BJRS
BRAZILIAN JOURNAL OF RADIATION SCIENCES

doi.org/10.15392/2319-0612.2024.2675
2024, 12(4A) | 01-27 | e2675
Submitted: 2024-08-30
Accepted: 2024-11-22

Effects of Ionizing Radiation on the Color and Morphology Properties of Leather

Stanziani-Gibba*, J. L.; Oliveira, M.J.A.; Otubo, L.; Cipriano, J.; Vasquez, P.A.S.

Instituto de Pesquisas Energéticas e Nucleares [Nuclear and Energy Research Institute] (IPEN), 05508-000, São Paulo, SP, Brazil

*Correspondence: jsgibba@usp.br

Abstract: Effective conservation strategies for leather artifacts and art objects are essential for preserving cultural heritage, particularly given the inherent vulnerability of the material to biodegradation, as leather, an organic material, is especially susceptible to this process. Gamma radiation has emerged as a promising method for the disinfestation and disinfection of cultural heritage objects and archival materials. This study aimed to advance the understanding of gamma radiation as a conservation technique for vegetable-tanned snake and chrome-tanned bovine leather, specifically focusing on its effects on chromaticity, surface topology, fiber structure and thermal behavior. Gamma radiation was applied at controlled doses of 1 and 3 kGy, and its impact on the morphology of the leather was assessed using colorimetry within the CIELAB color space and field emission gun scanning electron microscopy (FEGSEM). The findings indicated that gamma radiation at these doses induced minimal alterations in the morphological properties of the leather. The color differences for irradiated and non-irradiated samples were negligible, with total color differences (ΔE) remaining within acceptable limits ($\Delta E < 3$). Moreover, FEGSEM analysis demonstrated that the fiber structure and surface morphology were not significantly compromised by the irradiation process. Thermogravimetric analyses showed similar thermal decomposition between non-irradiated and irradiated samples for both bovine and snake leather, with detailed data analysis indicating thermal stability. The results supported the efficiency of gamma radiation as a conservation technique for both bovine and snake leather artifacts, preserving their aesthetic and structural integrity.

Keywords: gamma radiation, leather conservation, cultural heritage

SBPR

BJRS
BRAZILIAN JOURNAL OF RADIATION SCIENCES

doi.org/10.15392/2319-0612.2024.2675
2024, 12(4A) | 01-27 | e2675
Submitted: 2024-08-30
Accepted: 2024-11-22

Efeitos da Radiação Ionizante sobre a Cor e Propriedades Morfológicas do Couro

Resumo: Estratégias eficazes de conservação para artefatos de couro e objetos de arte são essenciais para preservar o patrimônio cultural, especialmente dada a vulnerabilidade inerente do material à biodegradação, já que o couro, um material orgânico, é especialmente suscetível a esse processo. A radiação gama surgiu como um método promissor para a desinfestação e desinfecção de objetos do patrimônio cultural e materiais de arquivo. Este estudo teve como objetivo avançar a compreensão da radiação gama como uma técnica de conservação para couro de cobra curtido ao vegetal e couro bovino curtido ao cromo, focando especificamente em seus efeitos na cromaticidade, topologia da superfície e estrutura da fibra e comportamento térmico. A radiação gama foi aplicada em doses controladas de 1 e 3 kGy, e seu impacto na morfologia do couro foi avaliado usando colorimetria dentro do espaço de cores CIELAB e microscopia eletrônica de varredura por canhão de emissão de campo (FEGSEM). As descobertas indicaram que a radiação gama nessas doses induziu alterações mínimas nas propriedades morfológicas do couro. As diferenças de cor para amostras irradiadas e não irradiadas foram insignificantes, com diferenças totais de cor (ΔE) permanecendo dentro de limites aceitáveis ($\Delta E < 3$). Além disso, a análise FEGSEM demonstrou que a estrutura da fibra e a morfologia da superfície não foram significativamente comprometidas pelo processo de irradiação. As análises termogravimétricas apresentaram decomposição térmica similar entre as amostras não irradiadas e irradiadas tanto para o couro bovino quanto para o couro de cobra, a análise dos dados detalhados indicaram estabilidade térmica. Os resultados apoiaram a eficiência da radiação gama como uma técnica de conservação para artefatos de couro bovino e de cobra, preservando sua integridade estética e estrutural.

Palavras-chave: radiação gama, conservação de couro, patrimônio cultural

SBPR

1. INTRODUCTION

The intrinsic connection between humanity and the natural environment, characterized by the necessity to adapt and utilize available resources, is exemplified by leather — one of the most ancient materials used by humans [1]. Throughout history, leather has been a significant element, providing essential insights into human life and activities [2]. An analysis of ancient leather artifacts and the proteins contained within them provides meaningful information regarding early human practices. [3].

Leather, a durable and non-putrescible material, is produced from animal hides through a complex, multi-stage process involving cleaning, tanning for stabilization, and finishing [4, 5]. Natural leather is expected to be more biodegradable than certain synthetic polymer materials since it is primarily composed of collagen [6]. Due to its versatility, leather is extensively used in various industries, including fashion, furniture, and automotive sectors [1, 7, 8].

Furthermore, leather artifacts and art objects have historically and culturally been of profound significance across diverse societies [9, 10, 11]. They are vital elements of cultural heritage, whose safeguarding is critically important and essential for forthcoming generations to comprehend the evolution of human civilization [11, 12]. Safeguarding these objects requires a multidisciplinary approach that includes risk assessment, conservation, and restoration [13].

In the field of conservation-restoration, three critical stages are recognized: knowledge, diagnosis, and preservation [14]. The knowledge stage establishes the theoretical and technical framework necessary to inform actions and assess risks, while diagnosis, through scientific methodologies, provides a detailed analysis of artifact's condition. Preservation then encompasses both preventive conservations, aimed at minimizing future deterioration risks, and corrective treatments, including curative conservation and restoration. This framework is particularly pertinent regarding leather artifacts, which are

primarily composed of collagen, as each type of leather is characterized by a group of related products with common features. However, variations in properties and responses to conservation treatments pose significant challenges [15].

In conservation treatments, the unique challenges posed by different materials necessitate tailored approaches. Unlike ceramics and metals, leather artifacts are highly susceptible to biological degradation, underscoring the need for specialized methods to mitigate risks associated with traditional conservation practices [11, 15, 16]. In addition, environmental factors such as humidity, temperature fluctuations, light exposure, and the presence of pollutants can induce, accelerate, and promote modifications to the aesthetic attributes, configurations, and structures of artifacts [9, 16].

Considering this scenario, ionizing radiation has emerged since the 1970s as an effective alternative for treating biological degradation in artifacts and art objects of cultural heritage [17]. The growing adoption of gamma radiation within scientific and museum collections underscores its efficacy as a nontoxic and advantageous option to traditional conservation methods [18]. This technique offers several additional benefits, including significantly reduced treatment times, the absence of chemical residues, and streamlined logistics in the handling of artifacts [19, 20, 21].

It is essential to further evaluate the biocidal efficacy of gamma radiation which is particularly well-suited for inhibiting biodegradation; specifically, hazardous organisms such as insects and fungi can be effectively eradicated through controlled exposure to gamma rays, considering the precise dose adapted to the target organism [17, 22]. The efficacy of gamma radiation is attributed to its high penetration capability, which allows it to target pests throughout the entirety of an irradiated object, reaching beyond surface layers and acting effectively across all life stages of insects and microorganisms, ensuring comprehensive eradication [22, 23].

Despite the advantages and effectiveness of gamma radiation in conservation, concerns persist regarding potential side effects. Gamma radiation interacts with the

electronic structure of the target material, leading to both direct and indirect ionization and electronic excitation [18]. While in many instances these excited electrons recombine without causing alterations, there remains a risk of inducing initial molecular changes, potentially triggering reactions that could result in changes in appearance, particularly in color and structure, due to chemical and physical modifications before stabilization is achieved [17].

This study aimed to evaluate the use of gamma radiation as a preservation technique for bovine and snake leather artifacts, with initial findings focusing on its effects on morphological characteristics, particularly chromaticity, topology, and fiber architecture. Gamma radiation was administered at doses of 1 and 3 kGy, selected based on disinfestation protocols [24]. Using CIELAB color space, colorimetry was used to measure chromatic variations and quantify color attributes objectively. Field emission gun scanning electron microscopy (FEGSEM) was employed to investigate potential morphological changes within the internal fiber structures, particularly their topology. Thermogravimetric analysis was conducted to assess the thermal behavior of the material.

2. MATERIALS AND METHODS

2.1. Sample selection

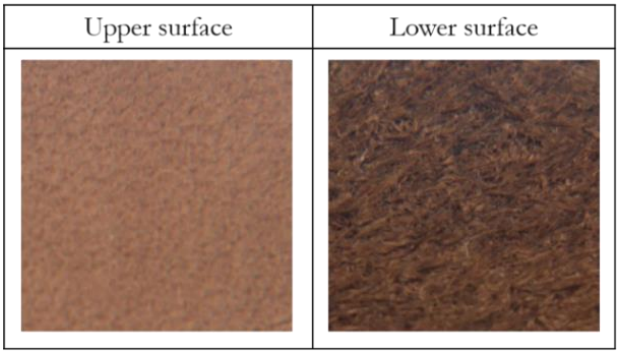
The experimental samples comprised two distinct types of leather that were specifically selected from bovine and snake species. The leading information regarding identification, classification, and general characteristics is presented in Figure 1. The bovine leather sample was provided by the company CR2 Indústria e Comércio de Calçados Ltda., and the snake sample was acquired from Stein Comércio de Cutelaria e Insumos Ltda. under Brazilian import license number 7799757.

Figure 1: Classification of leather samples

Sample	Species	Tanning Process	Color	Identification
S1BC	Bos taurus (Domestic cattle)	Mineral (Chrome)	Caramel (Dyed)	
S2CK	Acrochordus javanicus ("karung" in some regions)	Vegetable	Natural (Undyed)	

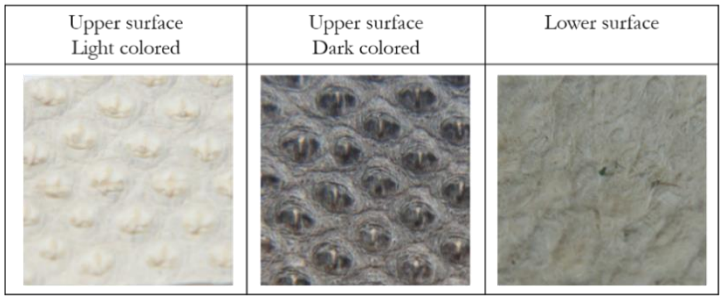
The bovine sample was a nubuck leather with unidirectional ultra-fine fibers and a soft, velvety texture, which is attained through a polishing process that results in a napped finish. It originates from the top grain of the hide and exhibits a uniform caramel hue with subtle shading variations due to the natural grain [25] (Fig. 2).

Figure 2: Bovine sample – upper surface and lower surface



Originating from Asia, the snake sample was a natural-colored leather from *Acrochordus javanicus*, a nonvenomous aquatic species [26] that is known for its loose skin and small, granular scales. The leather exhibits a brown dorsal side and pale-yellow ventral side (Fig. 3).

Figure 3: Snake sample – upper surface and lower surface



The samples were analyzed in their original state, except for FEG-SEM analysis, which required a gold-palladium coating to improve conductivity and enable clearer visualization of the surface morphology.

2.2. Ionizing radiation process

The irradiation process was conducted at the Cobalt-60 Multipurpose Irradiator, located within the Radiation Technology Center (CETER) at the Nuclear and Energy Research Institute – (IPEN), and connected to the National Nuclear Energy Commission (CNEN) as one of its institutions.

The installation project is classified as Category IV by the International Atomic Energy Agency (IAEA) and contains a panoramic irradiator equipped for storing wet radioactive sources within a pool of deionized water, reaching a depth of 7 meters with a capacity of 1,000,000 Curies of ^{60}Co [27, 28].

The samples were encased in corrugated cardboard packages and subjected to irradiation under standard atmospheric conditions at ambient temperature, with radiation doses of 1 kGy and 3 kGy administered.

2.3. Colorimetry

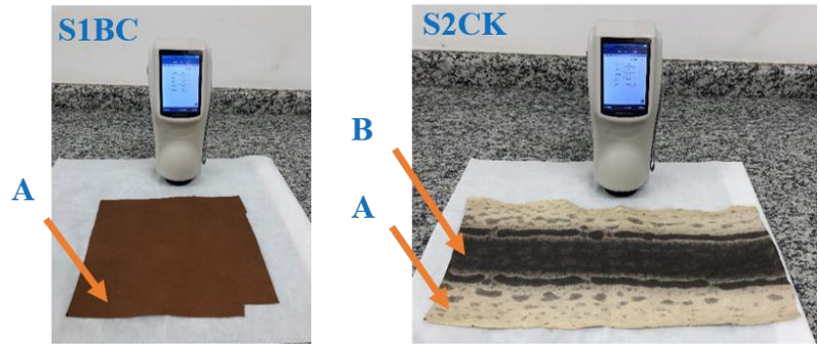
Colorimetry is the science of quantifying the physical attributes of colors by examining light absorption within the visible spectrum (380–780 nm), thereby excluding subjective interpretations by observers. This process is fundamental to understanding how colors are

perceived and quantified because colors are not intrinsic properties of objects but sensations generated by the nervous system, which are influenced by emotional and cultural factors. Human eye sensitivity varies with wavelength, peaking at approximately 550 nm. Color perception arises through the additive mixing of primary colors, which results in a broad range of hues. The perceived color also depends on the interaction of light with colored substances, which absorb light at specific wavelengths proportional to their concentration, as well as on the type of light source, which influences color interpretation. Standardized colorimetric methods enable a more objective definition of colors that is independent of illumination and subjective perception [29, 30].

The colorimetric characterization was based on the CIELAB color space, defined by the International Commission on Illumination (Commission Internationale d'Eclairage - CIE). This three-dimensional model represents all perceivable colors and is commonly used for accurate color measurements. It was initially published in 1976 and was developed to achieve perceptual uniformity; thus, a variation in a color value should produce a corresponding change with approximately equivalent visual meaning. It was built upon the values L* for perceptual lightness (value range is from 0 for black and 100 for white), a* for the red-green chromatic coordinate (positive values for red and negative for green), and b* for the blue-yellow chromatic coordinate (positive values for yellow and negative for blue), with the relative difference between two points in color space expressed as delta E (ΔE) calculated using the CIEDE2000 formula [23, 29, 31].

The samples were subjected to colorimetric analysis, with data consistently collected at the same location before and after each irradiation application to ensure process linearity. Measurements were performed at a single collection point for each bovine sample (Fig. 4 S1BC) owing to the uniform color of the material. For the snake samples, two collection points were selected due to the presence of distinct colors corresponding to light- and dark-colored areas (Fig. 4 S2CK).

Figure 4: Colorimetry – Sampling points for S1BC (A) and S2CK (A and B)



A PCE Instruments colorimeter model PCE-CSM 8 was used to measure color, operating with the SQC8 color management system. The equipment was programed with a measurement geometry of 45/0 (45° annular illumination, 0° viewing angle), wavelength range of 400–700 nm (10 nm pitch), and measuring aperture of Ø 8 mm. The colorimeter was configured to take three sequential measurements, providing the media of the obtained color coordinates.

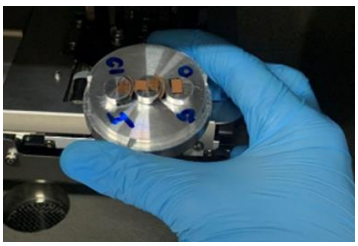
2.4. Field emission gun scanning electron microscopy analysis (FEG-SEM)

The field emission scanning electron microscope (FEG-SEM) used was a JEOL, model JSM-6701. The FEG-SEM was operated at an accelerating voltage of 5 kV, which is optimal for imaging nonconductive samples, such as leather samples, with minimal charging effects.

A magnification of 250x was employed to obtain detailed images of the leather samples, allowing visualization of the surface, cross-section, and posterior side morphology.

The samples were prepared by sectioning them along the surface and cross-sectional planes, followed by affixation to aluminum specimen stubs using carbon tape. Subsequently, they were coated with a thin layer of gold-palladium to enhance conductivity and ensure high-quality imaging (Fig. 5).

Figure 5: Sample preparation



This conductive coating mitigates the charging effects that can distort electron images and improves the clarity and resolution of the captured surface features by microscopy.

2.5. Thermogravimetric analysis

The thermal behavior of the samples was carried out using a TA SDT Q600 thermobalance. The temperature range used was for the stydy ranged from 20 °C to 600 °C with a heating rate of 20 °C/min, under a dynamic nitrogen (N_2) atmosphere with a flow rate of 100 mL min^{-1}.

3. RESULTS AND DISCUSSIONS

Color analysis

The results were analyzed to determine color consistency and accuracy for different doses and timelines, ensuring that any variations could be identified. Considering that the analysis involved organic materials characterized by heterogeneous surfaces, the inherent variability in color responses must be considered [23, 32]. To address this issue, the Hardeberg criteria [33] were applied. They proposed a range of acceptable values for color difference (ΔE*) rather than a single threshold. As indicated in Table 1, the Hardeberg criteria determine that ΔE* values less than 3 are nearly imperceptible to the human eye, ensuring that minor color deviations are negligible. Although noticeable, values between 3 and 6 fall within the acceptable range for most applications while maintaining the visual integrity of the materials. However,

ΔE* values exceeding 6 are deemed unacceptable because they signify substantial color variations that could compromise the material's consistency and potentially affect its application in precision-dependent contexts. This approach allows for a more nuanced interpretation of color variations, mainly when dealing with complex organic materials [23, 32].

Table 1: Criteria for the results for perception of the color difference (ΔE*)

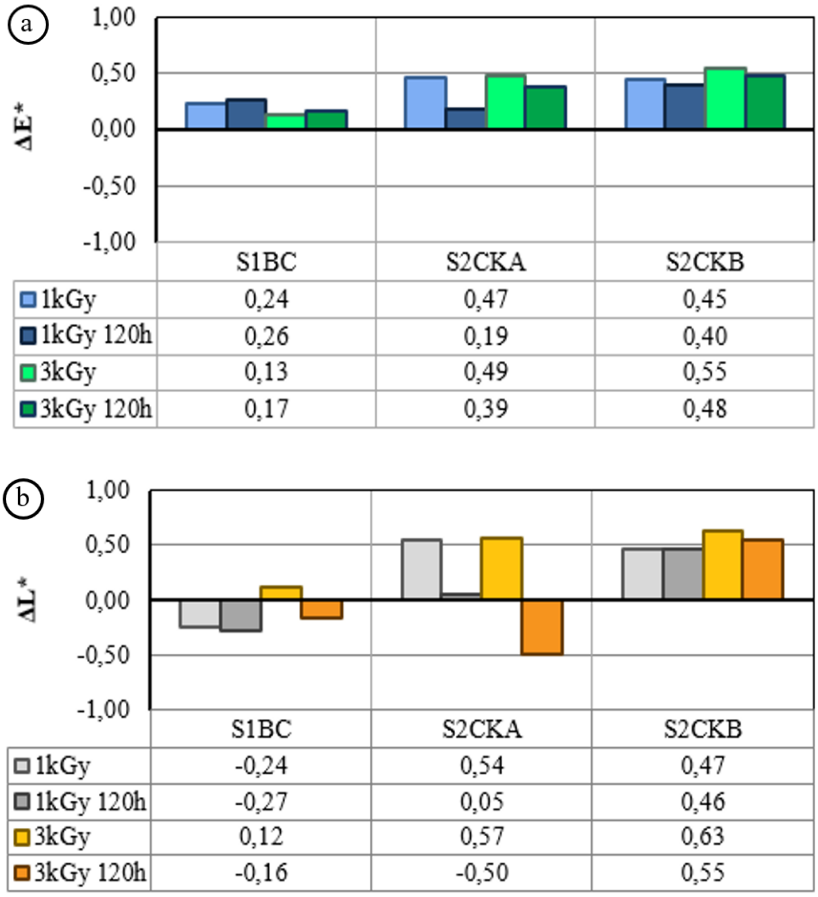
ΔE*	EFFECT
< 3	Hardly perceptible
3 < 6	Perceptible, but acceptable
> 6	Not acceptable

As reported by Ponta *et al.* [34], the functional and aesthetic properties of leather and parchment are minimally impacted by radiation decontamination at doses up to 10 kGy. The findings from Marušić *et al.* [23] demonstrated that gamma radiation doses below 10 kGy on goat leather samples resulted in color changes that were considered hardly perceptible.

The graphs in Figure 6 present a detailed analysis of the color differences (ΔE*) and luminosity variations (ΔL*) observed at the measurement points of the bovine and snake samples before and after the application of gamma radiation at doses of 1 and 3 kGy, with measurements taken immediately after irradiation and again after 120 h.

The color difference ΔE* graph (Fig. 6 a) shows that the variation in ΔE* for the bovine sample (S1BC) was relatively low under all tested conditions, with a maximum value of 0.26 observed after 120 h of exposure to 1 kGy. This suggests that S1BC exhibits considerable chromatic stability with minimal color changes that are barely perceptible to the human eye. In contrast, the snake leather samples (S2CKA and S2CKB) exhibited higher ΔE* values, particularly under 3 kGy exposure, with ΔE* reaching 0.55 for S2CKB after 120 h. Therefore, the samples are slightly susceptible to color changes.

Figure 6: Values of color difference ΔE* (a) and lightness difference ΔL* (b) after irradiation (1 kGy and 3 kGy)



	S1BC	S2CKA	S2CKB
1kGy	0,24	0,47	0,45
1kGy 120h	0,26	0,19	0,40
3kGy	0,13	0,49	0,55
3kGy 120h	0,17	0,39	0,48

	S1BC	S2CKA	S2CKB
1kGy	-0,24	0,54	0,47
1kGy 120h	-0,27	0,05	0,46
3kGy	0,12	0,57	0,63
3kGy 120h	-0,16	-0,50	0,55

Despite these differences, the color variations remained within the established thresholds and were categorized as "hardly perceptible" (ΔE*<3) to the human eye, indicating the insignificance of the radiation effects.

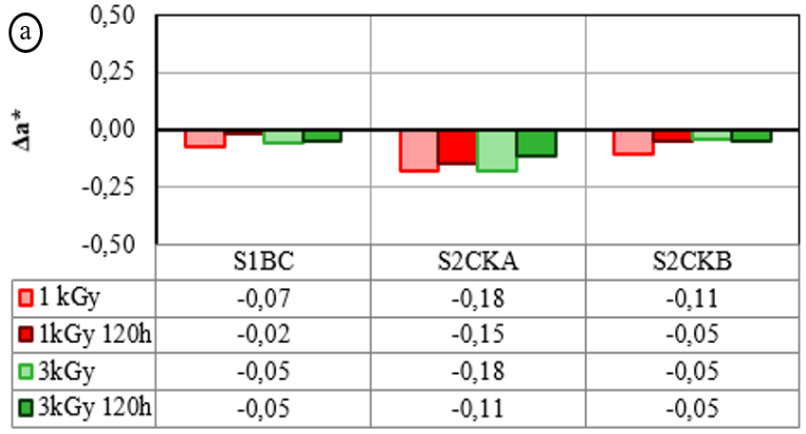
In the luminosity difference ΔL* graph (Fig. 6 b), the results for the bovine sample (S1BC) indicate negative ΔL* values at the 1 kGy dose, suggesting darkening of the sample after exposure. However, at 3 kGy, there was a slight recovery in luminosity (ΔL* = 0.12), although the sample darkened again after 120 h. These results suggest that the S1BC sample exhibits nonlinear behavior in terms of luminosity changes, although the values remain below 0.5. The snake leather samples (S2CKA and S2CKB) demonstrated an increase in luminosity, indicating surface lightening in most measurements, with minor variations observed in the

lighter-colored sample (S2CKA), particularly after 120 h. The darker sample (S2CKB) exhibited the greatest difference, with a ΔL* of 0.63 after 120 h at 3 kGy, suggesting a significant increase in light reflection.

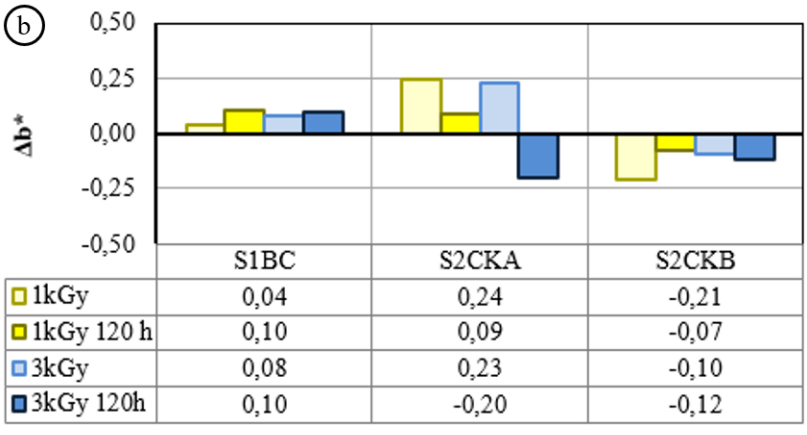
The presented data revealed distinct behaviors among the samples in response to radiation. While the bovine leather demonstrated greater chromatic stability, the snake leather exhibited higher susceptibility to changes in both color and luminosity. Nonetheless, all values remained within minimal thresholds, indicating preservation of the original color and pattern.

The graphs in Figure 7 show the differences in red-green (Δa*) and yellow-blue (Δb*) chromatic coordinates for the three samples (S1BC, S2CKA, and S2CKB) under the previously presented conditions.

Figure 7: Values of red-green coordinate difference Δa* (a) and yellow-blue coordinate difference Δb* (b) after irradiation (1 kGy and 3 kGy)



	S1BC	S2CKA	S2CKB
1 kGy	-0,07	-0,18	-0,11
1kGy 120h	-0,02	-0,15	-0,05
3kGy	-0,05	-0,18	-0,05
3kGy 120h	-0,05	-0,11	-0,05



	S1BC	S2CKA	S2CKB
1kGy	0,04	0,24	-0,21
1kGy 120 h	0,10	0,09	-0,07
3kGy	0,08	0,23	-0,10
3kGy 120h	0,10	-0,20	-0,12

The Δa* difference in the S1BC sample was minimal, with slightly negative values ranging from -0.02 to -0.07, indicating a slight shift toward green. This suggests that bovine leather is relatively stable regarding chromatic change along the red-green axis, regardless of the radiation dose and the time elapsed after exposure. The S2CKA snake leather sample (light color) exhibited more pronounced variations in Δa*, especially at the 3-kGy dose, where the difference reached -0.18 immediately after exposure and -0.11 after 120 h. The magnitude of these variations suggests that S2CKA is more susceptible to chromatic alterations along the red-green axis, particularly in response to higher radiation doses. In contrast, the S2CKB sample (dark color) showed moderate changes in Δa*, with values ranging from -0.05 to -0.11, indicating a shift toward green, although the changes were less pronounced than those in S2CKA.

The analysis of Δa* and Δb* coordinates revealed different chromatic responses; bovine leather exhibits relative chromatic stability with minor shifts in both color directions. In contrast, snake leather exhibits greater susceptibility, with significant shifts toward green and distinct yellow-blue oscillations between light and dark colors.

The results reveal varying degrees of chromatic stability among the samples; however, the observed differences remained within a minimal range of -0.25 to +0.25, suggesting only a minor influence of the irradiation process on color stability. These results align closely with previous studies by Ponta *et al.* [34] and Marušić *et al.* [23], further supporting the resilience of leather's aesthetic properties under gamma radiation exposure up to 3 kGy.

Field emission gun scanning electron microscopy analysis (FEG-SEM) analysis

Vadrucci *et al.* [35] observed in their studies on historical leather that, starting at a dose of 1 kGy, irradiated samples exhibited signs of fiber structure disorder, with significant damage recorded at a dose of 5 kGy. On the other hand, research on newly processed leathers by Gaidau *et al.* [36] identified minor fiber changes only starting at a dose of 25 kGy. This

study aligns with the findings of Kovacheva *et al.* [37], who reported an absence of significant morphological changes or fiber structure damage in leather at doses of 15 kGy and below.

In Figures 8, 9 and 10 are showed micrographs of bovine leather samples before and after exposure to gamma radiation at doses of 1 and 3 kGy, corresponding to the results for the upper surface, cross-section, and lower surface.

Figure 8: Upper surface of sample S1BC non–irradiated (Zero) and irradiated (1 kGy and 3 kGy)

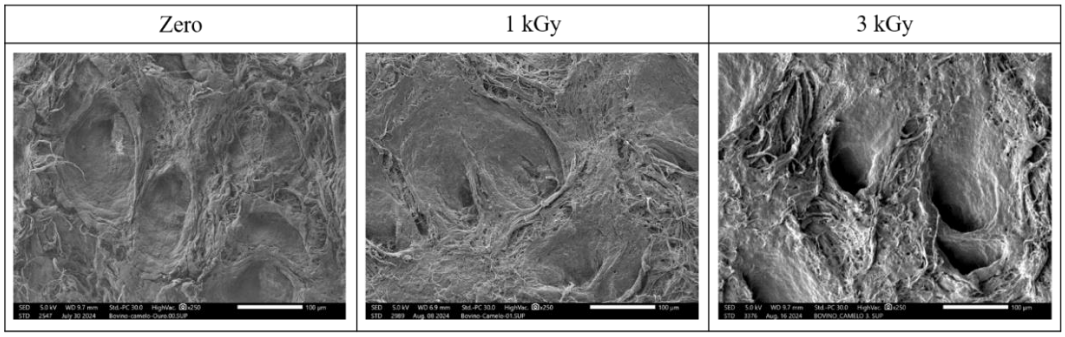


Figure 9: Cross-section of sample S1BC non–irradiated (Zero) and irradiated (1 kGy and 3 kGy)

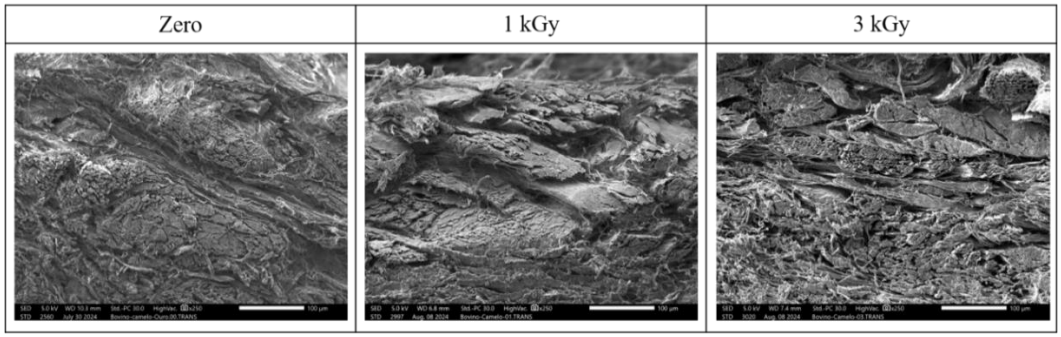
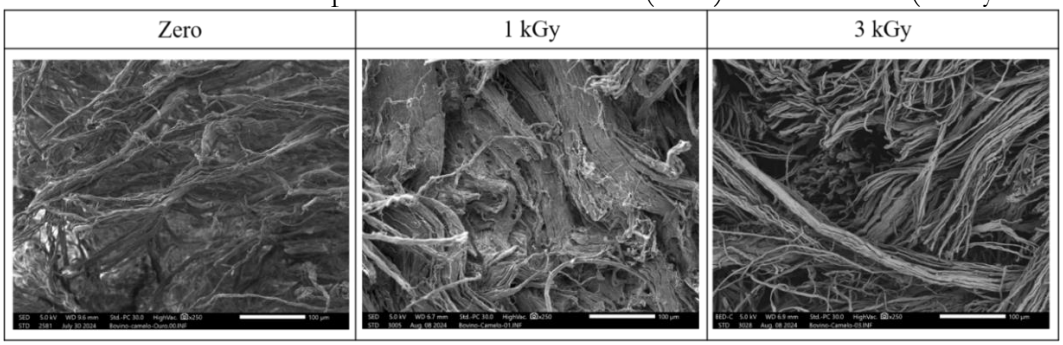


Figure 10: Lower surface of sample S1BC non–irradiated (Zero) and irradiated (1 kGy and 3 kGy)



The micrographs of upper surface of the bovine leather (Fig. 8) shows the unirradiated sample with the collagen fibers tightly interwoven, displaying a robust and intact structure. After irradiation at 1 and 3 kGy, the fibers began to show slight separation with minor gaps and a less dense appearance perceptible only at the applied magnification, however, the fiber structure remained intact without ruptures. Vadrucci *et al.* [35] observed similar results but with historical leather samples, as the samples in this research are newly produced leather, these results may have been influenced by the heterogeneity of leather surfaces, as described by Thomasset and Benayon [32] and Marušić *et al.* [23].

Figure 9 shows the leather cross-section, revealing a compact, layered arrangement of fibers with well-defined lamellar structures in both nonirradiated and irradiated samples, without any noticeable loosening or impact on the structural integrity of the fiber architecture. Similarly, Figure 10 illustrates the posterior side of the leather samples, where the nonirradiated samples exhibit a dense, closely packed fiber arrangement, which remains consistent in appearance after irradiation at 1 and 3 kGy.

Comparative analysis of bovine leather samples before and after ionizing radiation at doses of 1 and 3 kGy revealed that gamma radiation did not produce notable changes in the structural layers, effectively preserving the morphology of the grain across the upper surface, cross-section, and posterior side. These findings align with observations by Gaidau *et al.* [36] and Kovacheva *et al.* [37].

Figures 11, 12, and 13 present FEG-SEM micrographs of karung snake leather samples in non-irradiated and gamma-irradiated conditions at doses of 1 and 3 kGy, showcasing the upper surface, cross-section, and lower surface positions.

In all positions, the non-irradiated samples (Zero) display an intricate and well-preserved network of collagen fibers. The topography remains uniform, with fibers densely packed and interconnected, reflecting the material's natural morphology.

Figure 11: Upper surface of sample S2CK non–irradiated (Zero) and irradiated (1 kGy and 3 kGy)

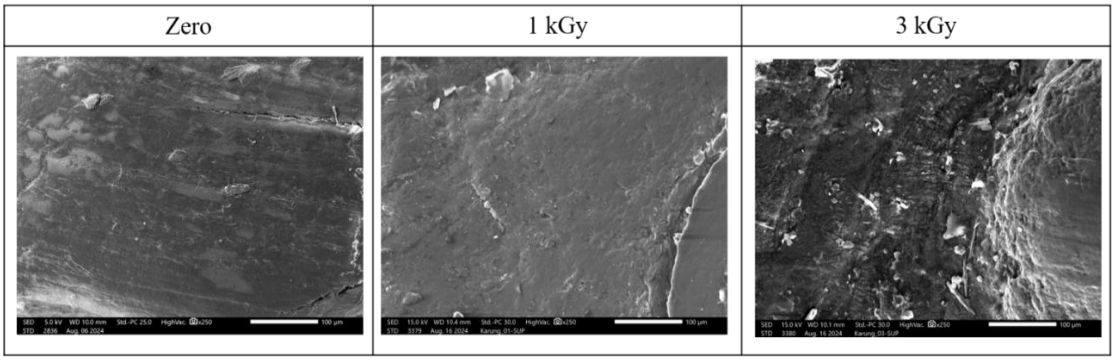


Figure 12: Cross-section of sample S2CK non–irradiated (Zero) and irradiated (1 kGy and 3 kGy)

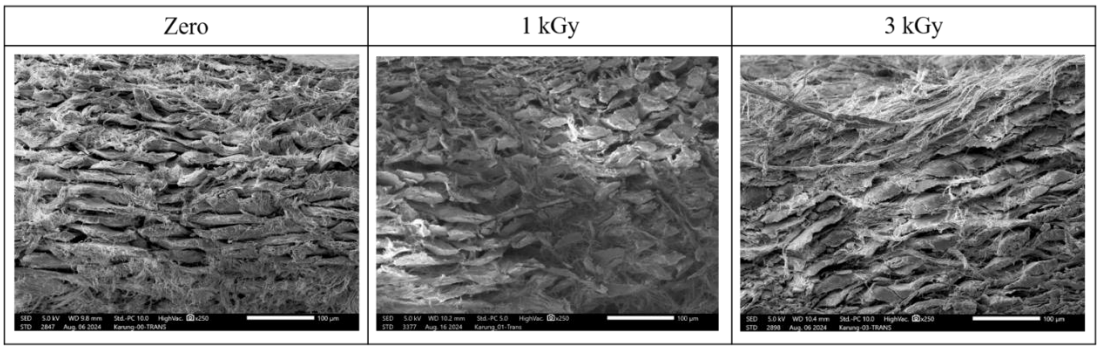
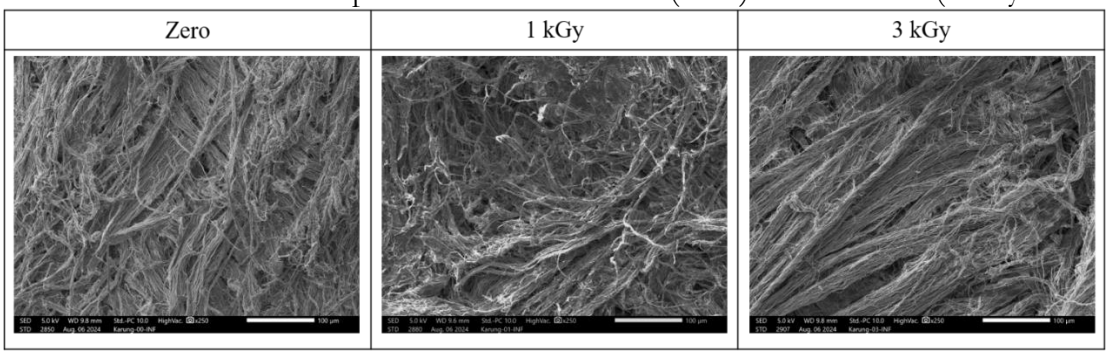


Figure 13: Lower surface of sample S2CK non–irradiated (Zero) and irradiated (1 kGy and 3 kGy)



Following irradiation at a dose of 1 kGy, no significant changes in fiber structure or surface morphology are observed. The fibers retain their arrangement, and the topological characteristics remain consistent with those of the non-irradiated sample, indicating that this dosage does not compromise the leather's structural integrity. Similarly, the sample irradiated at 3 kGy exhibits a morphology nearly identical to that of the non-irradiated and 1 kGy irradiated samples, supporting findings by Gaidau *et al.* [36] and Kovacheva *et al.* [37].

In summary, the FEG-SEM analysis corroborates that gamma irradiation up to 3 kGy does not substantially affect the fiber structure or surface topology of snake leather. These findings support the potential use of gamma radiation as a conservation method for snake leather artifacts, preserving both their structural and aesthetic properties.

Thermogravimetric analysis

Overlays of thermogravimetric (TG) curves and their derivatives (DTG) for non-irradiated and irradiated samples at doses of 1 kGy and 3 kGy are shown in Figure 14 for camel bovine leather (S1BC) and Figure 15 for karung snake leather (S2CK). In general, the TG curves revealed thermal decomposition characterized by two main events, regardless of the radiation dose applied. The first event corresponded to a gradual mass loss from the beginning of the analysis, attributed to the removal of adsorbed water; the second event represented the thermal decomposition of the material itself, consistent with previously reported findings [38, 39, 40]. The results suggest that the TGA curves for leathers irradiated at doses of 1 kGy and 3 kGy closely resemble those of non-irradiated samples, indicating that irradiation at these doses does not markedly affect leather weight loss.

The details of peak decomposition temperatures are shown in Tables 2 and 3 for camel bovine leather and karung snake leather samples, respectively. For camel bovine leather samples (Fig. 14), a slight increase was observed in the peak decomposition temperature of irradiated samples compared to non-irradiated samples (341.71 °C). At the 1 kGy dose, the peak temperature reached 343.22 °C, while at the 3 kGy dose, it slightly decreased to 342.72 °C, suggesting thermal stability within the applied radiation doses. These results are consistent with previous studies conducted by Carsote *et al.* [41] and Kovacheva *et al.* [37], however, no onset of the denaturation process was observed as reported by Chebwogen *et al.* [42].

Figure 14: TG (a) and DTG (b) curves - Sample S1BC non–irradiated and irradiated (1 kGy and 3 kGy)

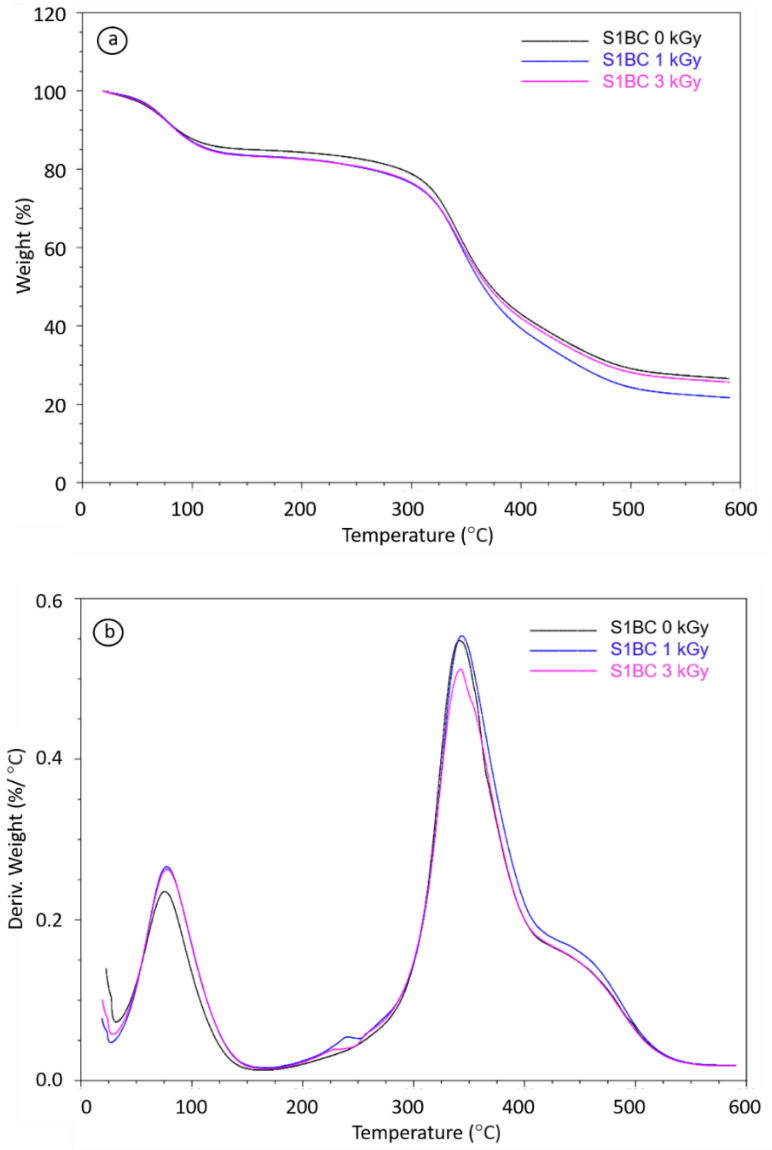


Table 2: Temperature values (°C) of the main peak - Sample S1BC

DOSE (kGy)	TEMPERATURE VALUES (°C)
0	341,71
1	343,22
3	342,72

Figure 15: TG (a) and DTG (b) curves - Sample S2CK non–irradiated and irradiated (1 kGy and 3 kGy)

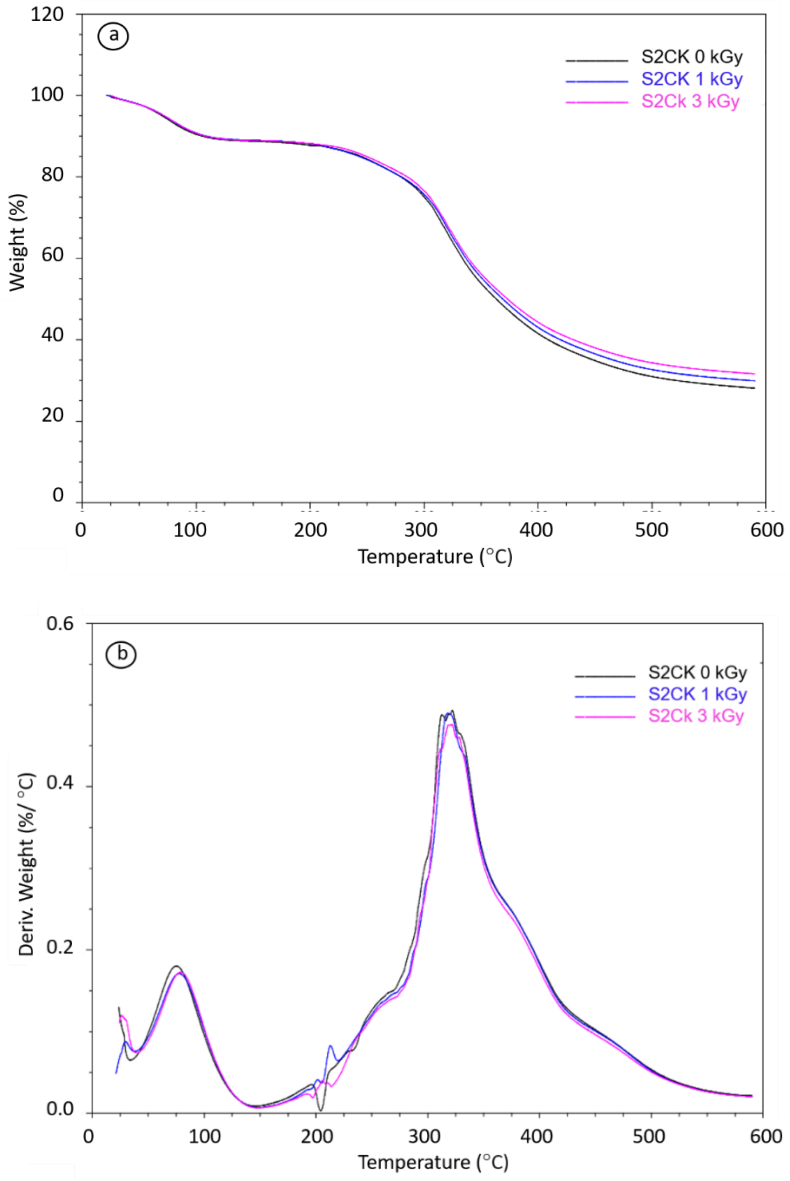


Table 3: Temperature values (°C) of the main peak - Sample S2CK

DOSE (kGy)	TEMPERATURE VALUES (°C)
0	322,00
1	318,46
3	320,49

For the karung snake leather samples (Fig. 15), a slight decrease in thermal stability was observed at the 1 kGy dose (318.46 °C), followed by a partial recovery at the 3 kGy dose. However, the decomposition temperature did not return to that of the original sample (322 °C). These findings are consistent with observations by Carsote *et al.* [41] and Kovacheva *et al.* [37]. Additionally, Czirok *et al.* [39] related that tannin-tanned leather exhibits greater sensitivity to thermal decomposition compared to chrome-tanned leather.

4. CONCLUSIONS

This study demonstrated that gamma radiation could be safely applied to vegetable-tanned snake leather and chrome-tanned bovine leather at doses up to 3 kGy, without compromising their morphological integrity. The findings indicated that doses of 1 kGy and 3 kGy induced only negligible changes in color and fiber structure, with color differences between irradiated and non-irradiated samples remaining imperceptible and well within the established acceptable threshold ($\Delta E < 3$). The minor variations observed in the color parameters, including luminosity (ΔL^*), red-green (Δa^*), and yellow-blue (Δb^*) coordinates, further suggested that the original color and pattern of the leathers were largely preserved. Furthermore, FEG-SEM analysis corroborated that the topographical morphology and internal fiber structures remained largely unaffected by the irradiation process at the tested doses. Thermogravimetric analyses showed similar thermal decomposition between non-irradiated and irradiated samples for both bovine and snake leather, with detailed data analysis indicating thermal stability. These results supported the viability of gamma radiation as a conservation technique for leather artifacts, effectively preserving their aesthetic and structural integrity.

ACKNOWLEDGMENT

The authors would like to thank the International Atomic Energy Agency (IAEA) and This research is supported by the project number 2020.06.IPEN.02.

CONFLICT OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

REFERENCES

[1] COVINGTON, A. D.; WISE, W. R. Introduction. *In*: COVINGTON, A. D.; WISE, W. R. **Tanning Chemistry: The Science of Leather.** London, UK: Royal Society of Chemistry, 2019. p. 027–031. https://doi.org/10.1039/9781839168826. PDF ISBN: 978-1-83916-882-6

[2] NAVARRO, D.; WU, J.; LIN, W.; FULLANA-I-PALMER, P.; PUIG, R. Life cycle assessment and leather production. **Journal of Leather Science and Engineering.** n. 2, p. 1–13, 2020. https://jlse.springeropen.com/articles/10.1186/s42825-020-00035-y

[3] ELNAGGAR, A.; OSAMA, A.; ANWAR, A.M.; EZZELDIN, S.; ELHASSAN, S. A. E.; EBEID, H.; LEONA, M.; MAGDELDIN, S. Paleoproteomic profiling for identification of animal skin species in ancient Egyptian archaeological leather using liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS). **Heritage Science.** n. 10, p. 1–10, 2022. https://heritagesciencejournal.springeropen.com/articles/10.1186/s40494-022-00816-0

[4] FERRARI, W. A.; PACHECO, J. W. F.; RAVACCI, H. C. J. [et al.]; MARTINES, A. M. [et al.]. Descrição do processo industrial. *In*: FERRARI, W. A.; PACHECO, J. W. F.; RAVACCI, H. C. J. [et al.]; MARTINES, A. M. [et al.]. **Guia técnico ambiental de curtumes**. 2. ed. São Paulo: Companhia Ambiental do Estado de São Paulo (CETESB)., 2015. p. 027–032. ISBN 978-85-61405-40-3

[5] SHI, J.; SHENG, L.; SALMI, O.; MAIS, M.; PUIG, R. Life cycle assessment insights into nanosilicates-based chrome-free tanning processing towards eco-friendly leather manufacture. **Journal of Cleaner Production**, v. 434, p 1–9, 2024. https://www.sciencedirect.com/science/article/pii/S0959652623040507

[6] WANG, Y.; ZHANG, Y.; WANG, Z. Biodegradability of leather: a crucial indicator to evaluate sustainability of leather. **Collagen and Leather**. ed 6, 1–9, 2024. https://jlse.springeropen.com/articles/10.1186/s42825-024-00151-z

[7] DICKINSON, E.; HIGH, K.E. The use of infrared spectroscopy and chemometrics to investigate deterioration in vegetable tanned leather: potential applications in heritage science. **Heritage Science**. n. 10, p 1–13, 2022. https://heritagesciencejournal.springeropen.com/articles/10.1186/s40494-022-00690-w

[8] DAVIS, M. A.; CULLETON, B. J.; ROSENCRANCE, R. L.; JAZWA, C. S. Experimental observations on processing leather, skin, and parchment for radiocarbon dating. **Radiocarbon**. Published online, p. 1–23, 2023. https://www.cambridge.org/core/journals/radiocarbon/article/experimental-observations-on-processing-leather-skin-and-parchment-for-radiocarbon-dating/29BFB589CE24129A802A8E22132C6B2B#

[9] ZHANG, M., FAN, J., LIU, J.; CHEN, Y.; LU, Y.; LEI, Y.; KAYA, M. G. A.; TANG, K. A comprehensive evaluation of a historical leather armor from Yanghai Cemetery, Turpan. **Heritage Science**, n. 12, p. 1–11, 2024. https://heritagesciencejournal.springeropen.com/articles/10.1186/s40494-024-01275-5

[10] ZHANG, M.; ZHANG, Z.; WANG, F.; LIU, J.; LEI, Y.; KAYA, M. G. A.; TANG, K. A.; TANG, K. A novel identification method for collagen-based cultural heritage: Integrating thermokinetics and generalized master plots. **Journal of Cultural Heritage**, n. 67, p. 226–236, 2024. https://www.sciencedirect.com/science/article/pii/S1296207424000657?via%3Dihub

[11] ZHANG, Y.; CHEN, Z.; LIU, X.; SHI, J.; CHEN, H.; GONG, Y. SEM, FTIR and DSC Investigation of Collagen Hydrolysate Treated Degraded Leather. **Journal of Cultural Heritage,** v. 48, p. 205–210, 2021. https://www.sciencedirect.com/science/article/pii/S1296203620301954

[12] UNITED NATIONS EDUCATION, SCIENTIFIC AND CULTURAL ORGANIZATION (UNESCO). **World Heritage.** Available at: https://www.unesco.org/en/world-heritage. Accessed on: 15 apr. 2024.

[13] DRUMOND, M.C.P. Preservação e Conservação em Museus. *In*: INSTITUTO do PATRIMÔNIO HISTÓRICO e ARTÍSTICO NACIONAL (IPHAN). **Caderno de Diretrizes Museológicas 1 ed. 2**. Belo Horizonte: Secretaria de Estado da Cultura/Superintendência de Museus, 2006, p. 105–135. http://portal.iphan.gov.br//uploads/publicacao/caderno_diretrizes_museologicas_2a_edicao.pdf

[14] COELHO, B.; QUITES, M. R. E. **Estudo da escultura devocional em madeira**. Belo Horizonte: Fundação João Pinheiro, 2014. ISBN: 978-8580542189.

[15] THOMSON, R. The Nature and properties of leather. *In:* Kite, M., Thomson, R. **Conservation of Leather and Related Materials**. New York, USA: Butterworth-Heinemann, 2011. p. 01–03. ISBN: 978-0-7506-4881-3.

[16] ZHANG, M.; YADI, H.; LIU, J.; PEI, Y.; TANG, K.; LEI, Y. Biodeterioration of collagen-based cultural relics: A review. **Fungal Biology Reviews**. v. 39, p. 046–059, 2022. https://www.sciencedirect.com/science/article/pii/S1749461321000622

[17] CORTELLA, L.; ALBINO, C.; TRAN, Q.; FROMENT, K. 50 years of French experience in using gamma rays as a tool for cultural heritage remedial conservation. **Radiation Physics and Chemistry**. v. 171, p. 1–13, 2020.

[18] VUJCIC, I.; MASIC, S.; MEDIC, M.; MILIĆEVIĆ, B.; DRAMICANIN, M. The influence of gamma irradiation on the color change of wool, linen, silk, and cotton fabrics used in cultural heritage artifacts. **Radiation Physics and Chemistry**. v. 156, p. 307–313, 2019. https://www.sciencedirect.com/science/article/pii/S0969806X18307163?via%3Dihub

[19] RIZZO, M. M.; MACHADO, L.D.B.; BORRELY, S.I.; SAMPA, M.H.O.; RELA, P.R.; FARAH, J.P.S.; SCHUMACHER, R.I. Effects of gamma rays on a restored painting from the XVIIth century. **Radiation Physics and Chemistry**. v. 63, p. 259–262, 2002. https://www.sciencedirect.com/science/article/pii/S0969806X01005096

[20] VASQUEZ, P. A. S. The State of the Art in Radiation Processing for Cultural Heritage in Brazil *In:* **Uses of Ionizing Radiation for Tangible Cultural Heritage Conservation**. Vienna, AT: International Atomic Energy Agency. ed. 1, 2017. p. 197–201. ISBN 978–92–0–103316–1.

[21] PONTA, C. C.; HAVERMANS, J. B. G. A. Trends in disinfection. *In:* **Uses of Ionizing Radiation for Tangible Cultural Heritage Conservation**. Vienna, AT: International Atomic Energy Agency. ed. 1, 2017. p. 31–37. ISBN 978–92–0–103316–1.

[22] CORTELLA, L. Khroma the frozen baby mammoth. *In:* **Uses of Ionizing Radiation for Tangible Cultural Heritage Conservation**. Vienna, AT: International Atomic Energy Agency. ed. 1, 2017. p. 137 – 139. ISBN 978–92–0–103316–1.

[23] MARUŠIĆ, K.; MLINARIĆ, N. M.; MIHALJEVIĆ, B. Radiation treatment of cultural heritage objects made of leather treated with common preservatives. **Radiation Physics and Chemistry**. v. 197, p. 1–6, 2022. https://www.sciencedirect.com/science/article/pii/S0969806X22001682

[24] PONTA, C. C.; HAVERMANS, J. B. G. A.; BOUTAINE, J. L. Disinfection of cultural artefacts using irradiation. *In*: **Uses of Ionizing Radiation for Tangible Cultural Heritage Conservation.** Vienna, AT: International Atomic Energy Agency. ed. 1, p. 93–103, 2017. ISBN 978–92–0–103316–1.

[25] SINGARAJ, S. P.; MURALI, R. C.; KUMARESAN, A.; GUNASEKARAN, B. Characteristic Analysis of Sisal Fabric and Cow Nubuck Leather for Developing Leather Lifestyle Accessories. **Journal of Natural Fibers**. v. 20, p. 1–16, 2023. https://www.tandfonline.com/doi/epdf/10.1080/15440478.2023.2218120?needAccess=true

[26] ROVATSOS M.; ALTMANOVÁ M.; POKORNÁ M. J.; AUGSTENOVÁ B.; KRATOCHVÍL L. Cytogenetics of the Javan file snake (*Acrochordus javanicus*) and the evolution of snake sex chromosomes. **Journal of Zoological Systematics and Evolutionary Research.** v. 56, p. 117–225, 2017. https://onlinelibrary.wiley.com/doi/epdf/10.1111/jzs.12180

[27] INTERNATIONAL ATOMIC ENERGY AGENCY (IAEA). Radiation safety of gamma, electron and X Ray Irradiation Facilities IAEA **Safety Standards Series.** No. SS-G-8, 2010. https://www.iaea.org/publications/8401/radiation-safety-of-gamma-electron-and-x-ray-irradiation-facilities.

[28] INSTITUTO DE PESQUISAS ENERGÉTICAS E NUCLEARES (IPEN). Irradiador Multipropósito. Available at: https://www.ipen.br/portal_por/portal/interna.php?secao_id=2500&campo=1798. Accessed on: 15 apr. 2024.

[29] LORUSSO, S.; NATALI, A.; MATTEUCCI, C. Colorimetry applied to the field of cultural heritage: examples of study cases. **Conservation Science in Cultural Heritage.** v. 7, p. 187–220, 2007. https://conservation-science.unibo.it/article/view/1252

[30] SHRESTHA, Y. K.; SHRESTHA, S. K. **Fundamentals of Colorimetry.** 2024. https://www.intechopen.com/chapters/87730.

[31] SHARMA, G.; WU, W.; DALAL, E. The Development of the CIE 2000 Colour-Difference Formula: CIEDE2000. **Color Research and Applications**, vol. 30, p. 340–350, 2001. https://onlinelibrary.wiley.com/doi/abs/10.1002/col.1049

[32] THOMASSET, A.; BENAYOUN, S. Assessing the durability of diverse leather tanning techniques for the manufacturing of leather goods through artificial aging processes. **Cleaner Engineering and Technology**. Elsevier, v. 22, p. 1–16, 2024. https://www.sciencedirect.com/science/article/pii/S2666790824000879

[33] HARDEBERG, J.Y. **Acquisition et reproduction d'images couleur: approches colorimétrique et multispec-trale. Interface homme-machine** [cs. HC]. 1999. 253p. Thèse (Docteur Specialité: Signal et Images) Ecole Nationale Supérieure des Télécommunications - Télécom ParisTech, Français.

[34] PONTA, C. C.; HAVERMANS J. B. G. A.; TRAN, Q. K.; CORTELLA, L. Effects of ionizing radiation on materials. In: INTERNATIONAL ATOMIC ENERGY AGENCY. **Uses of ionizing radiation for tangible cultural heritage conservation**. IAEA Radiation Technology Series Nº 6. Vienna, p. 61–85, 2017.

[35] VADRUCCI, M.; DE BELLIS, G.; MAZZUCA, C.; MERCURI, F.; BORGOGNONI, F.; SCHIFANO, E.; UCCELLETTI, D.; CICERO, C. Effects of the Ionizing Radiation Disinfection Treatment on Historical Leather. **Frontiers in Materials**, v. 7, p. 1–9, 2020. https://www.frontiersin.org/journals/materials/articles/10.3389/fmats.2020.00021/full

[36] GAIDAU, C.; STANCULESCU, I. R.; STANCA, M.; CUTRUBINIS, M.; TRANDAFIR, L.; ALEXANDRU, M.; ALEXE, C. A. Gamma irradiation a green alternative for hides and leather conservation. **Radiation Physics and Chemistry**, v. 182, p. 1–9, 2021. https://www.sciencedirect.com/science/article/pii/S0969806X21000190#:~:text=Gamma%20irradiation%20allows%20preserving%20not,potential%20for%20leather%20final%20products.

[37] KOVACHEVA, A. P.; BOSHNAKOVA, M. N.; ZHEKOV, M. E. D. Studying side-effects of gamma-irradiation processing of leather materials. **International Scientific Journal**, n. 5, p. 228–231, 2017. https://stumejournals.com/journals/i4/2017/5/228

[38] BANON, E.; GARCÍA, A. N.; MARCILLA, A. Thermogravimetric analysis and Py-GC/MS for discrimination of leather from different animal species and tanning processes. **Journal of Analytical and Applied Pyrolysis**, v. 159, p. 1–13, 2021. https://www.sciencedirect.com/science/article/pii/S0165237021002308

[39] CZIROK, I. S.; JAKAB, E.; CZÉGÉNY, Z.; BADEA, E.; BABINSZKI, B.; TÖMÖSKÖZI, S.; MAY, Z.; SEBESTYÉN, Z. Thermal characterization of leathers tanned by metal salts and vegetable tannins. **Journal of Analytical and Applied Pyrolysis**, v. 173, p. 1–13, 2023. https://www.sciencedirect.com/science/article/pii/S0165237023001791

[40] MOTHÉ, C. G.; MOTHÉ, M. G.; RIGA, A. T.; ALEXANDER, K. S. Thermal analysis of a model bio-membrane: Human and snake skins. **Journal of Thermal Analysis and Calorimetry**, v. 106, n. 3, p. 637–642, 2011. https://akjournals.com/view/journals/10973/106/3/article-p637.xml

[41] CARSOTE, C.; SENDREA, C.; MICU, M. C.; ADAMS, A.; BADEA, E. Micro-DSC, FTIR-ATR and NMR MOUSE study of the dose-dependent effects of gamma irradiation on vegetable-tanned leather: The influence of leather thermal stability. **Radiation Physics and Chemistry**, v. 189, p. 1–12, 2021. https://www.sciencedirect.com/science/article/pii/S0969806X21003625

[42] CHEBWOGEN, M.; NALYANYA, K. M., AMOLLO, T. A., MATHENGE, S. G. Effect of Gamma Irradiation on the Stability of Tanned Leather. **Textile & Leather Review**, v. 7, p. 550–568, 2024. https://www.tlr-journal.com/tlr-2024-038-chebwogen/

LICENSE