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Effect of Gamma Irradiation on the Stability of Tanned Leather

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ABSTRACT

Leather tanning involves several processes of converting putrescible hide to stable leather resistant to harsh environmental conditions. Severe conditions such as high temperatures and UV radiation, when exposed to the leather materials, cause degradation and decrease physical, chemical, and structural properties. The effect of gamma irradiation on viscoelastic properties and stability of tanned leather against thermal and photodegradation was studied using the Dynamic Mechanical Analysis (DMA) technique. The thermal stability of chrome and mimosa-tanned leather was inferred from the peak of storage modulus graphs. Gamma irradiation of samples with low doses increased the storage modulus of chrome and mimosa-tanned leathers. Doses up to 20 kGy decreased the stability of thermally aged chrome-tanned leather. However, for mimosa-tanned, there was an increase at higher doses as a result of gamma irradiation inducing additional bonds that enhance the stability of the tanned leather. Nevertheless, there is a variation in the stability of chrome-tanned leather at different doses of irradiation.

KEYWORDS

gamma irradiation, leather, thermal stability, photostability, viscoelasticity

INTRODUCTION

Leather a by-product of the meat industry forms an important raw material in the leather industry. The applicability of leather majorly depends on the mechanical properties that are remarkably determined by the tanning agents used during the tanning process [1]. A series of chemical and mechanical processes that alter the physical properties are performed on the hide to ensure the stabilization of the end product [2,3]. These complex chemical processes are under continuous ecological attention. Vegetable tanning agents have been incorporated instead of chromium salts but presented bleak prospects. Studies show that chromium sulfates, among other mineral tanning agents, confer superior mechanical stability compared to vegetable tanning agents [3,4]. The complex bridges and crosslinks induced by these salts during the tanning process enhance mechanical strength and thermal stability [5] and generally improve the viscoelastic properties of the finished leather [1]. However, the mechanical stability of leather is degraded when exposed to high temperatures and

ultraviolet radiations due to the presence of chromophoric amino groups (tyrosine and phenylalanine) in leather [6,7]. When leather is exposed to UV radiations it induces photochemical reactions by radical mechanisms where chemical compounds split off to form free radicals [8]. These free radicals immediately react with oxygen to form peroxide radicals and further react with leather components, which break the bonds between the tannins and collagen. Both thermal and photodegradation weaken the bonds in the leather and eventually mechanical properties hence the lower quality.

High-energy irradiation has been touted as one of the chemical crosslinkers that can be used to enhance the stability of leather against harsh conditions. Studies show that progressive thermal destabilization up to 100 kGy doses was evident for thermally stable vegetable-tanned leather and maintained leather-like properties. However, the unstable vegetable tanned underwent thermal destabilization and de-tanning when irradiated with 10 kGy [2]. Studies done using unilateral NMR revealed that there are modifications induced by gamma radiation that as crosslinking and dehydration at 25 kGy doses and chain degradation at higher doses [9]. In this paper, the impact of gamma irradiation on the viscoelastic properties and the stability of the processed leather against photo and thermal degradation using a Dynamic Mechanical Analyzer (DMA) is discussed.

EXPERIMENTAL

Sample Preparation

Fresh bovine hide was procured from the abattoir and salted to temporarily preserve the hide at the Kenya Industrial Research and Development Institute (KIRDI). The conventional process was done up to the pickling stage, as described in Table 1. The pelt was cut into two halves, and six (6) samples of 200 g were further cut from each half one sample was kept as a control sample and five samples were irradiated at different doses (10, 20, 30, 40, and 50 kGy) of radiation. The samples were irradiated at Kenya Agricultural and Livestock Research Organization (KALRO)-Biotechnology Research Institute at Muguga with a Co-60 gamma irradiator (Model GC 220E) at room temperature and normal atmospheric conditions.

Table 1. Beam house operation.

Process/ Step	% Chemicals	Duration	Remarks
Dirt soaking	166 % water	45 minutes	Run slowly in the drum
	0.2 % detergents		
Main soaking	166 % water	Overnight	
	0.01 % bactericide		
De-hairing	133 %Water	30 minutes	
	1 % Na ₂ S		

Process/ Step	% Chemicals	Duration	Remarks
Liming	133% Water	25 minutes	Run slowly in the drum
	25 % lime		
Re-liming	0.5 % Na ₂ S	2 hours	Drain and wash
	Add 1.5 kg lime		
Fleshing and scudding	0.5% Na ₂ S	20 minutes	Run slowly in the drum
De-liming	166 % water	30 minutes	Drain and wash
	4.2 % Ammonium sulphate		
	166 % water, 3.3 % Ammonium sulphate	25 minutes	
Bating	Add: 5 % Microbates	20 minutes	Run slowly in the drum
	1.7 % ammonium sulphate		
	Soak		
	Add: 25 % salt	15 minutes	
Pickling	2.5 % formic acid	10 minutes	
	1.7 % formic acid	10 minutes	
	1.7 % formic acid	10 minutes	

Sample preparation at the tanning stage

Before tanning, each of the 200 g pelts was cut into two after irradiation and tanned with chrome and mimosa tanning agents, respectively as described in Table 2. The samples were toggled and dried and from each treatment, samples of dimensions 30 × 9.3 × 0.93 mm were cut for dynamic mechanical analysis.

Table 2. Tanning process

Process/ Step	% Chemicals	Duration	Remarks
	6 % chrome		pH. 2.5
Chrome-tanning	Add: 7.5 % sodium formate	20 minutes	Run slowly in the drum
	7.5 % sodium bicarbonate	20 minutes	
	7.5 % sodium bicarbonate	20 minutes	Final pH 3.8
	50 % mimosa tannins		Run slowly in the drum
Vegetable-tanning	Add: 7.5 % sodium formate	20 minutes	
	7.5 % sodium bicarbonate	20 minutes	
	7.5 % sodium bicarbonate	20 minutes	Final pH 5

Sampling and Sample Conditioning

The specimens for dynamic mechanical analysis were kept at 23 °C and 50 % RH for at least 24 hours according to ISO 2419 [10]. Sampling was done following the standard ISO 2418 [11], whereby the

samples were cut within the official sampling position, in which the variation in strength properties and anisotropy were gradual and minimal [12].

Thermal and photoaging of samples in the heat and UV chamber

Samples of dimension $30 \times 9.3 \times 0.93$ mm were cut for dynamic mechanical analysis. They were aged in a heat-adjustable cabinet at 80 °C for 24 hours and in a UV cabinet (UV light of wavelength 254 nm-UV-C) for 144 hours. The samples were conditioned in a standard atmosphere for 48 hours before testing [10].

Dynamic Mechanical Analysis

Dynamic Mechanical Analysis (Model 2980 from TA Instruments, USA) was used for dynamic mechanical analysis. Samples were cut from irradiated and non-irradiated leather and mounted one by one onto the film tension clamp, run in multifrequency mode. The segment method was set to equilibrate at 35 °C, data storage off, isothermal for 1 minute, frequency sweep (this segment turns on the data storage, steps through the frequency table, and turns off data storage after the final frequency), increment of 5 °C while repeating the loop from isothermal to increment. The experiment was conducted in a multifrequency mode at 30 Hz in a static air environment and temperature ranging from 35 °C to 260 °C. Before each experiment, position, and clamp calibration was done to enhance the reliability of the results. Storage modulus, loss modulus, and $\tan \delta$ were determined as functions of temperature. The average data for storage modulus, loss modulus, and $\tan \delta$ versus temperature or frequency for each irradiated and non-irradiated sample were extracted from the DMA TA software and used to draw graphs. The magnitudes for each parameter and erratic changes were used to infer the thermal and photostability of the samples.

RESULTS AND DISCUSSION

Effect of gamma irradiation on viscoelastic properties of leather

The effect of gamma irradiation on viscoelasticity was inferred by plotting graphs of individual viscoelastic properties versus temperature for chrome-tanned and mimosa-tanned leathers on different graphs. The comparison at different temperatures enabled us to conclude the effect.

Storage modulus (E')

The E' of chrome-tanned leather irradiated at different doses of gamma irradiation is shown in Figure 1.

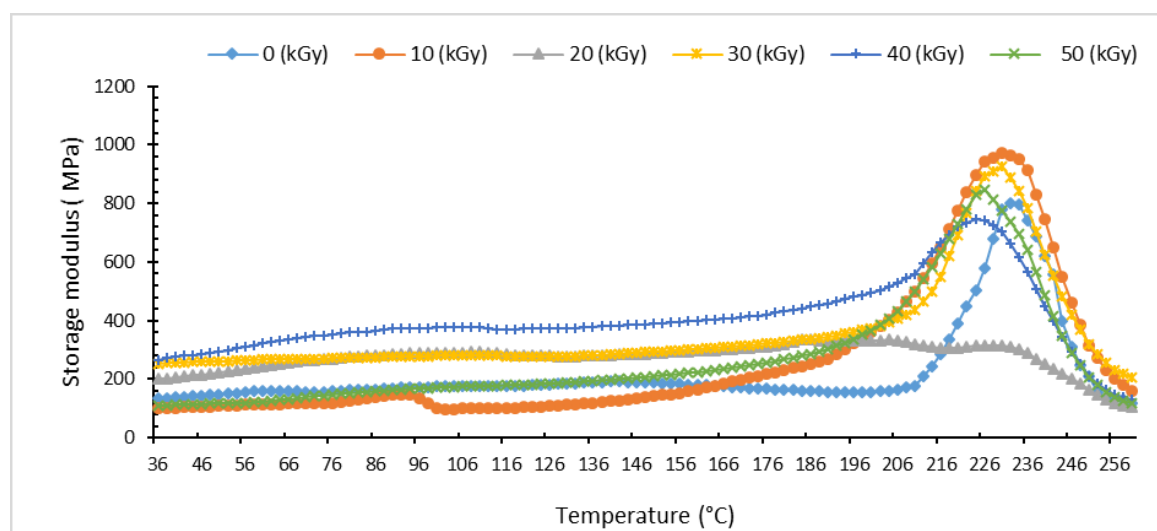


Figure 1. Effect of gamma irradiation on storage modulus of chrome-tanned leather

The E' increases linearly with increasing temperature, and at around 200 °C, the E' sharply increases, decreasing to almost zero. The initial increase with increasing temperature is due to dehydration, which happens as the temperature rises, and excess tannins that are not removed during the tanning process form additional crosslinks [13,14]. Also, increased crosslinking of chains between collagen and tannins increases E' as the temperature increases [3]. The increase in E' with increasing irradiation dose was also observed. This was attributed to irradiation in the presence of water, which forms radicals, a process called water radiolysis, which ionizes the carboxyl group in collagen, quickly forming amide in the presence of amine [15]. The denaturation temperature of non-irradiated leather is high, and as the irradiation dose increases, the denaturation temperature decreases. Herman et al. [16] report that irradiation with low doses induces additional crosslinks, and higher doses initiate the rupture of already-formed bonds, leading to a loss of mechanical strength and stability.

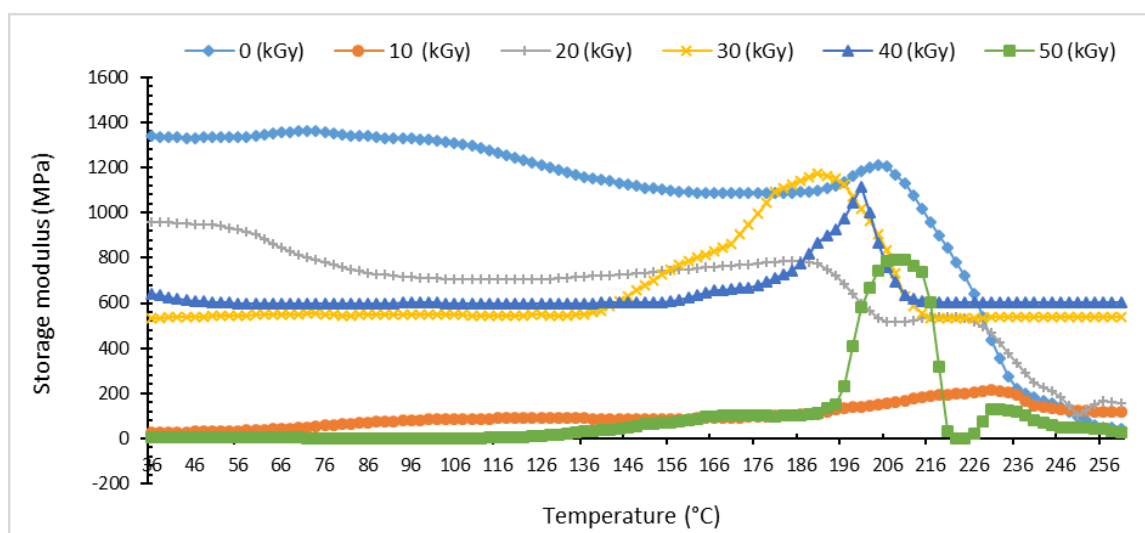


Figure 2. Effect of gamma irradiation on storage modulus of mimosa-tanned leather

For mimosa-tanned leather, non-irradiated mimosa-tanned leather exhibited a decrease in E' as temperature increased. It also had the highest E' , and as the irradiation dose increased, it decreased, as shown in Figure 2. The E' of the irradiated sample increased with temperature and interrupted with peaks at higher temperatures. At lower temperatures, the interaction between the tannins and protein collagen is through ionic bonds, and as temperature increases, covalent bonding predominates [17,18]. Irradiation with a 30 kGy dose and above, the E' of samples shows a sharp increase at higher temperatures and a drastic drop afterwards. This can be explained by the fact that gamma irradiation produces hydroxyl radicals through water radiolysis, which, in turn, enhances the interaction of the tannins with the protein collagen. At temperatures higher than 80 °C, only covalent bonds dominate the interaction of the collagen protein [18], which increases the E' . The denaturation temperature of non-irradiated leather is 206 °C. As the irradiation dose increased to 10 kGy, the denaturation temperature rose to 232 °C. This implies that lower irradiation doses enhance the stability of mimosa-tanned leather.

Tan delta ($\tan \delta$)

The loss factor of chrome-tanned leather irradiated at different doses of irradiation is shown in Figure 3.

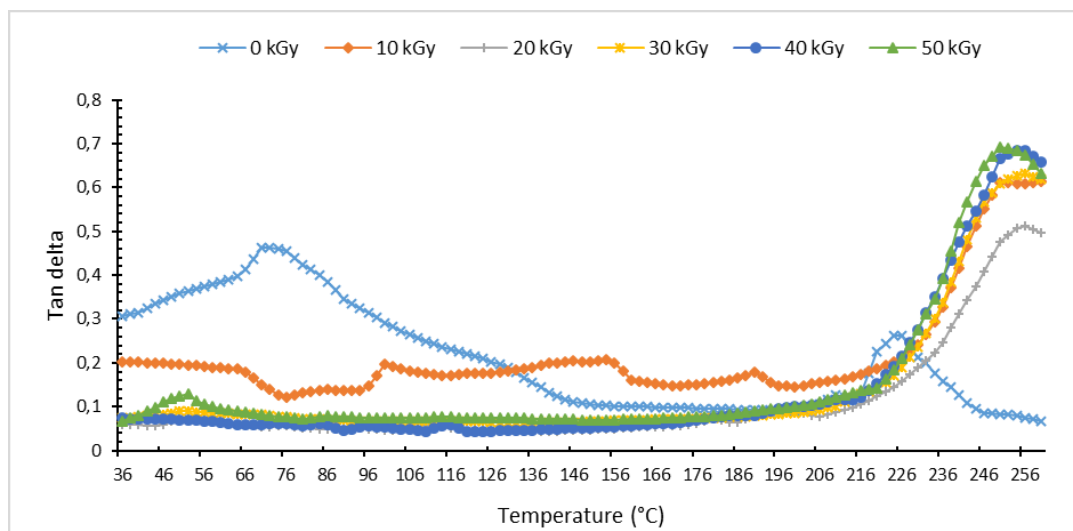


Figure 3. Effect of gamma irradiation on the tan delta of chrome-tanned leather

The loss factor of a material explains the dissipative capability of the material [9]. The irradiated and non-irradiated chrome-tanned leather loss factor is below the $\tan \delta$ threshold = 1; however, it increases with increasing temperature. In this study, the loss factor of non-irradiated leather displayed a slightly lower peak at lower temperatures than the peak reported by Nalyanya et al. at 235 °C [13]. The lower $\tan \delta$ of the irradiated leather is attributed to the rigidity of the crosslinks induced by gamma radiations [16]. The $\tan \delta$ of the non-irradiated leather is interrupted by peaks at 74 and 222 °C. The first peak is attributed to the melting of the unstable regions of collagen. The irradiated leather exhibited peaks at higher temperatures, related to the melting of both amorphous and crystalline regions of collagen [13]. The peak for the non-irradiated leather is noticeable at 222 °C, which is lower than for irradiated leather. The difference in peaks is attributed to the stiffness and compactness induced by gamma radiation between the amino acid and carboxyl side chains of the triple helical regions, which increases the peptide bonds [19–21]. The melting temperature of the non-irradiated leather agrees closely with the results reported by Cucos and Budrugaec of 229.8 °C for new leather [14].

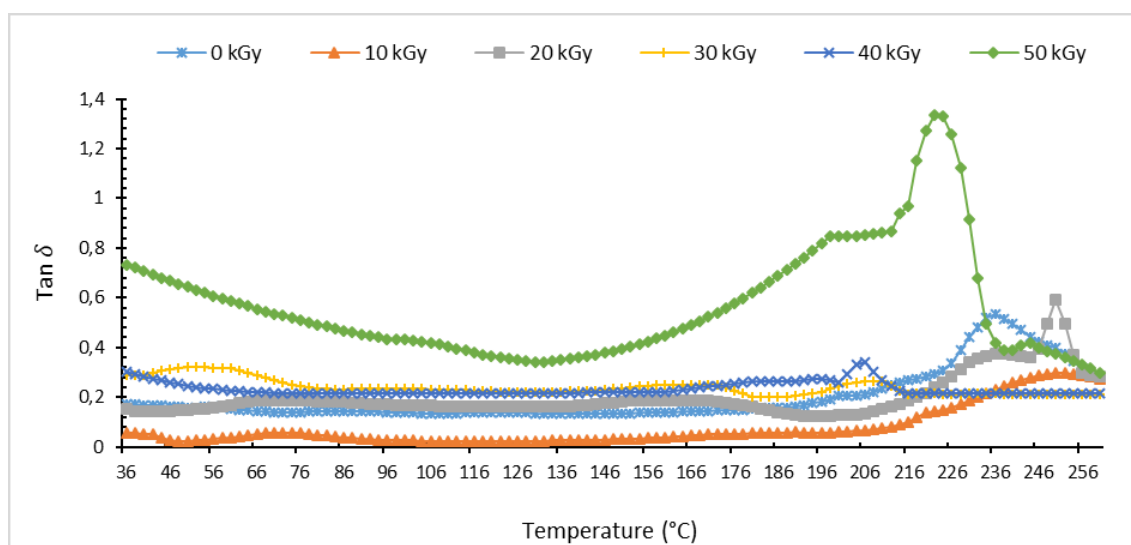


Figure 4. Effect of gamma irradiation on the tan delta of mimosa-tanned leather

The loss factor of radiated and non-irradiated mimosa-tanned leather is shown in Figure 4. The leather irradiated with 50 kGy radiation dose exhibited a higher tan delta than the other samples. The tan delta for non-irradiated was low, with a denaturation temperature of 234 °C. The lower tan delta is attributed to rigidity and compactness imposed by tannins. According to Jeyapalina et al., plant polyphenols reduce the rigidity of collagen through intermolecular hydrogen bonds [22]. More hydroxyl radicals were formed at higher radiation doses, which enhanced hydrogen bonding, thus decreasing the cohesive bond between adjacent tropocollagen molecules [22]. Irradiated leather exhibits an increase in denaturation temperature of up to 20 kGy, which is followed by a drop in denaturation temperature with increasing irradiation dose. The increase in denaturation temperature is because of the induced crosslinks by gamma irradiation, which improves the stability of the leather [16,21]. Nevertheless, as the irradiation dose increases, the denaturation temperature decreases due to the rupturing of previously formed bonds [2]; hence, more chains participate in the oscillation process. The tan delta of the sample irradiated with a 50 kGy dose is higher, implying that its dissipative power is also high.

Effect of gamma irradiation on thermal stability of tanned leather

The thermal stability of chrome and mimosa-tanned leather irradiated at different doses of gamma irradiation is inferred from the denaturation temperature of leather artificially aged in a heat-adjustable cabinet at 80 °C for 24 hours. The graphs were plotted as storage modulus versus temperature.

The storage modulus of chrome-tanned leather irradiated at different doses of irradiation is shown in Figure 5.

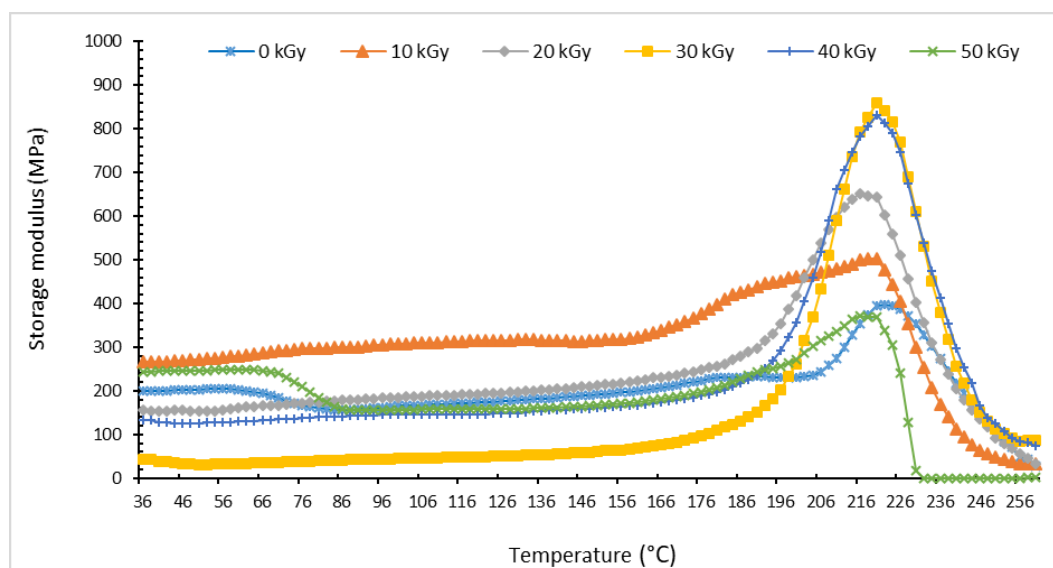


Figure 5. Effect of gamma irradiation on storage modulus of thermally aged chrome-tanned leather

The storage modulus of non-irradiated chrome-tanned leather increases with increasing temperature and is interrupted by a peak at 222 °C and decreases to almost zero. Increasing the irradiation dose to 20 kGy decreased the denaturation to 220 and 216 °C, respectively. The decrease can result from the thermal degradation of new ionized carboxyl functional groups necessary for chemical reactions. As the irradiation dose increased, the denaturation temperature increased to a higher temperature and decreased on irradiation with a 50 kGy radiation dose. Higher doses of radiation initiate the rupture of already-formed bonds, leading to a decrease in the denaturation temperature of leather [16]. This results in thermal destabilization. On the other hand, ionized carboxyl groups are more reactive and coordinate with chromium ions during tanning, stabilizing the collagen [23]. Thus, enhancing the stability of the tanned leather.

The storage modulus of mimosa-tanned leather irradiated with different doses of gamma radiation is shown in Figure 6.

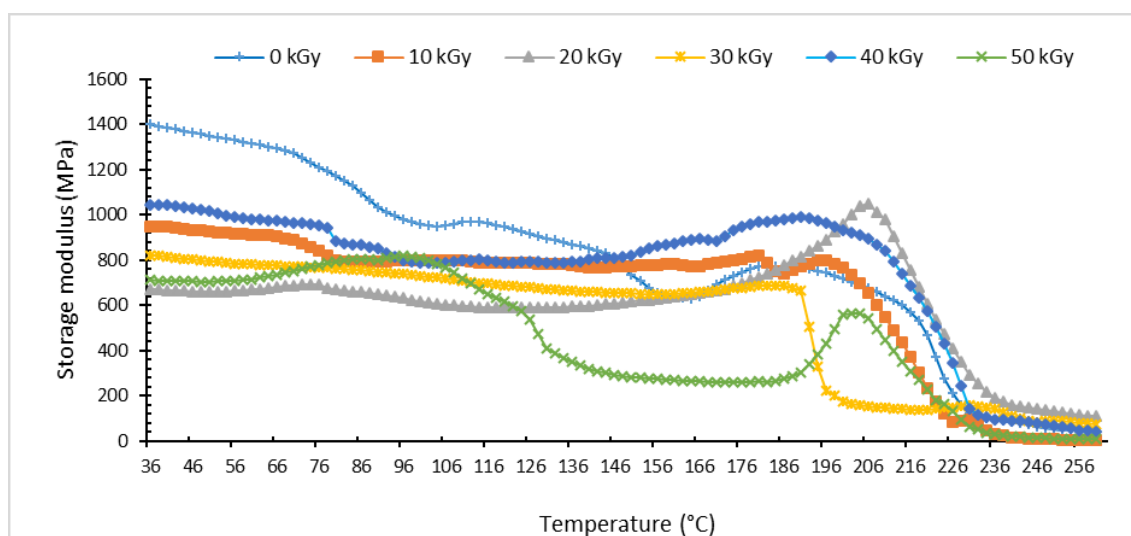


Figure 6. Effect of gamma radiation on storage modulus of thermally aged mimosa-tanned leather

The initial storage modulus of non-irradiated leather is high, and with increasing temperature, it decreases gradually and abruptly to almost zero at higher temperatures. The interaction of mimosa tannins with collagen is through hydrogen bonding [22], and with increasing temperature, water molecules are removed, destabilizing the collagen triple helix and decreasing the storage modulus. Water molecules are essential to the hydrogen bonding system because the bonds link up the triple helices [24]. Non-irradiated leather has the highest storage modulus up to 144 °C. It decreases as temperatures increase with denaturation temperature at 196 °C. Increasing doses of radiation increase the denaturation temperature to a higher value than that of the non-irradiated leather.

Effect of gamma irradiation on the photostability of tanned leather

The photostability of chrome and mimosa-tanned leathers irradiated at different doses is inferred from the denaturation temperatures of leather artificially aged in UV- cabinets at a wavelength of 254 nm (UV-C) for 144 hours.

Ultra Violet (UV) radiation is one of the most adverse external factors that cause chemical and physical effects on the hides and skins of organisms. The triple helix of collagen type I is sensitive to UV-254 nm radiation [26]. Aromatic amino acids such as tyrosine and phenylalanine enhance the absorption of UV radiation by hides and skins [3]. Absorbed energy breaks the collagen bonds into residues, creating free radicals that combine to form crosslinks or chain scission [15].

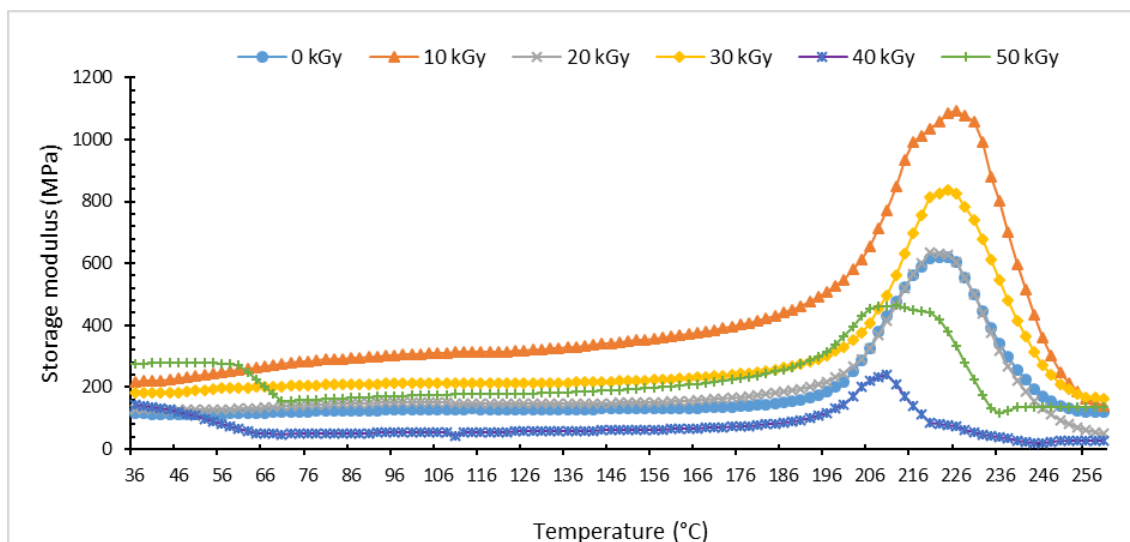


Figure 7. Effect of gamma irradiation on storage modulus of photo-aged chrome-tanned leather

The storage modulus of mimosa-tanned leather irradiated with different doses of gamma radiation and subjected to accelerated ageing is shown in Figure 8.

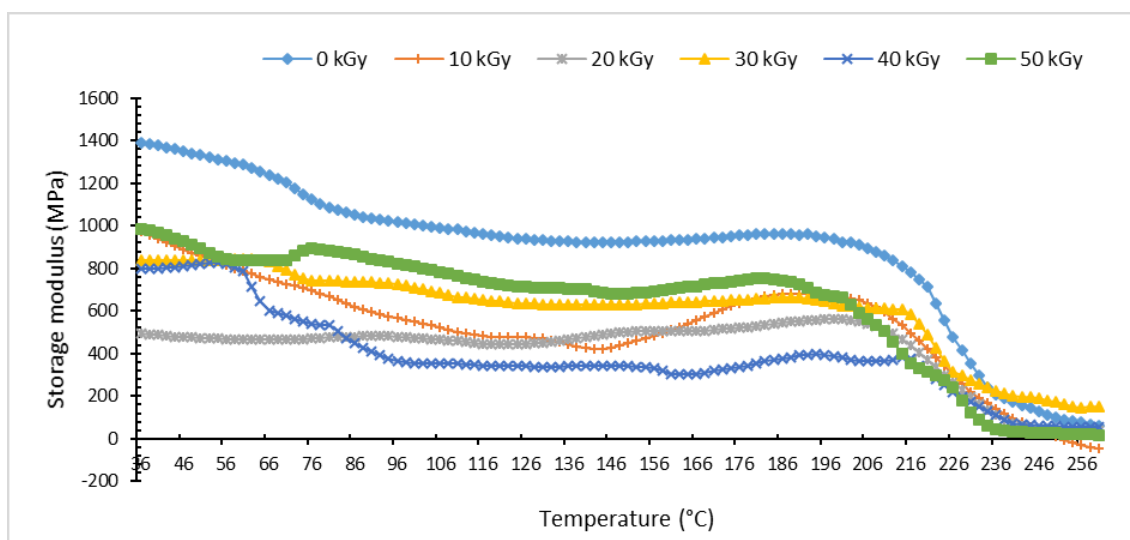


Figure 8. Effect of gamma irradiation on storage modulus of photo-aged mimosa-tanned leather

The storage modulus of the non-irradiated leather is higher, and as irradiation doses increase, the storage modulus decreases. The storage modulus of leather irradiated at 10 kGy up to 30 kGy increased, which is related to crosslinks induced by gamma radiation [2,26], irrespective of the degradation of collagen caused by UV radiation [3]. A decrease in storage modulus at 40 kGy radiation dose is due to the combined effect of gamma and UV radiation. Further irradiation shows an increased storage modulus but lower denaturation temperature.

Thermal stability

The thermal stability of chrome and mimosa-tanned leather was inferred from the denaturation temperature peaks of storage modulus at different irradiation doses.

The denaturation temperature of chrome-tanned leather thermally aged and non-aged and irradiated at different doses of irradiation is shown in Figure 9.

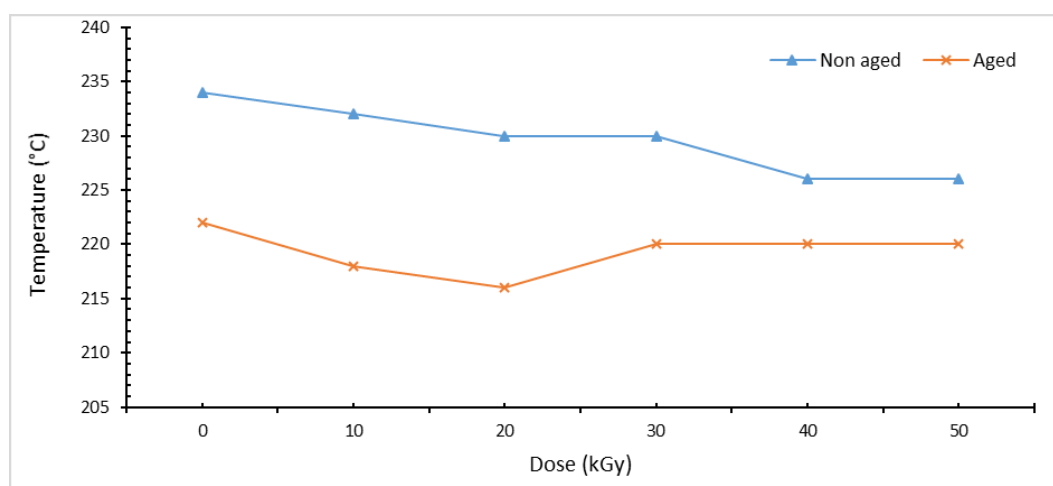


Figure 9. Denaturation temperature of chrome-tanned leather at different doses of irradiation

Non-aged leather shows a high denaturation temperature compared to thermally aged leather for all irradiation doses. Nevertheless, the non-irradiated leather shows the highest denaturation temperature; as the irradiation dose increases, the denaturation temperature decreases. This is because increased gamma irradiation initiates the breaking up of the already-formed bonds [16,27]. The thermally aged leather shows a slight decrease in the denaturation temperature up to 20 kGy doses of irradiation increase from 30 kGy and become constant up to 50 kGy. This suggests that high doses of gamma radiation prevent the leather from degradation. This can be related to the formation of C=O bonds, a chemical reaction with the help of free radicals produced during irradiation, hence the crosslinking reaction [28]. The denaturation temperature of both aged and non-aged mimosa-tanned leather irradiated at different doses of irradiation is shown in Figure 10.

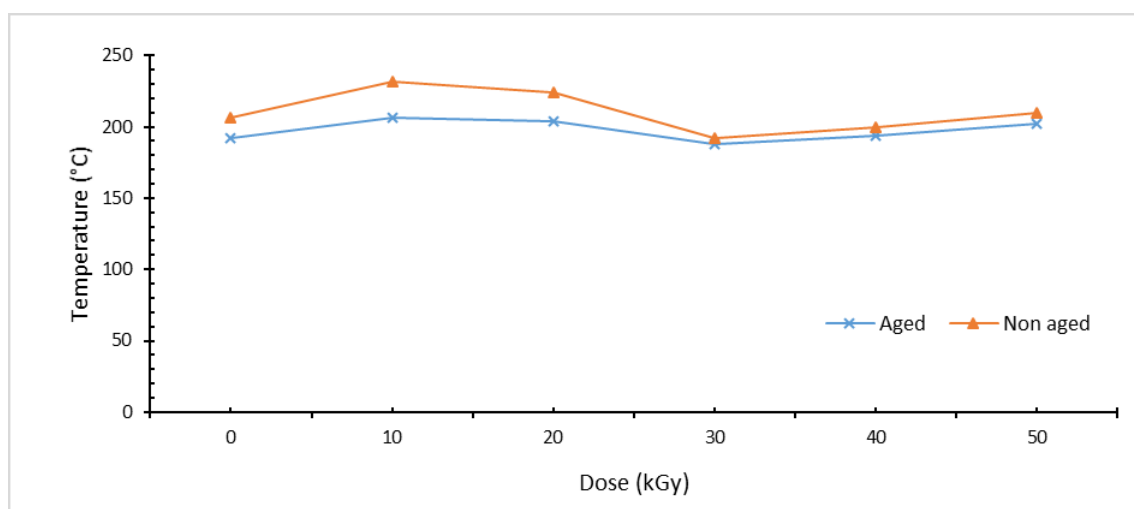


Figure 10. Denaturation temperature of mimosa-tanned leather at different doses of irradiation

The denaturation temperature of non-aged leather is higher than that of thermally aged leather at all irradiation doses. The denaturation temperature of both aged and non-aged leather increases up to 20 kGy dose of radiation and decreases at 30 kGy dose, nevertheless, at 40 and 50 kGy doses of radiation; the denaturation temperature increases. The aged mimosa-tanned leather shows a slight decrease in denaturation temperature, unlike chrome-tanned Leather in Figure 10, because mimosa tannins are plant polyphenols with antioxidant capability [29]. On the other hand, aged and non-aged leather for up to 10 kGy doses of radiation showed increased denaturation temperature and decreased denaturation temperature up to 30 kGy doses of irradiation. This results from accelerated ageing at high temperatures, causing thermal degradation of collagen. At 40 kGy irradiation dose, the denaturation temperature increases due to strong bonds formed due to crosslinking induced by gamma irradiation. Nevertheless, at 30 kGy irradiation dose, the denaturation temperature decreased to a lower temperature due to thermal degradation. This result agrees with the observations of Carsote et al. on mimosa-tanned goat leather [2].

Photostability

The photostability of chrome and mimosa-tanned leather was inferred from the denaturation temperature peaks of storage modulus graphs at different doses of irradiation.

The denaturation temperature of chrome-tanned leather, photoaged and non-aged, is shown in Figure 11.

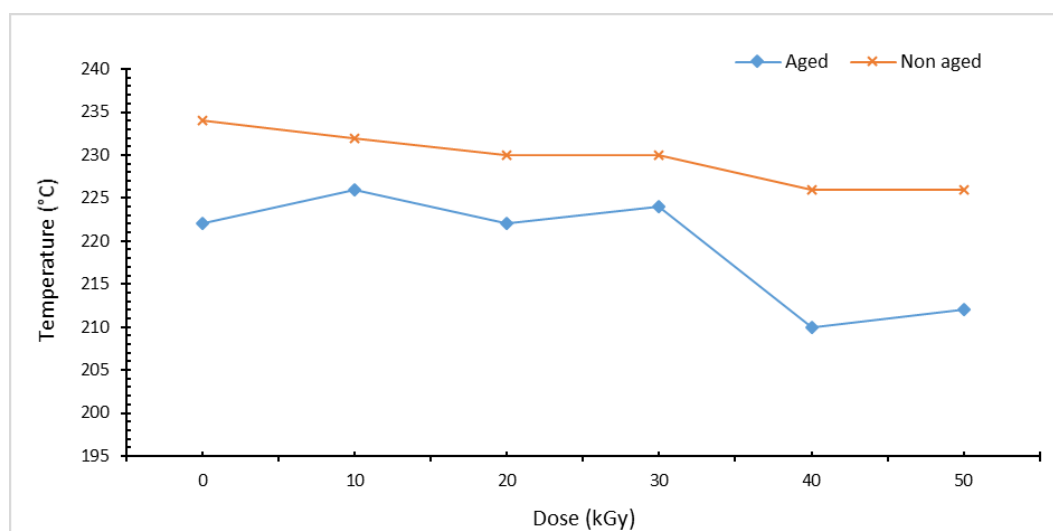


Figure 11. The denaturation temperature of chrome-tanned leather

Non-aged leather shows higher stability than aged leather at all irradiation doses. The denaturation temperature decreased with increasing irradiation dose for the non-aged leather. The aged leather display increased denaturation temperature up to 30 kGy radiation dose and decreased as the irradiation dose increased.

Studies by Nalyanya et al. have linked exposure of the leather to UV irradiation for a prolonged time to the initiation of photolysis and photodegradation, where the bonds already formed become weak, thus causing a decrease in storage modulus [3]. This further implies that the stability of the leather is decreased because of the decrease in the denaturation temperature. The denaturation temperature of the aged leather is significantly low, as shown in Figure 11, throughout the irradiation doses. The decrease is attributed to the presence of aromatic chromophores in the collagen structure and chromium ions which behave as synthetic polymers and are majorly associated with enhanced absorption of UV rays [30,31]. Increased absorption of these rays causes further degradation of the processed leather.

The denaturation temperature of mimosa-tanned leather aged and non-aged and irradiated with increasing doses of radiation is shown in Figure 12.

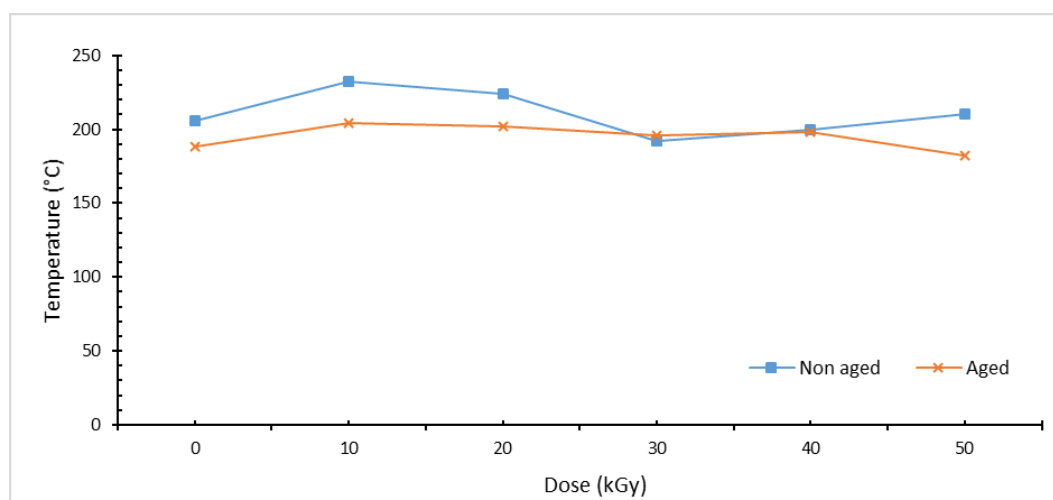


Figure 12. The denaturation temperature of mimosa-tanned leather

The denaturation temperature of non-aged leather is higher than that of aged leather throughout the irradiation range except at a 30 kGy irradiation dose. This is because, during the photoaging process, collagen peptide chains may have been ruptured randomly, leading to the destabilization of collagen fibres [32] and, therefore, lower denaturation temperature. The decrease in denaturation temperature at 30 kGy irradiation dose for non-aged is attributed to the rupture of already formed crosslinks caused by gamma radiations [16,27]. The denaturation temperature for non-irradiated samples was lower than that of irradiated samples. As the irradiation doses increased, the denaturation temperature of aged leather increased to a higher temperature and decreased at 50 kGy radiation dose. This is attributed to gamma irradiation inducing crosslinking at lower doses of irradiation and high doses of 50 kGy; degradation of the collagen structure dominates [16,27]. The UV ageing process also initiates the disruption of bonds, leading to decreased denaturation temperature [33].

CONCLUSION

This study investigated the impact of gamma irradiation on the viscoelastic properties and the stability of the processed leather against photo and thermal degradation using DMA. The mechanical stability and flexibility of leather are important for its usability. The storage modulus of the chrome-tanned leather increased at lower doses of irradiation, while there was a decrease for mimosa. However, with increasing doses of irradiation, there was an increase in storage modulus with increasing temperature. The loss factor of the chrome and mimosa-tanned leathers was less than one. This implies that leather retained its elastic property and thus increased applicability due to its flexibility. Aged chrome-tanned leather exhibited variation in stability with increasing irradiation dose. The aged mimosa-tanned leather exhibited an increase in denaturation temperature with increasing irradiation dose implying

that the processed leather became more resilient to degradation. This conforms to eco-friendly leather processing and improved leather quality. Gamma irradiations induced additional crosslinks to the substrate, increasing the leather strength. The bonds formed ensured increased stabilization of leather against harsh conditions. Therefore, leather industries should adopt the non-conventional leather processing approach to contribute to the cleaner processing of leather.

Author Contributions

Conceptualization – Chebwogen M, Nalyanya KM, Amollo TA; methodology – Chebwogen M, Nalyanya KM, Amollo TA; formal analysis – Chebwogen M, Nalyanya KM, Amollo TA; investigation – Chebwogen M, Nalyanya KM, Mathenge SM; writing-original draft preparation – Chebwogen M, Nalyanya KM; writing-review and editing – Chebwogen M; visualization – Nalyanya KM; supervision – Amollo TA. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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