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# Thermal and dynamic mechanical analysis of bovine hide

## Effect of chrome-tanning process

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**Abstract** Dynamic mechanical and thermal analysis has been used to investigate the effects of chrome tanning on the viscoelastic properties of an indigenous Kenyan Boran bovine hide. It has been shown that this technique can be used to assess the effects of the leather-making processes on the final leather. From the results, each process of the leather making can be customized for certain application fields. For instance, tanning has shown to enhance the storage modulus ($E'$), shear stress ($\sigma$) and thermal stability at all frequencies and temperatures while decreases the loss modulus ($E''$), loss factor, viscosity ($\eta$) and shear strain ($\varepsilon$). All the properties exhibited dispersion with two distinct frequency ranges: 0.1–30 and 30–100 Hz. The properties become less frequency dependent at frequencies higher than 30 Hz. Tanning enhances $E''$ at frequencies lower than 30 Hz but lowers $E''$ at higher frequency than 30 Hz. The dominant elastic nature of hides implies that the majority of the mechanical energy is dissipated by elastic deformation. The properties investigated showed an increase with temperature before drastic drops at specific temperatures. It can be noted that tanned hide stores more residue stress, and its molecular chains are easier to slide over each other when shearing forces are applied compared to pickled hide.

**Keywords** DMTA · Viscoelastic · Chrome-tanning · Temperature scans · Collagen · Bovine hide

## Introduction

Thermal and dynamic mechanical analysis is one of the thermoanalytical techniques that measure viscoelastic properties of materials against frequency/time and/or temperature [1–3]. Viscoelasticity provides probes into designing of materials and devices for certain purposes such as vibration abatement, rebouncy and mechanical shock reduction [3]. Viscoelastic behaviours, on the other hand, such as mechanical relaxation, are related to the physical processes such as phase transformation and thermal expansion in the material [3]. These behaviours therefore determine the performance-based properties of the materials during their relevant application [4]. In this technique, an applied sinusoidal stress on the sample produces strain, in which the modulus of the complex value can be resolved into real and imaginary components [5]. The real part is known as storage modulus, $E'$, and the imaginary part is known as loss modulus, $E''$. The ratio of the loss modulus to the storage modulus is loss factor or tan δ [2, 3]. This technique gives more precision and sensitivity compared to the alternative method, differential scanning calorimetry (DSC) since for every sine wave generated, the modulus value obtained can be used to sweep across the preselected temperature or frequency range [6, 7]. Storage modulus is related to the stiffness of the material, and it measures the degree of elasticity and hence resistance to deformation. Loss modulus measures the ability of the material to lose energy through dissipation in the form of heat [7]. It is related to the viscosity of the

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material, which measures the tendency of the material to shearing flows [8].

Leather, a by-product of the meat industry, is composed of a tight network of biopolymer collagen fibres, fibrils and elastin fibres that are viscoelastic in nature with industrial applications [9–12]. Conventionally, leather making involves a series of chemical, manual and mechanical processes; some of which are pickling and tanning processes [10, 13]. These processes are related to the ultimate quality of final leather products due to their impact on the physical–mechanical and structural properties of leather [10]. Leather being a viscoelastic material and the properties are related to the physical processes, such as phase transformation and thermal expansion, the thermal dynamic mechanical analysis can be used to investigate the effect of these leather-making processes [3, 14, 15]. Hence, this technique becomes novel in the assessment of the effect of some of the processes involved in the leather making on the quality of the final leather.

It has been shown that a diverse spectrum of viscoelastic response profiles over a wide temperature and frequency range is needed to fully characterize collagenous material [3, 16–19]. Use of dynamic mechanical and thermal analysis to characterize leather and parchments is well documented [1, 6, 13, 16]. However, effect of chrome tanning on the viscoelastic properties versus temperature and frequency/time is undocumented. This paper presents the comparison of the viscoelastic properties of pickled hide with tanned hide under wide temperature and frequency scans to elucidate on the effect of chrome-tanning process.

## Materials and methods

### Sample preparation

A commercially procured fresh bovine hide from an indigenous Kenyan Boran bovine breed was prepared to pickling stage using the standard conventional procedures at Kenya Industrial Research and Development Institute (KIRDI)—Leather Development Centre (see Table 1). The pelt was then cut along the backline into two identical halves. One half proceeded for chrome-tanning process (see Table 2) while the other half was left at pickled stage. Rectangular specimens from both the pickled and tanned hides, of dimensions 30 mm × 9.3 mm × 0.93 mm, were then sampled according to the official sampling method and sampling location ISO 2418: 2002 using a press knife. The specimens were then conditioned in a standard atmosphere, 23/50 (temperature 23 ± 2 °C, humidity 50 ± 5 % R.H.) for 48 h according to ISO 2419: 2002 prior to testing [20].

### Dynamic mechanical and thermal analysis

Dynamic mechanical and thermal analysis was carried out using Dynamic Mechanical Analyzer (DMA, Model 2980) from TA instruments (USA) with the help of thermal analysis control software. After position calibration, which was done before every experiment to enhance reliability of the results, samples were mounted onto the film tension clamp, one at a time. The experiment was conducted in multifrequency mode, from 0.1 to 100 Hz at interval of 10 Hz. For method segment, temperature was equilibrated at 30 °C and set to run until 240 °C. The ramp segment was set at a heating rate of 5 °C $min^{-1}$ in a static air environment. Isothermal segment was set at 5 min, and data storage segment was switched on. After each experimental run, data were transferred from TA to the Universal Analysis. With the help of this software, data for storage modulus ($E'$), loss modulus ($E''$), viscosities, shear stress and strain against temperature and/or frequency/time were then retrieved. For frequency sweeps, the Universal Analysis software gives the means/averages of the parameters for the entire temperature range. However, for temperature scans, the software gives the values of the parameters versus predetermined temperature range and interval for individual preselected frequencies. Hence, for temperature scans, the average means of the parameters for all the preselected frequencies were calculated. The graphs were drawn using Microsoft office 2013 Excel.

## Results and discussion

The loss modulus ($E''$) and storage 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 Fig. 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 0.1–30 Hz, tanned hide showed higher $E''$ compared to pickled hide. Both $E''$ curves for pickled and tanned hide decreased linearly with frequency to 30 Hz where the two curves had equal magnitudes. From 30 to 100 Hz, the increase in $E''$ for pickled hide was higher compared to tanned hide, although the curves showed weak frequency dependence. This indicates that tanning enhances $E''$ at frequencies lower than 30 Hz but lowers $E''$ at higher frequency than 30 Hz. It is also indicated that $E''$ decreases with frequency at frequencies lower than 30 Hz but increases with frequencies at frequencies higher than 30 Hz. This frequency dependence of viscoelastic properties agrees with Lakes [3]. Decreasing $E''$ in the range 0.1–30 Hz can be explained as follows: as frequency increases beyond 0.1 Hz, the available time for polypeptide

**Table 1** Sample preparation recipe of pickling

| Process/step | Chemicals/% | Temp/°C | Time | Remarks |
|---|---|---|---|---|
| Washing | 100 % $H_2O$, 1 % detergent | 23–25 | 10 min | Drain |
| Liming and unhairing | 100 % $H_2O$ | 23–25 | 1 h | Drum speed = 2–3 rpm |
| | 1.5 % $Na_2S$ | | | |
| | 1 % $Ca(OH)_2$ (Lime) | | | |
| | Add: | | | |
| | 100 % $H_2O$ | | 1 h | |
| | 1 % $Na_2S$ | | | |
| | 1 % $Ca(OH)_2$ (Lime) | | | pH = 12 |
| | Add: | | | Drain |
| | 50 % $H_2O$ | | 16 h | Fleshing and scudding |
| | 1 % $Ca(OH)_2$ (Lime) | | | |
| Washing | 300 % $H_2O$ | 25 | 10 min | Drain |
| Deliming | 100 % $H_2O$ | 25 | 1 h | |
| | 2 % $(NH_4)_2SO_4$ | | | pH = 8.3 |
| | 1 % Sodium metabisulphite | | | x-Section clear to phenolphthalein |
| Bating | 0.2 % microbates-1600 LVU | 35–37 | 1 h | Drum speed = 3 rpm |
| Washing | 200 % $H_2O$ | 20–25 | 20 min | Drain |
| 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 h | pH = 2.5 |
| Draining and washing | 200 % $H_2O$ | 25 | 20 min | 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 | 25–27 | 3 h | Drum speed = 3 rpm |
| | sulphate (33 % basic) | | 30 min | Penetration complete through x-section pH = 3.0 |
| | Add | | | |
| | 0.5 % Fungicide | | | |
| Basification | 0.5 % $NaHCO_3$ (1:10) | | 20 min | Drain |
| | Add | | | |
| | 0.5 % $NaHCO_3$ (1:10) | | 20 min | Final pH = 3.6 |
| | Add | | | |
| | 0.5 % $NaHCO_3$ (1:10) | | 20 min | Shrinkage temp = 100 °C |
| Draining and washing | 200 % $H_2O$ | 25 | 20 min | Drain |

chains to respond to the applied deforming sinusoidal strains starts to decrease. This impedes long chains to resonate with the oscillation. Hence, only the few short chains can participate in the oscillation and dissipation. This lowers the loss modulus. However, as frequency increases beyond relaxation, the entangled chains begin to unwind and oscillate increasing the participating polypeptide chains [21]. This gradually increases the loss modulus.

Storage modulus ($E'$) for tanned hide was significantly superior to pickled hide in the entire frequency range as

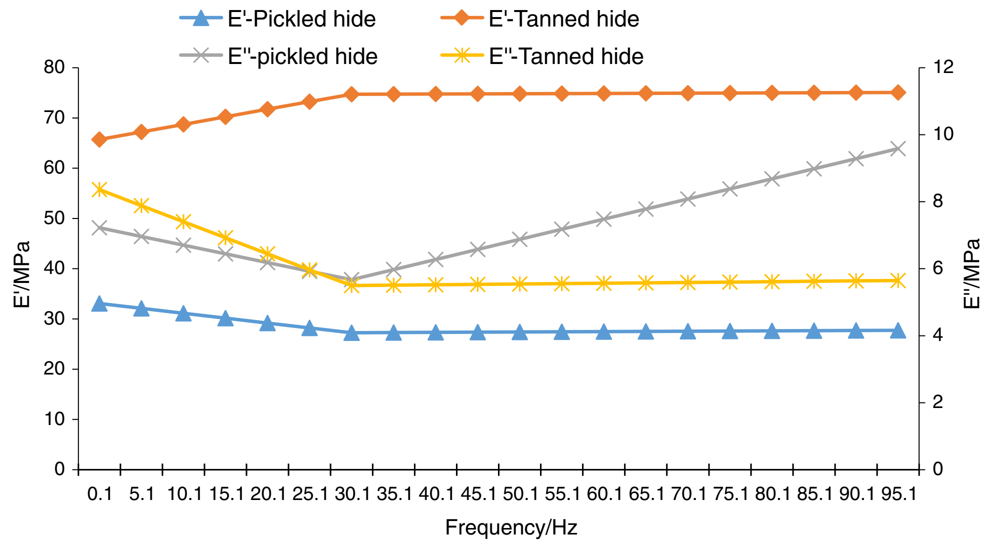


**Fig. 1** Effect of tanning on the E′ and E″ of bovine hide versus frequency

shown in Fig. 1. The $E'$ for both hides showed dispersion phenomenon [3]. For tanned hide, the $E'$ increased rapidly from 65.71 MPa at 0.1 Hz to 74.72 MPa at 30 Hz followed by a gradual increase, 74.72 MPa at 30 Hz to 75.07 MPa at 100 Hz. For pickled hide, $E'$ decreased from 33.08 MPa at 0.1 Hz to 27.26 MPa at 30 Hz followed by a gradual increase from 27.26 MPA at 30 Hz to 27.74 MPa at 100 Hz. It can be noted that the $E'$ becomes almost independent of frequency at frequencies higher than 30 Hz. Chrome tanning increases the molecular weight and induces intermolecular hydrogen bonds with the functional groups of the collagen that stabilizes the crystalline structure [6, 14, 22]. The synergistic effect of chromium ions with collagen molecules together with the increased molecular weight makes tanned hide stiffer than pickled hide [22]. Similarly, the presence of chromium ions in the hide increases the volume fraction. At low frequency, the collagen chains have more time to relax to a more favourable 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 [23, 24]. This increases the ability of the entanglement to store more imposed energy, and the collagen molecules behave more like elastic solid [25, 26]. This explains why storage modulus for tanned hide increased with frequency. However, during the prior processes of tanning, liming in alkali solution and sulphide swells the hide leaving a more open/loose structure. This disorients the recruitment process, resulting to spatial arrangement of collagen fibres [27]. Hence, this confirms the decreasing trend of $E'$ with frequency for pickled hide. As the frequency of oscillation increases further beyond 30 Hz, almost all collagen fibres get fully stretched and oriented in the direction of the applied strain. Here, the changes in the moduli with frequency become negligibly small.

The thermal variation of $E'$ and $E''$ for pickled and tanned hides is illustrated in Fig. 2. The $E''$ for both hides showed a significant increase with temperature and visible drastic drops at specific temperatures. The temperatures corresponding to the peaks for pickled hide were slightly lower 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 versus temperature was more intense and sharp 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. This can be attributed to the response of collagen to thermal energy. 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 [28]. This allows more chains to participate in the oscillation. Consequently, the loss of mechanical energy increases. The crosslinks in the tanned hide impose restrictions and rigidity on the segmental mobility of the chains [14, 22]. The implication of the restriction is that there remains limited number of collagen chains that take part in the oscillation, hence decreasing loss of the energy. This can explain 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 and 185 °C (Fig. 2). The crosslinks induced by the chrome-tanning agents conduce additional stiffness to the tanned hide compared to

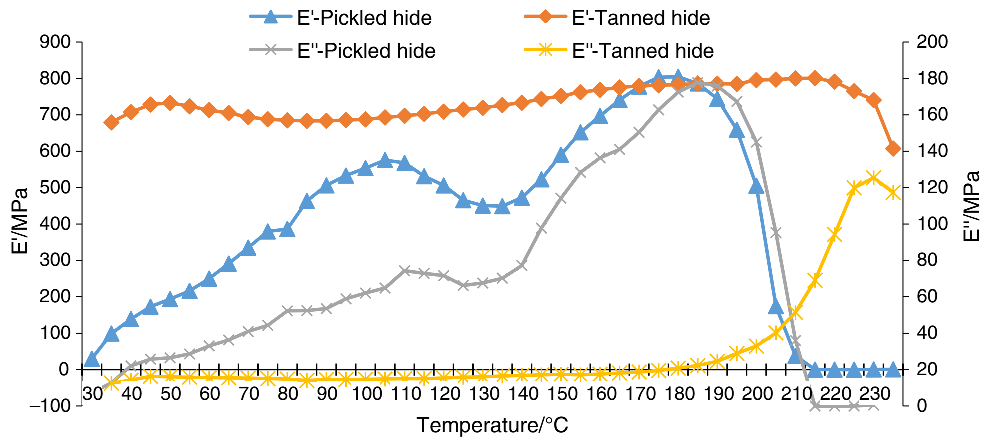


**Fig. 2** Effect of tanning on the E″ and E′ against temperature

pickled hide [22]. Tanned hide showed gradual increase in *E*′ and a slight drop at 220 °C, while pickled hide showed sharp peaks at 105 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 [15, 29]. For tanned hide, this transition occurred at slightly higher temperature due to the stabilizing effect of chrome-tanning agents. At higher temperatures, the components of the long backbone chains of the collagen begin to separate (molecular scission) and react with one another and eventually decompose, especially pickled hide [6]. This leads to drastic drop in storage modulus.

The *E*′ for both pickled and tanned hides was far greater than the corresponding *E*″ in the entire frequency and temperature range, implying that both hides are predominantly elastic in nature [20, 30, 31]. This also implies that the majority of the mechanical energy is dissipated by elastic deformation [14]. From Fig. 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 ($\eta$) and complex viscosity ($\eta$*) against frequency for tanned hide and pickled hide are illustrated in Fig. 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 crosslinked hydrogen bonds [22]. According to Sai and Babu [32], the intermolecular and intramolecular hydrogen bonding created during tanning are expected to increase viscosity. Both viscosities showed a decreasing trend: rapidly from 0.1 to 30 Hz followed by gradual from 30 to 100 Hz. As frequency increases, internal friction decreases due to smaller effective interactions among the collagen molecules [33]. The intermolecular interactions are reduced by the microstructural anisotropy, resulting from the shear deformation. As the frequency increases further, the orientation of the polymer chains is forced along the flow direction producing a drastic drop in the viscosity. Similarly, the number of entanglements that strengthen the flexibility of collagen chains decreases causing a significant drop in intermolecular bonds and hence lower viscosity [34, 35]. Both pickled and tanned hides exhibited a

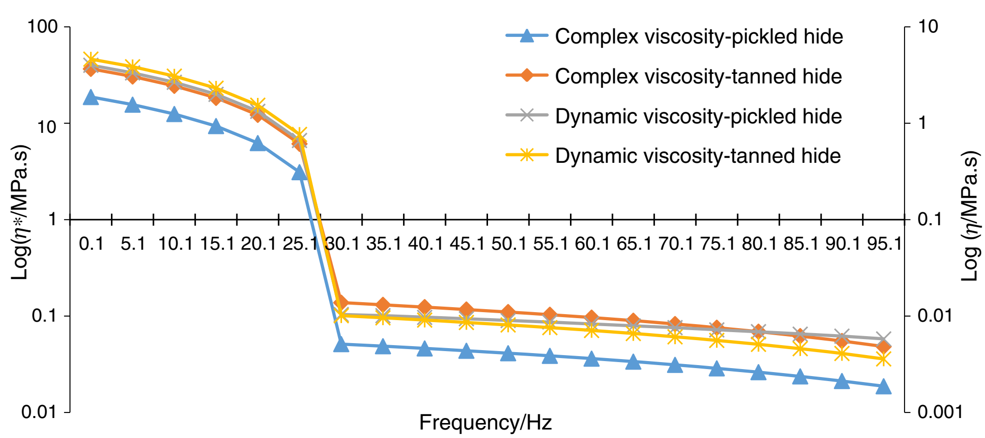


**Fig. 3** Effect of tanning on the $\eta_*$ and $\eta$ of bovine hide versus frequency

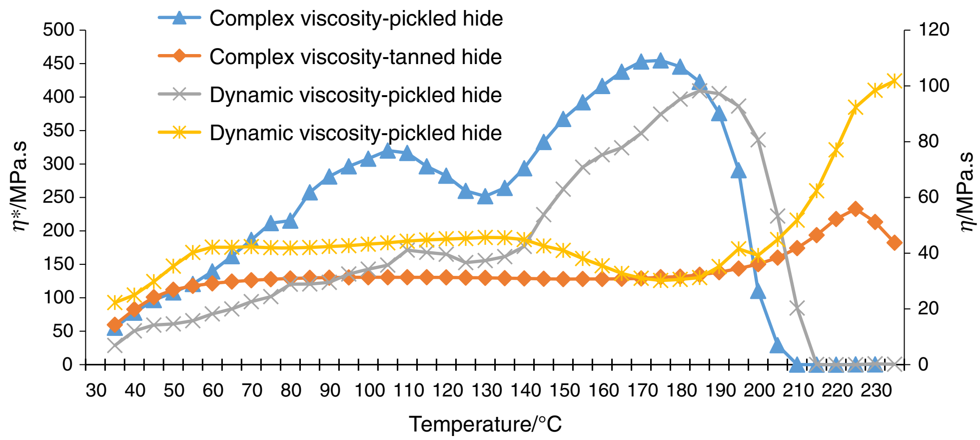


**Fig. 4** Effect of tanning on $\eta*$ and $\eta$ of bovine versus temperature

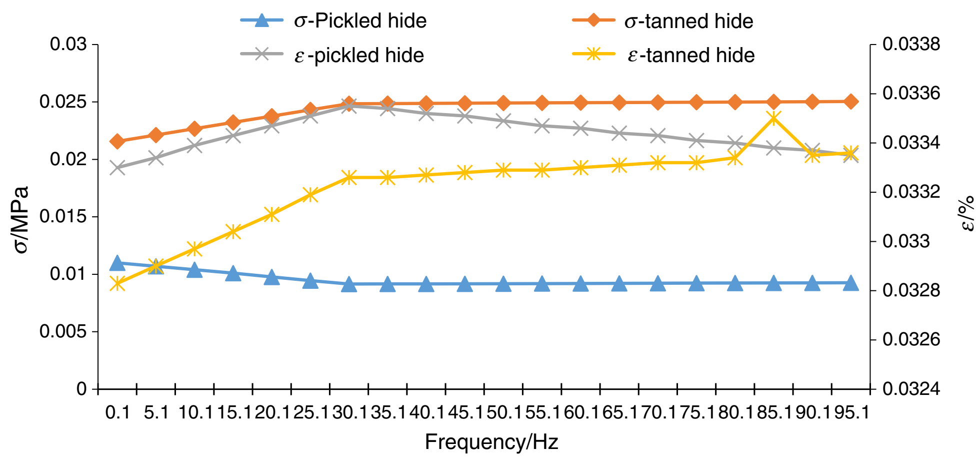


**Fig. 5** Effect of tanning on $\sigma$ and $\varepsilon$ of bovine hide versus frequency

weak structure as indicated by greater magnitudes of $\eta$* compared to the corresponding $\eta$ [36–38].

Figure 4 shows the effect of tanning on viscosities and variation of viscosities with temperature. It can be observed that resistance to flow or permanent deformation increases with temperature. This agrees with the observations made by Odlyha et al. [1] and Flory and Garrett [39]. The $\eta$* for pickled hide was greater than that for tanned hide in the temperature range 55–200 °C. The peaks in the $\eta$* for pickled hide occurred at 105 and 175 °C while at 110 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 [40]. The peaks in $\eta$ for pickled and tanned hides were observed at 185 and 235 °C, respectively. Heating drives the molecular mobility of the collagen chains and thus breaks the weak interactions such as hydrogen bonds [41]. 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) [42]. This causes abrupt decrease in the viscosity.

Figure 5 illustrates the effect of tanning on shear strain ($\varepsilon$) and shear stress ($\sigma$) and variation of ε and $\sigma$ 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 $\sigma$ than pickled hide (Fig. 5). This is probably due to the crosslinking by tanning, which enhances stiffness of the collagen molecules [22]. Greater ε values in pickled hide simply indicate 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 [42]. The swelling effect of liming with alkali solution and sulphide usually leaves the structure more open and loose during pickling [10, 20, 27]. In the frequency range of 30–100 Hz, $\sigma$ for both hides

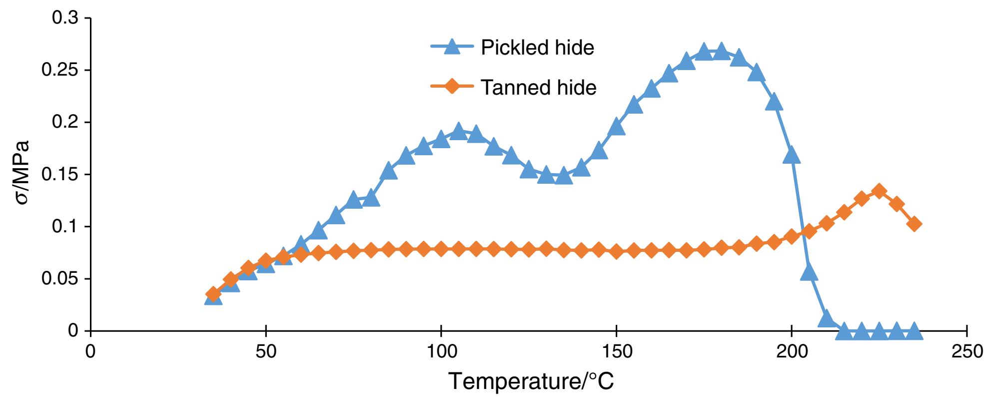


**Fig. 6** Effect of tanning on the $\sigma$ of bovine hide against temperature

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 did not 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 $\sigma$ with frequency.

Figure 6 illustrates the effect of tanning on the $\sigma$ and variation of $\sigma$ with temperature. Pickled hide had significantly greater $\sigma$ compared to tanned hide in the temperature range of 55–205 °C. The $\sigma$ for pickled hide increased rapidly with temperature to two peaks at 105 and 175 °C, while for tanned hide, the $\sigma$ increase was gradually forming two at 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 $\sigma$ decreased rapidly due to the irreversible decomposition of collagen crystalline molecules beyond their denaturation temperature [6, 20].

## Conclusions

Thermal dynamic mechanical analysis has been used to investigate the effects of chrome tanning on viscoelastic properties of bovine hide. It has been shown that this technique can be used to assess the effects leather-making processes on the quality of the final leather. From the results, the technique can be used to customize each leather-making process for specific application fields. The results show that tanning enhances the storage modulus ($E'$), shear stress ($\sigma$) and thermal stability at all frequencies and temperatures while decreases the loss modulus ($E''$), loss factor, viscosity ($\eta$) and shear strain ($\varepsilon$). All the properties exhibited dispersion with two distinct frequency ranges: 0.1–30 and 30–100 Hz. The properties become less frequency dependent at frequencies higher than 30 Hz. Tanning enhances $E''$ at frequencies lower than 30 Hz but lowers $E''$ at higher frequency than 30 Hz. The dominant elastic nature of hides implies that the majority of the mechanical energy is dissipated by elastic deformation. The properties investigated showed an increase with temperatures before drastic drop at specific temperatures. It can be noted that tanned hide stores more residue stress, and its molecular chains are easier to slide over each other when shearing forces are applied compared to pickled hide.

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