ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

TANNED LEATHERS PROPERTIES MODIFICATION AS A RESULT OF ARTIFICIAL AGEING

ROŞU Dan[1], VARGANICI Cristian-Dragoş[1], CRUDU Andra-Manuela[2], ROŞU Liliana[1], CRUDU Marian[2]

[1]Advanced Research Centre for Bionanoconjugates and Biopolymers
"Petru Poni" Institute of Macromolecular Chemistry Gr. Ghica Voda Alley 41A, 700487, Iasi, România,
drosu@icmpp.ro; lrosu@icmpp.ro; varganici.cristian@icmpp.ro

[2]National Research & Development Institute for Textiles and Leather Division:
Leather and Footwear Research Institute, Bucharest, Romania, mariancrudu@yahoo.com; andracrudu@yahoo.com

Corresponding author: Roşu, Dan, E-mail: drosu@icmpp.ro

Abstract: *Leather is a high tech material with different application fields, such as automotive, manufacturing of leatherwear articles or clothing and footwear. Leather is a biomaterial obtained by processing animal skins. Unfortunately, raw animal hides are practically inutilizable, due to their microbiological instability and are affected by rotting. Microbiological stability is achieved by tanning, when the protein is crosslinked, followed by drying. After crosslinking and drying, the new material shows the required properties of sustainability, availability and an esthetically pleasing aspect to the touch, making it available across its entire range of applications. From a structural point of view the animal skins are constituted of collagen, which is a fibrilar protein with a high degree of supramolecular organization in triple helix form that endows softness, elasticity and mechanical strength. High quality standards and lack of toxicity are required in all cases. Leather colour changes during exposure to light radiations are considered a consequence of the presence of some products with weak photochemical resistance during fabrication. The study aims to compare changes in properties of leathers obtained using mineral tanning agents such as Cr III salts and those obtained with the more environment-friendly technology using acid hydrolysis. Accelerated aging studies were conducted on tanned leathers by exposing the samples to UV radiation with different irradiation doses and two wavelengths (254 and 365 nm) under controlled humidity and temperature conditions. Structural changes caused by irradiation were studied by FTIR. Colour changes on the sample surfaces were assessed during irradiation with the CIEL a^*b^* system. The colour parameters variation (L^*, a^*, b^*) and colour differences have been discussed in correlation with structural changes, tanning method and irradiation conditions.*

Keywords: *Bovine skin, Tanning process, Titanium, Leather, UV radiation*

1. INTRODUCTION

Leather is a biomaterial, mostly comprised of collagen and obtained by processing animal skins with various uses, ranging from manufacturing of clothing, footwear and other accesories of daily use [1], [2]. Unfortunately, the raw animal hides are practically inutilizable, due to microbiological instability and rotting. Microbiological stability is achieved by tanning, when the protein is crosslinked, followed by drying. After crosslinking and drying the new material shows the required properties of sustainability, availability [3]. Chromium III salts are the best known tanning agents used for crosslinking of collagen based materials. It is well known that the manufacturing of

leather is one of the most polluting activities due to the inorganic chemical waste levels resulted during chemical operations. Chromium is known as the main source of pollution with heavy metals of the wastewaters resulted from tanning, wet finishing and mechanical processing of leathers. Therefore, the practical significance of chromium-free leather is constantly expanding. Attempts to replace chromium salts in the tanning process of hides with waste resulted from obtaining of ultrapure titanium technology are presented in literature [4], [5], [6]. It is expected that leather should be able to withstand exposure to extreme and varying environmental conditions, such as temperature, light, moisture and mechanical loading, over a series of years. The legal and economic consequences arising from any guarantee declaration force the manufacturers to know the ageing properties of their products and of the materials included in these products.

2. EXPERIMENTAL

2.1. Materials

The synthesis method of Ti–Al tanning agent and the obtaining of wet–white and wet–blue products were described in the literature [3].

2.2. Equipment

Material irradiation

The aging studies were conducted by exposing the leather surface samples (70x40x0.5 mm) to UV radiation up to 200 hours in the air. The samples were irradiated with UV filtred light emitted by two high intensity mercury vapor lamps (model R-52G, and B-100AP, manufactured by Analytik Jena Company, with emission maxima located at 254 and 365 nm.

A PMA 2100 radiometer manufactured by Solar Light Company equipped with PMA 2110 and PMA 2122 detectors with response spectral region 320-400 nm and respectively 249-251 nm was used to measure the irradiance and the irradiation dose during photochemical aging. The irradiance values were 23.3 Wm^{-2} for B-100AP lamp and 4.6 Wm^{-2} for R-52G lamp. Hourly irradiation doses were 36.8 kJm^{-2} for B-100AP lamp and 16.7 kJm^{2} for R52G lamp. These values were measured in irradiation chamber at the level of samples holder.

Colour modifications

Colour modifications during irradiation on the sample surfaces were followed with a Lovibond LC 100, RM 200 model apparatus manufactured by Tintometer Ltd., UK, using a white pellet from $BaSO_4$ as standard. The standard DIN 6174 (Farbmetrische 15 Bestimmung von Farbabständen bei Körperfarben nach der CIELAB-Formel, 1979) has been used for colour evaluation using D65 illuminant and the results in CIELAB ($L^*a^*b^*$) system has been expressed. In CIELAB ($L^*a^*b^*$) the colours are described by parameters L^* which defienes lightness, a^* which denotes the red/green value and b^* for yellow/blue value. The colour differences between the irradiated and non-irradiated samples were calculated with Eq. 1, where ΔL^*, Δa^* and Δb^* are the differences between each parameter after and before irradiation irradiation it is noted.

$$\Delta E = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2} \quad \textbf{(1)}$$

Fourier transform infrared spectroscopy (FTIR)

Through FTIR method one can obtain qualitative and quantitative detailed spectral analyses. The FTIR spectra were recorded with a Bruker Vertex 70 apparatus equipped with a MIRacle accessory designed for single or multi-reflection attenuated total reflectance (ATR). The ATR crystal plate was from diamond and the solid material was put in physical contact with the sampling

area through high pressure clamping for recording the spectra with high-quality and reproducibility. The spectra were recorded in the range 4000-600 cm^{-1} at a spectral resolution of 4 cm^{-1} and 64 scans.

3. RESULTS AND DISCUSSIONS

Structural changes during leather samples exposure to UV radiation were monitored by FTIR spectroscopy (Fig. 1). No significant changes were identified between the FTIR spectra of non-irradiated wet blue and wet white samples. Both the FTIR spectra contain specific vibrations of partially denaturated collagen. Thus, the broad signal in the range 3800 and 3000 cm^{-1} with the peak located at 3315 cm^{-1}, is a complex combination between –NH stretching vibrations from peptide linkages and OH groups of water molecules included in collagen structure.

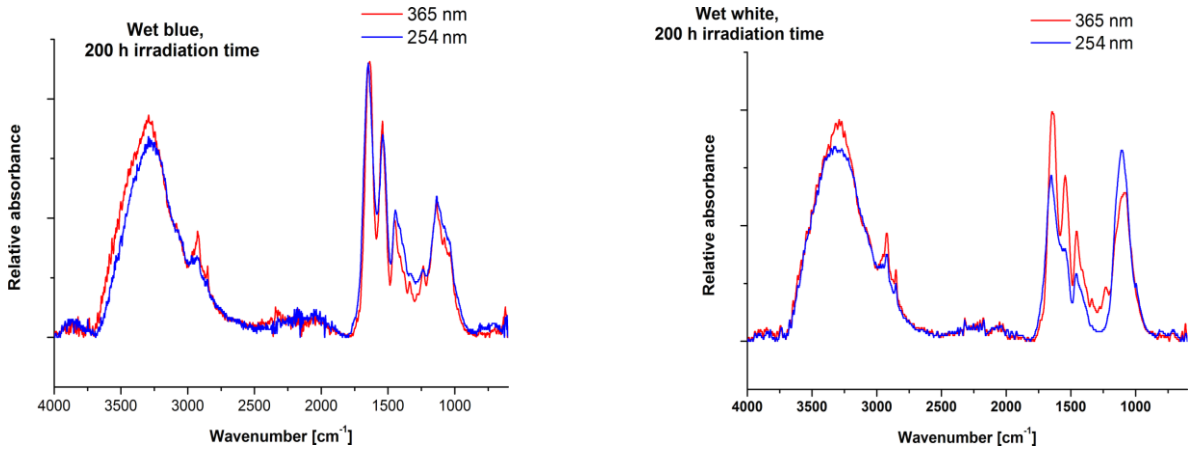
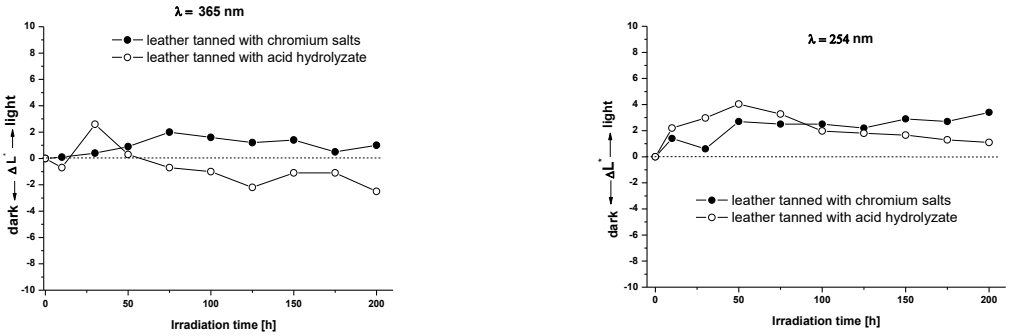


Fig. 1: *ATR-FTIR spectrum of bovine tanned skin*

The peak from 1454 cm^{-1} (Fig. 1a) was assigned to bending of C-H aliphatic groups from collagen structure and fatty acids, included as traces from early processing. The vibrations from 1637 cm^{-1} and 1552 cm^{-1} from Fig. 1(a) are characteristic to the peptide bond. The shifting of the peak from 3315 cm^{-1} to higher wavenumbers was found, regardless of the implied tanning method. The decrease of absorbance and displacement of this singal are indications of hydrogen bonds scission between intermolecular water molecule entities and protein chains. Loss of water molecules by evaporation accompanies the split of hydrogen bonds. Similar aspects were observed for the wet-white leather in Fig. 1(b), however with a more pronounced denaturation of collagen at 254 nm.
Mass losses continously occur during irradiation. In the case of the studied samples the mass losses are between 5 and 8 % after 200 hours irradiation time. These values are dependent on sample type and UV radiation wavelength. Highest mass losses have been recorded for wet blue samples irradiated at λ=254 nm (arround 8 % after 200h exposure time). Lower mass lossess have been recorded for wet blue samples exposed to lower energy UV radiations (λ =365 nm) (around 5 %).
Unlike to the wet blue samples, the wet white samples had comparable mass losses at both wavelengths (4.27% at λ = 365 nm and 3.65 % at λ = 254 nm).

ΔL^* values increase with irradiation time at both wavelengths. At 365 nm samples show similar behavior. The ΔL^* values was below 5 after 200 hours irradiation time. At lower wavelengths (λ=254 nm) the ΔL^* values were higher. The sample tanned with acid hydrolizate is characterized by lower ΔL^* differences. This observation proves a greater sensitivity of leather tanned with acid hydrolyzate. At 254 nm a slight increasing tendency of the lightness factor (L^*) may be observed for

both samples. The acid hydrolyzate tanned leather shows a slight tendency of darkening when the sample was exposed to 365 nm. This behaviour suggests that the wet white leather is more sensitive to photo-oxidation than the wet blue one.



(a) *(b)*

Fig. 2: *Variation of lightness factor differences with irradiation time*

4. CONCLUSIONS

Wet white leather was more sensitive to photo-oxidation than the wet blue one. Samples showed more intense photo-decomposition processes at 254 nm.

5. REFERENCES

[1] K. Joseph and N. Nithya, "*Material flows in the life cycle of leather*", J. Clean Product, vol 17, pp. 676-682, 2009

[2] C.-K. Liu, N. P. Latona, R. Ashby and K. Ding, "*Environmental effects on chrome-free lether*", J. Am. Leather Chem. As., vol. 101, pp. 368-375, 2006

[3] M. Crudu, V. Deselnicu, D.C. Deselnicu and L. Albu, "*Valorization of titanium metal wastes as tanning agent used in leather industry"*, Waste Manag., vol. 34, pp. 1806-1814, 2014

[4] M. Crudu, M. Niculescu, V. Deselnicu, D. Sutiman, D. Sibiescu, A. Cailean, N. Boca, *The process of obtaining and use of a range of chemicals with low toxicity to (pre) tanning natural leather*, Romanian Patent App. A/00941/17.11.2009

[5] M. Crudu, N. Boca, D. Sutiman, A. Ioanid, A. Caileanu, D. Sibiescu, "*Compounds with tanning capacityobtainedfrom Ti-end unrecyclable waste of the Ti-metalurgic industry"*, CERTEX ISBN 978-973-1716-54-1, 2009

[6] M. Crudu, C. Gaidau, A. Crudu, M. Popescu, M. Ionescu, *"Innovative material technology system with contribution to increasing eco-efficiency of industrial leather processing*", Annals of the University of Oradea, Fascicle of Textiles, Leatherwork, vol: XIV, ISSN: 1843-813X, 2013, pg. 95-100

ACKNOWLEDGEMENTS

Authors acknowledge the financial support of a grant of the Romanian National Authority for Scientific Research, CNCS−UEFISCDI Project number PN-II-PT-PCCA-2013-4-0436.