



Effects of ionizing radiation on the color and morphology properties of leather

Stanziani Gibba, J.L.¹, Otubo, L.², Oliveira, M.J.A.³, Vasquez, P.A.S.⁴

¹ jsgibba@usp.br, Instituto de Pesquisas Energéticas e Nucleares [Institute of Energy and Nuclear Research] (IPEN / CNEN - SP) Av. Professor Lineu Prestes, 2242, 05508-000 São Paulo, SP, Brazil

² lotubo@usp.br, Instituto de Pesquisas Energéticas e Nucleares [Institute of Energy and Nuclear Research] (IPEN / CNEN - SP) Av. Professor Lineu Prestes, 2242, 05508-000 São Paulo, SP, Brazil

³ mariahijo@gmail.com, Instituto de Pesquisas Energéticas e Nucleares [Institute of Energy and Nuclear Research] (IPEN / CNEN - SP) Av. Professor Lineu Prestes, 2242, 05508-000 São Paulo, SP, Brazil

⁴ pasalva@usp.br, Instituto de Pesquisas Energéticas e Nucleares [Institute of Energy and Nuclear Research] (IPEN / CNEN - SP) Av. Professor Lineu Prestes, 2242, 05508-000 São Paulo, SP, Brazil

1. Introduction

Leather has been present material for various applications throughout human history, valued for its versatility with unique properties. Leather is the result of processing skin through stages of cleaning, stabilization-tanning, and finishing, generating a stable and non-decomposable material [1] utilized in both industrial uses and the creation of cultural heritage artifacts. Preservation of cultural collections is essential [2] and requires a multifaceted approach, including risk assessment, conservation, and restoration, all guided by systematic strategies and common concepts, but with a priority on regional aspects [3].

The preservation of leather artifacts remains a significant challenge due to the susceptibility to biological degradation agents and risks of traditional methods. Each type of leather is made up of a group of related products with common characteristics, but varying in their properties and reaction to conservation treatments [4]. Brazil's predominantly tropical climate enhances infestation and biological infection. Consequently, cultural heritage artifacts containing leather in their composition are primarily threatened by humidity and biological factors.


In this context, ionizing radiation has emerged as a technique utilized since the 1970s as an efficient alternative for treating biological degradation. Its increasing application in scientific and museum collections underscores its viability as a non-toxic and advantageous option compared to traditional conservation methods. [5][6].

This study investigates the application of ionizing radiation as a preservation technique for bovine and snake leather samples with preliminary results of the effects on color and morphology properties of leather samples, two of the main characteristics of leather. Gamma radiation was applied to the samples at doses of 1 kGy and 3 kGy, which are minimum doses to establish the beginning of primary and secondary effects evaluation. Colorimetry using the CIELAB color space was utilized to objectively measure color differences and quantify color characteristics. Additionally, scanning electron microscopy (SEM) was used to investigate potential morphological alterations, especially on the surface and internal fiber structures.

2. Methodology

Sample selection

Two samples were selected from bovine and snake species. The main information regarding identification, classification, and general characteristics is presented in Figure 1. The bovine leather sample was provided by CR2 Indústria e Comércio de Calçados Ltda., while the snake sample was acquired from Stein Comércio de Cutelaria e Insumos Ltda., under Brazilian import license number 7799757.

| Sample | Species | Tanning Process | Color | Identification |
|--------|-------------------------------------|------------------|----------------|---|
| S1BC | <i>Bos taurus</i> (Domestic cattle) | Mineral (Chrome) | Caramel (Dyed) |  |


| | | | | |
|------|--|-----------|------------------|---|
| S2CK | <i>Bungarus fasciatus</i> (serpent or "karung" in some regions) | Vegetable | Natural (Undyed) |  |
|------|--|-----------|------------------|---|

Figure 1: Classification of leather samples.

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-CNEN/SP of the National Nuclear Energy Commission (CNEN). The installation project is classified as Category IV by the International Atomic Energy Agency (IAEA), containing a panoramic irradiator equipped for storing wet radioactive sources within a pool of deionized water, reaching a depth of 7 meters [7].

The samples were packaged in corrugated paper boxes and irradiated under normal atmospheric conditions at room temperature, with applied doses of 1 kGy and 3 kGy.

Colorimetry

The colorimetric characterization was based on the CIELAB color space, utilizing the numerical description of color developed by the International Commission on Illumination (Commission Internationale d'Eclairage - CIE). It was initially published in 1976 built upon the values L^* for perceptual lightness, a^* for the red-green chromatic coordinate, and b^* for the blue-yellow chromatic coordinate, with the relative difference between two points in color space expressed as ΔE (ΔE) calculated using the CIEDE2000 formula [8].

The equipment used was the PCE-CSM 8 colorimeter, with SQC8 color management system, measurement geometry of $0^\circ/45^\circ$, wavelength range from 400 to 700 nm, from the Colorimetry Laboratory at the Radiation Technology Center (CETER). Measurements were taken at one specific position on bovine leather and two positions of snake leather (light and dark) first on the non-irradiated samples, and after each irradiation process with a 120-hour interval.

Scanning electron microscopy analyses (SEM)

Scanning electron microscopic examinations were conducted to confirm potential differences in the structural layers, morphology, and fibrous structure of the corium in both non-irradiated (0 kGy) and effectively irradiated (3 kGy) leather samples. The samples were prepared by sectioning them along the surface and cross-sectional planes, affixing them to aluminum specimen stubs using carbon tape, and subsequently coating them with carbon. The samples were examined using a Hitachi TM3000 Tabletop Microscope, with observation conditions set to analyze mode and a magnification of 250 times.

3. Results and Discussion

Color analysis

The results of color analysis were compared against the criteria proposed by Hardeberg [9] for interpreting the color difference (ΔE^*) values, as presented in Table I. Values less than 3 have the effect of being nearly imperceptible to the human eye, from 3 to 6 the differences are noticeable yet acceptable, and above 6 are unacceptable.

Table I: Hardeberg Criteria for the results for perception of the color difference (ΔE^*)

| ΔE^* | Effect |
|--------------|-----------------------------|
| < 3 | Hardly perceptible |
| 3 < 6 | Perceptible, but acceptable |
| > 6 | Not acceptable |

The analyzed color parameters (ΔE^* , L^* , a^* , and b^*) exhibited slight variations suggesting the preservation of original color and pattern. Notably, color differences were categorized as "Hardly perceptible" ($\Delta E^* < 3$), indicating the insignificance of radiation effects. The most notable variation was observed in sample S2CKA for total color

difference (ΔE^*) at a dose of 1 kGy over a 120-hour interval, but it remained within established limits. The values of lightness (L^*) and chromatic scales (a^* , b^*) showed minimal fluctuation among applied doses and post-application periods, albeit with variances less than 1, remaining within acceptable thresholds (Fig. 2).

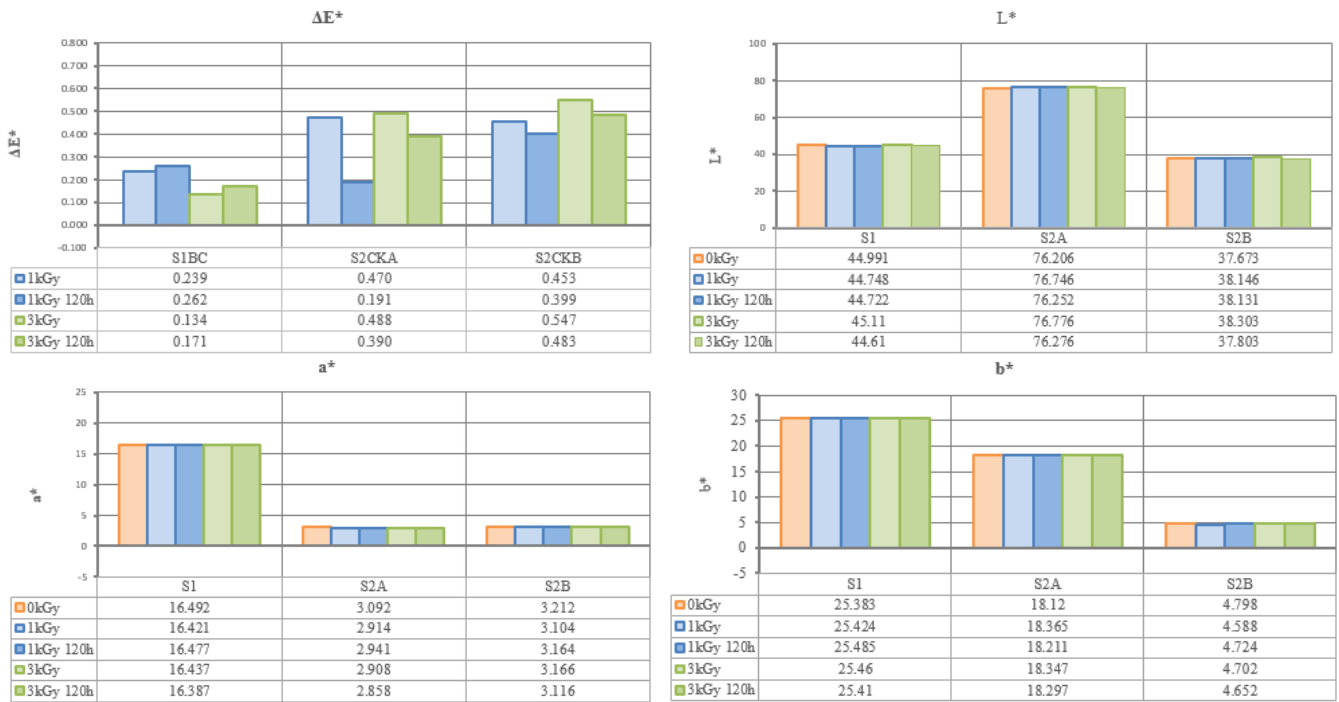


Figure 2: Values of total color difference (ΔE^*), and measurements of L^* , a^* and b^* of selected points before (0 kGy) and after irradiation (1 kGy and 3 kGy).

Scanning electron microscopy (SEM) analysis

The comparative morphological analysis conducted with the samples before and after the ionizing radiation process with 3 kGy revealed that the gamma radiation doses did not result in any remarkable changes in the structural layers, thereby preserving the morphology of the grain. Additionally, the images of cross-sections did not indicate any significant change in the protein leather fibers structure in the SEM micrographs (Figs. 3 and 4).

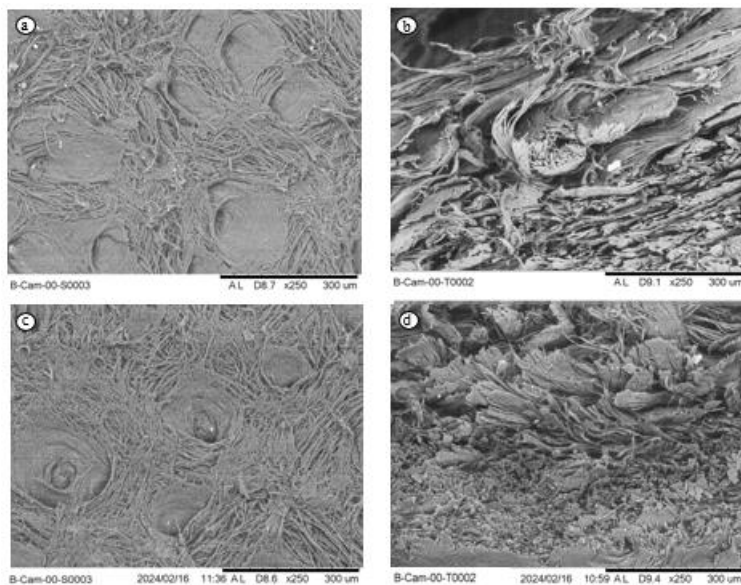


Figure 3: Sample S1BC non-irradiated a) surface b) cross-section and irradiated c) surface d) cross-section.

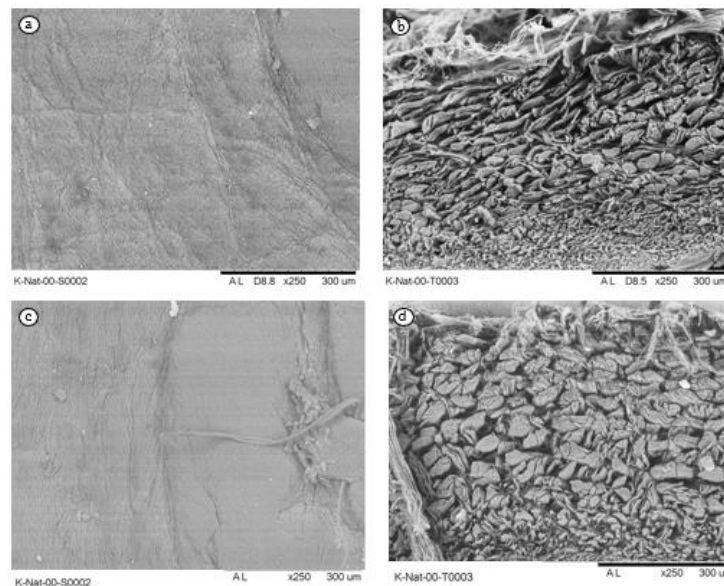


Figure 4: Sample S2CK non-irradiated a) surface b) cross-section and irradiated c) surface d) cross-section.

4. Conclusions

The study showed that gamma radiation applied to bovine and snake leather samples can be carried out safely with doses of up to 3 kGy, considering color and morphology properties. They revealed that doses of 1 kGy and 3 kGy led to negligible alterations in their colorimetric and morphologic characteristics. The color differences between non-irradiated and irradiated samples were imperceptible, and the measured values for total color difference fell within acceptable limits ($\Delta E < 3$), in accordance with established criteria. The analyzed color parameters (L^* , a^* , b^*) exhibited varying values; however, they clearly demonstrate slight differences, suggesting the preservation of the original color and pattern for each sample. SEM micrographs of the non-irradiated and 3 kGy irradiated samples presented no significant differences in the topographic morphology and internal structures of the fibers. In subsequent studies, this research aims to broaden its scope by incorporating higher irradiation doses, a more diverse array of leather samples, and additional characterization methodologies.

Acknowledgements

The authors thank the project the 2020.06.IPEN.02, International Atomic Energy Agency (IAEA).

References

- [1] Moreira, M. V., Teixeira, R. C., *Estado da arte tecnológico em processamento do couro: revisão bibliográfica no âmbito internacional*. Centro Nacional de Tecnologias Limpas, Porto Alegre, Brasil (2003).
- [2] “World Heritage” <https://www.unesco.org/en/world-heritage>. (2023).
- [3] Instituto do Patrimônio Histórico e Artístico Nacional (IPHAN), *Caderno de Diretrizes Museológicas 1*, Secretaria de Estado da Cultura/ Superintendência de Museus, Belo Horizonte, Brasil (2006).
- [4] Kite, M., Thomson, R., *Conservation of Leather and Related Materials*, Routledge, New York, USA (2011).
- [5] Rizzo, M.M., Machado, L.D.B., Borrelly, 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*, vol 63, pp. 259–262 (2002).
- [6] 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*. International Atomic Energy Agency. 1. Ed. Vienna, Austria. pp. 197- 201 (2017).
- [7] International Atomic Energy Agency (IAEA). *Radiation safety of gamma, electron and X Ray Irradiation Facilities IAEA Safety Standards Series No. SS-G-8*. IAEA, Vienna, Austria (2010).
- [8] Sharma, G., Wu, W., Dalal, E., “The Development of the CIE 2000 Colour-Difference Formula: CIEDE2000”, *Color Research and Applications*, vol. 30, pp. 340-350 (2000).
- [9] Hardeberg, J.Y. *Acquisition et reproduction d’images couleur: approches colorimétrique et multispec-trale. Interface homme-machine [cs.HC]*. Télécom ParisTech, Paris, Français (1999).