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EFFECT OF CHROME-TANNING PROCESS ON BOVINE HIDE USING DYNAMIC MECHANICAL AND THERMAL ANALYSIS (DMTA)

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ABSTRACT

The study reports the Dynamic mechanical Analysis of leather at pickling and tanned stage of processing. The study also discusses the effects of these two key processes in leather making on the viscoelastic properties. The technique of analysis has enabled recording of changes in the viscoelastic properties related to quality and hence functional performance as leather is further processed from pickling to tanning. Dynamic Mechanical Thermal Analysis of bovine hide can be to qualify and quantify leather tanning processes. The results have shown the possibility of using the technique to customize each leather tanning processes for specific application fields. Tanning enhances the E' , σ , and thermal stability while decreases E'' , loss factor, viscosity and ϵ . All the viscoelastic properties exhibited dispersion with two distinct frequency range: 0.1-30 and 30-100 Hz. The dominantly elastic nature of hides implies that the majority of the mechanical energy is dissipated by elastic deformation. Tanning: enhances E'' at frequencies lower than 30 Hz but lowers E'' at higher frequency than 30 Hz, increases E' at all frequencies and temperatures. Viscoelastic properties become less frequency-dependent at frequencies higher than 30 Hz. The viscoelastic properties investigated showed to increase with temperatures before drastic drop at specific temperatures. Tanned hide stores more residue stress and its molecular chains are easier to slide over each other when shearing forces are applied than pickled hide while pickled hide dissipates more than tanned hide at all temperatures and frequencies.

Key words: Storage modulus, Loss modulus, Viscosity, Shear stress, Dynamic Mechanical Thermal Analysis, Pickled and tanned cowhide, Viscoelastic properties.

INTRODUCTION

Dynamic Mechanical and Thermal Analysis is one of the thermo-analytical technique that measures viscoelastic properties of materials against time, temperature or frequency (Odlyha et al, 2000; Jin et al,

2001; Lakes, 2004). Viscoelasticity provides probes into designing of materials and devices for purposes such as vibration abatement, reboundy and mechanical shock reduction (Lakes, 2004). Viscoelastic behavior such as mechanical relaxation can also be related to the physical processes such as phase transformation and thermal expansion in the material (Lakes, 2004). These behaviors are important for they determine the suitability of the material in its relevant application field on the basis of performance (Kalachandra et al. 1995; Niska and Sain 2008; Shumigin et al. 2011). In this technique, an applied sinusoidal stress on the sample produces strain which the modulus of the complex value can be resolved into real and imaginary components (Wu et al, 2009). The real part is known as storage modulus, E' (Pa) and the imaginary part is known as loss modulus, E'' (Pa). The ratio of the imaginary part to the real part is referred to as $\tan \delta$ (Jin et al, 2001; Lakes, 2004). It has been shown that the technique gives more precision and sensitivity compared to the alternative method, Differential Scanning Calorimetry (DSC) (Cucos and Budrugaec, 2010). Similarly, for every sine wave generated, the modulus value obtained can be used sweep across the preselected temperature or frequency range (Arivazhagan and Masood, 2012). The E' measures the degree of elasticity and is related to the stiffness of the material. It also measures the resistance to deformation or sample's ability to store. The E'' measures the ability to lose energy through dissipation in form of heat (Arivazhagan and Masood, 2012). It is related to the viscosity of the material which measures the tendency of the material to shearing flows (Mas et al, 2002).

Leather is an inevitable byproduct of the meat industry, that otherwise will be thrown into waste, with wide applications in industries (Sturrock et al, 2004; Nalyanya et al, 2015a). Leather is composed of a tight network of biopolymer collagen fibres, fibrils and elastin fibres that viscoelastic in nature (Wright and Attenburrow, 2000; Tuckermann et al. 2001). Conventionally, leather making involves a series of processes aimed at stabilizing its structure (Nalyanya et al, 2015a). Among these processes, pickling and tanning processes stand out due to the changes they confer to the hide or skin structure (Jeyapalina et al, 2007; Nalyanya et al, 2015a). These processes affect the mechanical stability, resistance to flow and deformation (Chen et al, 2001). Since leather is a viscoelastic material, dynamic mechanical analysis can be used to study the effects of the processes involved in its processing (Nalyanya et al, 2015b). Viscoelasticity can also make it possible to explore possible applications such as mechanical shock absorbing ability. This is because viscoelastic effects are related to physical processes such as phase transformation and thermal expansion (Lakes, 2004). Hence, the technique can be used to quantify and qualify some of the processes involved in the leather making. Use of Dynamic Mechanical Thermal Analysis to characterize leather and parchments is well documented (Bosch et al. 2000; Odlyha et al, 2000; Jeyapalina et al. 2007; Cucos and Budrugaec 2010). However, literature concerning effect of tanning, temperature and frequency/time on the dynamic mechanical properties of hide at pickled and tanned stage is scarce if not unavailable. Since viscoelastic properties are dependent not only on temperature, but also on frequency and the state of the material (Flossmann et al. 2001; Lakes, 2004; Gautieri et al. 2012), then characterizing mechanical behavior of hide should involve a wide profile of responses over a wide range of temperatures, time and frequencies to give diverse spectrum (Rameshwaram and Dao, 2013). Hence, this paper presents the results of Dynamic mechanical analysis of both pickled and tanned leather under temperature and frequency scans to determine the effect of tanning and pickling processes. Properties such as storage modulus, loss modulus, dynamic viscosity and complex, shear stress and strain have been determined.

MATERIALS AND METHODS

Sample preparation

Samples were prepared to pickling and tanning stage using the standard procedures outlined in tables 1 and 2 at Kenya Industrial Research and Development Institute (KIRDI). Rectangular specimens of dimensions $30\text{ mm} \times 9.3\text{ mm} \times 0.93\text{ mm}$ sampled according to the official sampling method and sampling location ISO 2418: 2002 were cut using a press knife. The samples were then conditioned in a standard atmosphere,

23/50 (temperature 23 ± 2 °C, humidity $50 \pm 5\%$ R.H.) for 48 hours according to ISO 2419: 2002 prior to testing.

Table 1: Sample preparation recipe of pickling

Process/ step	(%) Chemicals	Temp/°C	Time	Remarks
Washing	100% H ₂ O, 1% detergent	23-25	10 min	Drain
Liming and unhairing	100% H ₂ O, 1.5% Na ₂ S, 1% Ca(OH) ₂ (Lime), Add: 100% H ₂ O, 1% Na ₂ S 1% Ca(OH) ₂ (Lime) Add: 50% H ₂ O 1% Ca(OH) ₂ (Lime)	23-25	1hr 16 hrs	Drum speed=2 – 3 r.p.m pH. =12 Drain Fleshing and scudding
Washing	300% H ₂ O,	25	10 min	Drain
Deliming	100% H ₂ O 2% (NH ₄) ₂ SO ₄ , 1% Sodium metabisulphite	25	1hr	P.H.=8.3 x-section clear to phenolphthalein
Bating	0.2% microbates-1600 LVU	35-37	1	Drum speed=3 r.p.m
Washing	200% H ₂ O,	20-25	20 min	Drain
Pickling	80% H ₂ O, 8% NaCl 1% H ₂ SO ₄ (98%),(1:10) 1% Sodium Formate,	20-22	10 min	Drum speed=3 rpm
Drain & washing	200% H ₂ O,	25	1 hr 20 min	P.H=2.5 Drain
Splitting				Split 1.0 mm
Horse up				
Sammy				

Table 2: Sample preparation recipe of tanning

Process/ step	(%) Chemicals	Temp/°C	Time	Remarks
Tanning	6% Chromium Sulphate,(33% basic) Add	25-27	3 hrs	Drum speed= 3 rpm Penetration complete through x-section pH = 3.0 Drain
Basification	0.5% Fungicide 0.5% NaHCO ₃ (1:10) Add		30 min 20 min	
	0.5% NaHCO ₃ (1:10) Add		20 min	Final pH = 3.6
	0.5% NaHCO ₃ (1:10)		20 min	Shrinkage temp = 100°C
Drain and washing	200% H ₂ O,	25	20 min	Drain

Dynamic Mechanical Analysis

Thermal-mechanical analysis was carried out using Dynamic Mechanical Analyzer (DMA, Model 2980) from TA instruments, USA. The samples were mounted onto the film tension clamp, one at a time, and the temperature was equilibrated at 30 °C. The experiment was set to run until 240 °C at a heating rate of 5 °C min⁻¹. This is the ideal heating/cooling rate for film tension geometry and the experiment was performed in a static air environment. Storage modulus (E'), loss modulus, viscosities, shear stress and strain were determined against temperature or frequency, with the aid of Thermal Analysis (TA) instrument control

software. This software analyses the data at different frequencies and presents the means in graphical form. Calibration of the DMA was done before any experiment to enhance reliability of the measurements.

RESULTS AND DISCUSSION

Loss Modulus versus Frequency

The storage modulus (E') and loss modulus (E'') curves for pickled and tanned hides were plotted on single graphs for convenient comparison. Effect of chrome-tanning process on the E' and E'' versus frequency is illustrated in figure 1. 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'' of 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. As frequency increases beyond 0.1 Hz, the available time for polypeptide chains to respond to the applied deforming sinusoidal strains decreases. This makes it difficult for long chains to resonate with the oscillation and only the fewer short chains can participate in the oscillation, lowering 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 participating oscillating chains hence increase in los modulus is observed (Patel et al. 1992).

Storage modulus, E' for tanned hide was significantly greater compared to pickled hide in the entire frequency range (Figure 1). The E' 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 Budrugaec, 2010; Chen et al, 2001; 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).

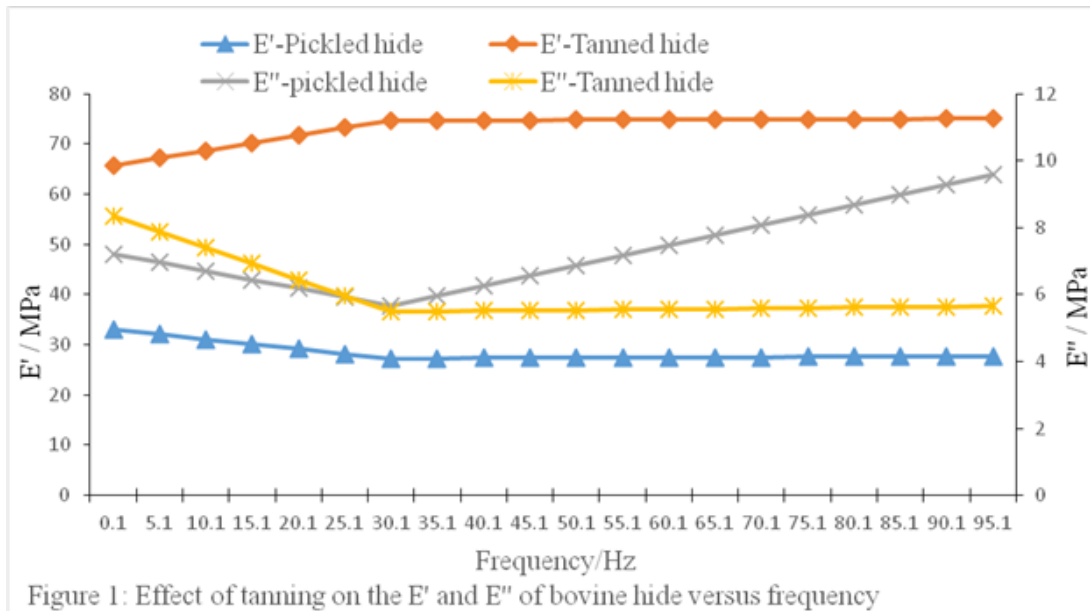
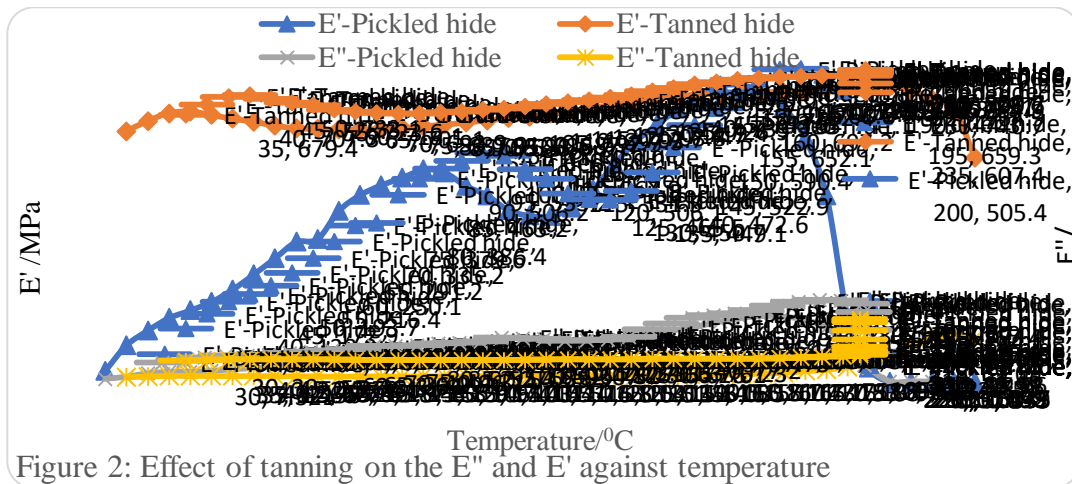


Figure 1: Effect of tanning on the E' and E'' of bovine hide versus frequency

Figure illustrates the variation of E' and E'' with temperature for pickled and tanned hides. The E'' for both hides showed a significant increase with temperature and visible drops at higher temperatures. The peaks for pickled hide occurred slightly lower temperature than for tanned hide. The E'' for pickled hide was higher than tanned hide implying that chrome-tanning decreases E'' . The increase in E'' for pickled hide with temperature was more intense and sharp peaks compared to tanned hide. Multiple peaks were noticed in pickled hide at 110 and 185 °C while tanned hide had only one peak at 230 °C. When hide is heated, collagen gets softened enabling substantial parts of the peptide chains to free themselves from the entanglements and align themselves in a more cohesive crystalline orientation (Billmer, 1984). This allows more chains to participate in the oscillation. Consequently, the loss of mechanical energy increases at higher temperatures. The crosslinks in the tanned hide impose restrictions and rigidity on the segmental mobility of the chains (Covington, 1997; Chen et al, 2001). The implication of the restriction is that there remains limited number of chains that take part in the oscillation hence decreased loss of the energy. This explains why tanned hide exhibited lower E'' than pickled hide.

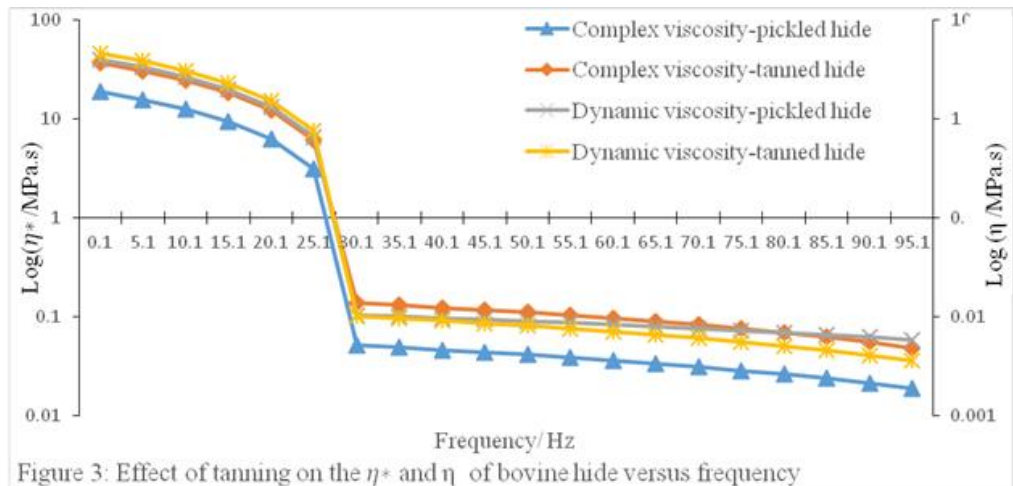
The storage modulus (E') for tanned hide was significantly higher compared to pickled hide throughout the temperature range except between 170 °C to 185 °C (Figure 4). The crosslinks induced by the tanning agents conduce additional stiffness to the tanned hide compared to pickled hide (Covington 1997). Tanned hide showed gradual increase in E' and a slight drop at 220 °C while pickled hide showed sharp peaks at 105 °C and 180 °C and further dropped to almost zero at 215 °C. The drastic drops in E' at 180 °C for pickled hide and 215 °C for tanned hide can be attributed to the transition of collagen structure from the orderly triple-helical to the random coil (Lai et al. 2008; Nalyanya et al. 2015b). For tanned hide, this transition occurred at slightly higher temperature due to the stabilizing effect of chrome-tanning effect. At higher temperatures, the components of the long backbone chains of the collagen begin to separate (molecular scission) and react with one another to alter the properties of the hide. This brings about decomposition especially pickled hide leading to drop in storage modulus at higher temperature (Cucos and Budrugaec, 2010).



The E' for both pickled and tanned hides were far greater than the corresponding E'' in the entire frequency and temperature range implying that both hides are predominantly elastic in nature (Kasapis and Mitchell, 2001; Korhonen et al. 2001). This also implies that the majority of the mechanical energy is dissipated by elastic deformation (Chen et al. 2001). From figure 2, the ratio of E'' to E' which gives the loss factor for pickled hide is greater than that for tanned hide almost in the entire temperature range.

The curves of dynamic viscosity (η) and complex viscosity (η^*) against frequency for tanned hide and pickled hide are illustrated in figure 3. Both viscosities for tanned hide were significantly higher compared to pickled hide. 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 created causes an increase in viscosity. This result agrees with the study by Sai and Babu, (2001). Both viscosities a decreasing trend: rapidly from 0.1 to 30 Hz then gradual from 30 to 100 Hz. 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. As the frequency increases further, the orientation of the polymer chains are forced along the flow direction producing a drastic drop in the viscosity. Similarly, the number of entanglements that strengthen the flexibility of collagen chains decrease causing a significant drop in intermolecular bonds hence translating to lower viscosity (Duan et al. 2013; Ju et al. 2013). Both pickled and tanned hides exhibited a weak structure as indicated by greater magnitudes of η^* than the corresponding η (Carnali 1991; Lapasin and Prici 1995; Morris et al. 1996).

Figure 4 show the effect of tanning on viscosities and variation of viscosities with temperature. The graphs took the same trend as the graphs for storage modulus against temperature. This means that resistance to flow or permanent deformation increases with temperature. This agrees with the observation made by Odlyha et al. (2000) and Flory and Garrett, (1958). The η^* for pickled hide was greater than that for tanned hide in the temperature range 55-200 °C. The peaks in the η^* for pickled hide occurred at 105 °C and 175 °C while 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 had collapsed at the temperatures (Pietrucha, 2005).



The peaks in η for pickled and tanned hides were observed at 185 and 235 °C, respectively (Figure 4). Heating drives the molecular mobility of the collagen chains and thus breaks the weak interactions such as hydrogen bonds (Xue and Sethi, 2012). Further heating causes the collapse of the triple helical structure (denaturation) that results in sudden fall in 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 abrupt decrease in the viscosity.

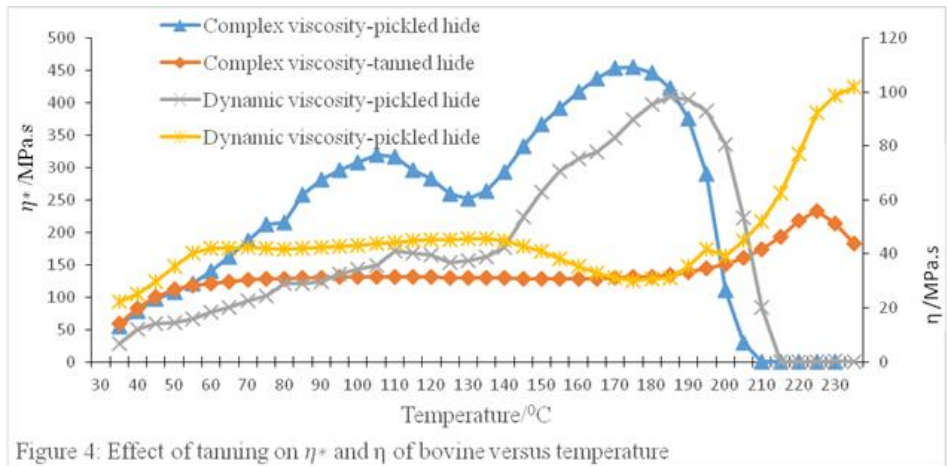


Figure 5 illustrates the effect of tanning on shear strain (ϵ) and shear stress (σ) and variation of ϵ and σ with frequency. The ϵ for pickled hide showed higher values than for tanned hide in the entire frequency range. In both pickled and tanned hides, the ϵ increased with frequency to a maximum value 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 (Figure 5). 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.

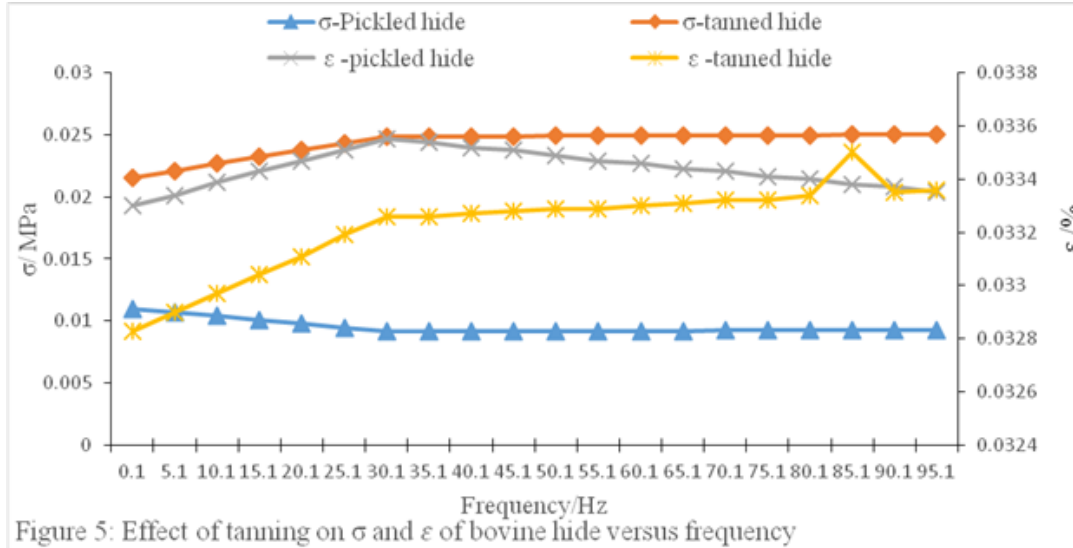


Figure 5: Effect of tanning on σ and ϵ of bovine hide versus frequency

Figure 6 illustrates the effect of tanning on the σ and variation of variation of σ with temperature. Pickled hide had significantly 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 110 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 σ decreased rapidly due to the irreversible decomposition of collagen crystalline molecules beyond their denaturation temperature (Cucos and Budrugaec 2010).

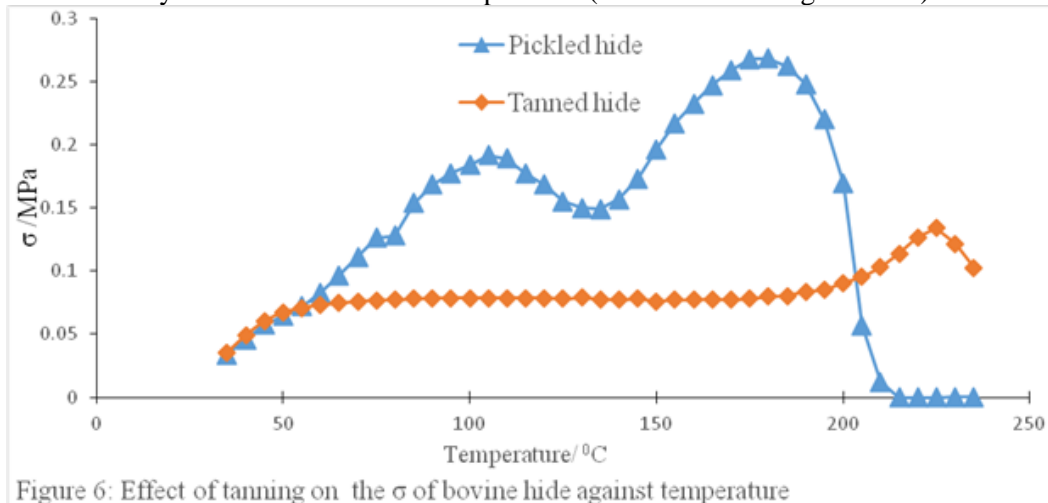


Figure 6: Effect of tanning on the σ of bovine hide against temperature

CONCLUSIONS

Dynamic Mechanical Thermal Analysis of bovine hide can be used to qualify and quantify leather tanning processes. The results have shown the possibility of using the technique to customize each leather tanning processes for specific application fields. Tanning enhances the E' , σ , and thermal stability while decreases E'' , loss factor, viscosity and ϵ . All the viscoelastic properties exhibited dispersion with two distinct frequency range: 0.1-30 and 30-100 Hz. The dominantly elastic nature of hides implies that the majority of the mechanical energy is dissipated by elastic deformation. Tanning: enhances E'' at frequencies lower than 30 Hz but lowers E'' at higher frequency than 30 Hz, increases E' at all frequencies and temperatures. Viscoelastic properties become less frequency-dependent at frequencies higher than 30 Hz. The viscoelastic properties investigated showed to increase with temperatures before drastic drop at specific temperatures. Tanned hide stores more residue stress and its molecular chains are easier to slide over each other when shearing forces are applied than pickled hide while pickled hide dissipates more than tanned hide at all temperatures and frequencies.

CONFLICT OF INTEREST

The work described here is original and has not been published before nor under any consideration for publication anywhere else and has been approved by all co-authors and the responsible authorities. Authors have declared that they have no conflict of interest existing.

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