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Effect of Solar Radiation on Viscoelastic Properties of Bovine Leather: Temperature and Frequency Scans

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Abstract This work presents both analytical and experimental results of the effect of unfiltered natural solar radiation on the thermal and dynamic mechanical properties of Boran bovine leather at both pickling and tanning stages of preparation. Samples cut from both pickled and tanned pieces of leather of appropriate dimensions were exposed to unfiltered natural solar radiation for time intervals ranging from 0 h (non-irradiated) to 24 h. The temperature of the dynamic mechanical analyzer was equilibrated at 30 °C and increased to 240 °C at a heating rate of $5\,^{\circ}\mathrm{C} \cdot \mathrm{Min}^{-1}$, while its oscillation frequency varied from 0.1 Hz to 100 Hz. With the help of thermal analysis (TA) control software which analyzes and generates parameter means/averages at temperature/frequency range, the graphs were created by Microsoft Excel 2013 from the means. The viscoelastic properties showed linear frequency dependence within 0.1 Hz to 30 Hz followed by negligible frequency dependence above 30 Hz. Storage modulus (E') and shear stress (σ) increased with frequency, while loss modulus (E''), complex viscosity (η^*) and dynamic shear viscosity (η) decreased linearly with frequency. The effect of solar radiation was evident as the properties increased initially from 0 h to 6 h of irradiation followed by a steady decline to a minimum at 18 h before a drastic increase to a maximum at 24 h. Hence, tanning industry can consider the time duration of 24 h for sun-drying of leather to enhance the mechanical properties and hence the quality of the leather. At frequencies higher than 30 Hz, the dynamic mechanical properties are independent of the frequency. The frequency of 30 Hz was

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observed to be a critical value in the behavior in the mechanical properties of bovine hide.

Keywords Bovine leather · Collagen · Dynamic mechanical analysis · Solar radiation · Viscoelastic properties

1 Introduction

Thermal–mechanical properties of leather materials, especially viscoelasticity materials, play a pivotal role, for instance, in determining appropriate processing techniques, application fields of the resulting products and probable quality performance during their use [1]. These properties include loss modulus, storage modulus, tan δ, complex/dynamic shear viscosity and shear stress [2]. Loss modulus measures mechanical energy dissipated as the material resists forces of deformation, while tan δ gives the index ratio between viscosity and elasticity or damping behavior of the material. The implication of this statement is that materials with higher values of tan δ or loss modulus take a longer time to regain their shape and size after the withdrawal of force of deformation or dampen any applied shocks more efficiently [3]. On the other hand, high values of viscosity indicate greater thickness or resistance to flow [4]. Either way, an increase or decrease in the mentioned properties signifies the stabilization or degradation of the materials, respectively [2]. Hence, these properties, which depend on temperature and molecular weight/stiffness, are also used to determine thermal stability and transition processes of the collagen with increasing temperatures [5–7].

Bovine leather and its products are versatile raw materials for many industries: the potential of their applications lies solely in the unique physical and mechanical properties [8]. The industrial processing and use subject these materials to extreme environmental factors such as natural solar radiation, humidity, environmental pollutants, abrasion, rain, and the wind [9]. Solar radiation spectrum, for instance, contains a measurable ultraviolet (UV) and infrared radiation that reach the earth's surface which causes significant physical, chemical and photochemical modification of collagenous polymers [9–13]. The change attributes to the findings that collagen contains an aromatic group of amino acids, chromophoric in nature, such as tyrosine, phenylalanine and other substances that absorb the solar radiations, especially in the UV region [9,14]. Absorption of these radiations by the collagens leads to the formation of free radicals that later recombine to form bond scissions, crosslinks or molecular fragments [9,11,14–18]. Since the elastins and collagens, components that make up more than 90 % of leather, determine the mechanical stability of leather matrix, exposure of leather to these radiations should alter its mechanical stability [15,16].

Significant studies have investigated the effect of solar radiation on collagen-based materials [11–13]. Nalyanya et al. [16] have reported an investigation on the effect of artificial ultraviolet radiation on the viscoelastic and dynamic viscosity of both pickled and tanned leathers. However, to our knowledge, there appears no documented investigation into the effect of unfiltered solar radiation on the mechanical properties of bovine leather. Therefore, this study presents the results on effects of natural solar radiations on the viscoelastic properties of bovine leather using thermal and dynamic mechanical analyses. This investigation also reports the effects of oscillation frequency and furnace temperature on the viscoelastic properties of leather. The study also makes a comparison of the effect of solar radiation on tanned leather and pickled leather to explore the effect of chrome-tanning on the solar radiation absorption of bovine leather.

2 Experimental

2.1 Sample Preparation

Raw pelt was processed to pickling and tanning stages using the standard conventional tanning procedures as described in Nalyanya et al. [8] at Kenya Industrial Research and Development Institute-Leather Development Centre (KIRDI-LDC). Samples of dimensions 30 mm × 9.3 mm × 0.93 mm were cut from both pickled pelts and tanned leather and exposed to unfiltered natural solar radiation for time intervals ranging from 0 h to 24 h. The irradiation was carried out during the month of September 2014 at Egerton University, Njoro-Kenya (0°55″S, 35°04″E). Egerton University region receives an estimated irradiance of 7.1 $\text{kWh}\cdot\text{m}^{-2}$ per day during the month of September [19]. Therefore, the irradiance to each sample was 0.0825 W per hour, based on the dimensions of the samples. Before testing, the samples were conditioned in a standard atmosphere of temperature 23 ± 2 °C and humidity 50 ± 5 % R.H. for 48 h. The variation of solar radiation doses was done by increasing the time of exposure to the sun [20].

2.2 Dynamic Mechanical Analysis

Dynamic mechanical analysis is a combination of thermal and mechanical analyses, which provides a sensitive technique for determining the time dependence or frequency/temperature dependence of the mechanical parameters of materials. Theoretically, perfectly elastic materials store all the energy supplied to them, while a purely liquid (viscous) material dissipates all during deformation. However, polymeric materials scatter a part of the energy that excites them. The mechanical response of the material is given in two distinct components. These components are an elastic part, storage modulus, E', and the viscous part, the loss modulus, E''. The ratio of loss modulus to storage modulus gives damping factor. Damping factor is also referred to as loss factor or loss tangent or tan δ. Characterization involves monitoring the changes in any of the three mentioned properties with temperature and frequency of oscillation. In this investigation, dynamic mechanical analyzer (DMA, model 2980) from TA Instruments, USA, was used. The device gives a choice of modes like creep/relaxation, iso-strain, multi-frequency, multi-stress/strain, controlled force/strain. Samples were mounted on the film tension clamp, one at a time. The experiment ran in the multi-frequency mode from 0.1 Hz to 100 Hz in the static air environment. The temperature was equilibrated from 30 °C to 240 °C at a heating rate of 5 $°\text{C}\cdot\text{min}^{-1}$. Thermal Analysis software in the DMA accessories was used to generate the graphs of storage and loss moduli, tan δ, dynamic shear and complex viscosity and shear stress versus temperature or frequency. This software analyzes raw data obtained by the DMA to give mean averages of the parameters at the preselected range of furnace temperatures and the oscillation frequency of the movable film tension clamp. The resources generated were used to produce graphs using Microsoft Excel 2013.

3 Results and Discussion

3.1 Dynamic Frequency Scans

Figures 1, 2, 3, 4 and 5 show the effects of solar radiations on the storage and loss moduli, complex and shear dynamic viscosities and shear stress of tanned leather. Figures 6, 7, 8 and 9 illustrate the effect of solar radiations on the storage and loss moduli, complex viscosity and shear stress of pickled leather. The properties showed a linear dependence with frequency. However, the relationship declined to almost zero at frequencies greater than 30 Hz. The same observation has been reported by Rammensee et al. [21]. The storage modulus and shear stress showed an increase in frequency from 0.1 Hz to 30 Hz, whereas loss modulus, complex viscosity and dynamic shear viscosity showed a linear decrease in the same frequency. This trend

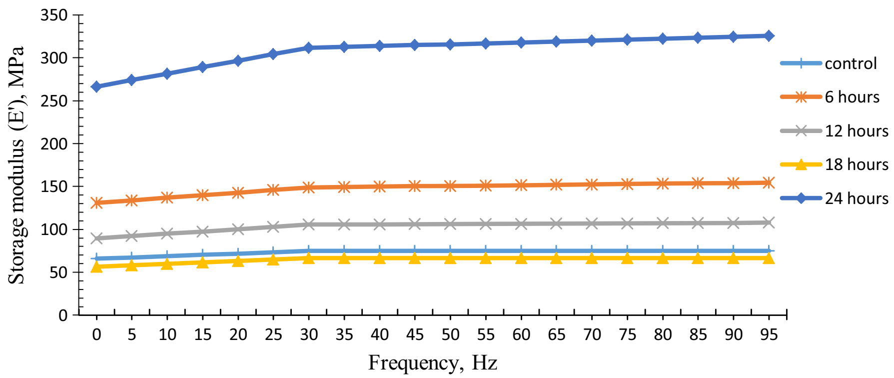

Fig. 1 Effect of solar radiation on the storage modulus (E′) of tanned leather

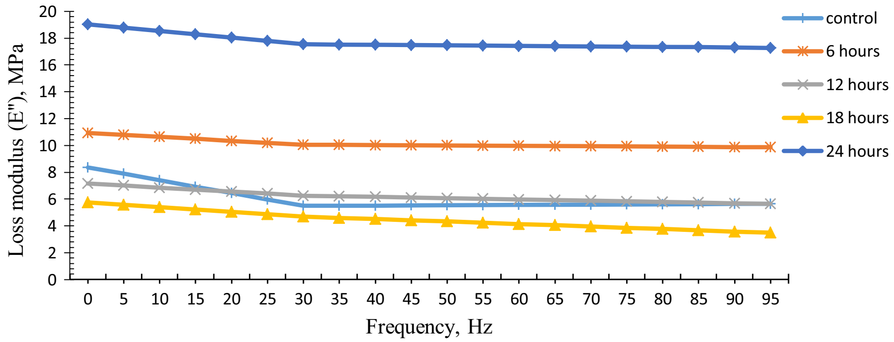

Fig. 2 Effect of solar radiation on the loss modulus (E″) of tanned leather

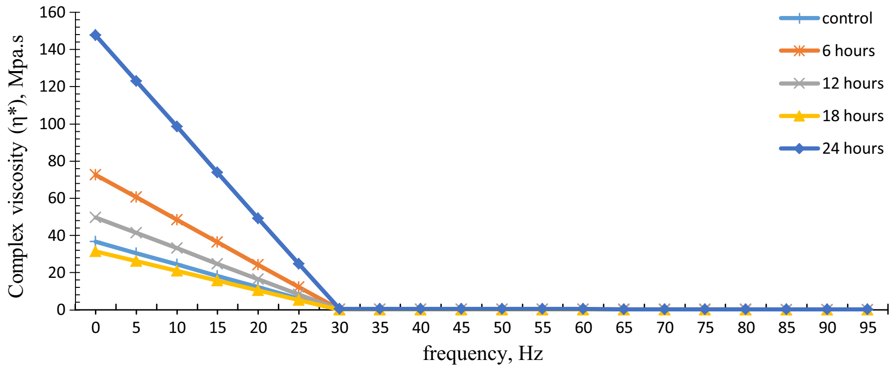

Fig. 3 Effect of solar radiation on the Complex viscosity (η*) of tanned leather

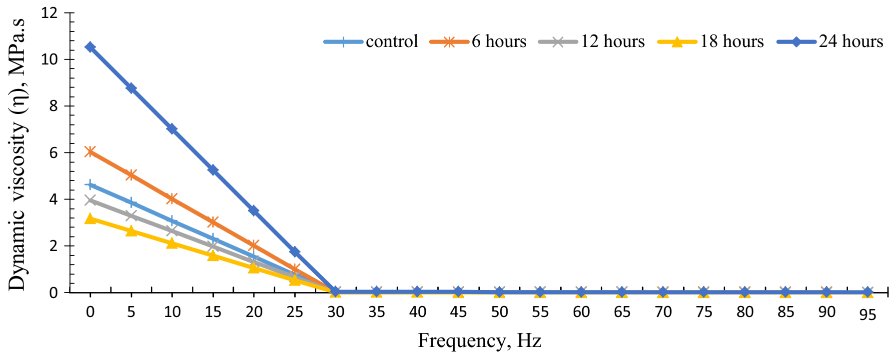

Fig. 4 Effect of solar radiation on the dynamic viscosity (η) of tanned leather

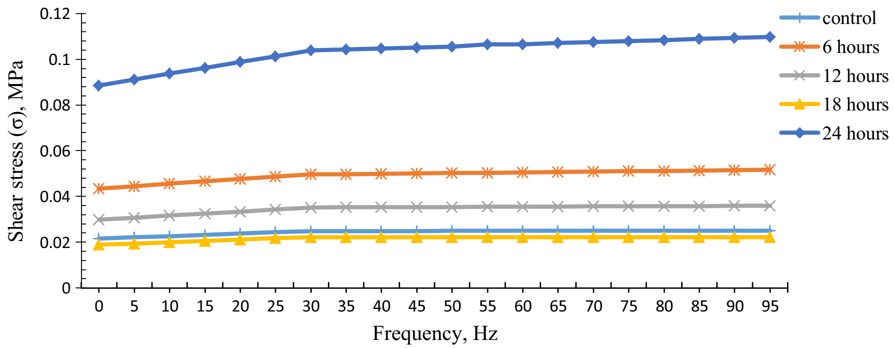

Fig. 5 Effect of solar radiation on the shear stress (σ) of tanned leather

implies that elasticity as indicated by storage modulus increases with frequency, while thickness, as demonstrated by loss modulus, decreases with the frequency within the frequency range of 0.1 Hz to 30 Hz. The same observation was made by Yi-Qiu et al. [2]. From these figures (Figs. 1, 2, 3, 4, 5, 6, 7, 8 and 9), the effect of solar radiation on the viscoelastic properties of both tanned and pickled leathers stands out. The

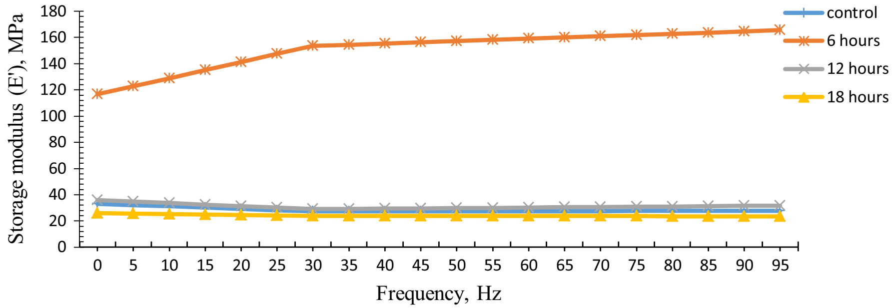

Fig. 6 Effect of solar radiation on the storage modulus (E′) of pickled leather

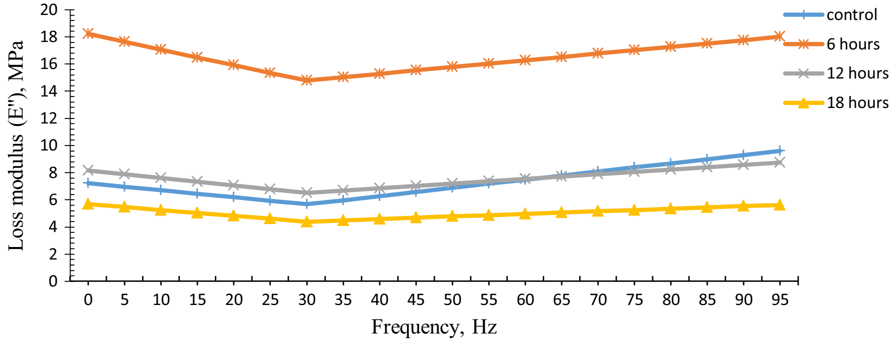

Fig. 7 Effect of solar radiation on the loss modulus (E″) of pickled leather

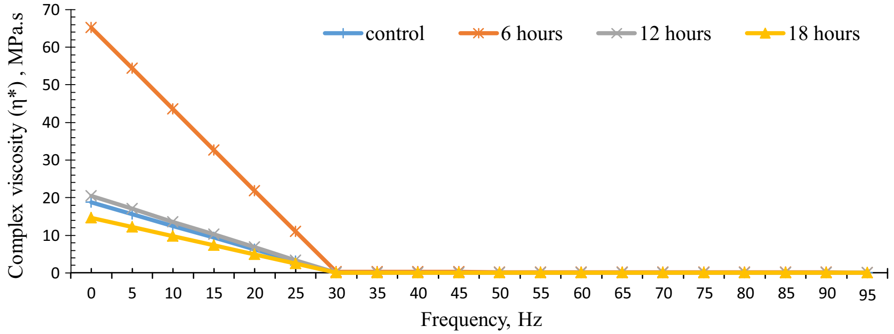

Fig. 8 Effect of solar radiation on the complex viscosity (η*) of pickled leather

characteristic trend showed an initial increase from 0 h to 6 h of irradiation followed by a steady decrease to minimum magnitudes at 18 h through 12 h before a noticeable increase to maximum for 24 h of irradiation.

Previous studies have elucidated that storage modulus is a more sensitive mechanical property due to the structural changes at low frequency than loss modulus and dynamic shear viscosity [22]. At low frequencies, the amorphous collagen particles maintain their random internal order and entanglements. With increasing frequency,

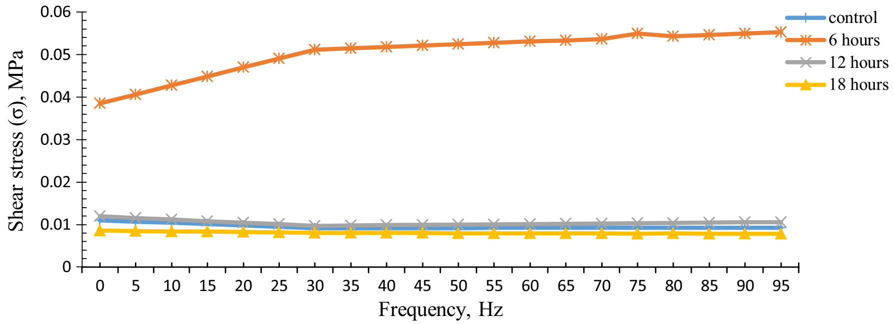

Fig. 9 Effect of solar radiation on the shear stress (σ) of pickled leather

the collagen particles in the hide disentangle because of the shearing forces and the collagen particles slip past each other more quickly. As the oscillation frequency increases, the particle flowability increases causing a decrease in viscosity [13]. Additionally, increasing frequency frees the entanglements, which strengthens the intermolecular bonds and hence internal friction among the collagen molecules decreases [23–25]. The decrease in internal resistance and the consequent decrease in energy dissipation causes a reduction in viscosity and loss modulus while the "freed" entanglements increase the bonds which in turn contribute to the stiffness and hence growth in storage modulus. Barnes [26] made the same observation and explained that the breaking down of the polymeric chain entanglements is more than the formation. At higher frequencies, the majority of the peptide chains align in the direction of the applied deformation strains. Probably, this can explain the behavior of the viscoelastic properties within these frequencies. Collagen fibrils in the leather matrix contain tightly bound water referred to as interstitial water. When leather is exposed to the unfiltered solar radiation, the collagen fibrils get dehydrated due to the near ultraviolet and thermal infrared component in the presence of atmospheric oxygen [13,27]. This water gets evaporated leading to a significant increase in the stiffness [28]. Dehydration and stiffness are related in such a way that the dehydration of this interstitial water brings the collagen sub-fibrils together forming additional interpeptide H-bonds or covalent crosslinks between tropocollagen sub-fibrils [20,28]. The crosslinks formed prevent free slippage between the collagen molecules and microfibrils [15,29]. The hierarchical structure of collagens become compact, and leather becomes stiffer [30]. The concept of dehydration and stiffness can be used to explain the initial increase in storage modulus, loss modulus, viscosity and shear stress [30]. Similarly, smaller doses of UV induce crosslinking interaction between collagen fibers [14]. However, as the dehydration continues with the time of exposure to the radiation, water which controls H–O–H collagen bonds is lost [31]. Additionally, the presence of the chromophoric tyrosine and phenylalanine enhances the solar UV absorption which initiates the breaking down of the hydrogen bonds, causing chain scission and molecular fragmentation [32]. When the scissions along the helix outweigh the crosslinking effect, this leads to a decrease in mechanical stiffness [20]. The initiated degradation of the aromatic amino acids leads to the formation of a crosslink called dityrosine and eventually additional

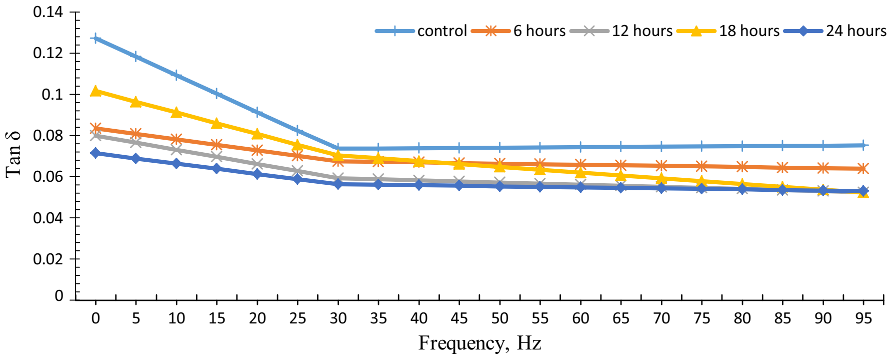

Fig. 10 Effect of solar radiation on the tan δ for tanned leather

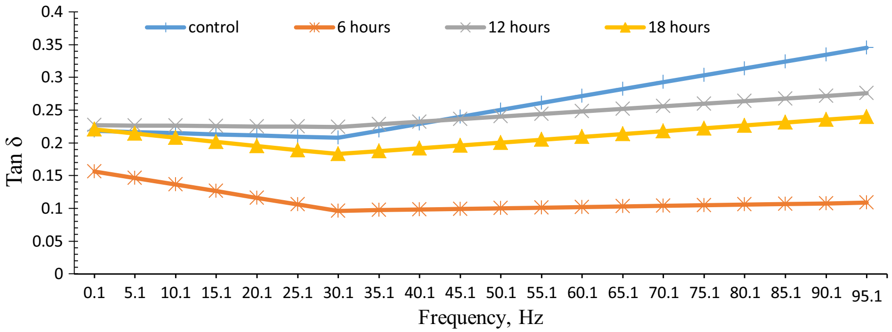

Fig. 11 Effect of solar radiation on the tan δ for pickled leather

crosslinks such as pentosidine and pyridinoline [33,34]. These competing processes of crosslinking and scission cause the variations in the mechanical properties on solar irradiation. The two competing processes explain the pronounced increase in moduli, viscosity and shear stress of tanned leather samples exposed to solar radiations for 24 h. The increase also attributes to the marked stiffness observed as a result of dehydration at this duration of irradiation [13].

Figures 10 and 11, respectively, show the effect of solar radiations on tan δ of tanned and pickle leathers. The trends observed between the tan δ of pickled and tanned leathers were different. Liu et al. [35] reported the same results of the variations in the mechanical properties of chrome-tanned and chrome-free leathers. The reason for the difference, in this case, is chromium compound. Tanned leather has chromium compounds within its structure, while pickled leather does not have.

At low frequencies where relaxation time is high, the polypeptide chains do not have sufficient time to cope with the deforming sinusoidal strains. Insufficiency of time means that only a few chains with shorter length can resonate with the oscillation [36]. As frequency increases beyond 30 Hz, the "freed" peptide chains from entanglements start to oscillate, increasing the dissipation as observed in the case of pickled leather in Fig. 11. However, the many crosslinks from the chromium ions restrict the segmental mobility in the tanned hide. Additionally, the higher molecular weight of tanned leather contributes to the restrictions of segmental mobility. Therefore, the extra "freed" peptide chains cause insignificant dissipation [36,37]. The constraints explain the constant dissipation in the frequency range of 30 Hz to 100 Hz. For tanned leather, the crosslinking effect conferred by chrome-tanning agents develops lateral network linkages between molecules and microfibrils drawing the collagen molecules close together [30,38]. Drawing closer the collagen together decreases the free volume or swelling and increases the fiber concentration per unit volume fraction of the polymeric matrix of the tanned leather [29,36]. The change in the molecular structure, hence polymeric heterogeneity, alters the permeability of both water and solar radiations. The structural alteration has the potential to improve the ultraviolet radiation absorption regardless of the similar collagen chromophoric residues as observed by Thurstan et al. [39]. Hence, the ultraviolet radiation absorption can be used to explain the differences found in Figs. 10 and 11.

Although other studies in elastomeric materials have found that viscoelastic properties linearly depend on oscillation frequency [40], the dependence in leather had not been done. Interestingly, all the graphs plotted are showing a particular trend in the behavior at the frequency of 30 Hz. Further investigations can verify the significance of this rate in leather. The 30 Hz can be a possible value for the natural frequency or resonant frequency of leather.

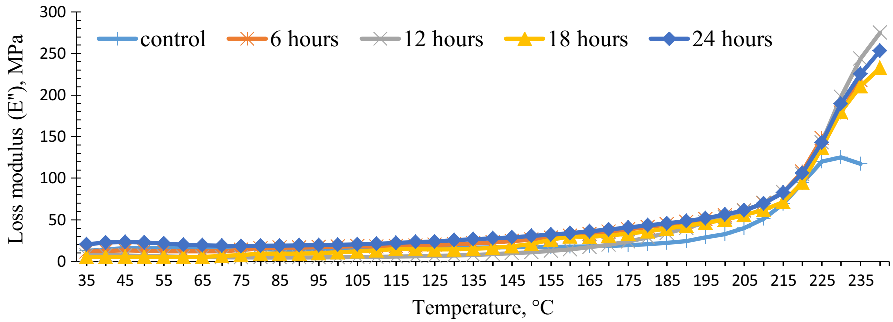

Fig. 12 Effect of solar radiation on the loss modulus (E″) of tanned leather

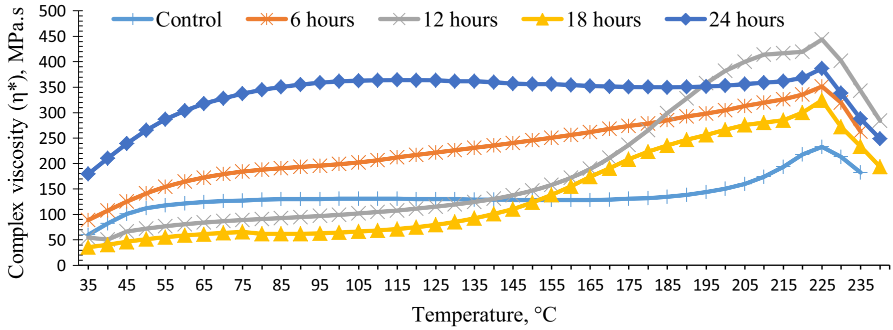

Fig. 13 Effect of solar radiation on the complex viscosity (η*) of tanned leather

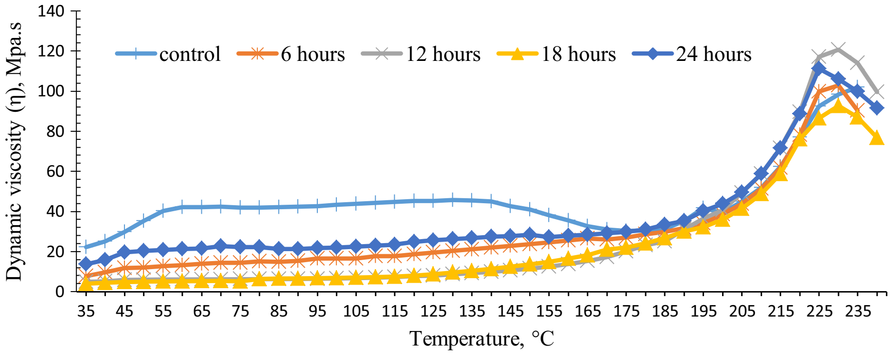

Fig. 14 Effect of solar radiation on the dynamic viscosity (η) of tanned leather

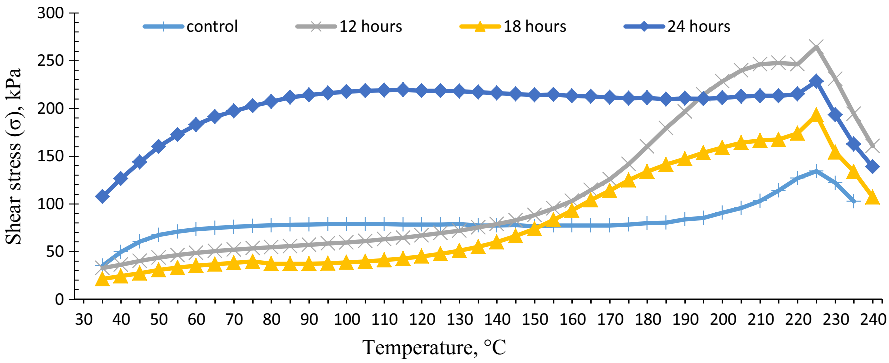

Fig. 15 Effect of solar radiation on the shear stress (σ) of tanned leather

3.2 Dynamic Temperature Scans

Effect of solar radiation on the loss modulus, complex viscosity, dynamic shear viscosity and shear stress of tanned leather as functions of temperature is illustrated in Figs. 12, 13, 14 and 15, respectively. Figures 16, 17, 18 and 19 show the effect of solar radiation on the loss modulus, complex viscosity, dynamic shear viscosity and shear stress of pickled leather as functions of temperature, respectively. Although there were overlaps at different temperatures, a common trend, similar to dynamic frequency sweeps, was noted. The properties recorded an initial increase as the time of exposure rose from 0 h to 6 h followed by a rapid decrease to a minimum at 12 h before a steady growth after that, to a maximum of 24 h through 18 h. There was an increase in the viscoelastic properties with temperatures forming peaks at a characteristic temperature of 225 °C as shown in Figs. 13, 14 and 15. The increase in loss modulus, viscosity and shear stress was observed with increasing temperature but was disrupted at higher temperature due to transition processes as indicated by two distinct peaks. For tanned leathers, the first peaks were not visibly different like in pickled leather, especially loss modulus. The peaks in viscosity and shear stress of tanned leather and pickled leather

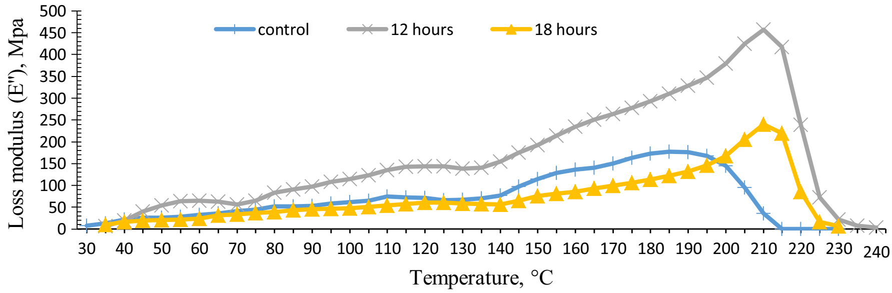

Fig. 16 Effect of solar radiation on the loss modulus (E″) of pickled leather

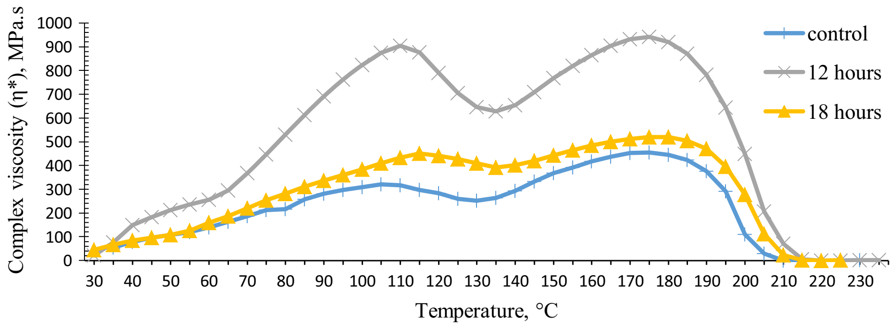

Fig. 17 Effect of solar radiation on the complex viscosity (η*) of pickled leather

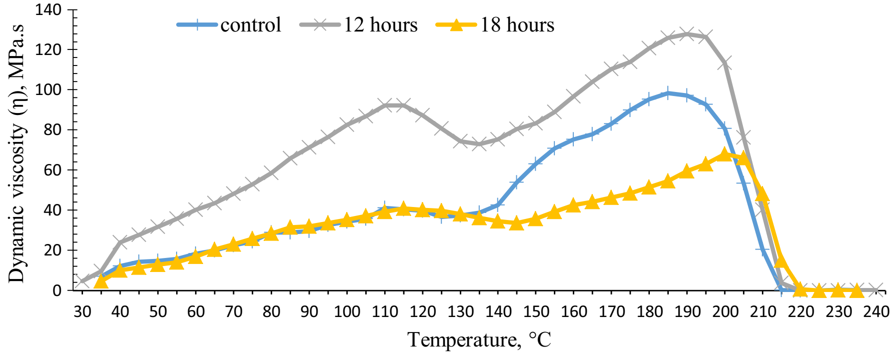

Fig. 18 Effect of solar radiation on the dynamic viscosity (η) of pickled leather

occurred at particular similar temperature ranges of 225 °C to 230 °C, and 175 °C to 210 °C, respectively.

The increase in temperature results in softening of the collagen chains. The softening allows more participation of the chains in the oscillation and flow. A significant number of peptide chains get freed from their entanglements to participate in the swing and dissipation. This disentanglement, in turn, increases the dissipation of mechanical energy. Increased dissipation, therefore, explains the growth of loss modulus with tempera-

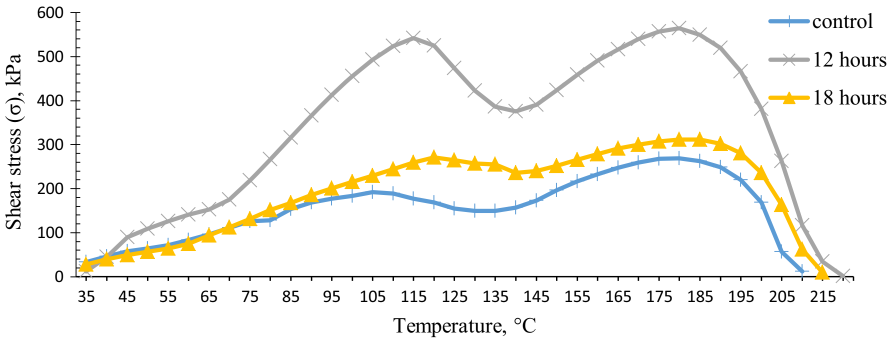

Fig. 19 Effect of solar radiation on the shear stress (σ) of pickled leather

ture. Furthermore, increasing temperature further dehydrates the collagen molecules. Dehydration reduces the space between particles, thereby increasing the inter- and intramolecular chemical bonds [30]. The changes in the collagen network, strengthening and shortening of the hydrogen bonds within the triple helix, confer stiffness in the collagen fibrils [27,38], resulting in the increase in the loss modulus, viscosity and shear stress. When the collagen structure loses the bound water, it melts and transforms the ordered triple helix to random coil [27,41]. The random coil rearrangement causes thermal depolarization which leads to dropping in loss modulus, shear stress and viscosity, as also observed by Ahmad et al. [42].

4 Conclusions

Within frequency the range from 0.1 Hz to 30 Hz, the properties showed linear dependence (dispersion phenomenon), but as frequency increased beyond 30 Hz, the frequency dependence became minimal, almost zero. The storage modulus and shear stress showed an increase in frequency from 0.1 Hz to 30 Hz, while loss modulus, complex viscosity and dynamic shear viscosity showed a linear decrease with frequency from 0.1 Hz to 30 Hz. Hence, the performance of the bovine leather and its products is better at frequencies higher than 30 Hz. At these frequencies, the properties are less dependent on the oscillation frequency. More investigations are recommended to identify the importance of this transition frequency, 30 Hz, and factors that determine this change rate. Solar radiation indeed has an influence on the viscoelastic properties of leather. Viscoelastic properties of leather showed an initial increase from 0 h to 6 h of sunlight followed by a steady decrease to minimum magnitudes at 18 h through 12 h before a drastic increase to a maximum at 24 h of irradiation. As functions of temperature, a common trend formed showed an initial increase to 6 h followed by a rapid decrease to a minimum at 12 h before a steady growth to a maximum at 24 h through 18 h. The viscoelastic properties also increased with temperature forming peaks at a characteristic temperature at 225 °C. Hence, solar irradiation of the leather by tanning industry for 24 h, which is a common practice by tanners, can be encouraged to enhance some viscoelastic/mechanical properties. Longer irradiation periods can be recommended to elucidate more information about effects of solar radiations.

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Compliance with Ethical Standards

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

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