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Thermal and mechanical analysis of pickled and tanned cowhide: Effect of solar radiations

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ABSTRACT: Cowhide, a natural biopolymer of collagen, forms raw material for leather, biomaterials, and food, among others. Thermal and mechanical analysis was done using dynamic mechanical analyzer. Effect of tanning and natural solar radiations on the storage modulus, tan δ, and thermal stability of pickled and tanned cowhides has been investigated in the temperature range of 30–240°C. Tanning has been shown to enhance thermal stability and storage modulus. However, tanning decreases its dissipative capability. Thermal stability of both tanned and pickled hide decreased with time of exposure to irradiation. Storage modulus dropped drastically within the initial 6 h of natural solar radiations before rising progressively with the subsequent 12, 18, and 24 h, although still lower than that for nonirradiated sample. Thermal–mechanical analysis proved to be a useful technique for assessing effect of tanning and natural solar radiations on cowhide. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43208.

KEYWORDS: collagen; cowhide; dynamic mechanical analysis; solar radiations; thermal properties

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INTRODUCTION

Thermal and dynamic mechanical properties of cowhide are key to its industrial processing techniques, eventual application fields, and functional performance of the resulting products in the high-end market.[1] Flayed cowhide usually undergoes a series of chemical and mechanical operations to form leather, a more mechanically stable and heat-resistant hide, in a process called tanning. Prior to tanning, all noncollagenous components of the hide such as hairs, epidermis, subcutaneous fats, muscular layer, and lipids among others are removed leaving dermis that proceeds to pickling and tanning process.[2] The collagen, which majorly constitutes dermis, self-organizes to form bundles or a meshwork that determines the mechanical strength, the elasticity, and the geometry of the leather.[3] Tanning forms new crosslinks in the collagen that had otherwise been broken by the acids and alkalis used prior to tanning.[4] However, collagen makes the outdoor applications of cowhide materials sensitive to natural environmental conditions such as solar ultraviolet radiations, oxygen, water vapor, and heat.[5] In the natural environment, the hide is exposed to factors such as solar radiations, atmospheric oxygen, casual oxidizing and acid atmospheric pollutants, environmental temperatures, and humidity. Solar radiations contain significant amount of ultraviolet radiations, visible light, and infrared rays that affect the mechanical stability of collagenous materials.[6,7] Inevitably, these are the typical factors that hide is exposed to during leather making process and field of application. When exposed to this natural environment, collagen, like other naturally occurring polymers, absorbs and scatters the solar ultraviolet radiations, infrared radiations, water vapor, and oxygen which may initiate deterioration or mechanical improvement of the collagen.[6]

Characterization of collagen-based materials using optical spectral measurement in the UV–VIS field technique has been documented although; it has a limitation of not giving data timely.[8] A comparison of a TR-FTIR, GC-MS, and TGA analyses with multispectral imaging on parchment is also documented.[9] Analysis of the effects of heating and drying on collagen using X-ray diffraction has been published.[10] However, these techniques do not show the dynamic thermal–mechanical relationship of the materials. Thermal-mechanical analyses have been very useful for the assessment of leather deterioration/degradation.[11] They have been used to characterize collagenous materials such as leather, parchment, and collagen solution using differential scanning calorimetry (DSC), micro Hot Table (mHT), and dynamic mechanical analyzer (DMA).[12–20] Although effect of solar radiations on the collagen-based biomaterials has been studied,[6] there appears no publication on the effect of solar radiations on cowhide using thermal-mechanical analyses.

Table I. Sample Preparation Recipe of Pickling

Process/step	Chemicals (%)	Temperature (/°C)	Time	Remarks
Washing	100% H_2O, 1% detergent	23-25	10 min	Drain
Liming & unhairing	100% H_2O, 1.5% Na_2S, 1% $Ca(OH)_2$ (Lime), Add: 100% H_2O, 1% Na_2S 1% $Ca(OH)_2$ (Lime) Add: 50% H_2O 1% $Ca(OH)_2$ (Lime	23-25	1 h 1 h 16 h	Drum speed=2–3 rpm pH = 12 Drain Fleshing and scudding
Washing	300% H_2O,	25	10 min	Drain
Deliming	100% H_2O 2% $(NH_4)_2SO_4$, 1% Sodium metabisulphite	25	1 h	pH = 8.3 x-section clear to phenolthalein
Bating	0.2% microbates-1600 LVU	35-37	1	Drum speed = 3 r.p.m.
Washing	200% H_2O,	20–25	20 min	Drain
Pickling	80% H_2O, 8% NaCl 1% H_2SO_4 (98%), (1:10) 1% Sodium formate	20–22	10 min 1 h	Drum speed = 3 rpm pH = 2.5
Drain & washing	200% H_2O	25	20 min	Drain
Splitting				Split 1.0 mm
Horse up				
Sammy				

Therefore, this study reports the findings of the effect of natural solar radiations on the thermal and dynamic mechanical properties of pickled and tanned hide using dynamic mechanical analysis. Insightful comparison of the effects of natural radiations on the pickled hide and tanned hide is also reported to understand effect of tanning on cowhide.

EXPERIMENTAL

Sample Preparation

Freshly flayed cowhide pelt was prepared to pickling stage prior to tanning following the conventional standard tanning procedure as summarized in Table I at Kenya Industrial and Research Institute-Leather Development Centre (KIRDI-LDC) in Nairobi-Kenya. The pickled pelt was then sided along the backline into two identical pieces. One piece was further tanned using chromium sulfate as summarized in Table II. The samples were cut from both the pickled and tanned hide using matched trial to give a standard comparison of the effect of chrome-tanning. Rectangular samples of dimensions 30 × 9.3 × 0.93 mm, sampled according to official sampling method and location (ISO 2418: 2002), were cut using a press knife both along the backbone and in perpendicular directions as illustrated in Nalyanya *et al.*[21] The choice of the sample sizes was dictated by the film tension geometry of the DMA and to minimize the variations arising from the anisotropic nature of cowhide with respect to the backbone and fibrous nature of cowhide.

Solar Irradiation

The suitably cut samples were exposed to the natural solar radiations for time intervals ranging from 0 (nonirradiated) to 24 h at Egerton University, Njoro-Kenya (0°55″S, 35°04″E) during the month of September 2014. This is the customary duration that tanning industry exposes the hide to the sun during leather making. Egerton University lies in the heart of Rift Valley, 22 km from Nakuru City, which receives solar radiations of irradiance approximately 7.1 kW m^{-2} each day during the month of September.[22] The time interval of exposure during the day was from 10 AM to 3 PM to minimize the variation of solar irradiance. Hence, each sample receives solar irradiance of approximately 0.08254 W each hour on average. The samples were then conditioned in a standard atmosphere of temperature 23 ± 2°C and humidity 50 ± 5% RH for 48 h prior to testing according to ISO 2419: 2002.

Thermal-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 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') and tan δ were determined as functions of temperature with the aid of thermal analysis (TA) instrument control software. This software analyses the data at different

Table II. Sample Preparation Recipe of Tanning

Process/step	Chemicals (%)	Temperature (/°C)	Time	Remarks
Tanning	6% Chromium sulphate (33% basic) Add 0.5% fungicide	25–27	3 h 30 min	Drum speed = 3 rpm Penetration complete through x-section pH = 3.0 Drain
Basification	0.5% $NaHCO_3$ (1:10) Add 0.5% $NaHCO_3$ (1:10) Add 0.5% $NaHCO_3$ (1:10)		20 min 20 min 20 min	Final pH = 3.6 Shrinkage temp = 100°C
Drain & washing	200% H_2O,	25	20 min	Drain
Horse up				

frequencies and present the means in graphical form. The temperatures corresponding to the peaks in tan δ were used to infer the thermal stability of the samples. Calibration of the DMA was done before any experiment to enhance reliability of the measurements.

RESULTS AND DISCUSSION

Effect of Tanning

Figure 1 illustrates the effect of chrome-tanning on the storage modulus of cowhide. Storage moduli (E') increased with increasing temperature for both pickled and tanned hides to two distinct major peaks, although only the second peak is noticeable for tanned hide. The increasing storage modulus can be explained by dehydration that takes place as temperature rises. Dehydration of collagen causes formation of additional cross-links 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.[2,23,24] These two effects combine to increase the storage modulus with temperature. This result has also been observed by Cucos *et al.*[18] who found out that dehydrated collagen fibrils are more mechanically stiff than hydrated collagen. However, tanned hide exhibited smaller increase in E' with increasing temperature than pickled hide showing that tanned hide has higher ability to function at varying strain and can survive long cycles than pickled hide. This can be attributed to the liming process of preparing the hide for tanning. During the liming, dermal swelling takes place increasing the porosity of the hide.[2] 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 y increasing temperature, pickled hide loses more water than tanned hide. This explains why the increase in storage modulus is higher for pickled hide as compared to the tanned hide. Throughout the temperature range, tanned hide recorded higher storage modulus values compared to pickled hide as shown in Figure 1. This is because tanning introduces synergistic effect on collagen with chromium ions generating strong cross-linkages that induce resistance to any forces of deformation on the dermal collagen, especially in compression tests.[2,25–27] 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.[25] This decreases the stiffness

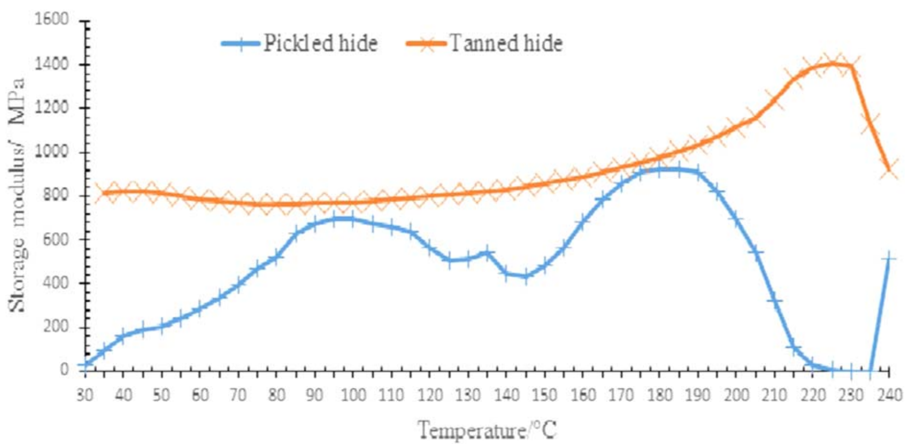

Figure 1. Effect of pickling and tanning on the storage moduli of hide. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

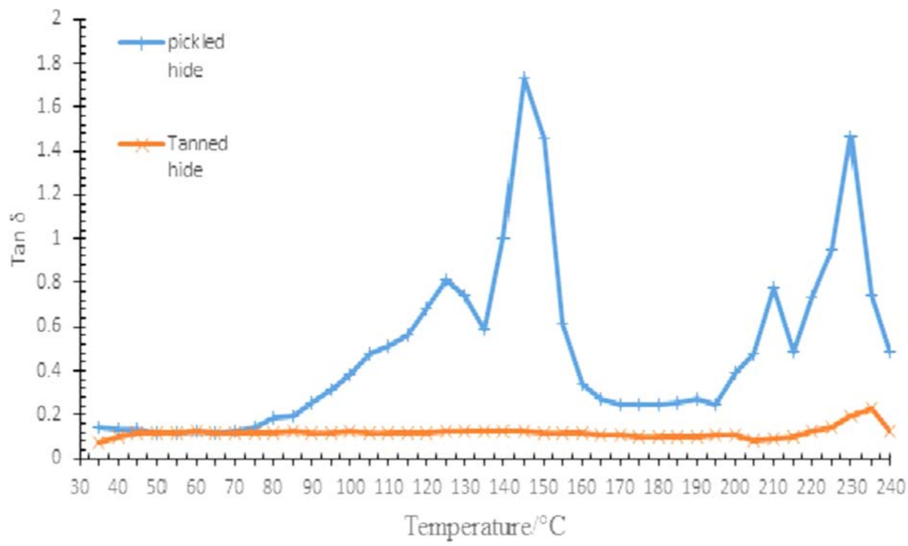

Figure 2. Effect of pickling and tanning on tan δ of hide. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of the pickled hide compared to tanned hide that has compact structure. This also explains why the temperatures corresponding to the peaks in storage modulus for tanned hide were slightly higher than for pickled hide (Figure 1). These results agree with those by Pekhtasheva *et al.*,[4] where it was observed that elastic properties of collagen increases with tanning. The temperature corresponding to the second peak of storage moduli for tanned hide was greater than that for pickled hide. This can also be attributed to the cross-linking effect of chrome-tanning.[28] 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.[14,27] 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,[17] 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.

Effect of chrome-tanning on tan δ of cowhide which determines the dissipative capability or the ability to lose mechanical energy imposed on is illustrated in Figure 2. The graph showed that tan δ for pickled hide is greater than for tanned hide which implies that tanning decreases the dissipative capability of cowhide. This also implies that tanned hide is more elastic/rubbery/elastomeric in nature than pickled hide.[29] This can probably be explained by chromium ions which act to decrease the free volume of the collagen matrix, enhancing the rigidity of the collagen molecules and increases molecular weight.[30] This depresses the molecular mobility in tanned hide, hence low dissipative capacity compared to pickled hide. Comparing Figures 1 and 2, temperatures corresponding to the peaks in tan δ were relatively higher than those in storage modulus. This is because temperatures in tan δ are determined by the entire volume fraction of the relaxing phase, hence its temperature is greatly affected by the amorphous phase of the collagen unlike the temperatures in storage modulus.[31] Tan δ increases as temperature rises due to increased polypeptide chains mobility which aids the chains to dissipate the applied

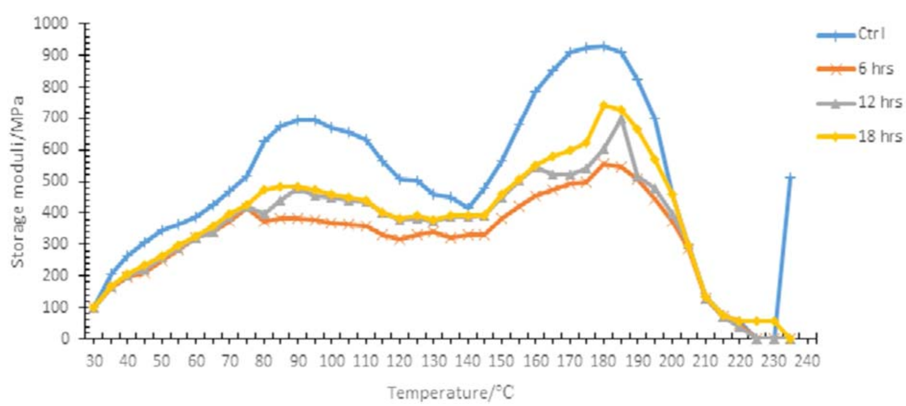

Figure 3. Effect of irradiation on storage moduli of pickled hide. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

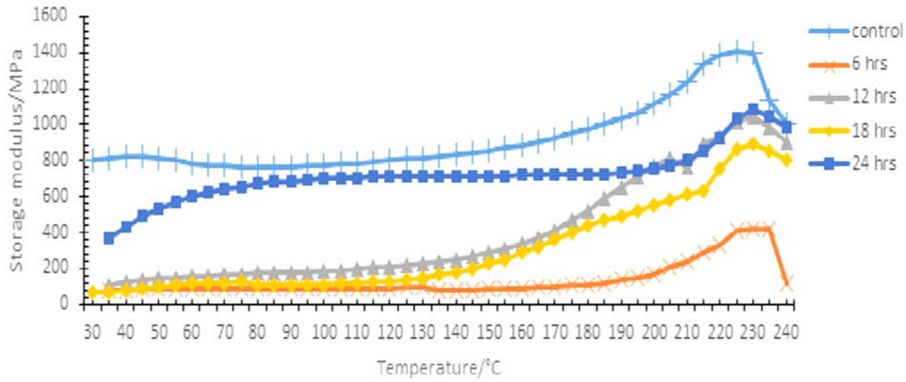

Figure 4. Effect of irradiations on storage moduli of tanned hide. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mechanical energy in form of heat.[32] The increasing tan δ with temperature was interrupted by the peaks which represent the dehydration of the collagen and melting of both amorphous and crystalline regions of collagen. In tanned hide, only the second peak was noticeable while pickled hide showed two distinct peaks. Therefore, the melting temperature of pickled hide occurred at 230°C, while for tanned hide occurred at 235°C. This implies that tanned hide is slightly more thermally stable than pickled as shown by their melting temperatures. The slight difference can be attributed to the rigidity imposed by the cross-links induced between amino acids and carboxy side chain of triple-helical regions during chrome-tanning hence increases peptide bonds.[17,25–28] The melting temperature for tanned hide agree closely with results reported by Budrugeac *et al.*[27] on new and historical leather which were 230 and 234.5°C using DMA and DSC, respectively. Odlyha *et al.*[33] found similar range of 230–234.5°C. Working on an extracted pure collagen, Cucos and Budrugeac[14] reported a slightly smaller value of 225.3°C. However, Budrugeac and Miu[11] working on the same extracted pure collagen reported the melting temperature range of 205–245°C.

Effect of Exposure to the Solar Radiations

Figures 3 and 4 illustrate the effect of solar radiations and other natural environmental factors on the storage moduli of pickled and tanned hides, respectively. The two graphs show that nonirradiated 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.[34,35] Absorption of these radiations, heat, and environmental water vapor by collagen in the presence of atmospheric oxygen causes oxidation.[9,34,36–38] This oxidation breaks covalent bonds in collagen peptide chains and the tanning agents forming highly reactive radicals and hydroperoxides.[37] The OH^- radicals, for example, induce chain scissions which weaken the mechanical properties of the hide.[6,34,39] Studies have shown that these radicals cause both chain scission and cross-linking of the collagen and the net effect depends on the irradiation dose or duration and pH of the medium.[6] Interestingly, as duration of irradiation increased, the storage modulus gradually increased although still lower than that of nonirradiated 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.*[36] observed that it increases the viscoelastic properties. The UV radiations and infrared cause dehydration of the collagen fibers which increase the stiffness, since dehydrated collagen is harder and stiff.[3,23,24,40] Similarly, the initial chain scission as a result of UV absorption by the aromatic/chromophoric amino acids

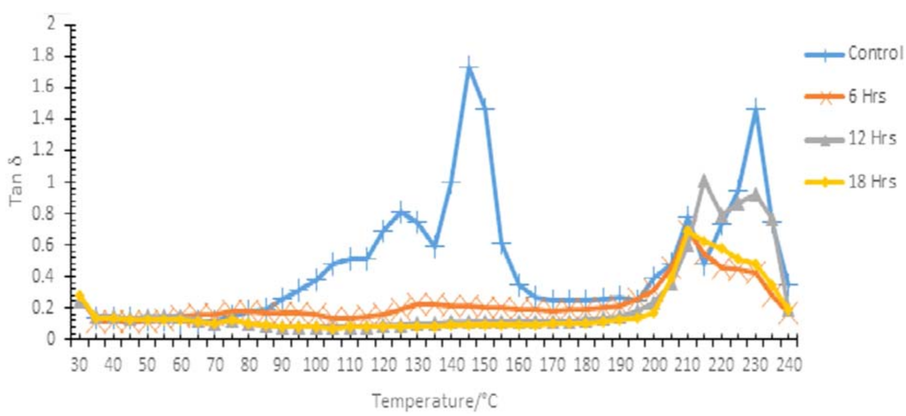

Figure 5. Effect of irradiations on tan δ of pickled hide. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

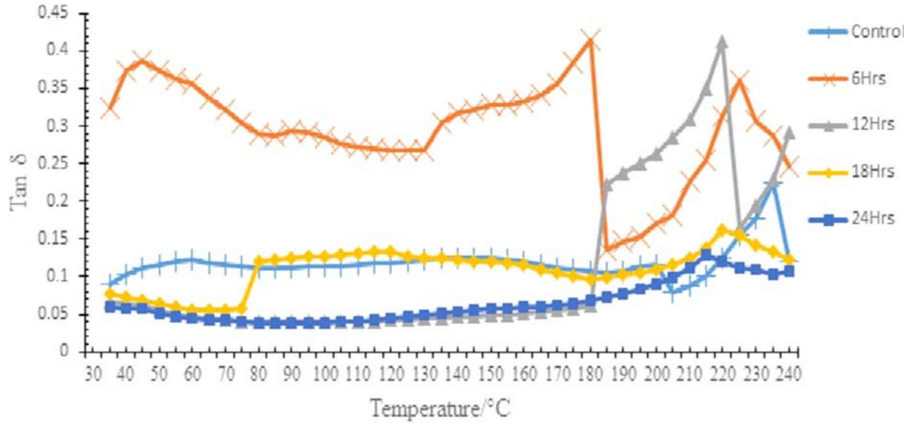

Figure 6. Effect of irradiations on tan δ of tanned hide. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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 cross-links that are aimed at increasing the stiffness.[41,42] 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 cross-links that induce stiffness.[43] This agrees with the observations made by Janko *et al.*[3] that the impact of irradiation is dependent on the environmental conditions and time of irradiation.

Tan δ for pickled hide behaved differently from that for tanned hide. The difference may probably be due to the chemical cross-linking effect of chrome-tanning that induces covalent bonds. These bonds decrease the collagen-free volume hence permeability to both water and radiations.[30] This increases molecular weight as well. For pickled hide, nonirradiated sample exhibited the highest tan δ (Figure 5). As time of irradiation increased, tan δ decreased, implying that irradiation decreases the dissipative capability of pickled hide. Only nonirradiated pickled hide sample recorded tan $\delta > 1$ at 140–155°C and 225–235°C. All irradiated samples had tan $\delta < 0.5$. For tanned hide, sample irradiated for 6 h had the highest tan δ followed by nonirradiated sample. All tanned hide samples had tan $\delta < 0.5$ (Figure 6). In Figures 5 and 6, it can be noted that cowhide is predominantly elastic in nature although tanned hide is more elastic but less dissipative than pickled hide as indicated by tan δ magnitudes. This can be attributed to the rigidity imposed on the tanned hide by the chromium ions and the increased molecular density.[17] The mobility and hence the dissipation in tanned hide is consequently restricted.

Thermal stability of cowhide, as indicated by the melting temperature of the crystalline fraction of collagen, was inferred from the temperatures corresponding to the peaks of tan δ[28] as shown in Figures 5 and 6. The effect of exposing the samples to the natural solar radiation on these temperatures and hence thermal stability is illustrated in Figure 7. 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.[30,44] The results agree with those reported by Pekhtasheva *et al.*[4] In both pickled and tanned hides, nonirradiated 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.*[45]

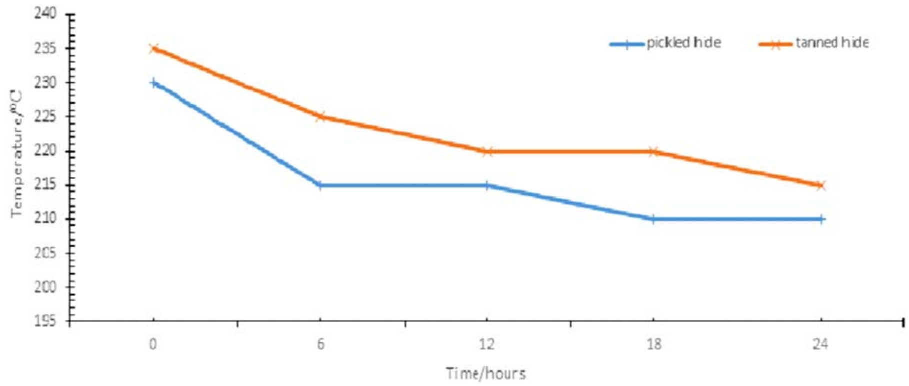

Figure 7. Effect of irradiations on melting temperatures of pickled and tanned hide. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

Chrome-tanning as a chemical cross-linking agent has been shown to enhance both thermal stability and storage modulus or stiffness of cowhide. However, the process decreases the dissipative capability or hysteresis or damping of the hide. This makes chrome-tanning inappropriate for materials used in the design of devices and materials for purposes of earplug, vibration abatement, reduction of mechanical shocks, instrument mounts, and controlling rebound and resisting rolling. As expected, thermal stability of both tanned and pickled hide decreased progressively with time of exposure to irradiation. Although storage modulus of both tanned and pickled hides dropped drastically within the initial 6 h of natural solar radiations like other polymers, the subsequent 12, 18, and 24 h improved the storage modulus gradually. Within the irradiation duration of 6–24 h, the modulus was still less than that for nonirradiated sample, revealing the negative impact of natural solar radiation. More researches are needed to extend the duration of irradiation beyond 24 h on this complex material to determine the duration at which the storage modulus starts to decrease with irradiation. Thermal-mechanical analysis proved to be a useful technique for assessing effect of tanning and natural solar radiations on cowhide. Leather industry, especially tanneries, needs to find an alternative technique for drying other than drying on the sun in order to guarantee quality leather.

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