STUDY ON MECHANICAL PROPRIETIES OF GAMMA IRRADIATED LEATHER AND PARCHMENT

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Cultural heritage is ineffably degrading due to physical, chemical and biological factors. If physical and chemical degradation can be delayed by controlling the storage conditions, the biological attack, once installed, can be stopped only by a drastic intervention. Among others, ionizing radiation treatment has the advantages of: the certainty of biocide effect, fast treatment, mass treatment, no harmful chemicals and residues. Although, because of the complexity and diversity of the constituents of cultural heritage items, there is always a question: if the radiation induces a supplementary degradation in the material. Literature reports show an increase use of radiation treatment for microbial decontamination of wood, painted wood and paper. Few experiments were conducted on leather and parchment. The purpose of this study is to test several mechanical proprieties of irradiated leather and parchment. Samples from leather and parchment were irradiated at doses from 10 kGy up to 50 kGy. For doses below 10 kGy we can consider that changes in mechanical strength of both parchment and leather samples is insignificant (lower than uncertainty of the measurement) but this should be confirmed by other analytical methods. Generally it is known that crosslinking is the predominant effect of irradiation in case of collagen. In our experiment an increase of the mechanical strength it was observed only in case of leather, for doses of 25 kGy and above. The absence of crosslinking in case of parchment can be explained by the lack of the sites which can support crosslinking.

Keywords: gamma irradiation, parchment, leather.

INTRODUCTION

Cultural heritage is ineffably degrading due to physical, chemical and biological factors. If physical and chemical degradation can be delayed by controlling the storage conditions, the biological attack, once installed, can be stopped only by a drastic intervention. Among others, ionizing radiation treatment has the advantages of: the certainty of biocide effect, fast treatment, mass treatment (large quantities), no harmful chemicals and residues. Although, because of the complexity and diversity of the constituents of cultural heritage items, there is always a question: if the radiation induces a supplementary degradation in the material. Literature reports show an increase use of radiation treatment for microbial decontamination of wood, painted wood and paper.

The Radiation Processing Centre of Horia Hulubei National Institute of Physics and Nuclear Engineering in Romania (IFIN-HH), achieves the preservation of artefacts by applying small doses of gamma radiation to destroy microorganisms and insects. The ongoing PN-II-PT-PCCA-2011-3-1742 research project "Improvement of occupational environment quality in cultural heritage deposits. Validation of gamma radiations treatment of textile and leather cultural goods (TEXLECONS)" coordinated by IFIN-HH intends to expand the results obtained in 3 previous projects on the radiation treatment of polychrome wood and paper to leather and textiles items (Stanculescu *et al.*, 2012).

The ionization induced by high energy photons leads to breaking of molecular bonds. Then, two mechanisms are competing in macromolecules: the chain scission (which is associated to the degradation of a material) and the formation of new molecular bonds. Crosslinking is a well known effect for certain synthetic or natural polymers and collagen is one of the natural polymers which are cross-linked under irradiation (Cataldo *et al.*, 2008).

The study of the degradation of cultural heritage items needs a variety of investigations with different analytical methods (Badea *et al.*, 2008). The mechanical properties are on highest interest but because of lack of availability of samples and large non-uniformity of the materials of natural origin, the studies are oriented for obtaining correlations with other physical and chemical properties.

The objective of the present study is to determine if there are any changes of mechanical properties induced by radiation treatment for leather and parchment and if so, how big they are.

MATERIALS AND METHODS

The mechanical tests were conducted on leather (fig. 1) and parchment (fig. 2) provided by INCDTP-ICPI. Where tested two types of leather: goatling-mimosa and sheep-quebracho and two types of parchment: goatling and goat.

Figure 1. Piece of leather for testing

Figure 2. Piece of parchment for testing

We used a Zwick Roel Universal Testing Machine with a 5 kN cell force. For determination of the tensile stress, the tensile strain and the modulus of elasticity we followed ISO 527-3 (film and foils) (1995) with 100 mm/min constant load speed for parchment and 200 mm/min constant load speed for leather. The samples were cut in a bone shape according to specimen number 5 of ISO 527-3 (6 mm in width and 80 mm the testing length). The reason in using this specimen was the ability to determine the modulus of elasticity. Thickness of the samples was measured with a general purpose micrometer.

The samples were irradiated at IRASM department of IFIN-HH with Co-60 radioactive sources at room temperature in a GC-5000 type irradiator. We applied doses of 9.9±0.6 kGy, 24.8±1.0 kGy and 49.6±1.4 kGy at a medium dose rate of 6.2 kGy/h with a dose non-uniformity DUR=1.276.

RESULTS AND DISCUSSIONS

We measured the thicknesses for both leather and parchment. The results are shown in table 1 for parchment and in table 2 for goat.

Table 1. Thickness values for parchment samples

Thickness	Goatling	Goat
Mean (mm)	0.31	0.46
Standard deviation (mm)	0.016	0.04
ν (%)	5.1	8.7
No. of samples	11	15

Table 2. Thickness values for sheep samples

Thickness	Goatling	Sheep
Mean (mm)	1.01	0.74
Standard deviation (mm)	0.091	0.038
ν (%)	9	5.1
No. of samples	11	15

The results for parchment show that goatling has lower thickness and better uniformity. One of the major problems when working with natural materials is the non-uniformity of the samples. This is caused by the animal constitution but also because of the manufacturing process, as it can be seen in figure 3 (the material is stretched with yarns and it alters the natural formation of material) (Hansen *et al.*, 1991).

In order to avoid some of the mentioned errors, all the tested samples were collected from the middle section, close to the back bone of the animal. In conclusion, we are looking to non-uniformities due to place of cutting the sample caused by the animal constitution and manufacturing process. Also for this case, the variation coefficient is rather high reflecting the non-uniformity of the samples.

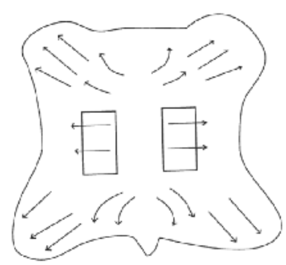

Figure 3. Stretching directions during the manufacturing of parchment (Hansen *et al.*, 1991)

The results obtained for maximum force and for elongation at break are shown in figure 4 and figure 5, respectively.

Comparing leather and parchment for maximum force (F_{max}), it can be observed that parchment has much higher values than leather. For parchment, the tensile strength apparently decrease with the increase of the irradiation dose but this decrease is inside de limits of the uncertainty of the measurement. In figure 4 the error bars represent the standard deviation for 5 samples in case of goatling parchment, 4 samples in case on goat parchment and 3 samples in case of leather. The number of samples was limited because of the available material from each type. A value of 7% is the usual uncertainty of the measurement for mechanical tests.

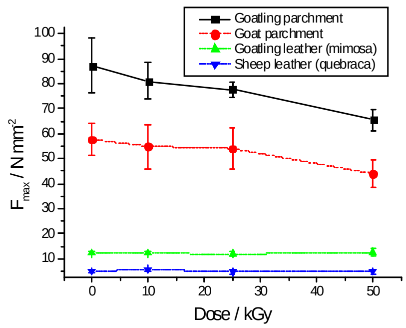

Figure 4. Tensile strength chart

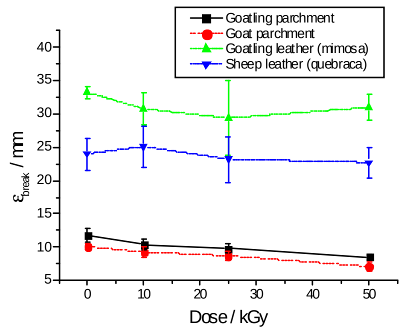

Figure 5. Elongation at break chart

For leather, the behaviour of tensile strength may suggest that crosslinking overcomes the chain degradation of collagen but this is still in the limits of the uncertainty of the measurement.

For the elongation at break (ε_{break}), it can be observed a very similar behaviour for the two parchment types. For leather, the results indicate crosslinking but also in the range of the uncertainty of the measurement.

The elasticity modulus was calculated according to the formula:

$$E_t = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1} \qquad (1)$$

where: E_t –tensile elasticity modulus (MPa); σ_1- stress at 0.05% strain (MPa); σ_2- stress at 0.25% strain (MPa).

The values for σ_1,σ_2, ε_1 and ε_2 where read from the curve recorded by the Zwick TestExpert software.

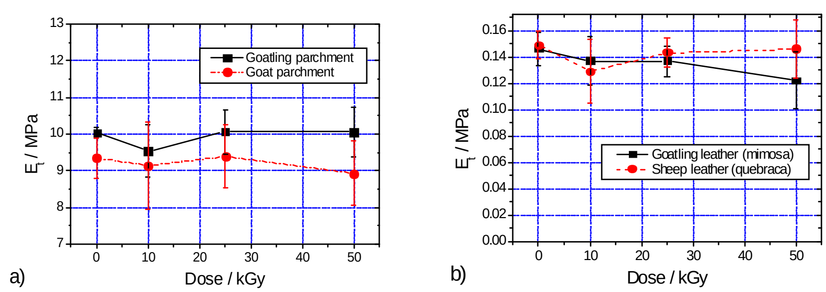

Figure 6. Modulus of elasticity: a) parchment, b) leather

In the figure 6 (a) it can be observed, for both parchment material, that the changes induced by radiation are relatively small, within the area of uncertainty of measurements. Both of materials behaved in the same way, goatling having higher values. At 10 kGy, the results indicated a slight crosslinking for all samples; for parchment, above 10 kGy, it seems that the elasticity module increases which may suggest some deterioration within the material. However, a similar behaviour was obtained for historical parchment in Portugal, by another method (texture test) which is also dependant on the elasticity modulus (Nunes *et al.*, 2012).

CONCLUSIONS

In the literature there are very few data on the behaviour of the physical and mechanical parameters of leather and parchment under irradiation with ionizing radiation an even fewer on historical (aged) leather and parchment (Nunes *et al.*, 2012).

Taking into account the non-uniformity of the historical materials and the size and number of samples required for mechanical testing, it is practically impossible and useless to test really old samples. We choose to test the effects of irradiation on new materials (not-aged) in order to avoid the non-uniformity induced by ageing degradation. The changes induced by ageing can be further evaluated by accelerating ageing methods. It is expected that the radiation induced degradation to be lower in case of aged samples (Nunes *et al.*, 2012). Generally it is known that crosslinking is the predominant effect of irradiation in case of collagen (wet state) (Cataldo *et al.*, 2008). In our experiment an increase of the mechanical strength it was observed only in case of leather, for doses of 25 kGy and above. The absence of crosslinking in case of parchment can be explained by the lack of the sites which can support crosslinking. For doses below 10 kGy we can consider that changes in mechanical strength of both parchment and leather samples is insignificant (lower than uncertainty of the measurement) but this should be confirmed by other analytical methods.

However, an extended comparative study for aged and non-aged samples irradiated at multiple doses, it is recommended to be performed with a method requiring less quantity on samples (thermal analysis or vibrational spectroscopy).

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