TREATMENT AND PROCESSING OF LEATHER MATERIALS USING GAMMA RADIATION

COSMIN HERMAN[1], OVIDIU CĂPRARU[1], BOGDAN LUNGU[1], IOANA STĂNCULESCU[1,2], MARIA STANCA[3], CARMEN GAIDĂU[3]

[1]*Horia Hulubei National Institute for Physics and Nuclear Engineering, Dept. IRASM, 30 Reactorului Str, 077125 Magurele, Ilfov, Romania*

[2]*University of Bucharest Dept. of Physical Chemistry, Regina Elisabeta Bld 4-12, 030018 Bucharest, Romania, istanculescu@nipne.ro*

[3]*INCDTP - Division: Leather and Footwear Research Institute, 93 Ion Minulescu st., Sector 3, 031215 Bucharest, Romania*

This paper presents a review on the functionalization methods of leather materials using gamma radiation. There are few studies regarding the effects of gamma irradiation on leather materials while the majority of studies are on the irradiation of collagen for medical purposes, decontamination and preservation of heritage leather objects and parchment documents. Recent studies on leather and parchment treated with bigger doses then the sterilization or decontamination doses and on gamma irradiated collagen, new information about the solubility of collagen, crystalline structure, shrinkage temperature and mechanical properties were obtained. The relation between the shrinkage temperature and the gamma radiation dose absorbed by the material were investigated with the MHT (Micro Hot Table) method. Evidences of cross-linking of the collagen were found at doses up to 25 kGy while for doses of 50 kGy and more the principal process was the scission of the peptide chains. The mechanical properties of tanned leather and parchment such as tensile strength and elongation at break were studied. The parchment tensile strength decreases with the increase of absorbed dose, for doses bigger than 10 kGy. The behaviour of tanned leather is different, an increase in the tensile strength at doses up to 25 kGy which can be a threshold for collagen cross-linking. More evidence of cross–linking of the collagen fibrils in leather materials were shown with the SEM-EDX and TG investigations. There were no substantial modifications in the structure of collagen for doses of 5, 10 and 15 kGy as shown by the SEM and TG analysis, but a slightly smaller loss of mass in the case of the dose of 25 kGy which can prove the cross-linking of collagen in the tanned leather material. Based on literature review a conceptual application model for gamma irradiation on leather materials was elaborated.

Keywords: leather, gamma irradiation, collagen

INTRODUCTION

Leather clothing, footwear, upholstery and other leather goods manufactured from animal hides and skins are subject to complex chemical processes which are under continuously ecological attention. From salt preservation of the animal hides in the purpose of preventing the decomposition to chromium salts tanning and biocide treatment of the wet blue leather against fungi, leather processing consists in many time and chemical consuming steps (Mesquita, 2013; Wu, 2009). This implies high costs and time consuming processing of the leather materials and residues and that is why innovative processes based on green technologies have to be developed.

Introducing gamma radiation as a treatment method to the leather industry is a new approach; few studies were conducted on leather materials, mostly in cross-linking of collagen chains (Guererro *et al.*, 2017). Other applications were found in medicine, in the purpose of sterilization or decontamination of medical collagen for different uses (Takitoh *et al.*, 2015). Gamma radiation was also used in cultural heritage conservation

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and restoration, as a nondestructive method of decontamination, and preservation of artifacts (IAEA, 2017; Vujčić *et al*., 2017).

Also, gamma irradiation can be used in leather industry for treatment of the leather materials in view of cross-linking activation of different polymeric substances to improve certain characteristic of the finished product (Catalina *et al*., 2010; Demeter *et al*., 2018).

Mechanical properties and elemental analysis showed evidence of cross-linking of the collagen for doses up to 25 kGy, and scission of the peptide chains for bigger doses, indicating a recommended dose for treatments on leather materials.

Processing of leather materials using gamma radiation to substitute steps in manufacturing and functionalization using different types of polymers can be cost effective and environmentally friendly and will be envisaged in the conceptual application model developed.

GAMMA IRRADIATION OF COLLAGEN BASED MATERIALS - STATE OF THE ART

Gamma Irradiation of Leather

Gamma radiation effects on leather materials were analysed on different hides and skins, vegetable tanned with extracts of quebracho, mimosa and with chromium salts (Carsote *et al*., 2016; Misra *et al*., 2018). The effects of gamma irradiation on the hides tanned with these commercial tanning agents have indicated supplementary cross-linking as a primary effect for doses up to 25 kGy, the material showing an increase in tensile strength, elongation at break and a smaller loss of mass according to thermogravimetric analysis. For bigger doses the main process is scission of the peptide chain, with evidence in shrinkage temperature and tensile strength decrease (Lungu *et al*., 2014; Sendrea *et al*., 2017). The four studies showed in Table 1 share the same conclusion.

Table 1. Studies on gamma radiation effect on tanned leather with a ^{60}Co gamma rays source

References	Material	Tanning agent	Analysed properties	Dose (kGy)
C. Sendrea *et al*., 2017	Calf leathers Sheep skins Goat skins	Quebracho extract Mimosa extract	Shrinkage temperature and intervals	10, 25, 50, 100
C. Sendrea *et al*., 2015	Calf leather	Quebracho and Mimosa extracts	Spin-lattice and spin-spin proton relaxation time	10,25 ,50, 100
Kovacheva *et al*., 2017	Calf leather Calf suede Pig skin	Not specified Chromium salts	Leather morphology and thermal decomposition	5, 10, 15
Lungu *et al*., 2014	Kid skin Sheep skin	Mimosa extract Quebracho extract	Tensile strength and elongation at break	10, 25, 50

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Gamma Irradiation of Parchment

Gamma radiation is used in decontamination and sterilization of parchment documents, for its non-destructivity and efficiency. Parchment documents were made usually from goat and sheep skins stretched and polished with calcium carbonate ($CaCO_3$) to achieve the white surface.

The dose of 30 kGy was proposed as a maximum dose of decontamination for parchment artifacts, indicating no changes in structural composition, colour and texture, as can be seen in Table 2 (Nunes *et al*., 2012). All small deviations in the measured properties were associated to structural diversity and different tanning methods (Nunes *et al*., 2012). For doses up to 10 kGy more recent studies showed cross-linking of the collagen fibrils, and deterioration for bigger doses applied on new parchment experimental models (Lungu *et al*., 2014). The tensile strength of the parchment documents decreased with the absorbed dose.

Table 2. Gamma irradiation of parchment documents with ^{60}Co gamma rays source

References	Material	Analysed properties	Dose (kGy)
Lungu *et al*., 2014	Goat parchment Kid parchment	Tensile strength and elongation at break	5, 10 ,15
Nunes *et al*., 2012	XV century parchment XVI century parchment XVII century parchment	Colour, texture and elasticity	10, 19, 22, 30

Gamma Irradiation of Collagen

Native and tanned collagen were irradiated with gamma rays from a ^{60}Co source, and the Electron Paramagnetic Resonance (EPR) spectrum was correlated with the absorbed dose, indicating different sensibility of collagen to gamma radiation due to the tanning process and tanning agent in comparison with native collagen, as can be seen in Table 3 (Duliu *et al*., 2001). Also, using gamma irradiation a stable hydrogel was obtained from an aqueous solution. The hydrogel that received a bigger dose of radiation revealed better mechanical properties, indicating cross-linking of collagen chains. At low doses, although chemical cross-links have been observed, the structure of the gelatine has not been significantly altered (Cataldo *et al*., 2007; Leontiu *et al*., 1993).

Table 3. Effects of gamma irradiation of collagen with a ^{60}Co gamma rays source

References	Material	Preparation method and irradiation	Analysis	Doses (kGy)
Catalado *et al*., 2008	Gelatine from porcine skin	Gelatine dissolved in demineralized water resulting in 28 ml homogeneous solution and irradiated in absence of air	Polarimetric measurements, FT-IR, spectra of electronic absorption, differential scanning calorimetry (DSC), thermogravimetric analysis with simultaneous differential thermal analysis (TGA-DTA)	12, 25, 50, 100, 150, 200

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References	Material	Preparation method and irradiation	Analysis	Doses (kGy)
Duliu *et al*., 2001	Tanned collagen membranes	1% Fibrous collagen gel in HCL solution 1% Fibrous collagen gel in HCL solution + formaldehyde 1% Fibrous collagen gel in HCL solution + $Cr(OH)(SO_4)_2$ 1% Fibrous collagen gel in HCL solution + $Al(OH)(SO_4)_2$	EPR spectroscopy	1, 3, 7, 11, 15
Maslennikova *et al*., 2015	Rat tail collagen	Rat tails dissected after 24 h, 7 days, 1, 2 and 3 months	Laser scanning microscopy, cross-polarization optical coherence tomography, differential scanning calorimetry	2, 4, 6, 8, 10 20, 30, 40
Grant *et al*., 1973	Rat tail collagen	Washed in saline solution and dried pre-irradiation Washed in saline solution and irradiated in saline solution Washed in saline solution and cross-linked with 5% glutaraldehyde	Electron microscopy, amino acid analysis, histology, solubility, enzyme reaction	From 50 to 1000
Gotoh *et al*., 1977	Dry collagen film	Regenerated with electrochemical method before irradiation	Elemental analysis, thickness, mass and tensile strength	40, 80, 100
	Wet collagen film	Regenerated with electrochemical method before irradiation		20, 40, 50
	Collagen film	Regenerated with electrochemical method under gamma irradiation		10, 20, 25

Gamma radiation was found to be useful for tannery wastewater harmful substances decomposition (Iqbal *et al*., 2015).

Conceptual Model for Leather Treatment with Gamma Radiation-a "Green Chemistry" Tool

As gamma irradiation equipments are more and more accessible and gamma radiation represents an ecological and effective alternative for chemical preservation, sterilization and cross-linking, the application in leather industry needs only advanced knowledge and economical approaching.

Based on the state of the art of the gamma irradiation applications in the field of collagen based materials processing a conceptual model is proposed in view of further developments (Fig. 2):

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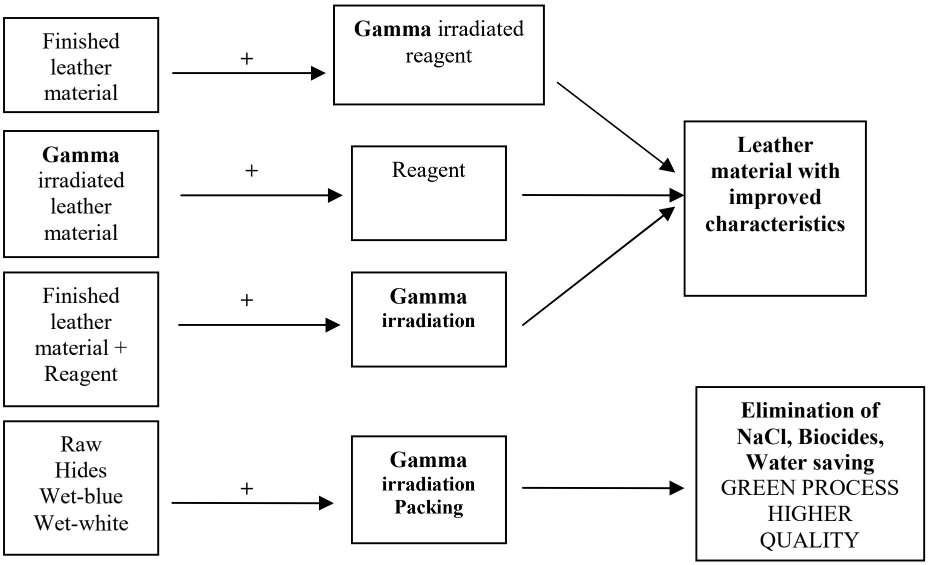

Figure 2. Conceptual model for leather processing by gamma irradiation

CONCLUSIONS

The application of gamma irradiation in leather industry represents an ecological approach for chemical and water saving with potential impact on leather quality improving. The knowledge in the area of gamma radiation application on collagen based materials are few and needs research efforts for innovative methods development.

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