STUDYING SIDE-EFFECTS OF GAMMA-IRRADIATION PROCESSING OF LEATHER MATERIALS


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Abstract: The paper describes part of the results of the first year of the IAEA Coordinated Research Project F23032, Contract № 20567 on “Studying Side-Effects of Gamma Irradiation Treatment for Disinfestation of Cultural Heritage Artefacts”. Calf leather, calf suede and pig skin patterns were selected and analyzed by Scanning electron microscopy (SEM), and Thermal gravimetric analysis (TGA) before and after the gamma-irradiation treatment with 5 kGy, 10 kGy and 15 kGy absorbed doses at low dose rate. The irradiation of the leather materials was performed in the gamma-irradiation facility BULGAMMA based on JS-850 60Co type gamma irradiator at Sopharma JSC. No significant changes in the leather morphology and thermal decomposition were observed as a result of the gamma-irradiation treatment. Conclusions on the applicability of gamma-irradiation treatment for preservation of leather items with insecticide and fungicide doses were done.

Keywords: GAMMA-IRRADIATION, LEATHER, LOW DOSE RATE, MORPHOLOGY, THERMAL DECOMPOSITION

1. Introduction

Preservation of cultural heritage artefacts is one of the major objectives of archaeologists, restorers and museum workers. Biological attack of insects, larvae, fungi and bacteria is a serious problem in the preservation and long-term keeping of natural materials (wood, paper, leather, textiles, religious icons, etc.) when stored in improper conditions. Successful application of nuclear techniques (gamma irradiation and electron beam treatment) for disinfestation of archives and cultural heritage artefacts has been demonstrated in the last decades. There are several advantages of radiation disinfestation, compared to the traditional chemical treatment, including higher effectiveness, reliability, lack of toxic residues, applicability on large amount of objects etc [1-7]. However there are not enough data on the side-effects of gamma irradiation on leather items, especially at fungicide radiation doses. This impedes the development of methodology for gamma irradiation treatment for their disinfestation and preservation. Cultural heritage artefacts are often unique and their structure can not be simulated easily. Studies of the effects on irradiated items require the different extent of aging to be considered. Investigations of the side-effects on leather samples will contribute to clarify the structural and morphological changes and select appropriate doses for treatment and allow widening the preservation of leather-containing items by gamma-irradiation. Gamma-irradiation at low radiation dose rate is found to cause accelerating aging of the items, due to radical formations [2, 8]. The radiation induced oxidative degradation is observed to increase at low dose rate values due to increased time for oxygen diffusion [8]. Thus the application of low dose rate gamma-irradiation might contribute to determine the effects of gamma irradiation on artefacts by using model samples.

The Co-60 industrial radiation facility BULGAMMA, situated at Sopharma JCS is used for sterilization of health care products, disinfection of pharmaceuticals, drugs, cosmetics and food irradiation. However gamma-irradiation treatment until now is not regularly accepted for disinfestation of cultural heritage artefacts in the country. The aim of the current study is to increase knowledge on side-effects of gamma-irradiation treatment of leather materials in order to implement the radiation disinfestation of leather artefacts in the country. This paper presents part of the results, obtained during the first year of Contract № 20567 “Studying Side-Effects of Gamma Irradiation Treatment for Disinfestation of Cultural Heritage Artefacts”. Side effects of gamma-irradiation treatment of leather materials with 5 kGy, 10 kGy and 15 kGy at low dose rate (0.006 - 0.06 Gy/s) were investigated. The radiation induced changes in the thermal decomposition and morphology of the samples were studied by using Scanning electron microscopy (SEM), and Thermal gravimetric analysis (TGA/DTG).

2. Materials and Methods

2.1. Samples description

Three natural leather patterns were chosen for this study: calf leather, calf suede and pig skin. Pictures of their both sides are presented in Figure 1. No chemical treatment of the leather samples was performed before and after the gamma-irradiation.

![Fig. 1. Physical observation of the selected leather patterns.](image-url)
2.2. Gamma irradiation

The irradiation of the leather patterns was performed in the gamma-irradiation facility BULGAMMA based on JS-850 $^{60}$Co type gamma irradiator at Sopharma. JS-850 $^{60}$Co gamma irradiator is a wet storage, tote-box irradiator, produced by MDS Nordion, Canada. JS-850 is an elevator type irradiator. It was replenished in 2007 with total irradiator activity 98.484 Ci after source reloading.

The absorbed dose distributions were measured with Ethanol Chlorobenzene routing dosimeters, consisting of dosimetric solution encapsulated in glass ampoule with diameter 10.7 mm and volume 2 mL. The absorbed dose was calculated from a calibration curve connecting it with the electric conductivity of the dosimetric solution measured with oscillograph. This dosimeter consists of an aerated solution of Chlorobenzene and water in ethanol to which a small quantity of acetate was added. The absorbed dose was calculated from a calibration curve connecting it with the electric conductivity of the dosimetric solution measured with oscillograph.

The maximum of the combined uncertainty of dose determination did not exceed 7.2 % (for 2 standard deviations).

Irradiator BULGAMMA is certified by the Quality Management System ISO 9001: 2008, applicable to Processing, decontamination and sterilization of products by gamma-irradiation for industrial, medical and scientific purposes. The samples (calf leather, calf suede and pig skin) were packed in plastic bags separately, closed in paper envelopes and irradiated by: 5 kGy, 10 kGy and 15 kGy absorbed doses at low dose rate (0.037 Gy/s).

2.3. Methods of investigations

The general morphology of the non-irradiated and gamma-irradiated leather samples was studied by SEM. A scanning electron microscope Lyra 3 XMU (Tescan with Quantax EDS detector - Bruker) was employed. Prior to the measurements, the samples were covered with a thin film of carbon. Analysis of the non-irradiated leathers was performed by SEM-EDX in order to obtain information on the elemental composition of the samples and the tanning methods.

The thermal properties of the samples were studied by thermogravimetry (TG/DTG) in pure argon, using Perkin-Elmer TGS-2.

3. Results and discussion

3.1. Morphology

The morphology of carbon-coated leather samples before and after gamma-irradiation at dose rate of 0.037 Gy/s with 5, 10 and 15 kGy was observed in several SEM images, at three different magnification ranges: x 200, x 500 and x 2000. Selected SEM images of the leather patterns before and after gamma-irradiation with 5, 10 and 15 kGy at low dose rate are presented on Figs. 2 - 7.

The SEM images of the external and internal surfaces of the studied leather samples did not show changes of the morphology as a result of the gamma-irradiation treatment. Despite the non-uniformity of the leather surfaces, no irradiation induced damages on them; neither on the fibers could be noticed as a result of gamma-irradiation treatment up to 15 kGy.

The results of SEM-EDX analysis, revealed that the calf suede and the pig skin samples were chrome tanned and contained 4.56 % Cr (suede) and 6.74 % Cr (pig skin). The calf leather did not show elements, untypical for natural leather content and considering that it is light in color, harder and less flexible than the suede and pig skin, we supposed that it has been vegetable tanned.

Fig.2. SEM images of calf leather (external side) before and after gamma-irradiation with 5, 10 and 15 kGy dose at 0.037 Gy/s.

Fig.3. SEM images of calf leather (internal side) before and after gamma-irradiation with 5, 10 and 15 kGy dose at 0.037 Gy/s.

Fig.4. SEM images of calf suede (external side) before and after gamma-irradiation with 5, 10 and 15 kGy dose at 0.037 Gy/s.
3.2. Thermal decomposition

The data, obtained from the TG/DTG analysis of the initial leather samples and irradiated samples with 15 kGy at low dose rate (0.037 Gy/s) are presented on Figs. 7-11.

The TG curves of the three leather patterns have similar shapes (Figs. 8, 9). Highest weight percent remained in the calf leather after heating up to 650 °C (33.24 %), followed by pig skin (26.64 %) and calf suede (24.56 %). The irradiated samples of calf suede showed slight increase of the weight percent remained after heating up to 650 °C, as compared to the non-irradiated sample (from 24.56 % to 27.06 %). This effect can be due radiation induced changes in the molecular structure, e. g. cross-linking of the collagen.

As can be seen from Figs. 10-12, the DTG curves of the non-irradiated and irradiated samples practically overlap, which indicates no influence of gamma-irradiation with 15 kGy at dose rate 0.037 Gy/s on the weight loss of the studied leathers. The initial weight loss in the temperature range of 40 – 120 °C can be ascribed to the moisture volatilization or evaporation of some residual tanning solvent. The temperatures of maximum weight loss rate, corresponding to the main weight loss step was observed at 298 °C for calf leather, 317 °C for calf suede and 320 °C for pig skin patterns.
4. Conclusions

The studies on the effects of gamma-irradiation treatment of calf leather, calf suede and pig skin with 5 kGy, 10 kGy and 15 kGy at low dose rate showed no significant changes in the morphology and thermal decomposition of the selected leather materials, as revealed by the scanning electron microscopy and thermal gravimetric analysis. Further investigations on the side-effects of gamma-irradiation on the molecular structure and radical formation in leather materials would contribute to development of radiation treatment methodology for their disinfestation and preservation.

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