase with the induced strain by an angle δ (Wu *et al.*, 2009) as shown in figure 2.3. This phase lag is due to the excess time necessary for molecular motions and relaxations to occur. Therefore dynamic strain, ε, can be given as

$$\varepsilon = \varepsilon_0 \cos \omega t, \qquad (2.1)$$

and dynamic stress, σ as

$$\sigma = \sigma_0 \cos(\omega t + \delta)$$

$$= \sigma_0 \cos \delta \cos \omega t - \sigma_0 \sin \delta \sin \omega t, \qquad (2.2)$$

where ω is the angular frequency of the varying tensile strain, t is the time and $\sigma_\circ$ and $\varepsilon_\circ$ are the amplitudes of stress σ and strain ε, respectively.

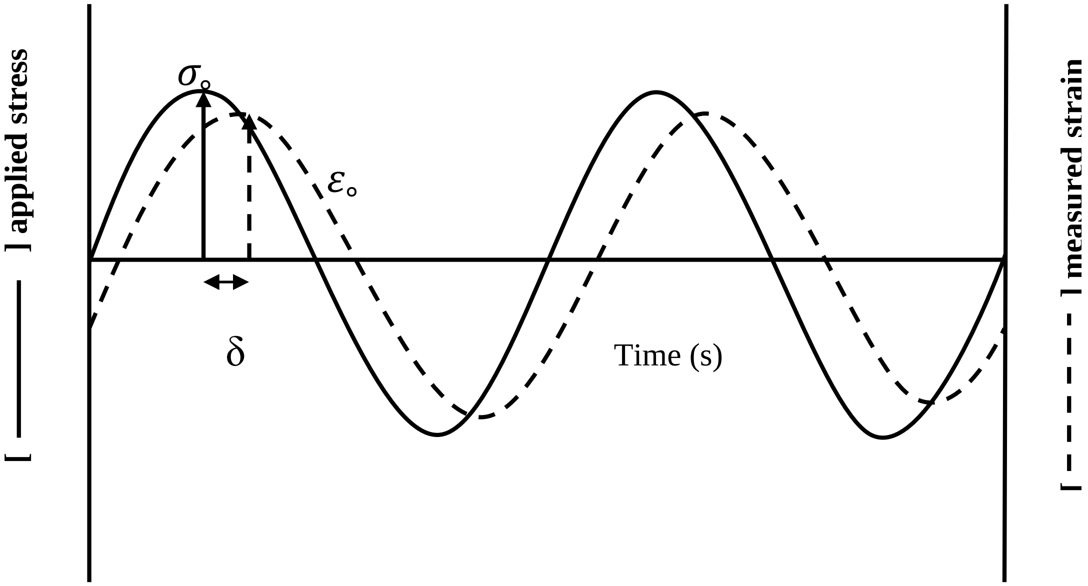

Figure 2.3: Response of a viscoelastic material (stress is out of phase with strain)

From equation (2.1), it follows that the applied stress consists of two components: $\sigma_\circ cos\delta$, which is in-phase with tensile strain and $\sigma_\circ sin\delta$, which is 90° out of phase with tensile strain. Therefore the material behaves partly as a solid and partly as a viscous liquid and the stress-strain relationship is expressed as;

$$\sigma = \varepsilon_0 E' \cos \omega t - \varepsilon o E'' \sin \omega t \qquad (2.3)$$

Dividing stress by strain yields two moduli: the storage, E' and the loss modulus, E'', which are given by;

$$E' = \frac{\sigma_\circ}{\varepsilon_\circ} \cos \delta \qquad (2.4)$$

and

$$E'' = \frac{\sigma_\circ}{\varepsilon_\circ} \sin \delta \qquad (2.5)$$

Hence strain and stress can be written as $\varepsilon = \varepsilon_\circ expi\omega t$ and $\sigma = \sigma_\circ expi(\omega t + \delta)$, respectively.

Equations (2.4) and (2.5) suggest that tensile modulus can be specified in complex form E^*. Thus, the strain and the stress cycles can be represented by the real parts of $\varepsilon^* = \varepsilon_\circ expi\omega t$ and $\sigma^* = \sigma_\circ expi(\omega t + \delta)$ respectively. Therefore,

$$E^* = \frac{\sigma^*}{\varepsilon^*} = \frac{\sigma_\circ}{\varepsilon_\circ} e^{i\delta} = \frac{\sigma_\circ}{\varepsilon_\circ} (\cos \delta + i \sin \delta) = (E' + iE'') \qquad (2.6)$$

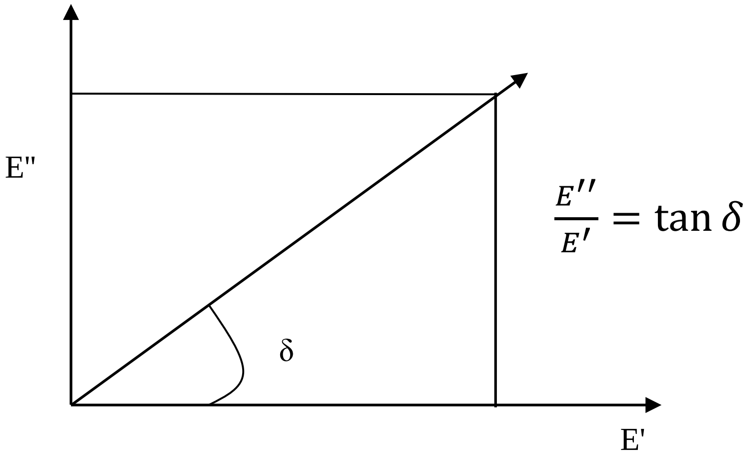

Figure 2.4: Storage modulus, E', loss modulus, E'' and tan δ

The real part of the modulus, E' in equation (2.6) is the storage modulus (E'). It is proportional to the peak of energy stored. It represents the elastic behavior of the material. Stiffness, K_s, of a specimen is defined as the ratio of the applied force to the amplitude of the deformation. It's an extrinsic property that is dependent on its geometry and relates to the E' by;

$$E' = K_s x(GF) = K_s x\left(\frac{L}{A}\right) \tag{2.7}$$

Where E' is the storage modulus and dimensions of the sample used to calculate Geometrical Factor (GF). For a sample of rectangular cross-section, the GF is related to the dimensions of the sample through equation 2.8,

$$GF = \frac{Length}{Cross\ section\ Area}. \tag{2.8}$$

The imaginary part of the modulus E'' is out phase with the strain in equation (2.6), is proportional to the net energy dissipated per cycle and is known as the loss modulus. It represents the viscous part of the material response. The ratio $\frac{E''}{E'} = \tan\delta$ is termed as the loss factor or damping factor as shown in figure 4. It's a dimensionless quantity and is the rate of energy lost per cycle to the energy stored and hence recovered per cycle. This loss factor gives information about the samples' viscous or elastic behavior. The storage modulus gives the amount of energy a sample stores, the loss modulus gives the amount of energy dissipated by the sample when a sinusoidal force is applied. The loss factor also called the damping factor is measured as an angle that indicates lag between the tensile stress and strain. Loss factor gives information regarding sample's viscous or elastic nature. The three parameters, E', E'' and $\tan\delta$ depend on the test frequency and/or temperature (Sperling, 2006). The parameters are used to characterize dynamic mechanical properties either at a given frequency or temperature or, preferably over a range of these variables (Sperling, 2006). They also play key role in evaluation of polymeric-based materials from the view point of performance (Kalachandra *et al.*, 1995).

2.3.2 Viscoelastic models

Mechanical models have been created to better visualize the stress and strain relationship in viscoelastic materials. These models use springs and dashpots to represent the dual nature of the behavior. These models include the Maxwell's model, the Kelvin-Voigt model and the Burger model:

Maxwell's Model

A Maxwell element exhibits a dynamic response. It consists of a purely elastic spring and a purely viscous damper connected in series as shown in figure 2.5. The application of a sinusoidal stress to a Maxwell element produces a strain with the same frequency as, but out of phase with, the stress. If E_M is the elastic modulus of the spring and η_M is the viscosity of the dashpot, then we have;

$$\sigma_M = E_M \varepsilon_{spring} = \eta_M \varepsilon_{dashpot}$$

and

$$\varepsilon_M = \varepsilon_{spring} + \varepsilon_{dashpot} = \frac{\sigma_M}{E_M} + \frac{\sigma_M}{\eta_M}, \qquad (2.9)$$

where subscript M denotes Maxwell, ε is the strain in the material, σ is the stress and E is the elastic modulus.

In Maxwell's model, the total strain is the summation of the individual strains of the spring and dashpot, the strain rate of an ideal spring and dashpot is given by;

$$\frac{d\varepsilon}{dt} = \left(\frac{1}{E}\right)\frac{d\sigma}{dt} + \frac{\sigma}{\eta} \tag{2.10}$$

where η is viscosity. For stress relaxation experiment, deformation at constant strain, then

$$\frac{d\varepsilon}{dt} = 0 = \left(\frac{1}{E}\right)\frac{d\sigma}{dt} + \frac{\sigma}{\eta}.$$

This implies that

$$\left(\frac{1}{E}\right)\frac{d\sigma}{dt} = -\frac{\sigma}{\eta}.$$

Solving for the equation,

$$\frac{d\sigma}{dt} = -\frac{E}{\eta}dt = -\frac{dt}{\tau},$$

where $\tau = \frac{\eta}{E}$, $ln\sigma(t) = ln\sigma_0 - \frac{dt}{\tau}$.

This implies that

$\sigma(t) = \exp(-\frac{t}{\tau})$. The stress decays to zero at infinite time.

$$E(t) = \frac{\sigma(t)}{\varepsilon o} = \frac{\sigma o}{\varepsilon o} \exp(-t/\tau) = E \exp(-t/\tau) \tag{2.11}$$

The response of the Maxwell model in a stress relaxation experiments corresponds to an elastic solid at $t \ll \tau$ and to a viscous fluid at $t \gg \tau$.

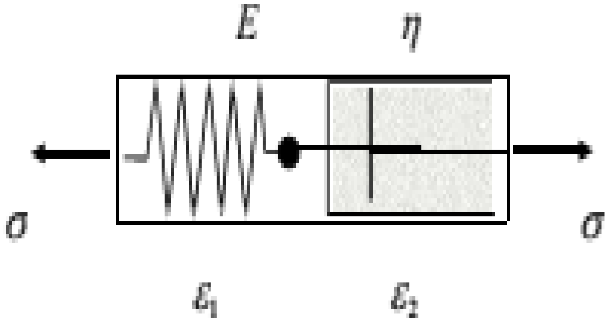

Figure 2.5: Schematic diagram for the Maxwell Model

The Kelvin-Voigt Model

This is a parallel assembly of dashpot and spring as shown in figure 2.6. In this case, the deformation are equal but the stresses are different:

$$\varepsilon_{Spring} = \varepsilon_{dashpot}$$

and $$\sigma_{spring} \neq \sigma_{dashpot},$$

where

$$\sigma_{spring} = E.\,\varepsilon_{spring}$$

and $\sigma_{dashpot} = \eta.\frac{d\varepsilon_{dash}}{dt}$, then

$$\sigma = E\varepsilon + \eta\frac{d\varepsilon}{dt}$$

If E_V is the elastic modulus of the spring, η_V is the viscosity of the dashpot and V denotes the Voigt model, then the constitutive relation can be given as

$\varepsilon_V = \varepsilon_{spring} = \varepsilon_{dashpot}$ and $\sigma_V = E_V\varepsilon_{spring} + \eta_V\varepsilon_{dashpot}$

$$\sigma_V = E\varepsilon + \eta\frac{d\varepsilon}{dt} \tag{2.12}$$

Stress relaxation experiment, deformation at constant strain, $\frac{d\varepsilon}{dt} = 0$

$$\sigma_V = E\varepsilon. \tag{2.13}$$

While this model provides a more reasonable representation of creep behaviour, it does not represent the stress-relaxation behaviour adequately.

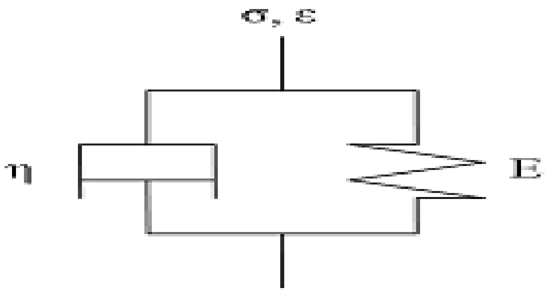

Figure 2.6: Schematic diagram for the Kelvin-Voigt Model

The Burger Model

According to the theory of viscoelasticity, the Burger model can be used to explain the rheological behavior of polymers in the dynamic mechanical analysis. The Burger model is a serial assembly of the Maxwell model (serial connection of spring/dashpot) and the Kelvin-Voigt model (Shames and Cozzarelli, 1992) as shown in figure 2.7.

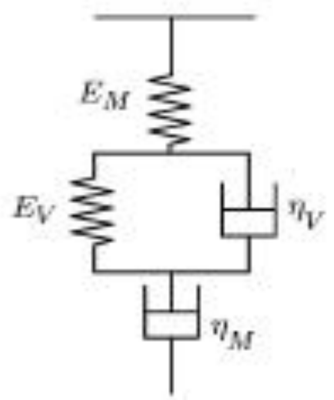

Figure 2.7: The Burger model of viscoelasticity (Li *et al.*, 2009)

2.4 Tensile Properties

Tensile properties are important functional and performance physical and mechanical properties of leather (Basil-Jones *et al.*, 2013). These properties include tensile strength, tear strength, percentage elongation among others. They determine both routine quality and serviceability assessment of the material, leather's usability, the state of usage, and inform the entire process of manufacturing goods from leather (Basil-Jones *et al.,* 2013). The properties vary according to the quantity of skin constituents (follicles, glands and erector muscles) and quantity of collagen fibre bundles (Jacinto *et al.*, 2004). The content of the rigid native triple-helices and fibril network of the collagen determine the strength and the compactness of the hide (Muralidhan and Ramesh, 2005).

2.4.1 Tensile Strength

Tensile strength is the ability of a material to withstand pulling/tensile force. It's measured in force per unit cross-sectional area. This property specifies the point at which a material goes from elastic to plastic deformation or stress needed to split a material apart.

There are kinds of tensile strength: yield strength that gives stress a material can withstand without permanent deformation, ultimate strength which is the maximum stress a material can withstand and breaking stress that gives a point of rupture on the stress-strain curve. Tensile strength sets a limit state at which the tensile stress leads to tensile failure in ductile failure way or brittle failure way. It determines how much a material elongates before hitting ultimate tensile strength and how much load a piece of material can accommodate before it loses its structural integrity. Here, two vises apply tension to a specimen by pulling at it, stretching the specimen until it fails. The maximum force it can withstand before breaking is recorded together with the elongation of the sample clamped between the vises. In leather, tensile strength is high where fibres are aligned more in the same direction as the applied stresses. In a case where fibres are aligned more in a direction normal to the stresses applied, the tensile strength is low (Salehi *et al.*, 2013). Tensile strength determines the structural resistance of leather to tensile forces hence its state and usability (SATRA, 2011; ESA, 2012).

2.4.2 Tear Strength

Tear strength is a measure of the resistance of a material to tear forces. The tear strength of a notched specimen is calculated by the maximum force or average of the peak forces recorded by the thickness of the material. The highest force exerted during tearing of the test piece is recorded and expressed in Newtons and the thickness is expressed in millimetres. Hence tear strength is measured in N/mm (Cloete *et al*., 2006). A rectangular test sample with a hole of specified shape is placed over turned up ends of a pair of holders attached to the jaws of a testing machine. A uniform pulling force is applied until breaking/deformation occurs. Tear strength is then calculated by dividing the force applied by the thickness of the material. It also depends on the viscoelastic and other dissipative processes occurring in the material. In bovine hide, this strength is contributed by the elastin and collagen bundles in the hide (Salehi *et al.*, 2013).

Tear strength of bovine hide has been correlated with collagen fibril diameters, showing that thicker fibrils give stronger material (Wells *et al.*, 2013). Collagen fibril orientation and orientation index (OI) vary significantly with sampling positions through the thickness of the skin in a consistent way (Basil-Jones *et al.*, 2013). The amount of collagen varies through the thickness of the leather from the grain to the corium, with a greater concentration of crystalline collagen measured toward the corium side. Stronger leather has the fibrils arranged mostly parallel to the plane of the leather surface (high OI), while weaker leather has more out-of-plane fibrils (low OI). The amount of collagen present depends on the breed of the animal, origin, sex and the age (Jacinto *et al*., 2004; Salehi *et al.*, 2013). Hence the quality of leather is intrinsically determined by the animal's breed.

2.4.3 Percentage Elongation

Percentage Elongation is a vital characteristic in leather industry: it determines the elasticity of a material. Upper leather and footwear should possess high flexibility to prevent the appearance of cracks and tears in the ball area (SATRA, 2011; ESA, 2012). High elasticity allows the material to withstand the elongation stresses to which it is subjected during footwear lasting, especially on the toe area (INESCOP, 2013). The percent elongation at failure is the plastic extension of the specimen at failure expressed as the change in original gage length divided by the original gauge length. This extension is the sum of the uniform and non-uniform elongations. Low elongation value results in easy tear while a high elongation value causes leather goods to become deformed very quickly or even lose usability. If stretched under the influence of a force, leather, just like a wire, first gets thinner and then breaks. Leather's elongation is directly related to fiber structure, orientation and fiber direction.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Sample preparation

A freshly flayed hide, commercially procured from Dagoreti Slaughter house, Nairobi (Kenya), was prepared using standard tannery chemicals process shown in table 3.1.

Table 3.1: Sample preparation recipe for pickling and tanning

Process/ Step	**(%) Chemicals**	**Temp (°C)**	**Time**	**Remarks**
Washing	100% H_2O, detergent	23-25	10 min	Drain
Liming & Unhairing	100% H_2O,	23-25	1hr	Drum speed=2 – 3 r.p.m
	1.5% Na_2S,			
	1% $Ca(OH)_2$ (Lime),			
	Add:			
	100% H_2O,		1hr	
	1% Na_2S			
	1% $Ca(OH)_2$ (Lime)			pH =12
	Add:			Drain
	50% H_2O		16 hrs	Fleshing and scudding
	1% $Ca(OH)_2$ (Lime			
Washing	300% H_2O,	25	10 min	Drain
Deliming	100% H_2O	25	1hr	
	2% $(NH_4)_2SO_4$,			P.H.=8.3
	1% Sodium metabisulphite			x-section clear to phenolthalein
Bating	0.2% -microbates-	35-37	1	Drum speed=3 r.p.m
	1600 LVU,			Drain
Washing	200% H_2O,	20-25	20 min	
Pickling	80% H_2O,	20-22	10 min	Drum speed=3 rpm
	8% NaCl			
	1%H_2SO_4(98%),(1:10)			
	1% Sodium Formate,			
			1 hr	P.H.=2.5
Pelt was then sided into two identical halves along the backbone, one half for tanning				
Tanning	6% Chromium Sulphate, (33% basic)	25-27		Drum speed= 3 rpm
	Add		3 hrs	Penetration complete through x-section pH = 3.0
	0.5% Fungicide		30min	Drain
Basification	0.5% $NaHCO_3$ (1:10)		20 min	
	Add			
	0.5% $NaHCO_3$ (1:10)		20 min	Final pH = 3.6
	Add		20 min	Shrinkage temp = 100^{0}C
	0.5% $NaHCO_3$ (1:10)			
Drain& Washing	200% H_2O,	25	20 min	Drain
Horse up				
Sammy				
Splitting				Split 1.0 mm

All specimens were sampled/cut using a press knife, both along the backbone direction and in the perpendicular direction as illustrated in figure 3.1, according to the official sampling method and sampling location as specified by ISO 2418: 2002. Sampling direction refers to the orientation of cutting the hide with respect to the backbone.

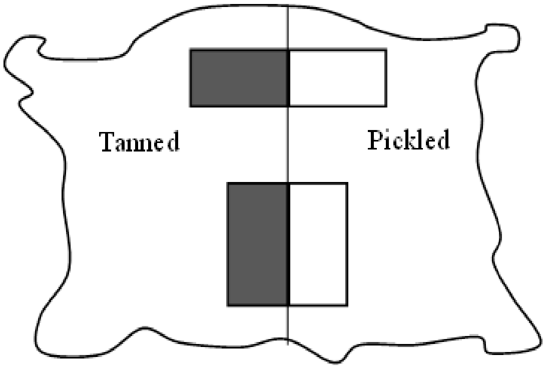

Figure 3.1: Schematic illustration of the sampling position and method for hide

The press knife cut out the specimen such that the angle formed at the cutting edge between the internal and external surfaces of the press knife was about 20° and the depth of the wedge of the cutting knife, *d* was greater than the thickness of the cut leather, as shown in figure 3.2.

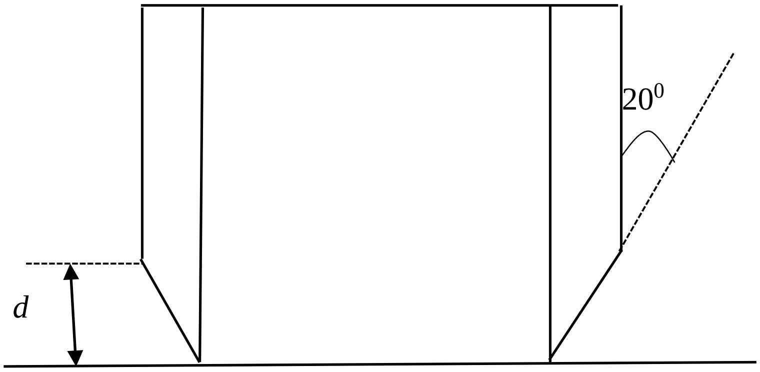

Figure 3.2: Schematic illustration of the shape of a press knife

3.1.1 Samples for tensile testing

For tensile strength and percentage elongation measurements, eight samples were cut in dumb-bell shape as shown in figure 3.3.

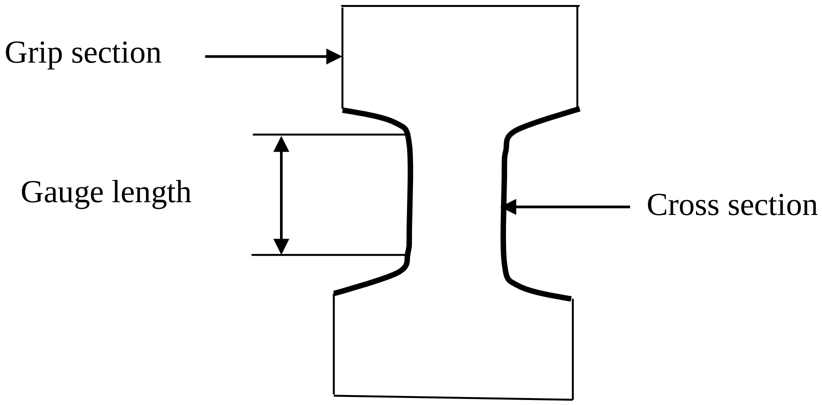

Figure 3.3: Schematic illustration of a standard tensile test sample

For tear strength measurements, eight rectangular specimens were cut, each 50 mm long and 25 mm wide with a template hole, as shown in figure 3.4.

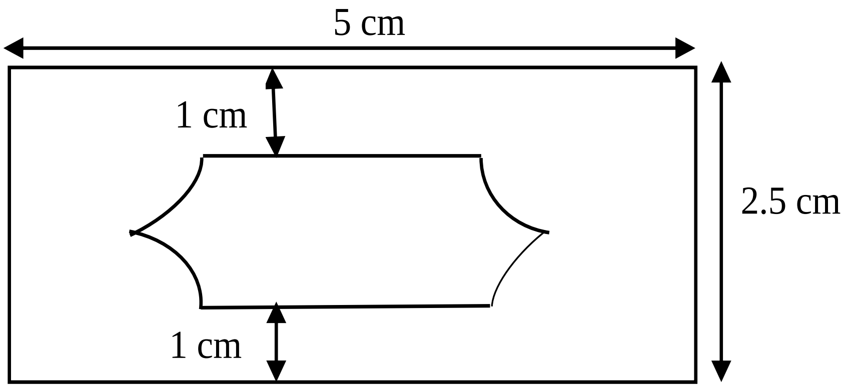

Figure 3.4: Schematic illustration of a standard sample for tear strength testing

The samples were then conditioned in a standard atmosphere, 23/50 (temperature of 23 ± 2 °C and humidity of 50 ± 5% R.H.) for 48 hours as specified by ISO 2419:2002 standard prior to testing. Thickness, *t* and width, *W* of each test sample were measured as specified by ISO 2589:2002 standard using digital Vernier calipers to the nearest 0.1 mm at areas between the grain side and the flesh side. Tensile strength and elongation were tested according to ISO 3376:2002 and ISO 3377-2:2002 standards for tear strength using Instron Testing Machine (Model 1101, UK) shown in plate 3.1.

Plate 3.1: A picture showing Instron Machine, Model 1101

The samples were clamped in the grips, one at a time, at the cross-sectional area of the gauge. A uniform jaws separation speed of 100 mm/min was selected with a gauge elongation length of 100 mm. The machine was run until the specimen was torn apart and the highest breaking force reached during tearing was recorded in Newtons (SLTC, 1996). The machine also recorded the elongation in mm directly from scale as described by Snyman and Jackson-Moss, (2000). Few samples were disposed due to slip-faults during testing. For a moment of testing, the absolute result was obtained only from the successful sample until the maximum force applied. For tear strength measurements, the pneumatic grips were replaced in the jaws of the Instron machine and the highest force was recorded. The tensile strength was then determined using equation 3.1;

$$Tensile\ strength = \frac{F}{Wt}\ (N/mm^2) \qquad (3.1)$$

where F is the highest recorded force, W is the width of the test sample and t is the thickness of the sample. Percentage elongation was determined using equation 3.2;

$$Percentage\ Elongation = \frac{L_{f-L_i}}{L_i} \times 100\% \qquad (3.2)$$

where L_f is the final free length and L_i is the initial free length of the sample. Tear strength was calculated from equation 3.3;

$$Tear\ strength = \frac{F}{t}\ (N/mm) \tag{3.3}$$

3.1.2 Solar irradiation of the samples

Rectangular samples of dimensions $30\ \text{mm} \times 9.3\ \text{mm} \times 0.93\ \text{mm}$ [measured by digital Vernier caliper according to ISO 2589:2002 (IULTCS/IUP 4)] were exposed to the natural solar radiation in the natural environment for time intervals of 0 to 24 hours. This is the customary duration that tanning industry exposes the hide to the sun during leather making. The samples were spread on an erected board by a tape to increase the solar irradiance. The solar irradiation was done during the month of September, 2014 at Egerton University, Njoro, Kenya ($0^0 55'' \text{S}, 35^0 04'' \text{E}$) and altitude of 1859 m (Owando *et al.*, 2013). Egerton University is in Rift Valley, 22 Km from Nakuru City, which receives solar radiations of irradiance approximately 7.1 kWm^{-2} each day during the month of September (Owando et al, 2013). The time interval of exposure during the day was from 10 AM to 3 PM to minimize the variation of solar irradiance. Therefore, on average, each sample received solar irradiance of approximately 0.08254 W each hour. The samples were then conditioned in a standard atmosphere of temperature 23 ± 2 °C and humidity 50 ± 5 % RH for 48 hours prior to testing according to ISO 2419: 2002.

3.1.3 UV irradiation of the samples

Rectangular specimens of dimensions $30\ \text{mm} \times 9.3\ \text{mm} \times 0.93\ \text{mm}$ were exposed to UV radiations in air at room temperature and at room relative humidity from an 8W UV fluorescent lamp (Model LF-204.LS) from UVITEC of wavelength 254 nm (UV-C) and of irradiance of 0.0475 W/m^2, which was positioned horizontally 15 cm away from the sample in an aluminum shutter. Various doses of UV irradiation were obtained by varying duration of irradiation from 0-30 hours. The specimens were then conditioned in a standard atmosphere, 23/50 (temperature $T = 23 \pm 2$ °C, humidity $\phi = 50 \pm 5\%$ R.H.) for 48 hours according to ISO 2419: 2002 (IULTCS) standard prior to testing. The pictures for both pickled and tanned hide samples are shown in plates 3.2 and 3.3, respectively.

Plate 3.2: Picture showing pickled hide sample for Film tension clamp of DMA 2980

Plate 3.3: Picture showing pickled hide sample for Film tension clamp of DMA 2980

3.2 Dynamic Mechanical Analysis

The storage modulus, E' and tan δ of samples prepared in section 3.1.2 and 3.1.3 were determined by a DMA (Model 2980) from TA instruments, using Thermal Analysis (TA) instrument control software installed in the DMA. A picture of Film Tension Clamp of DMA is shown in plate 3.4.

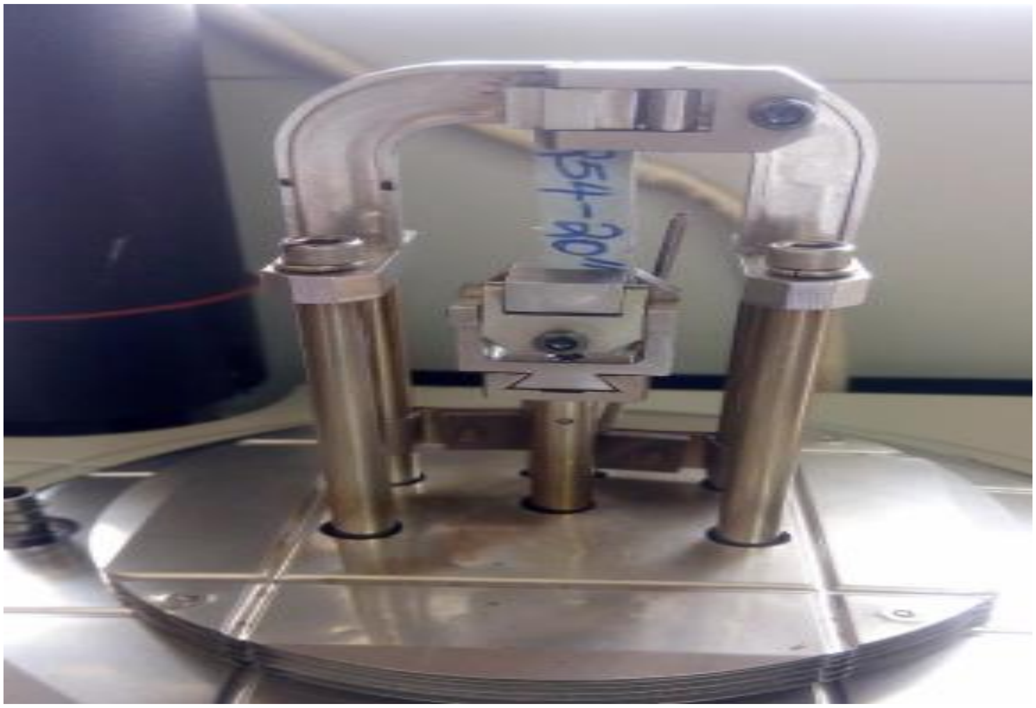

Plate 3.4: Picture showing Film tension clamp of a DMA 2980

The DMA was calibrated using standard samples which were accessories of the DMA 2980 before any measurements were taken to ensure the reliability of the results. The specimens were carefully mounted onto thin film clamp and the experiment run in multi-frequency mode with frequency range of 0.01-100 Hz equilibrated at room temperature 30 ^{0}C and heated at a rate of 5 ^{0}C per minute to 240 ^{0}C. The TA software displayed the data in graphical form. The results for E' and tan δ as functions of either frequency or temperature were obtained in graphical form.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Tear strength, tensile strength and percentage elongation

In this section, data were analyzed statistically by Microsoft Excel 2013 for t-test assuming unequal means and expressed as *p* to assess the statistical significance. The alpha (α) was set at 0.05. Therefore, significance of the null hypothesis was rejected whenever $p \leq \alpha$. The results for tensile strength, percentage elongation and tear strength for pickled and tanned hide are presented in tables 4.1 and 4.2, respectively.

Table 4.1 (a): Tensile strength, percentage elongation and tear strength of pickled hide sampled parallel to the backbone

Sample code	***Tensile strength (N/mm^2)***	***Percentage Elongation (%)***	***Tear strength (N/mm)***
A	34.0	46.80	186.13
B	32.78	52.00	151.61
C	32.78	53.20	190.00
D	34.04	52.53	179.10
E	24.61	69.20	181.87
F	33.95	53.20	171.70
Average	**32.24**	**54.49**	**176.74**

Table 4.1 (b): Tensile strength, percentage elongation and tear strength of pickled hide sampled perpendicular to the backbone

Sample code	*Tensile strength (N/mm^2)*	*Percentage Elongation (%)*	*Tear strength (N/mm)*
A	14.82	69.20	222.52
B	24.82	62.5	188.69
C	29.22	63.2	156.52
D	22.22	57.3	202.61
E	14.48	69.9	168.09
F	20.35	72.4	222.52
Average	**20.99**	**65.76**	**193.49**

Table 4.2 (a): Tensile strength, percentage elongation and tear strength of tanned hide sampled parallel to the backbone

sample code	*Tensile strength (N/mm^2)*	*Percentage Elongation (%)*	*Tear strength (N/mm)*
A	42.86	22.90	57.57
B	30.88	23.56	66.59
C	50.75	27.66	64.00
D	31.43	25.53	68.40
E	38.24	24.20	56.88
F	37.46	24.76	52.50

Table 4.2 (b): Tensile strength, percentage elongation and tear strength of tanned hide sampled perpendicular to the backbone

sample code	*Tensile strength (N/mm^2)*	*Percentage Elongation (%)*	*Tear strength (N/mm)*
A	25.28	36.33	61.60
B	29.49	29.16	88.11
C	36.18	29.67	95.00
D	26.54	31.16	78.00
E	29.65	29.16	86.18
F	22.93	32.16	92.57

4.1.1 Effect of sampling direction on tensile properties

From figures 4.1 and 4.2, specimens sampled perpendicular to the backbone direction had significantly higher tear strength (p = 0.00508) than parallel sampled specimens. In this case, the null hypothesis was rejected. It implies that numerically higher tear force is required to tear both pickled and tanned hide sampled in perpendicular direction than those sampled parallel to the backbone.

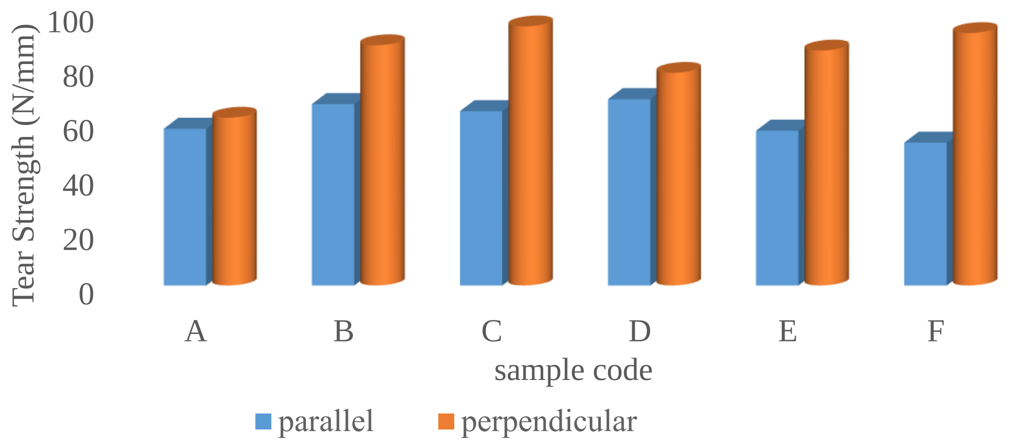

Figure 4.1: Effect of sampling direction on tear strength for tanned hide

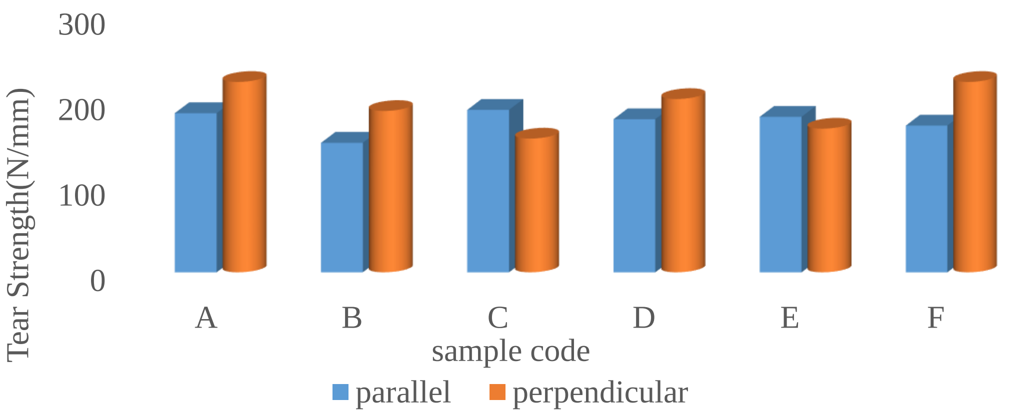

Figure 4.2: Effect of sampling direction on tear strength for pickled hide

From figures 4.3 and 4.4, percentage elongation for specimens sampled perpendicular to the backbone was significantly (p=0.00114) higher than for parallel sampled specimens. Hence null hypothesis was rejected. The values demonstrate that hide has greater elasticity in the perpendicular direction than parallel direction. This is a fact that can be exploited in shoemaking, where the leather is stretched over the form in perpendicular direction.

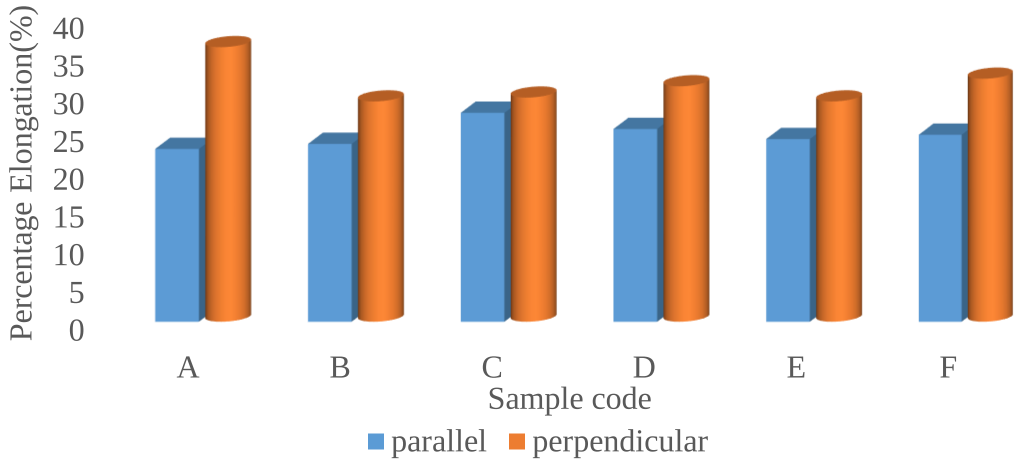

Figure 4.3: Effect of sampling direction on percentage elongation for tanned hide

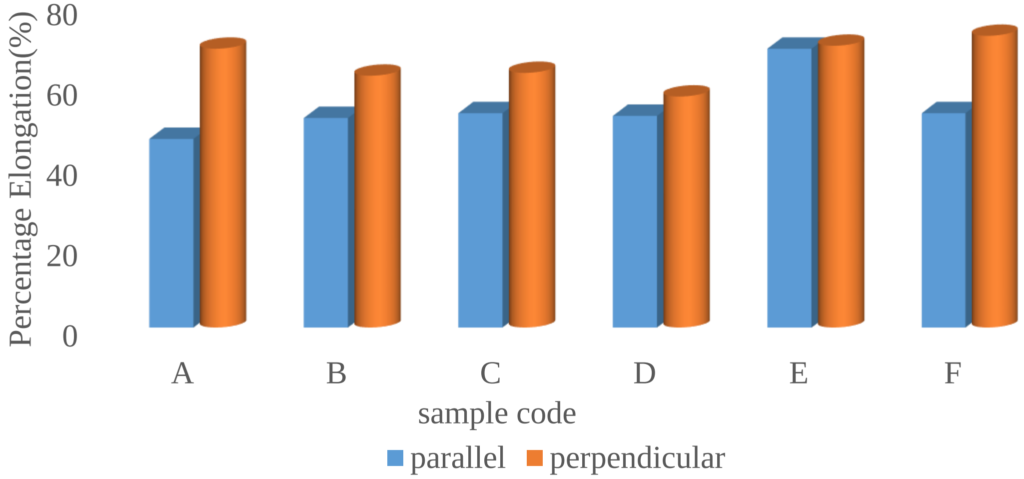

Figure 4.4: Effect of sampling direction on percentage elongation for pickled hide

Tensile strength values for specimens sampled parallel to the backbone were numerically higher than perpendicularly sampled specimens (*p* = 0.020986) for both pickled and tanned hide as shown in figures 4.5 and 4.6. Hence null hypothesis was rejected; sampling direction indeed has significant effect on tensile properties.

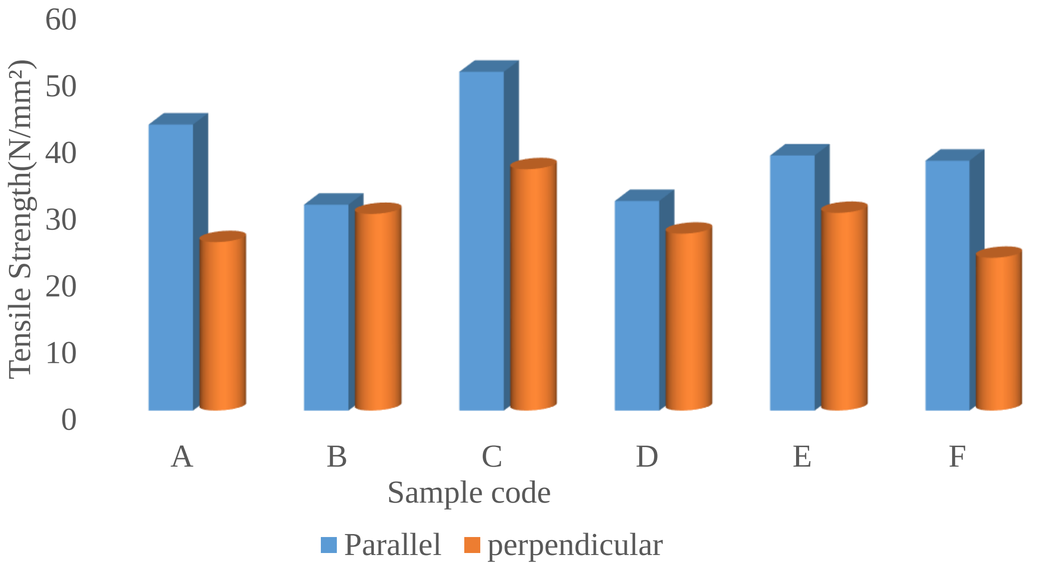

Figure 4.5: Effect of sampling direction on tensile strength for tanned hide

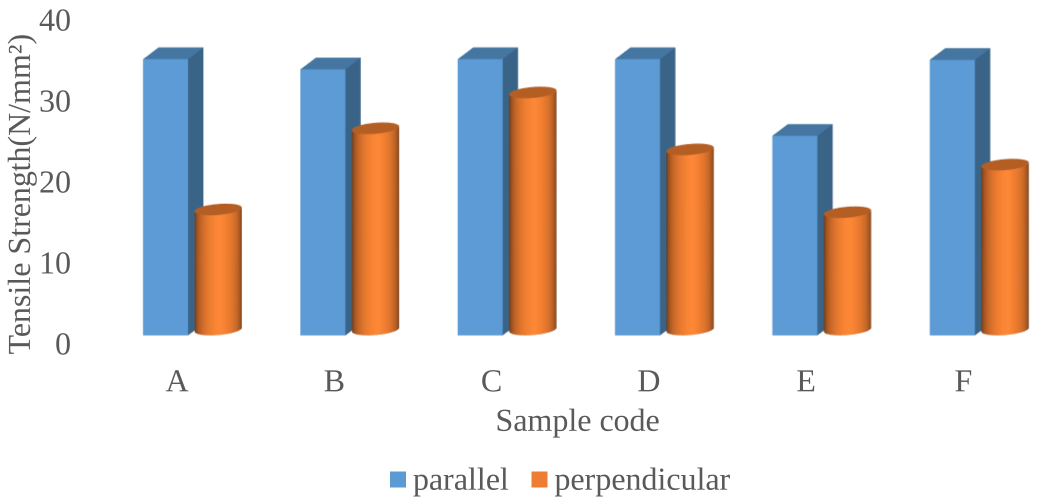

Figure 4.6: Effect of sampling direction on tensile strength for pickled hide

When fibres are aligned more in a direction normal to the stresses applied, then tensile strength becomes low (Salehi *et al*., 2013). The values for tensile strength and percentage elongation are in agreement with those reported by Sivasubramaniana *et al*. (2008) for cattle hide. Nevertheless, the results contradicted those reported by Oliveira *et al*. (2007), who reported that both tear and tensile strengths are significantly higher when the sample is perpendicularly sampled than parallel sampled. For both tensile and tear strengths, these variations might be explained by the anisotropic arrangement of the collagen fibres in the hide matrix (Craig *et al.*, 1987; Oliveira *et al.*, 2007). The degree of alignment of the collagen fibrils in the plane determines tear strength. High tear resistant materials have majority of their fibrils contained within parallel planes with little or no crossover between the top and the bottom surfaces (Sizeland *et al.*, 2013). In the perpendicular sampling direction, percentage elongation decreased with increased thickness. It can be pointed out that, when the samples for the tearing analysis are taken in parallel direction, the direction of tearing is perpendicular and when the samples are taken perpendicularly the tearing direction is parallel.

There were variations in values of tensile strength, tear strengths and percentage elongation for samples taken from different positions as a function of distance from the backline, as shown in figures 4.1 to 4.6 (indicated by different values for A, B, C, D, E and F). Leather, being an anisotropic material, its fibre bundles are oriented in diverse directions depending on the distance from the backbone, direction of sampling and the type of animal (Lin and Hayhurst, 1993). Samples taken closer to the backbone had higher tensile strength than those taken a distance from the backbone implying the influence of sampling position with respect to the backbone. These results agree with those obtained from merino sheep leather that showed a consistent decrease as the distance from the backbone increased (Gordon, 1995). The anisotropy can be used to explain the defection noticed in figure 4.2, sample code C and E.

4.1.2 Effect of tanning on tensile properties

Numerical values of both percentage elongation and tear strength were significantly higher for pickled hide than tanned hide (p = 0.000236 and p = 0.0176, respectively), whereas the values of tensile strength were numerically higher (p = 0.0344) for tanned hide than for pickled hide as shown in figures 4.7 - 4.12. Therefore, the null hypotheses were rejected in all the cases. Hence bovine hide tanning indeed has an effect on its tensile properties.

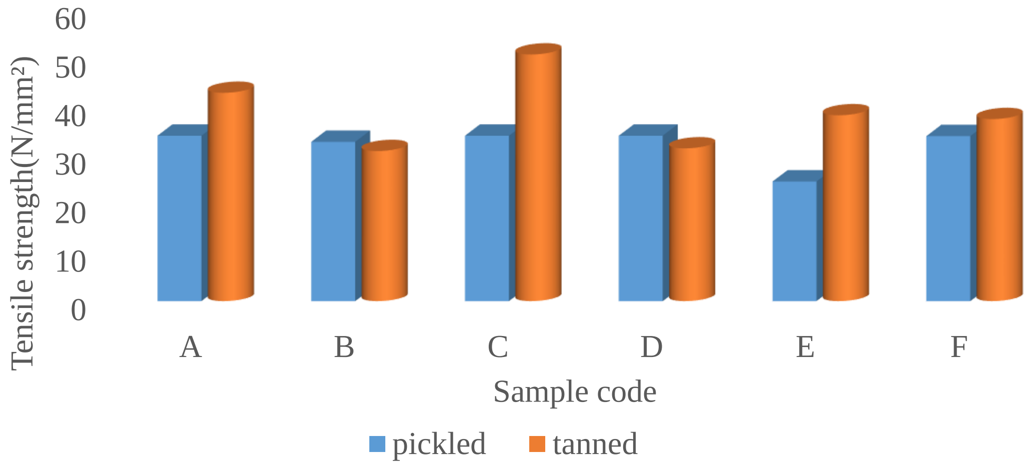

Figure 4.7: Effect of tanning on tensile strength for bovine hide in parallel sampling

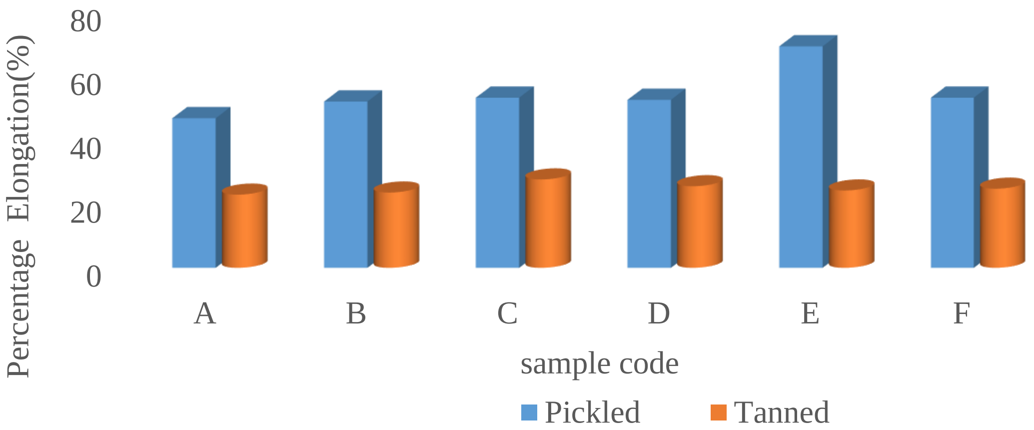

Figure 4.8: Effect of tanning on percentage elongation for hide in parallel sampling

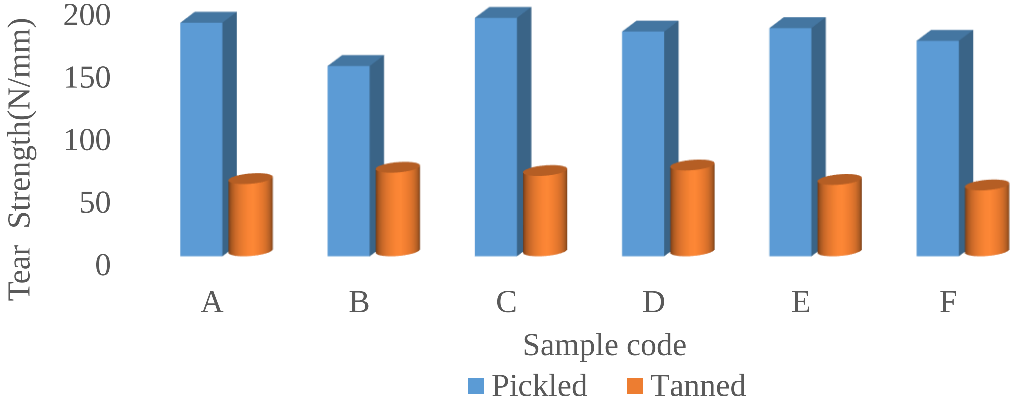

Figure 4.9: Effect of tanning on tear strength for bovine hide in parallel sampling

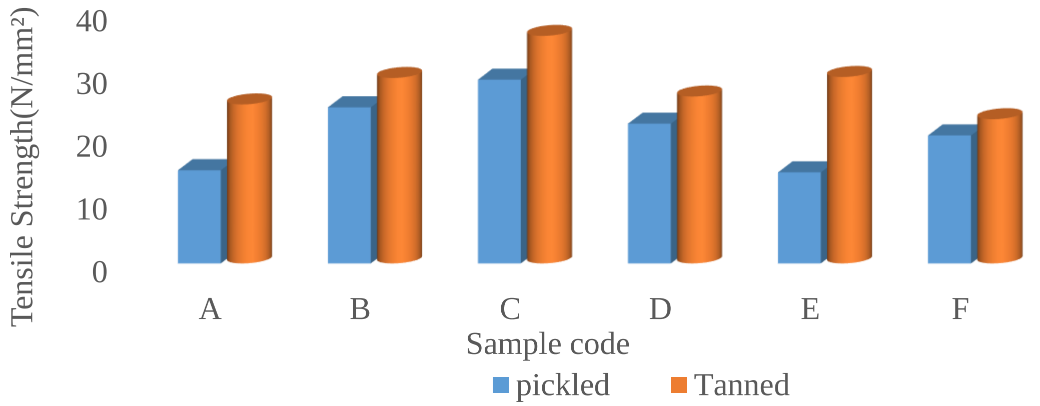

Figure 4.10: Effect of tanning on tensile strength for hide in perpendicular

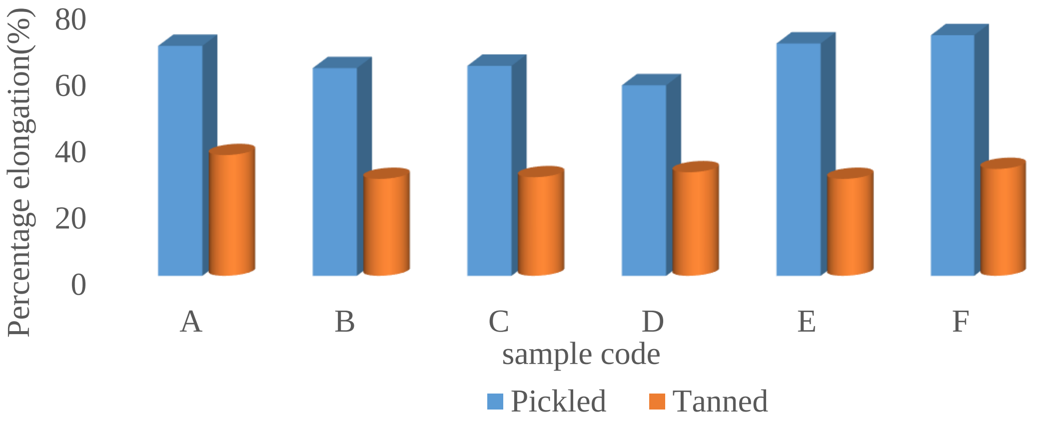

Figure 4.11: Effect of tanning on percentage elongation for hide in perpendicular

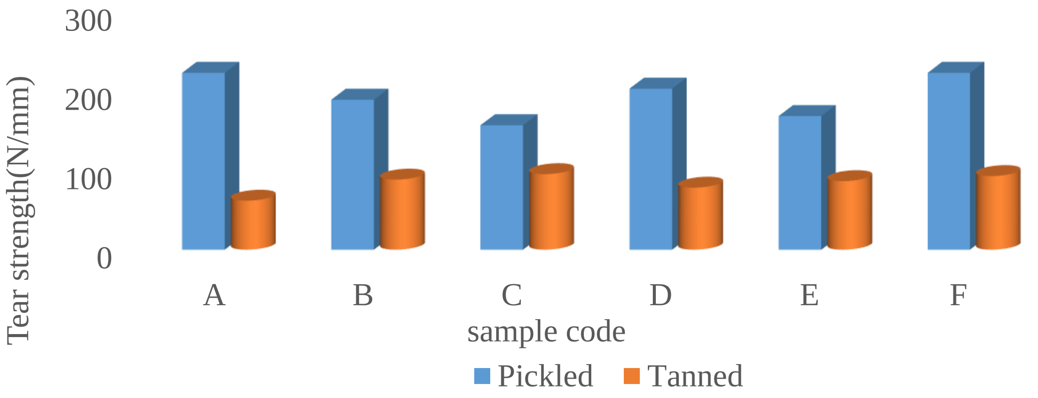

Figure 4.12: Effect of tanning on the tear strength for hide in perpendicular

The averages for tensile strength, tear strength and percentage elongation obtained for pickled and tanned hide are tabulated in tables 4. 1 and 4.2, respectively.

Table 4.3: Average results obtained for pickled hide

Picked hide

Tensile strength (N/mm^2)	Tear strength (N/mm)	Percentage Elongation (%)
26.61	185.12	60.13

Table 4.4: Average results obtained for tanned hide

Tanned hide

Tensile strength (N/mm^2)	Tear strength (N/mm)	Percentage elongation (%)
33.48	72.27	28.02

These averages agree with results reported by Ventre *et al*. (2006) for soaked calfskin and leather. Different values for tensile strength for the pickled and tanned hides can also be explained by the fact that the cross-sectional area of the pickled hide is higher than for tanned hide due to the osmotic swelling effect of liming process. Here, the collagen fibre bundles are loosened (Nalyanya *et al.*, 2015a). This decreases the load bearing collagen fibre concentration per given volume in the natural tissue in a water swollen state since the tensile strength is inversely proportional to cross-sectional area. The swelling also pushes the collagen fibres apart increasing the angle of weave hence decreasing the load transfer leading to a lower tensile strength. Additionally, the chemical process of tanning introduces additional crosslinks into the collagen between the adjacent polypeptide chains (Hansen *et al.*, 1993). This binds active groups to the functional groups of proteins causing resistance to slippage of chains over each other and hence increasing the tensile strength (Covington, 1997).

4.2 Viscoelasticity and thermal stability of hides

4.2.1 Effect of tanning on viscoelasticity and thermal stability

Effect of tanning process on the viscoelasticity was inferred by plotting graphs of individual viscoelastic property versus temperature for pickled and tanned hide on the same graph. The comparison at different temperatures enabled to infer the effect.

Loss modulus (E'')

The loss modulus (E'') for pickled hide increased with temperature to about 185 °C before a drastic drop to zero at 215 °C as shown in figure 4.13. The increase in E'' for tanned hide was gradual while for pickled hide, the increases were sharp and intense. The drop observed for pickled hide was slightly at lower temperature than for tanned hide. Again, pickled hide had multiple sharp and erratic peaks at temperatures 110 °C and 185 °C while tanned hide had only one peak at 230 °C.

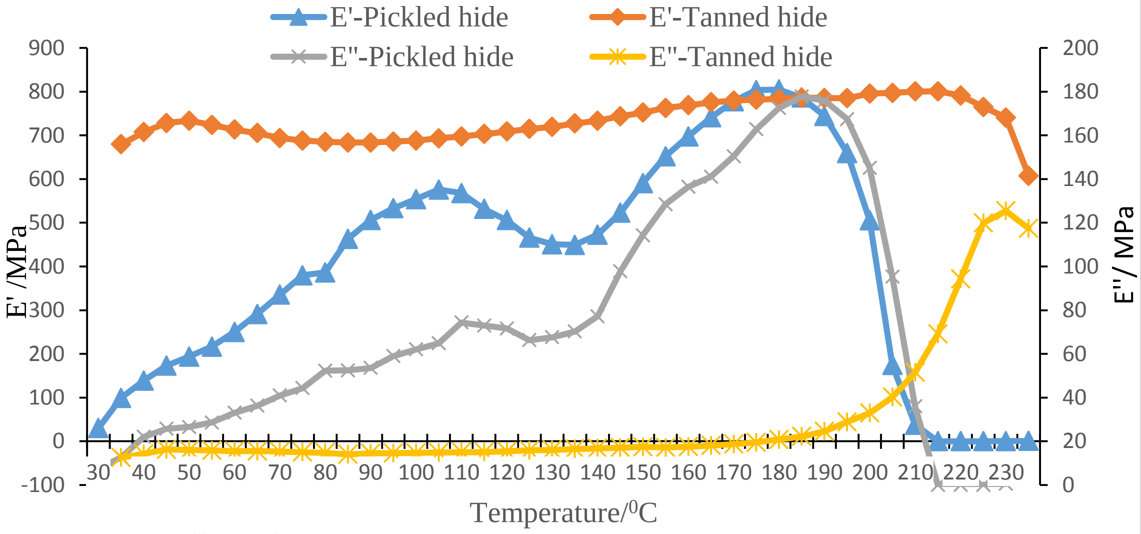

Figure 4.13: Effect of tanning on the E" and E' against temperature

When the hide is heated, collagen gets softened allowing more chains to participate in the oscillation. This increases the loss of mechanical energy, and hence high loss modulus. Heating also increases the rate of relaxation processes enabling substantial number of peptide chains to free themselves from their entanglements and align in a more cohesive crystalline orientation (Billmer, 1984). The crosslinks in the tanned hide impose restrictions on the segmental mobility reducing the number of peptide chains taking part in the relaxation process (Covington, 1997; Chen *et al.*, 2011). This explains why tanned hide had lower loss modulus than pickled hide especially at higher frequencies.

Storage modulus ($\boldsymbol{E'}$)

In figure 4.13, the storage moduli for both tanned and pickled hide increased with temperature to two distinct major peaks, although only the second peak was noticeable for tanned hide. The increasing trend of the storage modulus in both hides can be explained by dehydration taking place in the hide as temperature rises. Dehydration of collagen causes formation of additional crosslinks and stiffening effect of the hide. Removal of interstitial water pulls the collagen fibrils closer inducing intramolecular bonds and compacting the collagen structure into stiff and hard hide (Lischuk *et al.*, 2006; Kato *et al.*, 2001; Mogliner *et al.*, 2002). These two effects combine to increase the storage modulus with temperature. Same observation has been reported by Cucos *et al*. (2011) who found out that dehydrated collagen fibrils are more mechanically stiff than hydrated collagen. The storage modulus for tanned hide was higher compared to pickled hide throughout the experimental temperature range except between 170 ^{0}C to 185 °C. This can be attributed to the effect of tanning that induces crosslinks, which conduce additional stiffness (Covington, 1997). Storage modulus for tanned showed gradual increase and a slight drop at 230 °C while pickled hide showed erratic peaks at 100 °C and 185 °C and then dropped to almost zero at 225 °C. The steady increase in storage modulus for tanned hide can be attributed to the stabilization effect of tanning which compacts the collagen molecules and tanning agents unlike pickled hide that is amorphous from the swelling effect of liming (Nalyanya *et al.*, 2015b). During the liming, dermal swelling takes place increasing the porosity of the hide (Lischuk *et al.*, 2001). The opened up structure of pickled hide allows more absorption of water unlike the tanned hide which later is compacted by chromium ions. Hence, during dehydration by increasing temperature, pickled hide loses more water than tanned hide. This explains why the increase in storage modulus is higher and erratic for pickled hide as compared to the tanned hide. Stabilization shows that tanned hide has higher ability to function at varying strain and can survive long cycles than pickled hide. Tanning increases the molecular weight and induces intermolecular hydrogen bonds with the functional groups of the collagen that stabilizes the crystalline structure increasing the stiffness and stabilizing the structure of the crystalline collagen (Chahine, 2000; Covington, 1997). The synergistic effect of collagen with chromium ions together generate more cross linkages that induce resistance to any forces of deformation on the dermal collagen, especially in compression tests (Lischuk *et al.*, 2001; Chahine, 2000; Covington, 1997; Budrugeac *et al.*, 2004). This improves stiffness and compactness in the collagen matrix hence storage modulus. Similarly, swelling of the hide structure during pickling process increases the distance of separation between the reactive groups unlike in tanned hide where they are brought together by the chromium ions, hence weakening the intercollagen bonds (Chahine, 2000). This also affects the recruitment process and the resulting spatial arrangement of collagen fibres (Liu *et al*., 2009). This decreases the stiffness of the pickled hide compared to tanned hide that has compact structure. The compact structure implies that tanned hide has greater volume fraction compared to pickled hide. This also explains why the temperatures corresponding to the peaks in storage modulus for tanned hide were slightly higher than for pickled hide; 180 °C for pickled hide and 215 °C for tanned hide. These results agree with those reported by Pekhtasheva *et al*. (2012) where it was observed that elastic properties of collagen increases with tanning. This also explains why temperatures corresponding to the second peak of storage moduli for tanned hide was greater than for pickled hide (Paul and Bailey, 2003). After the second the peak, the storage moduli for both hides dropped drastically especially for pickled hide. At the second peak, melting of the crystalline collagen occurs, forming volatile compounds and "pearls-on-a-string-like-structures" especially for pickled hide causing irreversible decomposition as shown in plate 4.1 (Pekhtasheva *et al.*, 2012; Budrugeac et al, 2004). This is a transition of collagen structure from the orderly triple-helical to the random coil collagen which weakens the structure significantly (Lai *et al.,* 2008; Nalyanya *et al*., 2016). The associated mechanical relaxation and reorganization of the metastable amorphous causes a drastic drop in storage modulus. The results agree with those reported by Cucos and Budrugeac (2010) who reported the melting (softening) of the crystalline collagen which corresponds to denaturation of the collagen triple-helix causing a drop in storage modulus occurred at 225.3 °C.

Plate 4.1: Picture showing decomposed pickled sample after DMA 2980 experiment

Tan delta (tan δ)

Tan δ measures dissipative capability, in this case, ability of the hide to lose mechanical energy imposed on it. Figure 4.14 illustrates comparison of tan δ for pickled and tanned hide. Comparison helps is to determine the effect of tanning on tan δ. Tan δ for pickled hide was greater than for tanned hide in the entire temperature range except 50-60 ℃ . This means that tanning decreases dissipative activity of the hide. The chromium ions coupled with increased molecular weight enhances the rigidity of the collagen molecules (De Carvalho and Grosso, 2004). This depresses the molecular mobility in tanned hide hence low dissipative capacity of tanned hide compared to pickled hide. This implies that tanned hide is more elastic/rubbery/elastomeric in nature than pickled hide, as indicated by the lower tan δ magnitude (Korhonen *et al.*, 2001). In the temperature range of 140-155 °C and 225-235 °C, tan δ for pickled hide reached the threshold; tan δ=1, to cross from solid-like to liquid-like behavior (Al-Ruqaie *et al.*, 1997). This also implies that the majority of the mechanical energy is dissipated by elastic deformation (Lakes, 2004). Tan δ for both hides showed increases with temperature interrupted with peaks at certain temperatures due to the dehydration and melting of both amorphous and crystalline fractions of collagen. The increase with temperature can probably be due to polypeptide chains mobility which aid dissipation of the applied mechanical strain/deformation energy in form of heat (Asif *et al.*, 2005). Temperatures corresponding to the peaks in tan δ were relatively higher than temperatures corresponding to peaks in storage modulus since the response in tan δ is determined by the entire volume fraction of the relaxing phase hence its temperature is greatly affected by the amorphous phase (Sirear, 1997).

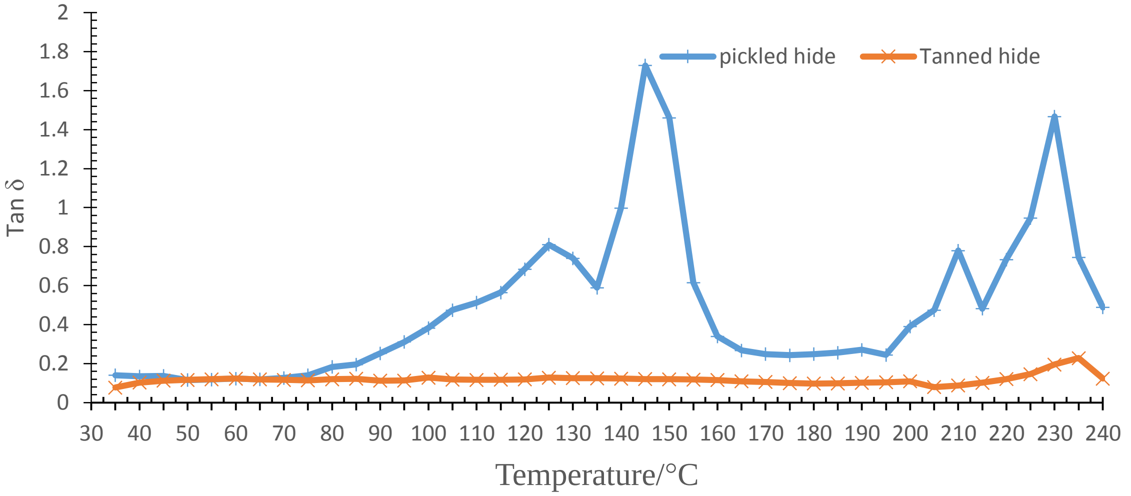

Figure 4.14: Effect of pickling and tanning on tan δ for bovine hide

Complex and dynamic viscosity (η)

The dynamic viscosity, η and complex viscosity, η* for pickled hide and tanned hide increased with temperature. This means that resistance to flow and permanent deformation increases with temperature. The complex viscosity for pickled hide was greater than that for tanned hide in the temperature range 55 °C to 200 °C. The increase in viscosity for pickled hide were more pronounced with two peaks at 105 °C and 175 °C while small peaks observed for tanned hide at 110 and 225 °C. Complex viscosity for pickled hide dropped to almost zero at temperature 210 °C as shown in figure 4.15. This is attributed to the breakage of bonds that once stabilized the secondary structure of collagen (Xue and Sethi, 2012). Dynamic viscosity, η for pickled hide was greater than that for tanned hide in the temperature range 140 °C to 205 °C. The peaks in η for pickled and tanned were observed at 185 °C and 235 °C respectively as shown in figure 4.16.

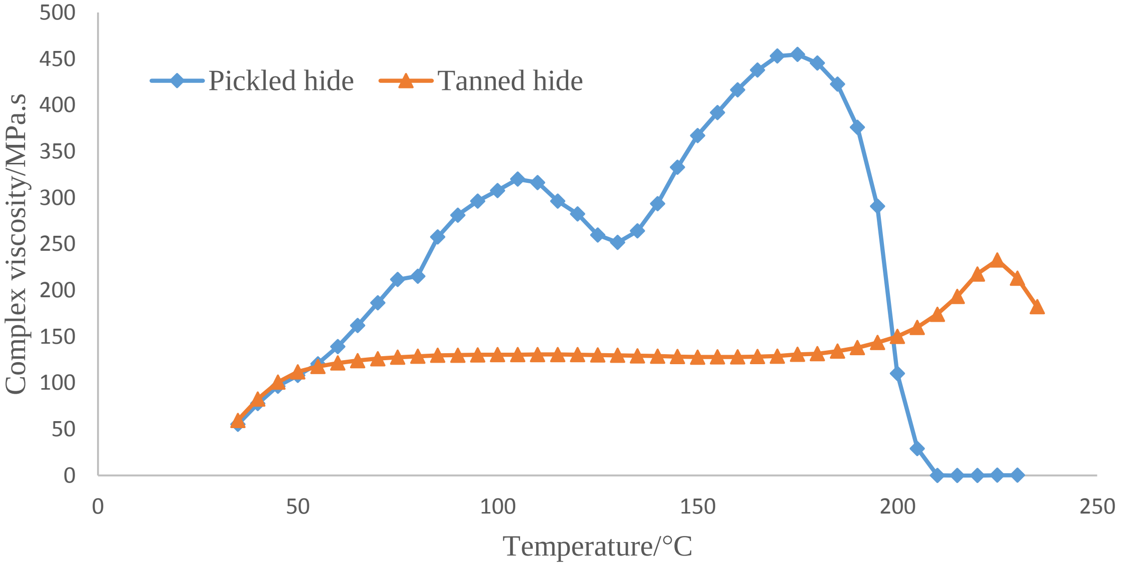

Figure 4.15: Schema showing complex viscosity for bovine hide

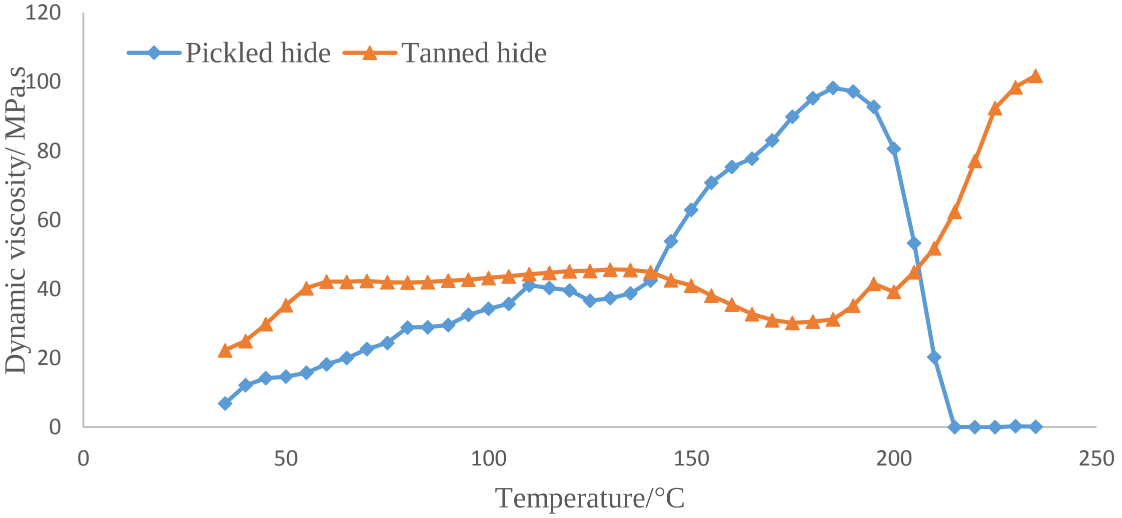

Figure 4.16: Schema showing η for bovine hide

Increase in temperature drives the molecular mobility of the collagen chains and breaks weak interactions such as hydrogen bonds (Xue and Sethi, 2012). Consequently, with an increased temperature, the viscosity response of the material is expected to increase (Odlyha *et al*., 2000). During denaturation, the collapse of the triple helical structure causes sudden fall in the viscosity. Any further heating beyond this temperature simply transforms the collagen from the triple-helix to the random coil configuration. The transition involves the breakage of hydrogen bonds between the adjacent polypeptide chains of collagen causing the intact trimers (γ) to break into either individual chains (α) or dimers (β). This causes decrease in the viscosity at temperatures beyond denaturation.

Shear stress (σ)

Figure 4.17 illustrates the effect of tanning on the σ and variation of variation of σ with temperature. Pickled hide had greater σ compared to tanned hide in the temperature range of 55-205 °C. The σ for pickled hide increased rapidly with temperature to two peaks at 105 and 175 °C while for tanned hide, the σ increase was gradual forming two peaks at 110 °C and 225 °C. The drastic drops after the second peaks can be attributed to the collapse of the triple-helical ordered structure of collagen to the random coil of amorphous region and crystalline fraction of collagen. As expected, drops for tanned hide occurred at relatively higher temperature than for pickled hide. This shows that tanning makes hide more thermally stable. Beyond the second peaks, the shear stress, σ decreased rapidly due to the irreversible decomposition of collagen crystalline molecules beyond their denaturation temperature (Cucos and Budrugeac, 2010).

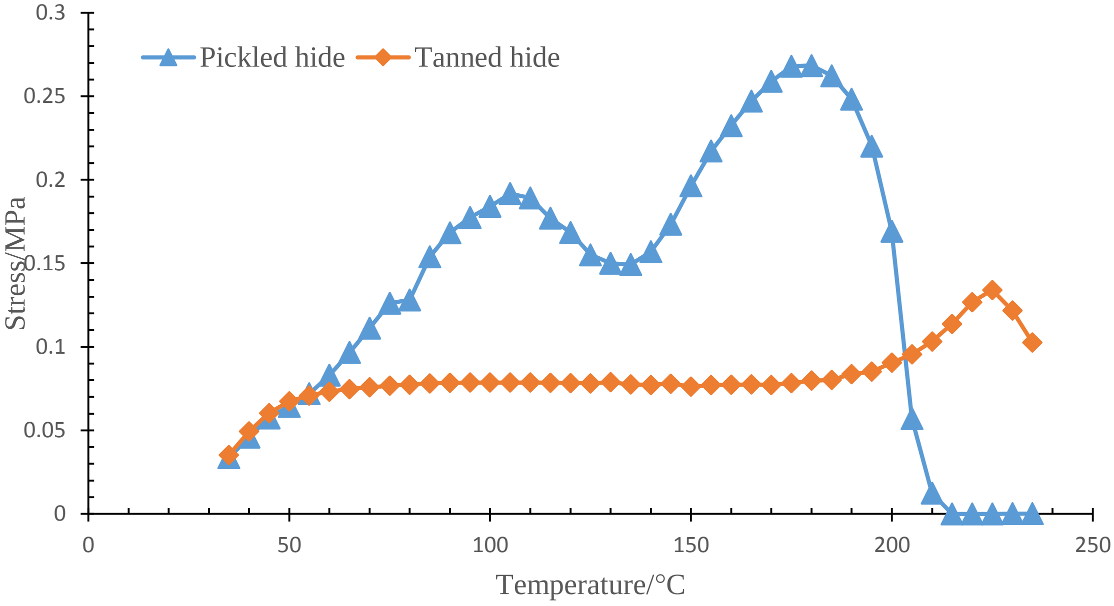

Figure 4.17: Schema of σ versus temperature for pickled and tanned hide

At higher temperatures, the shear stress, σ decreased rapidly especially in pickled hide. The decrease is due to the irreversible decomposition of collagen crystalline molecules beyond the denaturation temperature as shown in plates 4.2 for tanned hide (Cucos and Budrugeac, 2010).

Plate 4.2: Picture showing tanned hide sample after DMA 2980 experiment

Thermal stability

Transition temperatures for pickled and tanned hide were 90 and 130 °C, respectively as inferred from figure 4.14. The difference in these temperatures can be attributed to the tanning process. The additional crosslinks are induced between amino acids and carboxyside chain of triple-helical regions of the molecules during chrome tanning. This increases molecular density and molecular α-chains motions are restricted more than pickled hide. The rigidity strengthens peptide bonds in tanned hide hence greater thermal stability (Covington, 1997; Chahine, 2000; Paul and Bailey, 2003; Budrugeac *et al.*, 2004; Haroun *et al.*, 2009; Cucos and Budrugeac, 2010). Studies by Sathiyamoorthy *et al.* (2013) and Budrugeac and Miu (2008) reported TS for chrome tanned leather as 100 ℃ using Differential Scanning Calorimetry (DSC). This implies that the value by DSC is slightly lower than the value by DMA. This can be attributed to the water that DSC subjects the samples to during testing. Water decreases stability of the collagen chains. Denaturation temperature (Td) as inferred from the temperatures corresponding to the second peaks of tan δ for pickled hide and tanned hide were 180 ℃ and 225 ℃. The values agree with results reported by Budrugeac *et al.* (2004) on new and historical leather which were 230 and 234.5 ℃ using DMA and DSC, respectively. Cucos and Budrugeac (2010) reported 218 ℃ on crystalline zone of pure collagen. By using DSC analysis, Budrugeac and Miu (2008) reported the melting temperature of crystalline zone of collagen to be in the range of 205-245 ℃. Other relevant studies carried out on collagen of the aortic tissue by Samoillan *et al*. (1999) found 220 ℃. Odlyha *et al.* (2003) found similar range of 230-234.5 °C. Budrugeac and Miu (2008) working on the same extracted pure collagen reported the melting temperature range of 205-245 °C.

4.2.2 Effect of solar radiations on viscoelasticity and thermal stability

In order to infer effect of solar radiation on viscoelasticity, curves of each viscoelastic property for samples irradiated for different time durations were plotted on the same graphs to compare their magnitudes. The graphs of the properties were plotted as functions of temperature.

Storage modulus (E')

Figures 4.18 and 4.19 illustrate the effect of solar radiations on the storage moduli for pickled and tanned hides, respectively. The two graphs show that non-irradiated samples have highest storage moduli compared to the radiated samples. The drop in storage modulus after irradiation may be attributed to the combined effects of solar ultraviolet radiations, solar infrared radiations and atmospheric oxygen. Collagen contains aromatic/ chromophoric amino acids such as tyrosine, phenylalanine, histidine and cysteine which readily absorb these radiations especially in the UV- range (Miles *et al.*, 2000; Rabotyasgova *et al.*, 2008; Theodossiou *et al.*, 2002). Absorption of these radiations, heat and environmental water vapor by collagen in the presence of atmospheric oxygen causes oxidation (Manfredi *et al.*, 2015; Miles *et al.*, 2000; Izquierdo et al, 1994; Florian, 2009; Teddy *et al.*, 2006). This oxidation breaks covalent bonds in collagen peptide chains and the tanning agents forming highly reactive radicals and hydro-peroxides (Florian, 2009). The OH- radicals for example induce chain scissions which weaken the mechanical properties of the hide (Sionkowska *et al.*, 2006; Miles *et al.*, 2000; Thompson, 2006). Studies have shown that these radicals cause both chain scission and crosslinking of the collagen and the net effect depends on the irradiation dose or duration and pH of the medium (Sionkowska *et al.*, 2006). Interestingly, as duration of irradiation increased, the storage modulus gradually increased; although still lower than that of non-irradiated samples. This contradicted our hypothesis. However, exposure of the hide to the solar radiations exposes the sample to the heat due to the infrared rays, which Izquierdo *et al*. (1994) observed that it increases the viscoelastic properties. The UV radiations and infrared cause dehydration of the collagen fibres which increase the stiffness, since dehydrated collagen is harder and stiff (Janko *et al.*, 2010; Kato *et al.*, 2001; Mogilner *et al.*, 2002; Kaminska *et al.*, 1996). Similarly, the initial chain scission as a result of UV absorption by the aromatic/chromophoric amino acids causes degradation. Collagen degradation in the presence of oxygen at ambient temperatures induces the aromatic amino residues to form dityrosine and other photoproducts such as pentosidine and pyridoline, which are all crosslinks that are aimed at increasing the stiffness (Fathima et al, 2007; Metreveli et al, 2010). Furthermore, the modification of amine and carboxyl groups by the hydroxyl radicals from the UV splitting of the water molecules on the peptide backbone radicals (-NHC-CO-) together with their covalent bonds form the crosslinks that induce stiffness (Weadock *et al.*, 1995). This agrees with the observations made by Janko *et al*. (2010) that the impact of irradiation is dependent on the environmental conditions and time of irradiation.

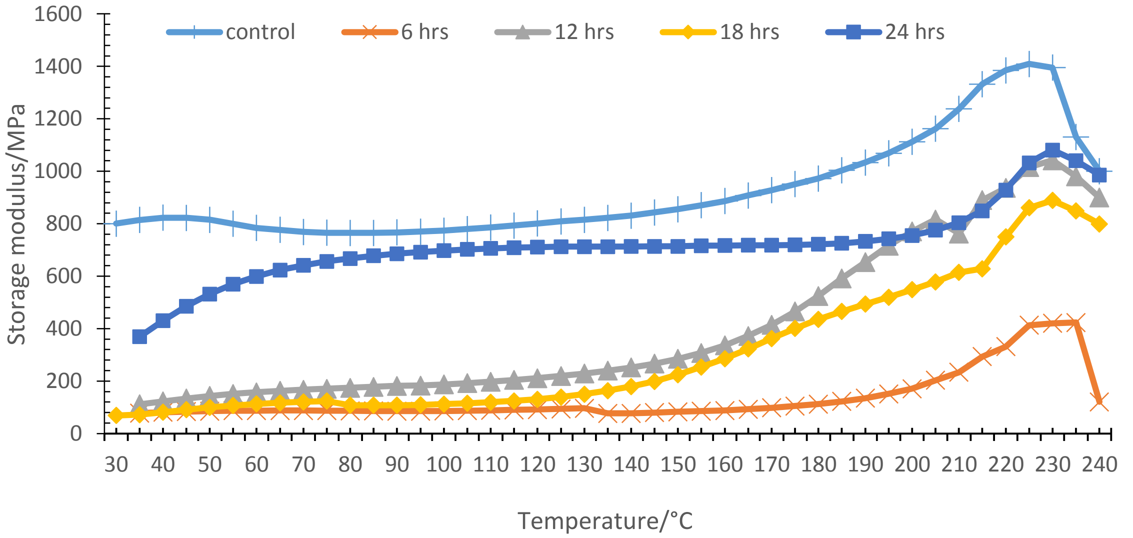

Figure 4.18: Effect of solar radiation on storage moduli for tanned hide

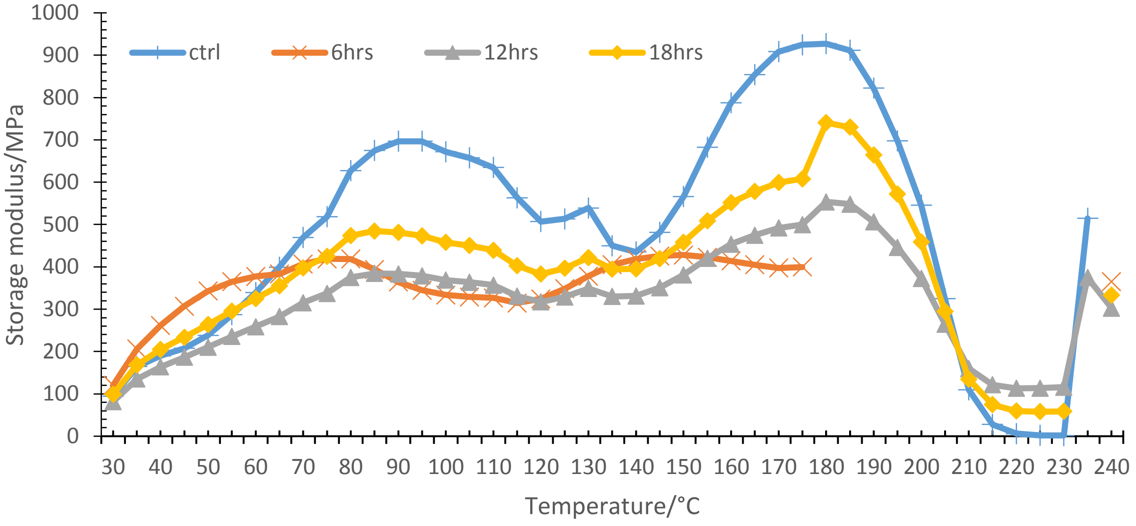

Figure 4.19: Effect of solar radiation on E' for pickled hide

Tan δ

Figures 4.20 and 4.21 illustrate the effect of solar radiations on tan δ for pickled and tanned hide, respectively. Tan δ for pickled hide behaved differently from that for tanned hide. The difference may probably be due to the chemical crosslinking effect of chrome-tanning that induces covalent bonds. These bonds decrease the collagen free volume hence permeability to both water and radiations (De Carvalho and Grosso, 2004). This increases molecular weight as well. For pickled hide, non-irradiated sample exhibited the highest tan δ. As time of irradiation increased, tan δ decreased, implying that irradiation decreases the dissipative capability of pickled hide. Only non-irradiated pickled hide sample recorded tan δ greater than 1 at 140-155 °C and 225-235 °C. All irradiated samples had tan δ less than 0.5. For tanned hide, sample irradiated for 6 hours had the highest tan δ followed by non-irradiated sample. All tanned hide samples had tan δ less than 0.5. It can be noted that bovine hide is predominantly elastic in nature although tanned hide is more elastic but less dissipative than pickled hide as indicated by tan δ magnitudes. This is due to the rigidity imposed on the tanned hide by the chromium ions and the increased molecular density which efficiently restrict the mobility and hence dissipation (Cucos and Budrugeac, 2010).

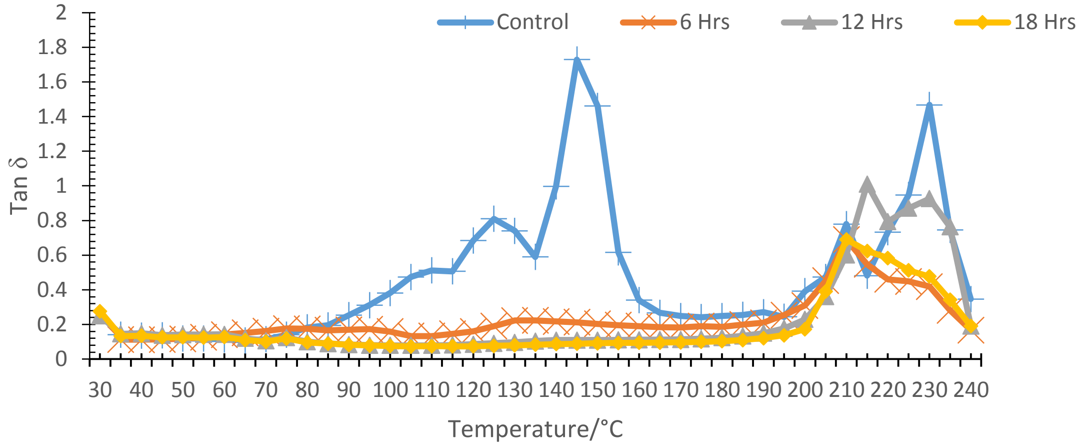

Figure 4.20: Effect of solar radiation on tan δ for pickled hide

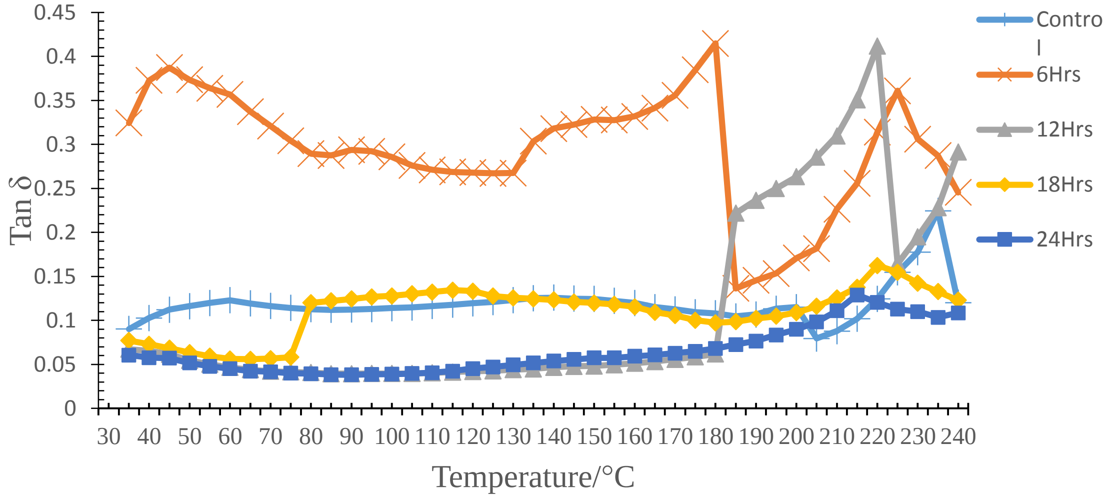

Figure 4.21: Effect of solar radiation on tan δ for tanned hide

Thermal stability

The effect of solar radiation on thermal stability for pickled and tanned hide is illustrated in figure 4.22. Thermal stability of bovine hide, as indicated by the melting temperature of the crystalline fraction of collagen, was inferred from the temperatures corresponding to the peaks of tan δ (Paul and Bailey, 2003) as shown in figures 4.20 and 4.21. The effect of exposing the samples to the natural solar radiation on these temperatures and hence thermal stability is illustrated in figure 4.22. The temperatures for tanned hides are slightly higher than those for pickled hide; a fact that makes chrome-tanning more necessary in leather making procedures. It improves the thermal stability by increasing the melting temperature, shrinkage temperature or denaturation temperature (De Carvalho and

Grosso, 2004; Bigi *et al.*, 2001). The results agree with those reported by Pekhtasheva *et al*. (2012). In both pickled and tanned hides, non-irradiated samples had the highest melting temperature compared to solar-irradiated samples. In both hides, temperatures decreased progressively with increasing time of irradiation. These results agree with those reported by Zheng *et al.* (2009). This trend can be explained by the fact that solar UV radiation leads to the rupturing of the collagen peptide bonds and the crosslinks that confer thermal stability. The breaking of inter and intramolecular hydrogen bonds (bond scission) consequently decreases the stability. These trends reflect the harmful effects of UV radiation in the solar radiation spectrum, which bring about photolysis and photo-ageing.

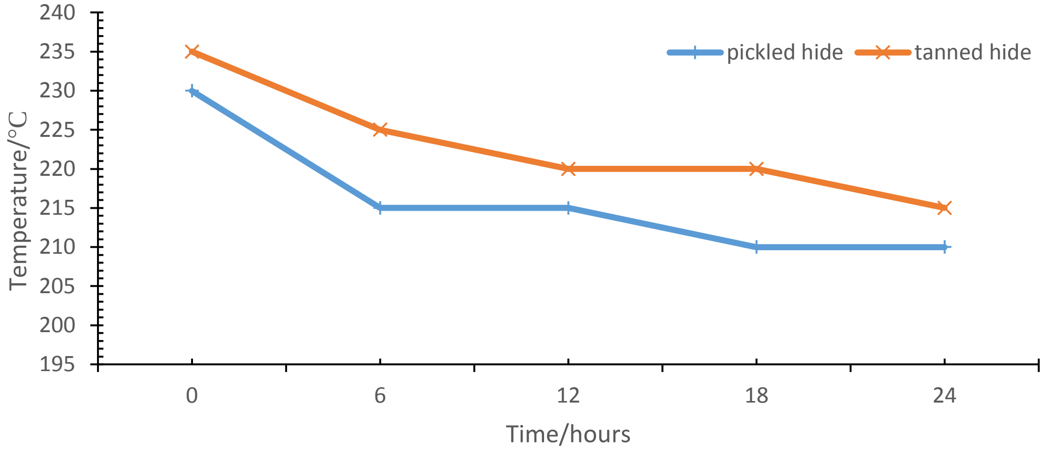

Figure 4.22: Effect of solar radiation on melting temperatures for bovine hide

4.2.3 Effect of frequency on viscoelasticity

Loss modulus (E'')

The storage modulus (E') and loss modulus (E'') curves for pickled and tanned hides were plotted on a single graph (figure 4.23). The effect of chrome-tanning process on the E' and E'' versus frequency was illustrated. The graphs show distinct linear frequency dependence divided into two regions: 0.1-30 Hz and 30-100 Hz. In the frequency range of 0.1 to 30 Hz, tanned hide showed significantly higher E'' compared to pickled hide. Both E'' curves for pickled and tanned hide linearly decreased with frequency until 30 Hz where the two curves had equal magnitudes. From 30 to 100 Hz, the increase in E'' for pickled hide was significantly higher compared to tanned hide, although, the curves showed weak frequency-dependence in this range. This result indicate that tanning enhances E'' at frequencies lower than 30 Hz but lowers E'' at higher frequency than 30 Hz. This also indicates that E'' for both hides decreases with frequency at frequencies lower than 30 Hz but increases with frequencies at frequencies higher than 30 Hz. Similarly, E'' for both hides is a frequency-dependent variable as observed by Lakes, (2004). Decrease in E'' of hide in the range 0.1-30 Hz is expected. The decrease in E'' of hide at lower frequencies indicates the relaxation process where the polypeptide chains do not have enough time to respond to the applied deforming sinusoidal strains making it difficult for the chains to resonate with the oscillation. Only the peptide chains with shorter chain length are able to oscillate. This decreases the number of participating oscillating chains and hence lower loss modulus. At 30 Hz, the chains are in relaxation process and beyond this frequency, the entangled chains begin to oscillate. This increases the number of the participating oscillating chains hence increase in loss modulus is observed (Patel *et al.*, 1992; Eidam *et al.*, 1995).

Storage modulus, E' for tanned hide was significantly greater compared to pickled hide in the entire frequency range. The storage modulus for both hides showed linear relationship with frequency agreeing with the results by Lakes, (2004). For tanned hide, the E' increased rapidly from 0.1 to 30 Hz followed by a gradual increase that almost became independent of frequency. For pickled hide, E'decreased from 0.1 to 30 Hz followed by a gradual increase, almost forming a plateau at higher frequencies. This implies that for both hides, the E' becomes less frequency-dependent at frequencies higher than 30 Hz. Chrome-tanning increases the molecular weight and also induces intermolecular hydrogen bonds with the functional groups of the collagen that stabilizes the crystalline structure (Cucos and Budrugeac, 2010; Covington, 1997). The synergistic effect of chromium together with the increased molecular weight make tanned hide stiffer than pickled hide (Covington, 1997). Similarly, the presence of chromium ions in the hide increases the volume fraction and droplet size of collagen phase. At low frequency, the collagen chains have more time to relax to a more favorable state by slippage of the entanglement point of chains. As the frequency increases, the chains become unable to respond to the applied forces. When the chains can no longer slip past each other readily, and the entanglements tightly fixed in the network, the polypeptide mobility decreases (Ward and Hadley, 1993; Gunasekaran and Ak, 2000). This increases the ability of the entanglement to store more imposed energy and the collagen molecules behave more like elastic solid (Clasen and Kulicke, 2001; Doi and Takimoto, 2003). This explains why storage modulus increased with frequency. As frequency of oscillation increased further beyond 30 Hz, almost all collagen fibres are fully stretched and oriented in the direction of the applied strain, hence E' becomes almost constant, independent of the frequency. During prior processes of tanning, liming in alkali solution and sulphide makes the hide to swell leaving a more open/loose structure. This affects the recruitment process and the resulting spatial arrangement of collagen fibres (Liu *et al*., 2009). This explains the decrease of E' of pickled hide. Both pickled hide and tanned hide showed a greater degree of dispersion with their moduli (Lakes, 2004).

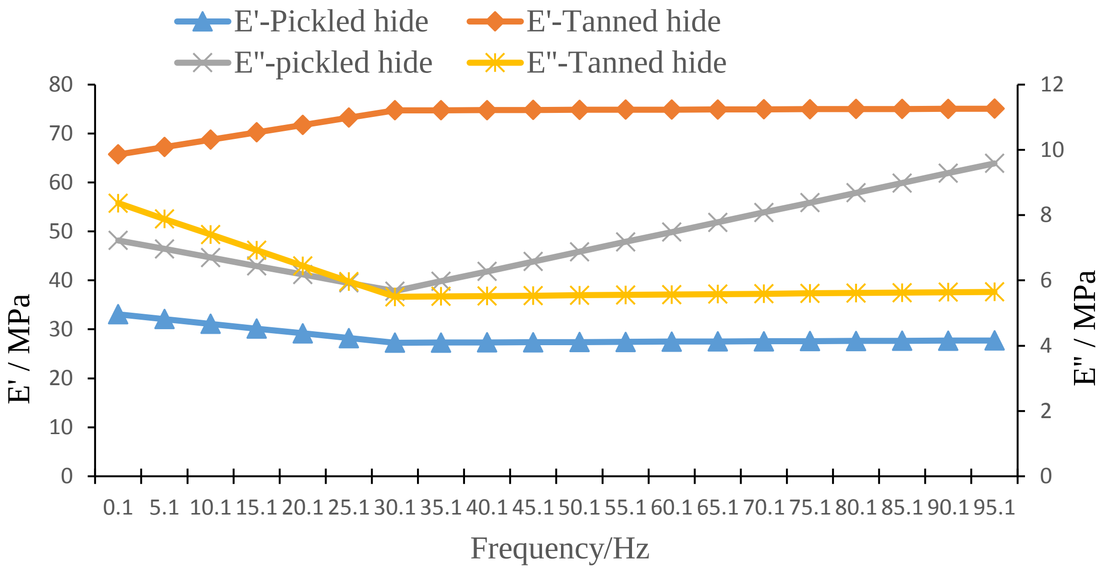

Figure 4.23: Effect of tanning on the E' and E" for bovine hide versus frequency

Tan δ

The magnitudes of tan δ for both pickled and tanned hides were less than a unit at all frequencies as shown in the figures 4.24. This implies that both hides are predominantly elastic in nature and hence implying that much of the energy was dissipated by elastic deformation (Korhonen *et al*., 2001). Tan δ for pickled hide was greater than for tanned hide throughout the frequency range. These results agree with those reported by Kasapis and Mitchell, (2001). Tan δ for both hides decreased linearly from 0.1 Hz to 30 Hz followed by linear increase from 30 to 100 Hz. The increase for tanned hide was smaller, almost forming a plateau compared to the increase for pickled hide. The crosslinks in the tanned hide impose restrictions on the segmental mobility and therefore reducing the number of peptide chains taking part in the relaxation process (Chen *et al*., 2011). This explains why tan delta for pickled hide was higher than for tanned hide especially at higher frequencies.

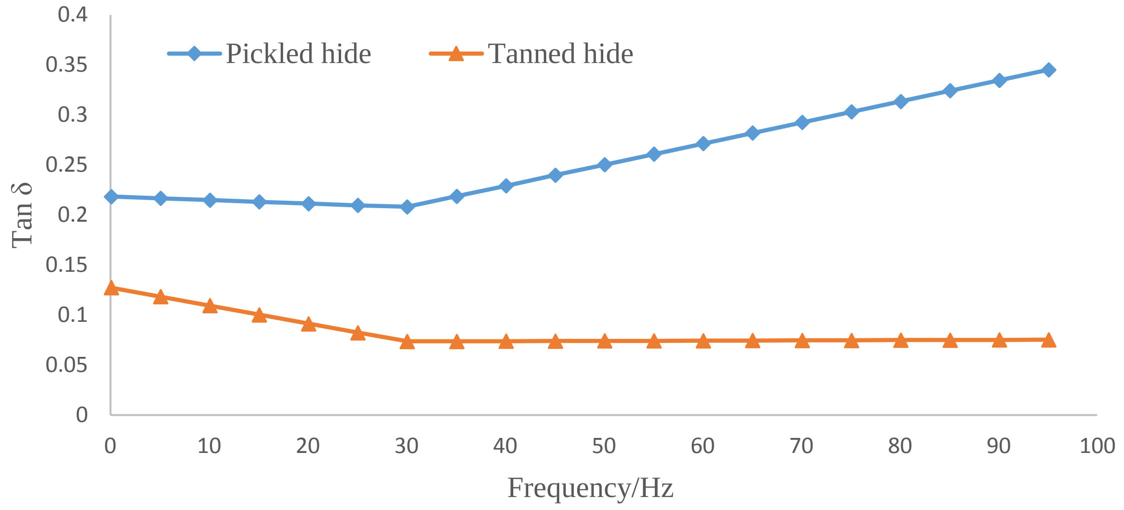

Figure 4.24: Frequency dependence of tan δ for bovine hide

Complex and Dynamic viscosity

The complex viscosity and dynamic viscosity, η for tanned hide was higher than that for pickled hide as shown in figure 4.25. This is attributed to the crosslinking effect of tanning that improves the strength and stiffness of the hide. Both η and the complex viscosity for both pickled hide and tanned hide decreased linearly and rapidly with increase in frequency from 0.1 to 30 Hz, followed by weak dependence on frequency from 30 to 100 Hz for both hides. Both hides exhibited weak structure indicated by greater complex viscosity than the corresponding η. The results are in agreement with the findings reported by Carnali (1991); Lapasin and Pricl (1995) and Morris *et al.* (1996).

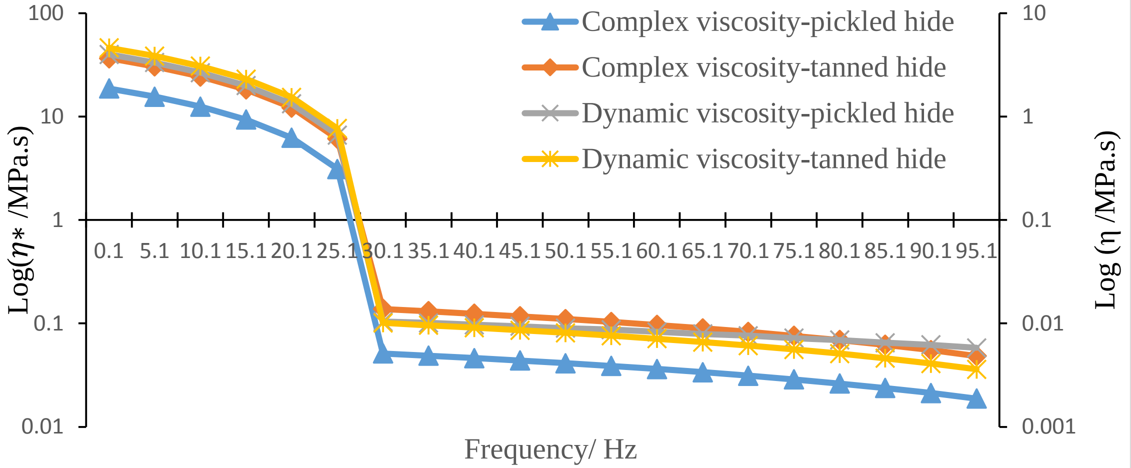

Figure 4.25: Effect of tanning on $\eta *$ and η for bovine hide versus frequency

Tanned hide has higher molecular weight per unit volume due to the presence of chromium ions and cross-linked hydrogen bonds (Covington, 1997). The intermolecular and intramolecular hydrogen bonding increases the viscosity of tanned hide compared to pickled hide. The results agree with those obtained in a study by Sai and Babu (2001). As frequency increases, internal friction decreases due to smaller effective interactions among the collagen molecules (Machado *et al*., 2002). The intermolecular interactions are reduced by the micro-structural anisotropy resulting from the shear deformation. Further increase in frequency forces the orientation of the polymer chains along the flow direction resulting in a drop in the viscosity. Similarly, increase in frequency decreases the number of entanglements that strengthen the flexibility of collagen chains hence reducing the intermolecular bonds which translates to lower viscosity (Duan *et al*., 2013; Ju *et al*., 2013).

Shear strain (ε) and shear stress (σ)

Figure 4.26 illustrates the effect of tanning on shear strain (ε) and shear stress (σ) versus frequency. The ε for pickled hide showed higher values than for tanned hide in the entire frequency range. In both pickled and tanned hides, the ε increased with frequency to a maximum value at 30 Hz. At 95.1 Hz, the curves of ε for both pickled and tanned hides overlapped. In the entire frequency range, tanned hide had greater σ than pickled hide. This is probably due to the crosslinking by tanning which enhances stiffness of the collagen molecules (Covington 1997). Greater ε values in pickled hide simply indicates that the molecular chains are easier to slide over each other when shearing strains are applied compared to tanned hide. This also indicates the stronger ability of tanned hide to store more residual stress (Edali *et al.*, 2001). The swelling effect of liming with alkali solution and sulphide usually leaves the structure more open and loose during pickling (Liu *et al.*, 2009; Nalyanya *et al.*, 2015a). In the frequency range of 30-100 Hz, σ for both hides showed weak frequency-dependence. When hide is subjected to any shear strain, collagen molecules have enough room to distribute the stress with different relaxation times. At lower frequency, almost all the stress distribution modes are fast enough for the operation, hence stress was minimal. As frequency increased, most of the collagen molecules didn't have enough time to relax during the cycle $(^{2\pi}/_{\omega})$. Hence the collagen chains remain stretched throughout the oscillation cycle. This explains the increasing trend of σ with frequency.

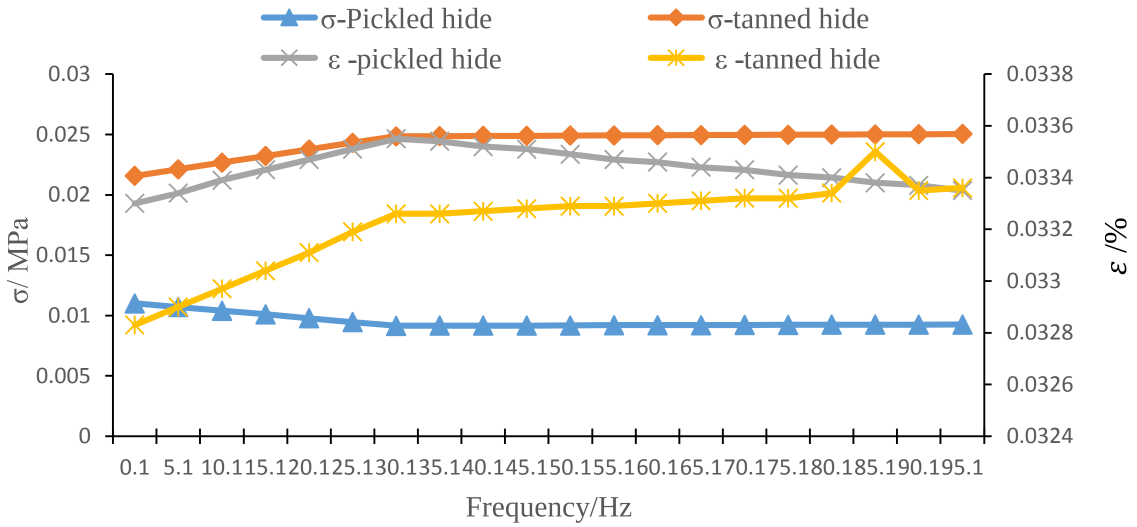

Figure 4.26: Effect of tanning on σ and ε for bovine hide versus frequency

4.3 Effect of artificial UV radiations on viscoelasticity

In this section, curves of viscoelastic properties for samples irradiated for different time durations were plotted on the same graphs to compare their magnitudes across the experimental temperature and frequency sweeps. The comparison of the curves enabled inferences of the effect of the radiation on the properties.

4.3.1 Storage modulus (E')

Storage modulus (E') with no UV radiation

The storage moduli **(**E'**)** of non-irradiated (control) pickled and tanned hides are shown in figure 4.27. Pickled hide showed progressive increase in E' with temperature to two distinct peaks of 1192 and 1101 MPa at temperatures 110 °C and 195 °C, respectively. There was a minimum E' of 820 MPa at 135 °C and a drop to almost zero at 210 °C. Tanned hide similarly showed a peak of 1418 MPa at 225 °C. Minimum E' of 813 MPa and 765 MPa occurred at 40 °C and 85 °C respectively. During pre-tanning, tanning processes and exposure to the atmosphere, collagen matrix absorbs water into its structure (Mandal *et al.*, 2010). Increase in temperature dehydrates the collagen of the water making the fibrils and bundles to come together making the structure more compact and stiff increase in E' (Budrugeac *et al.*, 2010; Cucos *et al.*, 2011). After the first peak, E' decreases due to melting of the amorphous fraction of the collagen. An increase in temperature beyond the second peak causes water molecules in the collagen to compete for energy with the hydrogen bonds that maintain the triple-helix configuration causing unwinding of the triple-helix (denaturation) and finally formation of localized gel in the case of pickled hide (Cucos *et al.*, 2011). Denaturation causes a decrease in the storage modulus**.** This process has also been referred to as melting of the native crystalline (rigid) collagen or shrinkage of the native collagen both denoting glass transition (Gangopadhyay *et al.*, 2000; Jeyapalina *et al.*, 2007). During this melting, there is increased mobility of the macromolecular chains that weaken the intra and inter collagen bonds hence decreased storage modulus.

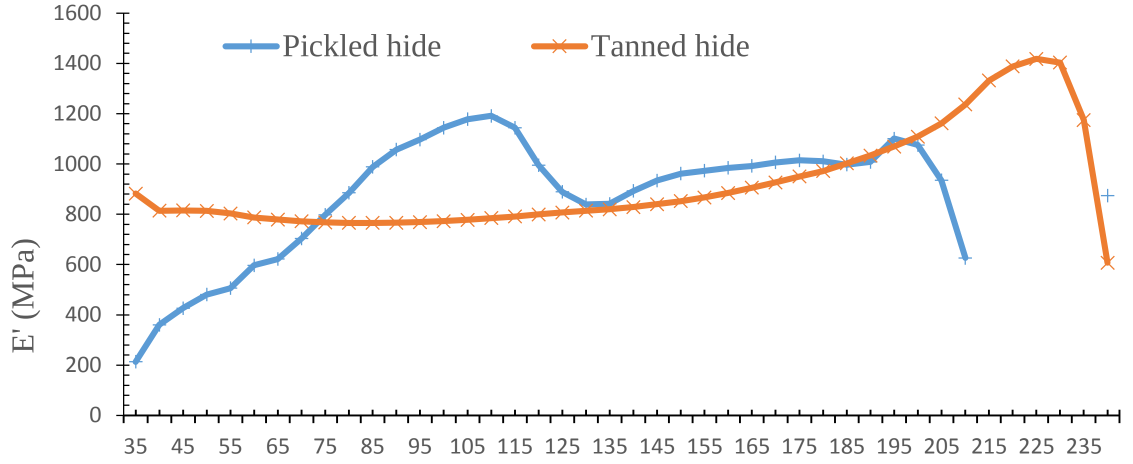

Figure 4.27: Effect of tanning on $\boldsymbol{E'}$ for bovine hide

Storage modulus ($\boldsymbol{E'}$) with UV radiation

The effect of UV irradiation on E′ for pickled hide is illustrated in figure 4.28. At temperatures lower than 110 °C, the control sample had the lowest E′with the irradiated samples showing inconsistent increase and decrease. However, there was a visible characteristic trend such that the sample irradiated for 30 hours had the highest E′ followed by 24 hours, 12 hours followed by 18 hours then 6 hours. Higher irradiation showed significant increases in E′. Results agree with the study by Liu *et al.* (2011). Collagen amino acids possess endogenous chromophoric sites (aromatic residues) such as tyrosine and phenylalanine which absorb the UV irradiations in the range of 250-300 nm (Sionkowska *et al*, 1999; Sionkowska *et al.*, 2004; Metreveli *et al.*, 2010; Zhang *et al.*, 2011). The energetic UV radiations initiate photodegradation of these aromatic amino acids to form crosslinks called dityrosine (Kato *et al.*, 1994; Miles *et al.*, 2000; Paul and Bailey, 2003; Sionkowska *et al.*, 2004; Metreveli *et al.*, 2010). This increases the hardness and stiffness of the collagens hence E′(Theodossiou *et al.*, 2002; Metreveli *et al.*, 2010). Further absorption of the UV irradiation forms new photoproducts such as pentosidine and pyridinoline that add more crosslinks (Fathima *et al.*, 2007; Sionkowska *et al.*, 2013). However, the concurrent polypeptide chain scission and crosslinks initiated by the UV irradiation cause intermediate magnitudes of storage modulus. similarly, water molecules in the collagen matrix splits under UV irradiation forming radicals which attack peptide backbone radicals (-NHC-CO-). The radicals recombine forming covalent bonds together with the subsequent modification of the amine and carboxyl groups' crosslinks that increase the E′(Weadock *et al.*, 1995). This agrees with results obtained by Sionkowska *et al.* (2001) who cited the intermediate magnitudes to be as a result of competing processes of peptide bond scission events arising from the free radical mechanism of the aromatic residues donating free electrons.

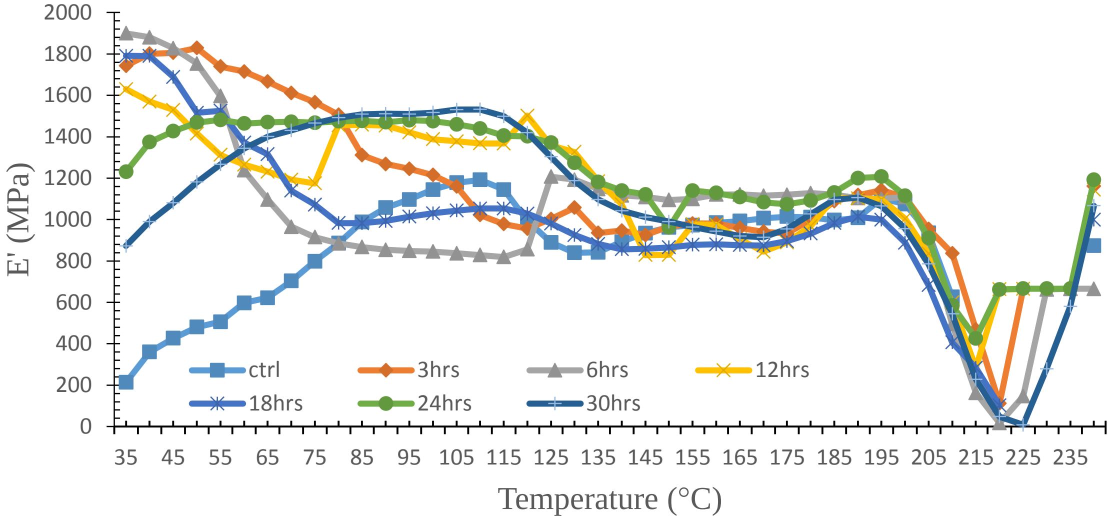

Figure 4.28: Effect of UV radiation on $\boldsymbol{E'}$ for pickled hide

The effect of UV radiation on the storage modulus for tanned hide is shown in figure 4.29. The samples irradiated for 30 minutes, 3 hours, 12 hours, and 30 hours had lower E' than the control sample while sample irradiated for 6 hours and 18 hours had higher E' than the control. From 30 minutes the E' increased to the highest value at 6 hours through 3 hours. Thereafter, E' decreased through irradiation time of 12 hours and 18 hours to 30 hours. From 0-30 minutes, the decrease in E' indicates the photodegradation of collagen along its main chains with scission of $-CH_2-N=$ and $=CH_2$ bonds. It is likely due to the breaking of $N-H\cdots O=C$ inter-chains hydrogen bond as well as losing the bonding water in collagen (Kaminska and Sionkowska, 1996). Thereafter, E' starts to increase slowly to 6 hours where the magnitude is highest. This can be attributed to the crosslinking as a result of formation of dityrosine, pentosidine and pyridinoline. Further irradiation and increased absorption causes photodegradation and photolysis that weaken the bonds and decrease the storage modulus. Comparing figure 4.28 and 4.29, the trends are different.

Apart from the tyrosine, phenylalanine, pentosidine and pyridinoline that increase UV absorption, the presence of chromium ions act as synthetic polymer or special inorganic pigment increasing absorption (Sionkowska, 2000; Christner, 2007). Similarly, tanning makes the leather structure compact lowering the percentage reflectance and increasing the absorption (Christner, 2007). This absorption complicates further the polypeptide crosslinking and chain scission. Absorption coefficient is affected by hydration level owing to direct absorption by water molecules and subsequent vaporization (Fisher and Hahn, 2004). At higher irradiation duration, the maximum of absorption/scattering is almost the same. Pickled hide behave as undyed crust which has high reflectance of the UV radiations that scatter the radiation hence their impact on the structure is minimized (Ionita *et al.*, 2010). Free radicals appearing in collagen water solutions under UV radiation and evoking photodegradation of macromolecule (Metreveli *et al.*, 2008).

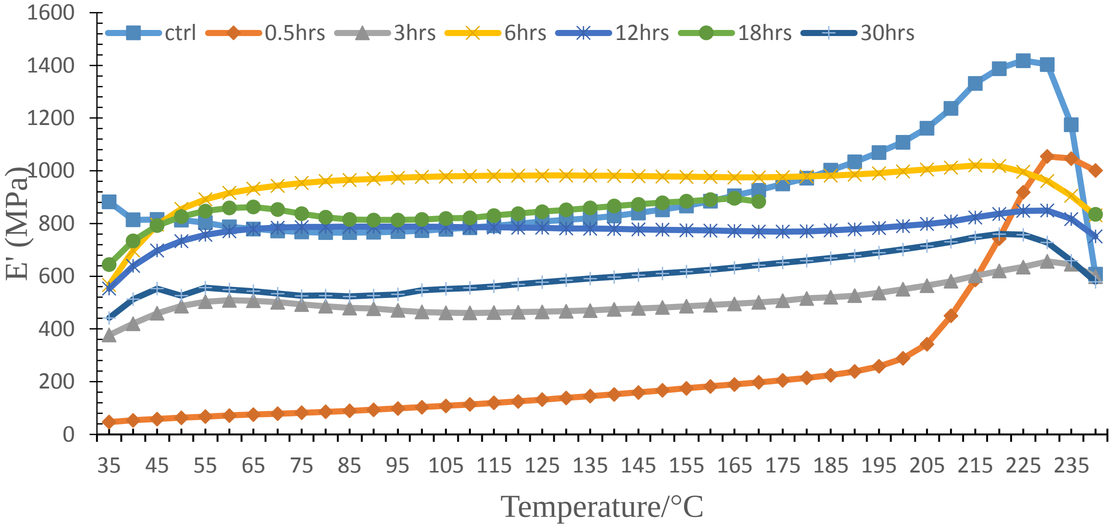

Figure 4.29: Effect of UV radiation on E' for tanned hide

4.3.2 Tan δ

Tan δ with no UV radiation

Effect of tanning on tan δ is illustrated in figure 4.30. Both pickled and tanned hide possess some damping capability useful to dissipate cyclic mechanical energy imposed on it during deformation. As it can be seen in the figure 4.30 in the temperature range 55-165 °C, tanning slightly increases the dissipative capability of the collagen fibres as indicated by slightly higher tan δ of tanned hide compared to pickled hide. However, this damping is higher in pickled hide than tanned at temperatures higher than 165 °C.

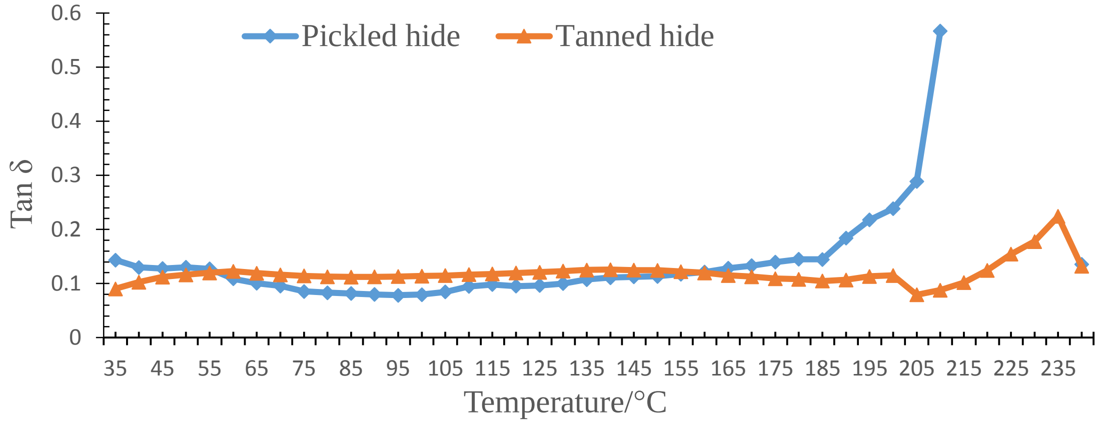

Figure 4.30: Effect of tanning on tan δ for bovine hide

Tan δ with UV radiation

Figure 4.31 illustrates the effect of UV radiation on tan δ of pickled hide. Although there were overlapping in tan δ due to smaller values in the temperature range 35-210 °C, there appears a characteristic trend. Tan δ was highest in the specimen irradiated for 18 hours then it decreased in the order 12 hours, 6 hours, 3 hours then control. In the temperature range 35-210 °C, the magnitudes of tan δ were less than 0.5 implying the elastic nature of the hide. Tan δ increased rapidly higher than 210 °C, although only samples irradiated for 12 hours and 18 hours recorded tan δ greater than one. This implies that pickled hide is predominantly elastic in nature within this temperature and frequency range. The viscous component is only noticed at higher temperature when the mobility of the peptide chains associated with the dissipation of energy in form of heat is high (Asif *et al.*, 2005).

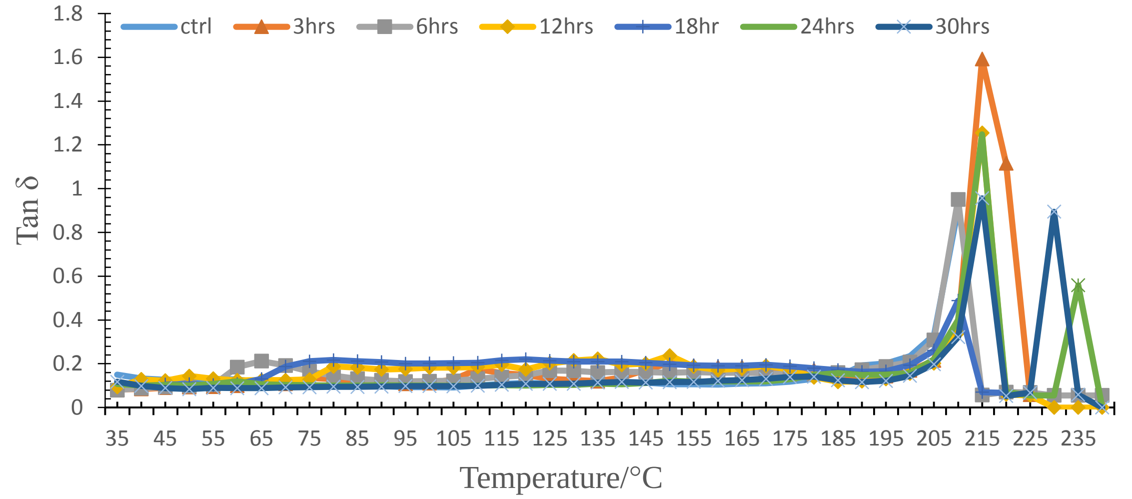

Figure 4.31: Effect of UV radiation on tan δ for pickled hide

The effect of UV radiation on tan δ for tanned hide is illustrated in figure 4.32. In all the samples, the tan δ increased rapidly temperatures greater than 180 °C. This is due to increased chain mobility that increases the energy dissipation in form of heat.

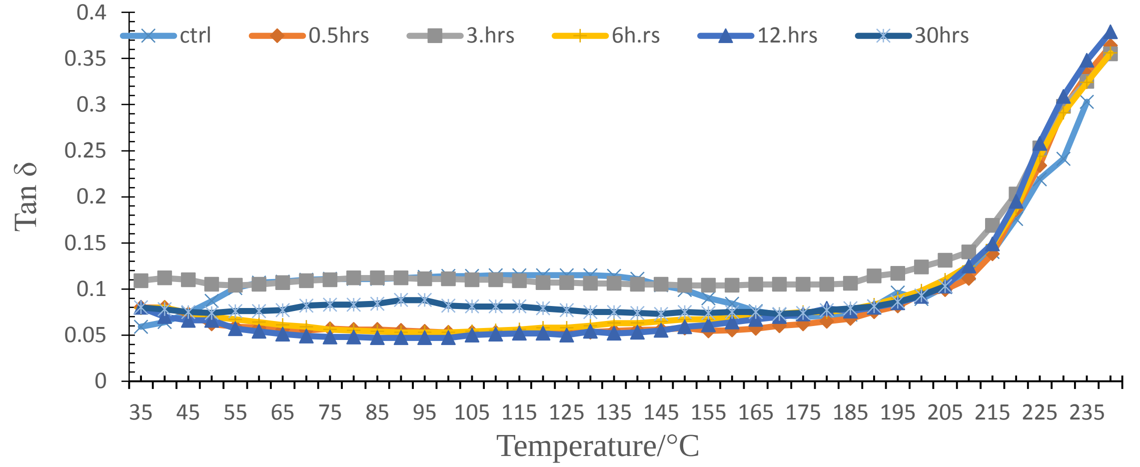

Figure 4.32: Effect of UV radiation on tan δ for tanned hide

4.3.3 Dynamic Viscosity (η)

Dynamic Viscosity (η) and complex viscosity (η*) with no UV radiation

The effect of tanning on dynamic viscosity and complex viscosity is illustrated in figure 4.33. The dynamic viscosity, η increased with temperature for both hides, forming peaks at different temperatures. This means that resistance to flow or permanent deformation increases with temperature, an observation that agreed with the results obtained by Odlyha et al. (2000). The initial increase of η with temperature is possibly due to the increasing hydrophobic interactions among the collagen molecules as collagens associate more at high temperatures (Li *et al.*, 2014). With increasing temperature, energy for heat motion of the polypeptide chains increases and thus the resistance to segment motion becomes weaker leading to drop in η (Zhang *et al.*, 2010). In addition, the increase drives the molecular mobility of the collagen chains and thus breaks the weak interactions such as hydrogen bonds (Xue and Sethi, 2012). During melting or denaturation of the collagen, the triple-helix of collagen collapse to a random coil with weak intra and inter molecular hydrogen bonding that hold the secondary structure of collagen (Sai and Babu, 2001; Pietrucha, 2005; Fathima *et al.*, 2009). This leads to a decreasing trend in η. At temperatures higher than 195 °C, the η of pickled dropped continuously while it increased rapidly in tanned hide. This is probably due to the chrome tannins that generate additional crosslinks of collagen fibrils leading to reinforcement of the tanned hide at higher temperatures (Cucos and Budrugeac, 2010). The η curves peaks in pickled hide were sharper than those observed in tanned hide. The major peaks in dynamic viscosity for pickled hide were at 115 and 195 °C of magnitudes 60 and 90 MPasec, respectively and a minimum of 45.65 MPasec at 130 °C while at 135 °C of 45.55 MPasec in tanned hide. However, the major peaks in complex viscosity for pickled hide occurred at 105 °C and 175 °C but at 110 °C and 225 °C for tanned hide. Beyond 175 °C for pickled hide and 225 °C for tanned hide, the viscosities dropped drastically to almost zero. The breakage of the bonds that once stabilized the secondary structure of collagen collapsed at the temperatures (Pietrucha, 2005). This is due to collapse of the triple-helical structure (denaturation) that results in sudden fall in viscosity Both dynamic viscosity, η and complex viscosity for pickled hide was greater than tanned hide in the temperature range 75-205 °C. The collagen spaces created by the swelling processes in tanned hide are filled up by the chromium ions. This leaves little space for water absorbed. This explains why the increases and the peaks in tanned hide were less sharp and small.

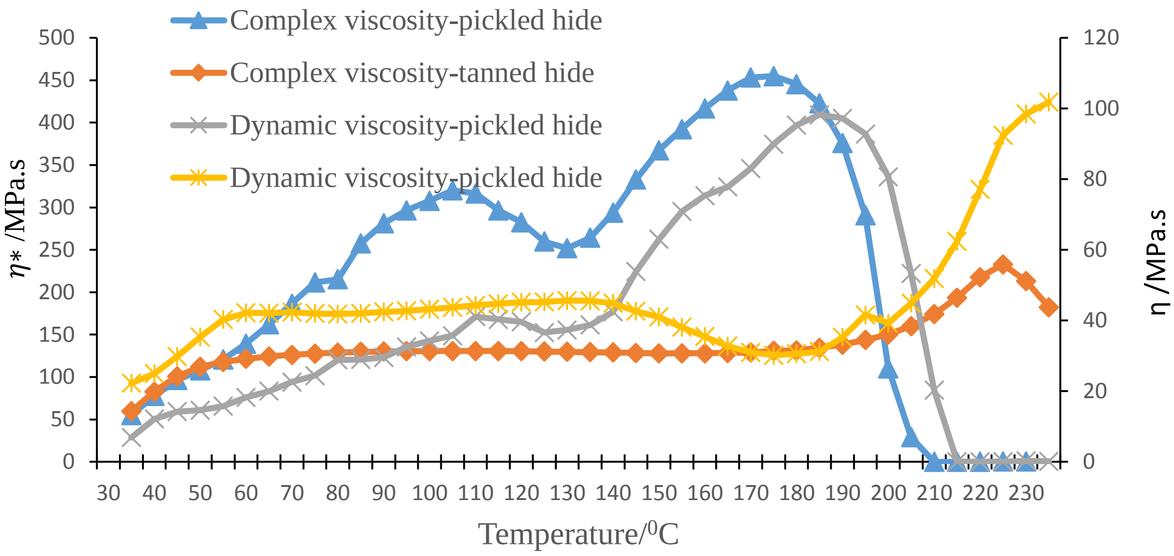

Figure 4.33: Effect of tanning on $\eta*$ and η for bovine hide versus temperature

Dynamic Viscosity (η) with UV radiation

Figure 4.34 illustrates the influence of artificial UV radiation on η of pickled hide. Control sample had the lowest η followed by the sample irradiated for 30 hours with the specimen irradiated for 30 minutes having the highest η with a minimum of 439 MPasec and a maximum of 949 MPasec at 185 and 100 °C, respectively. All the specimens showed a distinct common trend, whereby the η reached maximum at 90-130 °C.

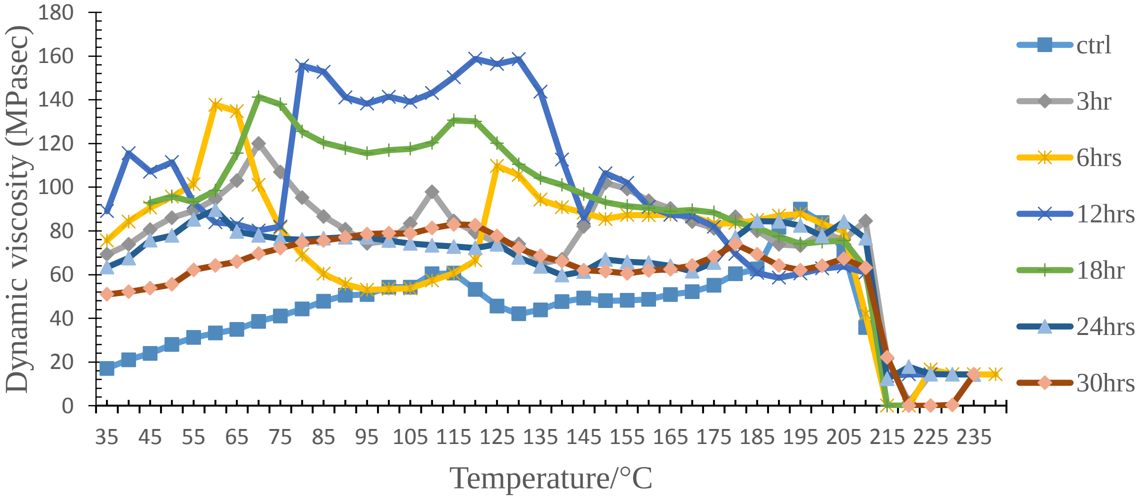

Figure 4.34: Effect of UV radiation on η for pickled hide

The effect of UV radiation on the η of tanned hide is illustrated in figure 4.35.

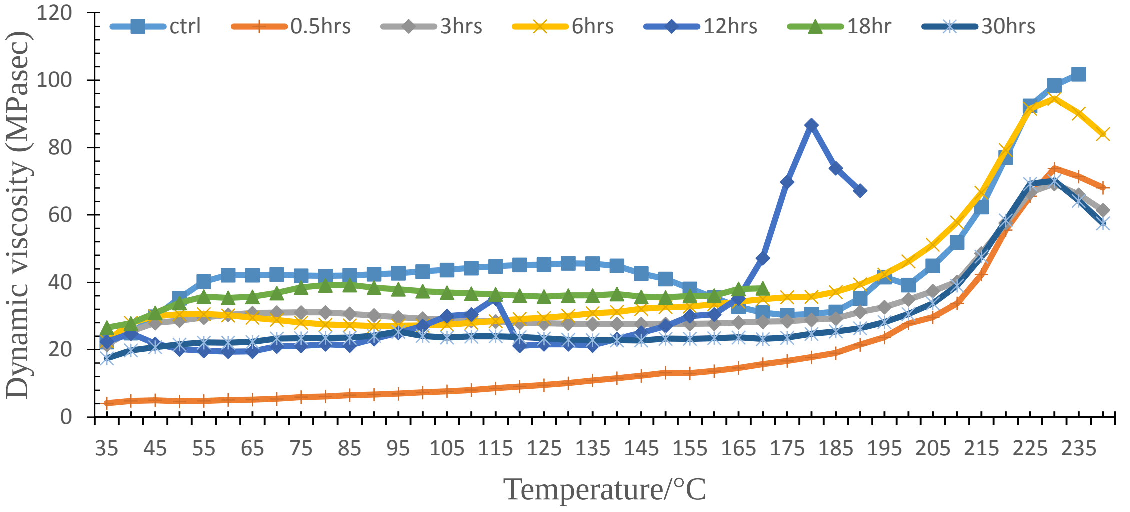

Figure 4.35: Effect of UV radiation on η for tanned hide

On the contrary, control sample had the highest η than the irradiated samples. This implies that η decreases with irradiation. This agrees with results from collagen studied by Sionkowska *et al.* (1999) and Sionkowska *et al.* (2013). In both investigations, relative viscosity decreased with time of UV radiation (Sionkowska *et al*., 2013). Results also agree with the viscosity measurements by Fathima *et al.* (2007) on both native and aldehydes-treated collagen (Fathima *et al.*, 2007). The reduction in η can be attributed to the free radicals causing breaking of intermolecular bonds of triple-helical molecule (Kato *et al.*, 1994; Fathima *et al*., 2007). The presence of chromium ions in the collagen matrix act the role of synthetic polymer that increase the absorption of UV radiation as observed in a study by Sionkowska (2000). Increased absorption causes major photodegradation and scission in the main chains and hence weak stability that leads to decreased η for irradiated samples (Fathima *et al.*, 2007). Similarly, the distinct bluish color of the tanned hide makes it good in absorbing UV radiation than the high reflecting undyed pickled crust which scatters most radiations hence minimizing their effect on the structure (Ionita *et al.*, 2010). These results closely correlate with those of Olle *et al.* (2011) whereby the chrome tanned leather was strongly affected by the UV radiation than the wet white leather.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

5.1.1 Tensile tests

Percentage elongation and tear strength of samples cut perpendicular to the backbone were significantly higher than for samples cut parallel to the backbone ($p = 0.00114$ and $p = 0.00508$, respectively). However, tensile strength for samples cut perpendicularly was significantly lower than for samples cut parallel to the backbone ($p = 0.02099$). Indeed tanning significantly increased the tensile strength ($p = 0.0344$) but decreased both percentage elongation or elasticity and tear strength ($p = 0.000236$ and $p = 0.0176$) of bovine hide. The measured values of tear strength, tensile strength and percentage elongation have shown that indigenous Kenyan Boran bovine hide meets the required standards for leather as per the United Nations Industrial Development Organization (UNIDO) and British Standards.

5.1.2 Solar radiation

Chrome-tanning has been shown to enhance majority of viscoelastic properties and thermal stability to temperatures as high as 235 ^{0}C. Tanning also decreases the dissipative or hysteric or damping ability of the hide

Solar radiation has shown to initially decrease storage modulus within 6 hours but subsequent 12, 18 and 24 hours improved the storage modulus gradually. However, within the entire irradiation duration of 6-24 hours, the modulus was still less than that for non-irradiated sample, which reveals the negative impact of natural solar radiation. Irradiation has shown to progressively decrease thermal stability. Indeed the leather industry needs to find an alternative drying technique other than sun-drying to guarantee good quality leather.

Thermal-mechanical analysis proved to be a useful technique for assessing the effect of tanning and natural solar radiation on hide.

5.1.3 Artificial UV radiation

It was found that UV radiation increases the storage modulus (E') of pickled hide whereas in tanned hide, irradiation increased E' up to maximum at 6 hours followed by consistent decrease with irradiation until 30 hours. It was noticed that tanning increases the damping capability as indicated by higher tan δ in tanned than pickled hide. The results also show the predominant elastic nature of hides. In pickled hide, tan δ consistently decreased with irradiation. Irradiation increases η in pickled hide while decreases η in tanned hide.

5.2 Recommendations

The tensile properties showed that Boran bovine hide meets the international UN standards for leather. The study therefore recommends the rearing of Boran breed since it is indigenous and adaptable to the local conditions. This would enhance the livelihood and ensure supply of raw materials for the leather sector.

Leather industry to use alternative drying mechanism other than drying on tanned hide since tanned hide absorbs more solar radiations. If possible, the sun drying process can be customized to individual needs of the application. Chrome should be customized based on the individual applications of the material especially design of devices and materials for purposes of earplug, vibration abatement, reduction of mechanical shocks, instrument mounts and controlling rebound and resisting rolling.

Solar radiation has shown to initially decrease storage modulus within 6 hours but subsequent 12, 18 and 24 hours improved the storage modulus gradually. However, within the entire irradiation duration of 6-24 hours, the modulus was still less than that for non-irradiated sample, which reveals the negative impact of natural solar radiation. Irradiation has shown to progressively decrease thermal stability. Of course this calls for more researches to be done at more than 24 hours of solar radiations. Indeed Kenyan leather industry need to find an alternative technique for drying other than sun-drying to guarantee quality leather.

REFERENCES

Afaq F, Adhami VM and Mukhtar H, (2005). Biological Effects of Ultraviolet Radiation, *Mutation Research/Fundamental and Molecular Mechanisms of Mutagenesis*, **571**, 153–173.

Aklonis JJ and McKnight WJ, (1983). (Ed.), Introduction to polymer viscoelasticity, John Wiley and Sons, New York, Chichester, Brisbane.

Al-Ruqaie IM, Kasapis S and Abeysekera R, (1997). Structural properties of pectin-gelatin gels. Part II: effect of sucrose/glucose syrup, *Carbohydr Polym*, **34**, 309-321.

Altaf K, Ashcroft IA and Hague RJM, (2011). Investigation of the effect of relative humidity on polymers by depth Sensing Indentation, *J Mater Sc*, **46** (23), 7551-7557.

Annumary A, Thanikaivelan P, Ashokkumar M, Kumar R, Sehgal PK and Chandrasekaran B, (2013). Synthesis and characterization of hybrid biodegradable films from Bovine hide collagen and cellulose derivatives for biomedical applications, *Soft Materials*, **11**, 181-194.

Asfaw A, (1997), Country report: Ethiopia. *In proceedings of a seminar on livestock development policies in Eastern and Southern Africa*. OAU/ IBAR and ministry of Agriculture and cooperatives, Swaziland, Mbabane, 343-345.

Asif A, Huang CY and Shi WF, (2005). Photopolymerization of waterborne polyurethane acrylate dispersions based on hyperbranched aliphatic polyester and properties of the cured films, *Colloidal Polymer Science*, **283**, 721–730.

Basil-Jones MM, Edmonds RL, Cooper SM, Kirby N, Hawley A and Haverkamp RG, (2013). Collagen Fibril orientation and tear strength across ovine skins, *Journal of Agricultural Food and Chemistry*, **61**(50), 1227-1233.

Beck K and Brodsky B, (1998). Supercoiled Protein Motifs: The Collagen Triple-Helix and the α-Helical Coiled Coil, *Structural Biology,* **122**, 17-29.

Bigi A, Burghammer M, Falconi R, Koch MH, Panzavolta S, Riekel C, (2001). Twisted plywood pattern of collagen fibrils in teleost scales: an x-ray diffraction investigation, *Journal of Structural Biology*, 136, 137-143.

Billmer WF, (1984). Textbook of polymer science, 3rd Edition. Applied science publishers, London, 366-367.

Brinckmann J, Notbohm H, Mueller PK and Eds, (2005). Collagen: Primer in Structure, Processing and Assembly, Springer-Verlag Heidelberg, the Netherlands.

Budrugeac P and Miu L, (2008). Effect of Temperature and Relative Humidity on Vegetable Tanned Leather Studied By Thermal Analysis, *J Cultural Heritage*, 9, 146–153.

Budrugeac P, Miu L, Popescu C and Wortmann JF, (2004). Identification of collagen-based materials that are supports of cultural and historical objects, *J Therm Anal Calorim*, **77**(3), 975-985.

Carnali JO, (1991). A dispersed anisotropic phase as the origin of the weak-gel properties of aqueous xantan gum, *Journal of Applied Polymer Science,* **43,** 929-941.

Chahine C, (2000). Changes in hydrothermal stability of leather and parchment with deterioration: a DSC study, *Thermochimica Acta*, **365**, 101-110.

Chaudhry B, Ashton H, Muhamed A, Bull S and Frankel D, (2009). Nanoscale viscoelastic properties of an aligned collagen scaffold, *J mater sc; mater in med*, **20**(1), 257-263.

Chen Y, Zhang M, Liu W and Li G, (2011). Properties of alkali-solubilized collagen solution cross-linked by N-Hydroxysuccinimide activated adipic acid, *Korea-Aust Rheol J.*, **23**(1), 41-48.

Christner J, (2007). TFL Ledertechnik AG, Switzerland, World Leather, Feb/March, 32-35.

Clasen C and Kulicke WM, (2001). Determination of viscoelastic and rheo-optical material functions of water soluble cellulose derivatives, *Progress in Polym Sc*, **26**, 1839-1919.

Cloete SWP, van Schalkwyk SJ, Brand TS, Hoffman LC and Nel CJ, (2006). The effects of dietary energy and protein concentrations on ostrich skin quality, *South African Journal of Animal Science*, **36** (1), 40-44.

Cohen NS, Odlyha M and Foster GM, (2000). Measurements of shrinkage behavior in leather and parchment by dynamic mechanical thermal analysis, *Thermochimica Acta*, **365** (1-2), 111-117.

Covington AD, (1997). Modern Tanning Chemistry, *Chem. Soc Rev*, **26** (2), 111-126.

Craig AS, Eikenberry EF and Parry DA, (1987). Ultrastructural organization of skin: classification on the basis of mechanical role, *Connective Tissue Res*, **116**, 213–223.

Cucos A and Budrugeac P, (2010). The Suitability of the DMA Method for the Characterization of Recent and Historical Parchments and Leathers, *Int J Conserv Sc*, **1**(1), 13-18.

Cucos A, Budrugeac P, Miumi L, Mitrea S and Sbarcea G, (2011). Dynamic Mechanical Analysis of Historical Parchments and Leathers: Correlation with DSC and XRD, *Thermochemica Acta*, **516**, 19-28.

DAGRIS, (2006). Domestic Animal Genetic Resources Information System (DAGRIS). Eds. Rege JEO, Ayalew W, Getabun E, Hanote O and Dessie D, International Livestock Research Institute, Addis Ababa, Ethiopia.

Daniels R and Landmann W, (2005). Hides and skins: temperature and physical change, World Leather, **5**, 44.

De Carvalho RA, Grosso CRF, (2004). Characterization of gelatin based films modified with transglutaminase, glyoxal and formaldehyde, *Food Hydrocolloid*, **18**, 717–726.

de Volder N, Hallmanns M and Levy J, (2007). Annoying energy. II. Solar heating of dark leather, in Proceedings of the XXIX International Union of Leather Technologists and Chemists Societies Congress, Washington.

Doi M and Takimoto JI, (2003). Molecular modelling of entanglement, *Philosophical Transactions of the Royal Society London A*, **361,** 641-652.

Duan L, Li J, Li C, and Li G, (2013). Effects of NaCl on the rheological behavior of collagen solution, *Korea-Aust Rheol J*, **25**(3), 137-144.

Edali M, Esmail MN and Vatistas GH, (2001). Rheological properties of high concentrations of carboxymethyl cellulose solutions, *J Appl Polym Sc*, **79**, 1787-1801.

Eidam D, Kulicke WM, Kuhn K and Stute R, (1995). Formation of maize starch gels selectively regulated by the addition of hydrocolloids, *Starch*, **47**(10), 378-384.

Ershad-Langroudia A, Mirmontahaia A and Vahidzadeh R, (2012). Viscoelastic behavior of treated historical leather with nanocomposite, Proceedings of the 4th International Conference on Nanostructures (ICNS4), 12-14 March, 2012, Kish Island, I.R. Iran.

ESA (Ethiopian Standards Agency) (2012). The quality standards for leather and leather products, Addis Ababa, Ethiopia.

FAO (Food and Agriculture Organization of the United Nations) (2010b). World Statistical Compendium for Hides, Skins, Leather and Leather Footwear. Tropical and

Horticultural Products Service, Commodities and Trade Division (ESC), FAO, Viale delle Terme di Caracalla 00100 Rome, Italy.

Fathima NN, Suresh R, Rao JR and Nair BU, (2007). Effect of UV Irradiation on the Physicochemical Properties of Collagen Stabilized Using Aldehydes, *J Appl Polym Sc*, **104**, 3642–3648.

Fisher BT and Hahn DW, (2004). Measurement of small signal absorption coefficient and absorption cross-section of collagen for 193nm excimer laser light and the role of collagen in tissue ablation, *Applied optics*, **43**(29), 5443-5451.

Florian MLE, (2009). The mechanisms of deterioration of leather In: KITE M and Thompson R (eds), *Conservation of leather and related materials*, Oxford, Butterworth-Heinemann.

Fujimori E, (1989). Cross-linking and fluorescence changes of collagen by glycation and oxidation, *Biochim Biophys Acta*, **998**:105–110.

Gangopadhyay S, Lahiri S and Gangopadhyay PK, (2000). Chrome-free Tannage by Sequential teratment with synthetic Resins and Aluminium or Titanium, *J soc leath Tech Chem*, **84**, 88-93.

Gelse K, Poshl E and Aigner T, (2003). Collagens-structure, function and biosynthesis, *Advanced drug delievry reviews*, **55**(12), 1531-1546.

Gordon PG, (1995). Australian Woolskin–their Value and Processing, *Wool. Tech. Sheep Breed*, **43**, 120-135.

Gorham SD, Light ND, Diamond AM, Willins MJ, Bailey AJ, Wess TJ, Leslie NJ, (1992). Effect of chemical modifications on the susceptibility of collagen to proteolysis. II. Dehydrothermal crosslinking, *Int J Biol Macromol*, **14**,129–138.

Gunasekaran S and Ak MM, (2000). Dynamic oscillatory shear testing of foods –selected applications, *Trends in Food Science & Technology*, **11,** 115-127.

Haile A, Ayalew W, Kebede N, Dessie T and Tegegne A, (2011). Breeding strategy to improve Ethiopian Boran cattle for meat and milk production. IPMS (Improving Productivity and Market Success) of Ethiopian Farmers Project Working Paper 26. Nairobi, Kenya, ILRI.

Haile-Mariam, (1994). Boran - indigenous African cattle with potential, Ph.D. Dissertation, Department of Animal Breeding and Genetics, Swedish University of Agricultural Sciences, Uppsala, Sweden.

Haines B, (1991). Natural ageing of leather in libraries. In Leather, its composition and changes with time; Calnan C and Haines B, eds. Northampton: The Leather Conservation Centre.

Hansen EF, Lee SN and Sobel H, (1993). Effects of Relative Humidity on some Physical properties of Modern Vellum, *J Amer Inst conserv*, **31**(3) 325-342.

Haroun M, Palmina K, Gurshi A and Covington D, (2009). Potential of Vegetable Tanning Materials and Basic Aluminum Sulphate in Sudanese Leather Industry, *J Eng Sc Tech*, **4**(1), 20 - 31.

Herascu N, Simileanu M, Radvan R, (2008). Color Changes In The Artwork Materials Aged By UV Radiation, *Romanian Reports in Physics*, **60** (1), 95–103.

Hu H, Zhang X, He Y, Guo ZS, Zhang J and Song Y, (2013). Combined effects of Relative Humidity and Temperature on dynamic viscoelastic properties and Transition of polyvinyl alcohol, *Appl Polym Sc*, **130** (5), 3161-3167.

INESCOP (Center for Technology and Innovation), (2013). http://www.manual for Oxazolidine Tanned Leather: Environmentally Friendly Oxazolidine-Tanned Leather (LIFE08 ENV/E/000140).com. Accessed on June 21, 2013.

Ionita I, Dragne AM, Gaidau C, Dragomir T, (2010). Collagen Fluorescence Measurements on Nanosilver Treated Leather, *Romanian Reports in Physics*, **62 (**3), 634–643.

ISO 2418:2002. Sampling for Physico-mechanical and Fastness Tests-sampling Location, Geneva, Switzerland Test.

ISO 2419: 2002 (IUP 3, SLP 3) Leather – Conditioning of Test pieces for Physical Tests.

ISO 2589:2002 (IULTCS/IUP 4): Determination of thickness

ISO 3376:2002. Leather Physical and Mechanical Tests. Determination of Tensile Strength and Percentage Extension.

Izquierdo E, Boissere M, Robinet L, Larreta-Garde V, Lavedrine B, (1994). Characterization of the effects of heat on vegetable tanned leather, cultural heritage conservation and sustainable development, Paris.

Jacinto MAC, Da Silva Sobrinho AG and Costa RG, (2004). Anatomic and structural characteristics of wool and non-wool sheep (*Ovis aries* L.) in regard to the physico-mechanical aspects of the leather, *Braz J Anim Sc*, **33** (4), 1001–1008.

Jankauskaitė V, Gulbinienė A, Mickus V, (2004). Effect of Leather Finishing Technology on Water Vapour Transmission. Part II. Water Vapor Transfer through Microporous Film Laminated leather, *Materials Science*, **10** (3), 249 – 254.

Janko M, Zink A, Gigler AM, Heckl, WM and Stark RW, (2010). Nanostructure and mechanics of mummified type I collagen from the 5300-year old Tyrolean Iceman, *Proc. R. Soc. B.*, **277**, 2301–2309.

Jariashvili K, Madhan B, Browdsky B, Kuchava A, Namicheishvili L and Metreveli N, (2012). UV damage of collagen: insights form model collagen peptides, *Biopolymers*, **97** (3), 189-198.

Jeyapalina S, Attenburrow GE and Covington AD, (2007). Dynamic Mechanical Thermal Analysis (DMTA) of Leather Part 1: Effect of Tanning Agent on the Glass Transition Temperature of Collagen, *J Soc Leath Techn Chem*, **91** (6), 236-242.

Ju H, Dan W, Hu Y, Lin H and Dan N, (2013). Dynamic rheological properties of type 1 collagen fibrils, *J Mech in Med and Biol*, **DOI: 10.1142/S0219519413400150.**

Kalachandra S, Minton RJ, Takamata T and Taylor TF, (1995). Characterisation of commercial soft liners by dynamic mechanic analysis, *J Mater sc: Mater Med*, **6**, 218-222.

Kaminska A and Sionkowska A, (1996). Effect of radiation on the infrared spectra of collagen, *J Polym Degrad Stabil*, **51**, 19–26.

Kaplan DL and Xu P, (2004). Nanoscale surface patterning of enzyme-catalyzed polymeric conducting wires, *Adv Mater*, **16**, 628–33.

Kasapis S and Mitchell JR, (2001). Definition of the rheological glass transition temperature in association with the concept of iso-free-volume, *Int J Biol Macromol*, **29**, 315-321.

Kato Y, Mori Y, Makino Y, Morimitsu Y, Hiroi S, Ishikawa T and Osawa T, (1999). Formation of N ε-(hexanonyl) lysin in protein exposed to lipid hydroperoxide, A plausible marker for lipid hydroperoxide-dervived protein modification, *J Biol Chem*, **274** (29), 20406-20414.

Kato Y, Uchida K, Kawakishi S, (1994). Aggregation of collagen exposed to UVA in the presence of Riboflavin: a plausible role of tyrosine modification, *Photochem. Photobiol*. **59**(3), 343- 349.

Kato K, Bar G and Cantow HJ, (2001). The interplay between surface micro-topography and mechanics of type I collagen fibril in air and aqueous media: An atomic force microscopy study, *Eur. Phys. J. E*. **2001**, 6, 7–14.

Katumin A, Hufenbach W, Kostka P and Holeczek K, (2010). Frequency dependence of the self-heating effect in polymer-based composites, *Achiev Mater Manufact Eng*, **41**, 9-15.

Khan MA, Rahman MM, Bhuyan MZR, Ahmad MU, (2002). Curing of Crust Leather by Ultraviolet Radiation with Urethane Acrylate: Role of Pigment, *J Appl Polym Sc*, 86, 692–697.

Korhonen M, Hellen L, Hirvonen J and Yliruusi J, (2001). Rheological properties of creams with four different surfactant combinations-effect of storage time and conditions, *Int J Pharm*, **221**, 187-196.

Lai GL, Li Y and Li GY, (2008). Effect of concentration and temperature on the rheological behavior of collagen solution, *Int J Biol Macromol*, **42**, 285-291.

Lakes RS (2004). Viscoelastic measurement techniques, *Amer Inst Phys*, **75**, 797-810.

Lapasin R and Pricl S, (1995). Rheology of industrial polysaccharides: theory and applications, Blackie Academic & Professional, London.

Lapshin RV, Alekhin AP, Kirilenko AG, Odintsov SL and Krotkov VA, (2010). Vacuum UV smoothing of nanometer-scale asperities of polymethyl methacrylate surface, *Surface Investigation. X-ray, Synchrotron and Neutron Techniques*, **4**, 1–11.

Larsen R, (2000). Experiments and observations in the study of environmental impact on historical vegetable tanned leathers, *Thermochimica Acta*, **365**, 85.

Lee CH, Singla A and Lee Y, (2001). Biomedical applications of collagen, *Int Pharm*, **221**, 1-22.

Lee-Sullivan P and Dykeman D, (2000). Guidelines for performing storage modulus measurements using the TA Instruments DMA 2980 three-point bend mode: Amplitude effects, *Polymer Testing*, **19**, 155-164.

Lewis DM, (1989). *Some Aspects of the Photochemistry of Fibrous Proteins*, Colorage 6, 25-31.

Li Y, Qiao C, Shi L, Jiang Q and Li T, (2014). Viscosity of collagen solutions: Influence of concentrations, Temperature, Adsorption and Role of Intermolecular Interactions, *J. of Macromol Sc, Part B: Physics*, **53** (5), 893-901.

Li Z, Paudercerf D and Yang J, (2009). Mechanical behavior of natural cow leather in tension, *Acta Mechanica Solida Sinica*, **22**.

Lin J and Hayhurst DR, (1993). Constitutive Equations for Multi-axial Straining of leather under uniaxial Stress, *Eur. J. Mechanics*, **12**(4), 471-492.

Lischuk V, Plavan V and Danilkovich A, (2006). Transformation of the collagen structure during beam-house process and combined tanning, *Proc. Estonian Acad. Sci. Eng*, **12**, 188–198.

Liu CK, Latona NP and Ramos M, (2011). Effects of Alpha-Tocopherol Addition to Polymeric Coatings on the UV and Heat Resistance of a Fibrous Collagen Material—Chrome-Free Leather, *J Appl Polym Sc*, **122**, 3086–3091.

Liu CK, Latona NP, Ashby R, (2006). Environmental effects on chrome-free leather, *JALCA*, **101**, 368-375.

Liu CK, Latona NP, Lee J and Cooke PH, (2009). Microscopic observations of Leather Looseness and its effects on mechanical properties, *JALCA*, **140,** 230-236.

Machado AAS, Martins VCA and Plepis AMG, (2002). Thermal and Rheological Behavior of Collagen Chitosan Blends, *J Therm Anal Calorim*, **67**, 491-498.

Mandal A, Meda V, Zhang WJ, Farhan MK and Gnanamani A, (2010). Synthesis, characterization and comparison of antimicrobial activity of PEG/TritonX-100 capped silver nanoparticles on collagen scaffold, *Colloids Surface B Biointerfaces*, **90**, 191-196.

Manfredi M, Bearmann G, France F, Shor P and Marengo E, (2015). Quantitative multispectral imaging for the detection of parchment ageing caused by light: a comparison with ATR-FTIR, GC-MS and TGA analyses, *Int J Conserv sc*, **6**, 3-14.

McKenzie RL, Björn LO, Bais A, Ilyasd M, (2003). Changes in biologically active ultraviolet radiation reaching the Earth's surface, *Photochem Photobiol Sci*, **2**, 5–15.

McKinlay A and Diffey BL, (1987). A reference action spectrum for ultraviolet induced erythema in human skin; Human exposure to Ultraviolet Radiations: *Risks and Regulations*, ed WF Passchier and BFM Bosnajakovic (Amsterdam: Elsevier) pp **83-**87.

Menard KP, (1999). Dynamic Mechanical Analysis: a practical introduction, CRC Press LLC, Boca Raton, FL.

Menter JM, Patta AM, Sayre RM, Dowdy J and Willis I, (2001). Effects of UV irradiation on type I collagen fibril formation in neutral collagen solutions, *photoderm photoimmunol photomed*, **17**(3), 114-120.

Metreveli NO, Namicheishvili LO, Jariashvili K, Svintradze DV, Dgebuadze M, Chikvaidze ED, Skopinska J and Sionkowska A, (2010). UV-Vis and FT-IR Spectra of Ultraviolet irradiated collagen in the presence of antioxidant ascorbic acid, *J Ecotoxicol Environm Safety, 7***3**,448-455.

Metreveli N, Namicheishvili L, Jariashvili K, Dgebuadze M, Chikvaidze ED, Sionkowska A, (2008). Identification of free radicals induced by UV irradiation in collagen water solutions, *J Photochem Photobiol B Biol*, **93**(2), 61–5.

Miles CA and Burjanadze TV, (2001). Thermal stability of collagen fibers in ethylene glycol, *Biophys J*, **80** (3), 1480-1486.

Miles CA, Sionkowska A, Hulin SL, Sims TJ, Avery NC and Bailey AJ, (2000). Identification of an intermediate state in the helix-coil degradation of collagen by ultraviolet light, *J. Biol. Chem*, **275**, 33014–33020.

Mishra AK, Mishra A and Chattopadhyay P, (2011). Herbal Cosmeceuticals for Photoprotection from Ultraviolet B Radiation: A Review, Herbal Cosmeceuticals for Photoprotection from Ultraviolet B Radiation: A Review, *Tropical Journal of Pharmaceutical Research,* **10** (3), 351-360.

Mogilner GI, Ruderman G, Grigera R, (2002). Collagen hydration and native state, *J. Molecular Graphic and Modelling*, 21, 209-213.

Morris ER, Gothard MGE, Hember MWN, Manning CE and Robinson G, (1996). Conformational and rheological transitions of wellan, rhamsan and acylated gellan, *Carbohydr Polym*, **30,** 165-175.

Muralidhan MR and Ramesh V, (2005). Histological and biomechanical studies of the skin of cattle and buffalo, *Indian journal of animal research*, **39**(1), 41-44.

Mwinyihija M, (2010). Hides, skins and leather value addition initiatives: the Kenyan Scenario. Leather and Leather Products Development Division, Ministry of Livestock Development, Mawingu Conference, 23-25.

Nalyanya KM, Rop RK, Onyuka A, Kamau J, (2015a). Tensile properties of indigenous Kenyan Boran pickled and tanned bovine hide, *Int J Sci Res*,**4** (3), 2149–2154.

Nalyanya KM, Rop RK, Onyuka A, Migunde PO and Ngumbu RG (2015b). Thermal and mechanical analysis of pickled and tanned cowhide: Effect of solar radiations, *J Appl Polym Sc*, 133, **DOI: 10.1002/app.43208**

Nalyanya KM, Migunde PO, Ngumbu RG, Onyuka AS and Rop RK, (2016). Influence of UV radiation on the viscoelastic properties and dynamic viscosity of bovine hide using dynamic mechanical analysis, *J Therm Anal Calorim*, **123**, 363-370.

Nguyen AL, Vu BT and Wilkes GL, (1974). The Dynamic Mechanical, Dielectric and Melting Behavior of Reconstituted Collagen, *Biopolymers*, **13**, 1023–1037.

Ninh C, Cramer M and Bettingera CJ, (2014). Photoresponsive hydrogel networks using melanin nanoparticle photothermal sensitizers, *Biomater Sci*, **2**, 766.

Ockerman HW and Hansen CL, (2000). *Animal by-product processing and utilization*. Lancaster, PA: Technomic Publishing Co., 463.

Odlyha M, Foster GM, Cohen NS and Larsen R, (2000). Characterization of leather samples by non-invasive dielectric and thermomechanical techniques, *Therm Anal Calorim*, **59**, 587-600.

Odlyha M, Cohen NS, Foster GM, Aliev A, Verdonck EV, Grandy D, (2003). Dynamic mechanical analysis (DMA) ^{13}C solid state nmr and microthermomechanical studies of historical parchment, *Therm Anal Calorim*, **71**, 939-950.

Ojango JM, Malmfors B and Okeyo AM. (eds). (2006). AGTR (Animal Genetics Training Resource, version II). International Livestock Research Institute, Nairobi, Kenya, and Swedish University of Agricultural Sciences, Uppsala, Sweden.

Oklahoma State Education, (2012). Indigenous cattle breeds in East Africa: Boran cattle in Kenya and Somalia, Available: www.ansi.okstate.edu/breeds/cattle/boran [Accessed: April 22, 2012].

Oliveira RJF, Costa RG, Souza WH and Medeiros AN, (2007). Influence of genotype on physico-mechanical characteristics of goat and sheep leather, *Small Rumin Res*, **73**,181-185.

Olle L, Jorba M, Font J and Bacardit A, (2011). Comparison of the effect of the tropical test on both chrome-tanned and wet-white upholstery leather, *J. Soc. Leath. Tech. Chem*, **95**,234-239.

Owando LM, Kinyua R, Ndeda JOH, Mangi SN and Kibwage JK, (2013). Investigation of solar energy potential in Nakuru Kenya and its implications on Kenya Energy policy, *Baraton Interdisciplinary Research journal*, **3**(2), 29-40.

Patel SK, Malone S, Cohen C, Gillmor JR and Colby RH, (1992). Elastic Modulus and Equilibrium Swelling of Poly (dimethylsiloxane) Networks, *Macromol*, **25,** 5241-5251.

Paul RG and Bailey AJ, (2003). Chemical Stabilization of Collagen as a Biomimetic, *the Scientific World Journal*, **3**, 138–155.

Pekhtasheva E, Neverov A and Zaikov G, (2012). Bio damages and protection of leather and fur, *J Chem & Chemic Tech*, **6**, 327-337.

Persikov AV, Ramshaw JAM and Brodsky B, (2005).prediction of collagen stability from amino acid sequence, *J Biol Chem*., **280**, 19343–19349.

Pietrucha K, (2005). Changes in denaturation and rheological properties of collagen-hyaluronic acid scaffolds as a result of temperature dependencies, *Int. J. Biol. Macromol*, **36**, 299-304.

Rabotyagova OS, Cobe P and Kaplan DL, (2008). Collagen structural hierarchy and susceptibility to degradation by UV radiation, *Mater Sc & Eng*, **28**, 1420-1429.

Robertshaw D and Finch V, (1976). The effects of climate on the productivity of beef Cattle in: ed. A.J. Smith Beef cattle production in developing countries. Edinburg, Centre for Tropical Veterinary Medicine, 281-293.

Sai BP and Babu M, (2001). Studies on Rana tigerrina skin Collagen, *Comp Biochem Physiol B: Biochem Mol Biol*, **128**, 81-90.

Salehi M, Lavvaf A and Farahvash T, (2013). Skin Quality and Physical Properties of Leather Based on Sex, Age and Body Parts of Goats Reared on Sub-Humid Hill Country, *Iranian Journal of Applied Animal Science*, **3** (4), 853-857.

Samia HA, (2014). Histological study of the skin and Leather characteristics in two types of Arabian Camels, *Journal of American Science*, **10**(9) 41-47.

Samoillan V, Dandrirand-Lods J, Lamure A, Maurel E, Lacabanne C, Venturini GAG, Casarotto D, Gherardini L, Spina MJ, (1999). Thermal analysis characterization of aortic tissues for cardiac valve bioprostheses, *Biomed Mater Res* **46**, 531–538.

Saraf H, Ramesh K, Lennon A, Merkle A, Roberts J, (2007). Mechanical properties of soft human tissues under dynamic loading, *Journal of Biomechanics*, **40**, 1960-1967.

Sathiyamoorthy M, Selvi V, Mekonnen D, Habtamu S, (2013). Preparation of eco-friendly leather by process modifications to make pollution free tanneries, *J Eng, Comp & Appl Sc*, **2**, 17-22.

SATRA, (2011). Testing Equipment Catalogue.

Shames IH and Cozzarelli FA, (1992). Introduction to non-linear viscoelastic behavior: creep. In: Elastic and inelastic stress analysis, Englewood Cliffs, Prentice Hall, 221-228.

Sionkowska A, (1999). Photochemical transformations in collagen in the presence of melanin, *Journal of Photochemistry and Photobiology A: Chemistry*, **124** (1-2), 91–94.

Sionkowska A, (2000). Modification of collagen films by ultraviolet irradiation, *Polym Degrad Stabil*, **68 (**2), 147–151.

Sionkowska A, Anecka PA, Lewandowska K, Kaczmarek B and Szarszewska P, (2013). Influence of UV-irradiation on molecular weight of chitosan, *Biopolym Res Gr*, **18**, 21-28.

Sionkowska A, Kaczmarek A, Wisniewski H, Kowalonek M and Skopinska J, (2004). Surface characteristics of UV-irradiated collagen/ PVP blended fills, *J Surf Sci*, **566**, 608-612.

Sionkowska A, Kaminska A, Miles CA and Bailey AJ, (2001). The effect of UV radiation on the structure and properties of collagen, *Polymers*, **46(**6), 379–389.

Sionkowska A, Wisniewski M, Skopinska J and Mantovani D, (2006). Effects of Solar Radiation on Collagen-Based Biomaterials, *Int J Photoenergy*, **2006**, 1–6.

Sirear AK, (1997). Elastomers. In: Thermal Characterization of Polymeric Materials. Turi, E.A. (Ed.), **1**, Academic Press, 970-1025.

Sivasubramaniana S, Murali Manoharb B and Puvanakrishnana R, (2008). Mechanism of Enzymatic Dehairing of Skins Using a Bacterial Alkaline Protease, *Chemosphere*, **70**, 1015 - 1024.

Sizeland KH, Basil-jones MM, Edmonds RL, Cooper SM, Kirby K, Hawley A and Haverkamp S, (2013). Collagen orientation and leather strength for selected mammals, *J Agr Food Chem*, **61** (4), 887-892.

SLTC (Society of Leather Technologist and Chemists), (1996). Official methods of analysis. (3rd Ed.). Redbourne, SLTC.

Snyman MA and Jackson-Moss CA, (2000). A comparison of leather properties of skins from ten different South African sheep breeds, *South African J Anim Sci,* **20,** 129-130.

Sperling L, (2006). *Introduction to Physical Polymer Science*.4th Edition, Willey interscience, Canada, 350 – 410.

Sturrock EJ, Boote C, Attenburrow GE, Meek KM, (2004). The effects of the biaxial stretching of leather on fibre orientation and tensile modulus, *J Mater Sc*, **39**, 2481 – 2486.

Svobodova A, Psotova J and Walterova D, (2003). Natural phenolics in the prevention of UV- induced skin damage, *Biomed Papers*, **147**,137–145.

Teddy T, Miu L, Giurginca M, Meghea A, (2006). Evaluation of degradation of parchment and leather by FT-IR and UV-VIS-NIR spectroscopy, *Revista de Chimie*, **57**, 466-471.

Theodossiou GS, Rapti V, Hovhannisyan E, Georgiou K and Yova PD, (2002). Thermally Induced Irreversible Conformational Changes in Collagen Probed by Optical Second Harmonic Generation and Laser-Induced Fluorescence, *Lasers in Medical Science,* **17**(1) 34–41.

Thompson R, (2006). The nature and properties of leather, In: Kite, M.; Thompson, R. (eds). Conservation of leather and related materials. Oxford. Butterworth-Heinemann.

Thomson R, (2002). Conserving historical leathers: Saving our past for the future, *J. Am. Leather Chem Ass,* **97**, 307.

Tuckermann M, Mertig M and Pompe W, (2001). Stress measurement on Chrome-tanned leather**,** *J Mater Sc*, **36**, 1789-1799.

Tyan YC, Liao JD, Klauser R, Wu ID and Weng CC, (2002). Assessment and characterization of degradation effect for the varied degrees of ultraviolet radiation onto the collagen-bonded polypropylene non-woven fabric surfaces, *Biomater*, **23**(1), 65-76.

Valeika V, Sirvaityte J, Beleska K, (2010). Estimation of Chrome-free Tanning Method Suitability in Conformity with Physical and Chemical Properties of Leather, *Materials science (Medziagotyra)*, **16**(4), 330-336.

Ventre M, Padovani M, Covington AD and Netti PA, (2006). Composition, Structure and Physical Properties of Foetal Calf Skin, IULTCS II. EUROCONGRESS, Istanbul.

Wang YL and Attenburrow GE, (1989). Strength of Brazilian Goatskin leathers in relation to skin and animal characteristics, *J Soc Leath Tech Chem*, **78**, 55.

Ward IM and Hadley DW, (1993). An introduction to the mechanical properties of solid polymers. John Wiley and Sons Ltd, New York.

Weadock KS, Miller JE, Bellincampi LD, Zawadsky JP and Dunn MG, (1995). Physical crosslinking of collagen fibres: comparison of UV irradiation and dehydrothermal treatment, *Biomedical Materials Research*, **29**, 1373-1379.

Wells HC, Edmonds RL, Kirby N, Hawley A, Mudie ST and Haverkamp RG, (2013). Collagen Fibril Diameter and Leather Strength, *J Agric Food Chem*, **61**(41) 11524-11531.

Wenger MPE, Bozec L, Horton AM and Mesquida P, (2007). Mechanical properties of collagen fibrils, *Biophysics*, **93**, 1255-1263.

Wu JY, Lin HC, Hsu JS, Yip MC and Fang W, (2009). Static and dynamic mechanical properties of polydimethylsiloxane/carbon nanotube nanocomposites, *Thin Solid Films*, **517** (17), 4895-4901.

Xing JY, Bai B and Chen ZH, (2011). Effects of UV irradiation on stabilization of collagen, *IEEE*, **4**, 2979-2982.

Xue D and Sethi R, (2012). Viscoelastic gels of guar and xanthan gum mixtures provide long-term stabilization of iron micro- and nanoparticles, *Journal of Nanoparticle Research*. **DOI: 10.1007/S11051-012-1239-0.**

Zhang F, Wang A, Li Z, He S and Shao L, (2011). Effect of UV irradiation on porcine dermis type 1 collagen from fresh water fish scales, *Food and Nutrition Sciences*, **2**, 818-823.

Zhang M, Chen Y, Li G and Du Z, (2010). Rheological properties of fish collagen solution: effects of temp and concentration, *Korea-Australia Rheology Journal,* **22**(2), 119-127.

Zheng X, Wang K, Tang K, Qin S, Liu J, (2009). Influence of UV Irradiation on the Properties of Tanned and Fatliquored Goatskin Leather, College of Materials Science and Engineering, Zhengzhou University, Henan 450052, P. R. China.

APPENDIX

List of Publications

1. **Nalyanya KM**, Rop RK, Onyuka A, Migunde PO and Ngumbu RG (2015). Thermal and mechanical analysis of pickled and tanned cowhide: Effect of solar radiations, *Journal of Applied polymer science (Wiley & sons)*, 133, **DOI: 10.1002/app.43208**
2. **Nalyanya KM**, Migunde P. O., Ngumbu R.G., Onyuka A.S. & Rop R.K. (2016). Influence of UV radiation on the viscoelastic properties and dynamic viscosity of bovine hide using DMTA, J Therm Anal Calorim (Springer) **123**, 363-370. **DOI: 10.1007/s10973-015-4851-2.**
3. **Nalyanya KM**, Rop RK, Onyuka A and J Kamau (2015). Tensile properties of Kenyan Indigenous Boran bovine Pickled and Tanned hide, *International Journal of Science and Research* **4** (3), 2149-2154.
4. **Nalyanya KM,** Migunde P. O., Ngumbu R.G., Onyuka A.S. & Rop R.K. Dynamic and rheological properties of pickled and tanned bovine hide, *J Therm Anal Calorim (Springer)* – Under review.
5. **Nalyanya KM**, Migunde P. O., Ngumbu R.G., Onyuka A.S. & Rop R.K. Rheological influence of global solar UV irradiation on the bovine hide, *International journal of Thermophysics (Springer)*- Under review.

Presentations

1. *"Effect of Chrome tanning and pickling on the quality of leather"* at **The 2nd Chuka University International conference,** Chuka University, from 28th-30th October, 2015.
2. *"Influence of global solar radiations on the viscoelastic characterization of both pickled and tanned bovine hide*" in: **The 9th Egerton University International Conference,** Egerton University, from 25th - 27th March, 2015.
3. *"Influence of terrestrial solar radiations on the viscoelastic properties and thermal stability of both pickled and tanned indigenous bovine hide*" at **The Winter College on Optics International workshop at ICTP-Trieste**, Italy, from 9th - 20th February, 2015 under the theme: *Light: a Bridge Between Earth and Space*".

a. *"Environmental impact on the ageing of natural biopolymers of polypeptide class"* at the **International Biopolymer Congress,** University of Manchester, London, UK, 16th to 19th June, 2016.

b. *"Effect of leather processing techniques and environmental conditions on the quality of Kenyan Indigenous leather"* at the **First World Congress on Innovation and Livestock Development (WCILD), Egerton University,** in June 2016.

c. *"Influence of UV radiation on the viscoelastic properties and dynamic viscosity of bovine hide using dynamic mechanical analysis" at the* **10th Egerton University International Conference, Egerton University, Kenya on 30th March to 1st April, 2016.**