



NEW ECO-EFFICIENT PRODUCTS USED IN LEATHER INDUSTRY

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Abstract: In today's move to "sustainable production" the leather industry, as well as many other industries is recognized as a polluting one. Traditional chemical operations are polluting because of the levels of inorganic chemical waste. Process chemicals which are not consumed within the reactions necessary to convert collagen to leather are currently discharged to waste. These are usually applied during bulk production, such as inorganic agents from beam house and tanning processes, e.g. lime, sulphide, ammonium salts, sulphuric acid and sodium chloride, mineral tanning agents – mainly Cr(III) and the less common Al(III), Zr(III), Ti(III), Fe(III) salts -, whereas depending on the tanning process and the leather article produced organic chemical waste discharged comprises aldehydic and polyphenolic tanning products, bating enzymes, organic carboxylic acids and excess electrolyte stable synthetic fat liquors. It is rare for chemicals and water to be recovered for re-use from several of these process steps. Moreover, tanners worldwide are required to operate within strict legislative boundaries. Serious drawbacks continuously arise concerning the chrome-tanning process in leather industry and the environmental hazardous consequences of chromium containing effluents. In order to overcome this impediment, a great deal of research has been focused on developing chrome-free tanning methods in the past years, such as titanium tanning. In the present study, Ti-Al tanned bovine leather was characterized by means of SEM microscopy, EDAX elemental analysis, ATR-FTIR spectroscopy, thermogravimetry TGA, and differential scanning calorimetry DSC techniques.

Key words: bovine skin, tanning process, titanium, leather, ATR-FTIR, SEM/EDAX

1. INTRODUCTION

It is a well known fact that the leather industry always has been one of the most polluting ones. This is due to the resulting of inorganic chemical waste levels during different chemical operations. Such waste results usually during bulk production, and usually consists of inorganic agents resulted during beam house and tanning processes (ammonium salts, lime, sodium chloride, sulphide, sulphuric acid and mineral tanning agents – mainly Cr(III) and the less common Zr(III), Ti(III), Fe(III), Al(III) salts. Other discharged chemical waste depends on the tanning process and the nature of the produced leather article [1-3]. The hazardous environmental consequences which usually arise in the leather industry from the chrome-tanning process are due to chromium based



effluents. It is therefore that a great deal of research has been conducted in overcoming this issue, and which is focused on developing chrome-free tanning methods, such as titanium tanning [4-6].

2. EXPERIMENTAL

2.1. MATERIALS

Wet salted bovine hides weighing 20-25 kg (Constanta, Romania), limed and delimed bovine hide waste, bovine hide waste pretreatment with titanium based product, tanning product based on titanium recovered from scrap metal, technical grade auxiliary materials used in leather processing - succinic anhydride.

2.2. EQUIPMENT

Differential scanning calorimetry (DSC)

The glass transition temperature domain (T_g) was determined by using the DSC technique. The thermograms were recorded on a DSC 200F3 Maia (Netzsch, Germany) calibrated with five metals (In, Sn, Bi, Hg, Co) according to standard procedures. Samples were heated in aluminium crucibles with pierced and pressed lids for removal of any volatiles released during heating. Sapphire is used for absolute heat capacity values determination. The used DSC device covers a temperature range of $-150\text{ }^{\circ}\text{C} \div 500\text{ }^{\circ}\text{C}$ and cooling is made with liquid nitrogen. The experiments were conducted in nitrogen, as inert atmosphere, with a heating/cooling rate of $10\text{ }^{\circ}\text{C}/-10\text{ }^{\circ}\text{C}$ and in the temperature range $-50\text{ }^{\circ}\text{C} \div 300\text{ }^{\circ}\text{C}$.

Fourier transform infrared spectroscopy (FTIR)

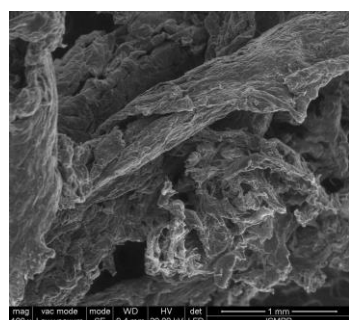
Through FTIR method one can obtain qualitative and quantitative detailed spectral analyses. The FTIR spectra were recorded with a Bruker Vertex 70 apparatus equipped with a MIRacle accessory designed for single or multi-reflection attenuated total reflectance (ATR). The ATR crystal plate was from diamond 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 $4000\text{-}600\text{ cm}^{-1}$ at a spectral resolution of 4 cm^{-1} and 64 scans.

Scanning electron microscopy (ESEM)

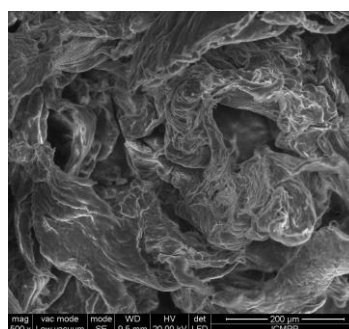
Samples materials surfaces were examined with a Quanta 200-FEI environmental scanning electron microscopy (ESEM). The investigations were performed in Low Vacuum mode using a secondary electron detector ETD at accelerating voltage of 20 kV. The Quanta 200 scanning electron microscope is equipped with an EDX system for allowing quantitative and qualitative compositional analysis. Double-sided carbon tape was used to mount the samples on aluminum stubs. The samples were covered in gold. The following chemical elements were identified through EDAX analysis: C, N, O, Na, Mg, Al, Si, S, Cl, Ti, V, Fe.

3. RESULTS AND DISCUSSIONS

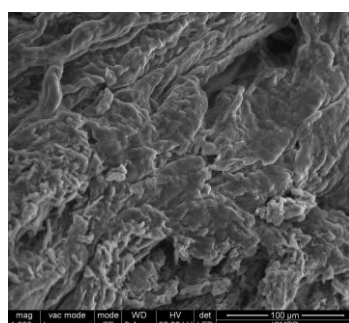
Relevant information regarding surface topology and sample structure was obtained with scanning electron microscopy SEM technique. *Figs. 1a-d* shows the SEM/EDAX micrographs of the studied sample in different sections and at different resolution values.



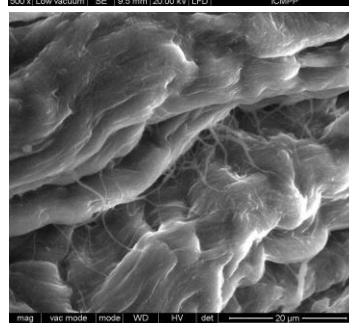
a



b



c



d

Fig. 1a: Micrograph of sample (1) at 100x
Fig. 1c: Micrograph of sample (1) at 1000x

Fig. 1b: Micrograph of sample (1) at 500x
Fig. 1d: Micrograph of sample (1) at 5000x

The micrographs in *Figs. 1a-d* evidence a fibrillar and relatively compact surface. At higher resolution (5000x) there may be observed thin cross-linking bridges (*Fig. 1d*).

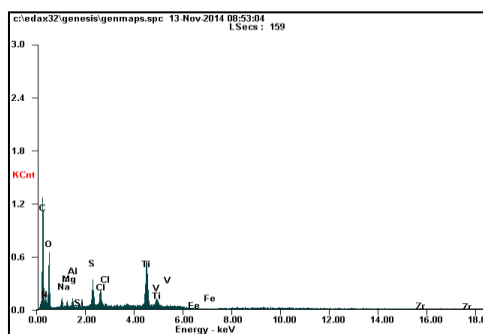


Fig. 2: EDAX analysis of bovine skin tanned with Ti-Al salts

By analyzing the ATR-FTIR spectrum in *Fig. 3* one may observe the presence of absorption bands specific to collagen structure. Bands at 1651 cm^{-1} and 1541 cm^{-1} are characteristic to polypeptides, which describe deformation vibrations of C=O structure (amide I band), and C–NH bonds vibration (amide II band). The vibration bands at 3427 cm^{-1} and 1030 cm^{-1} are proof of C–N bonds presence from primary amine groups existing in different types of collagen. The absorption band at 3427 cm^{-1} is a sign of humidity traces present in the tanned skin samples.

The DTG curve in *Fig. 4* indicates at least three consecutive stages of thermal degradation for the tanned bovine skin with maximum thermal decomposition rates recorded at $89\text{ }^{\circ}\text{C}$, $319\text{ }^{\circ}\text{C}$ and $386\text{ }^{\circ}\text{C}$, respectively, corresponding to DTG curve peaks.

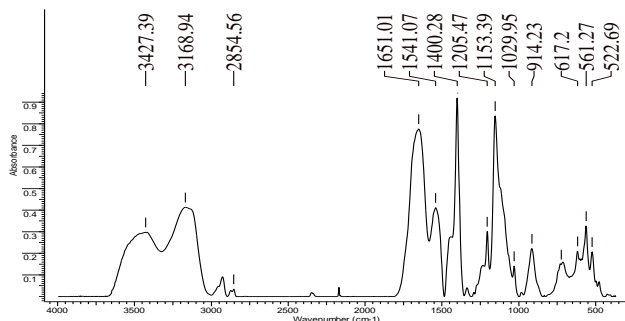


Fig. 3: ATR-FTIR spectrum of bovine skin tanned with Ti-Al salts

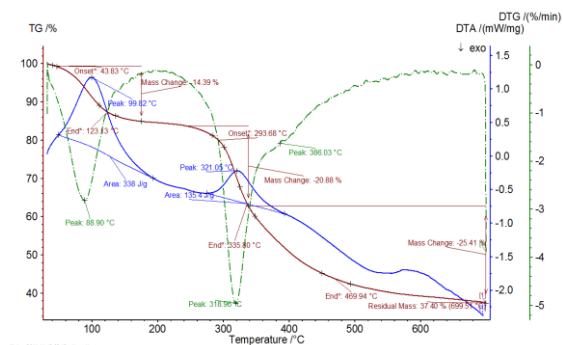


Fig. 4: TGA curve of bovine skin tanned with Ti-Al salts recorded in the temperature range 30–700 °C in nitrogen and at a heating rate of 10 °C min⁻¹

The DTA curve peaks indicated that all three thermal decomposition processes were endothermic. The first thermal decomposition stage ranges between 44 °C and 200 °C with a total mass loss of 14.4%. The second thermal decomposition stage ranges between 294 °C and 335 °C with a total mass loss of almost 21%. The third thermal decomposition stage ranges between 335 °C and 700 °C with a total mass loss of over 25%. The residue remained at the end of the thermal decomposition process of the studied material represented 37.4% of the initial sample mass.

REFERENCES

- [1] M. Seggiani, M. Puccini, S. Vitolo, C. Chiappe, C. S. Pomelli, D. Castiello, “Eco-friendly titanium tanning for the manufacture of bovine upper leathers: pilot-scale studies”, *Clean. Techn. Environ. Policy*, vol. 16, pp. 1795–1803, 2014.
- [2] M. Crudu, V. Deselnicu, I. Ioannidis, L. Albu, A. Crudu, “New wet white tanning agents and technology”, *ICAMS – 4th International Conference on Advanced Materials and Systems*, Bucuresti, Romania, 2012.
- [3] A.D. Covington, “*Tanning Chemistry: The Science of Leather*”, RSC Publishing, Cambridge; RSC Publishing: Cambridge, UK, 2011.
- [4] M. Crudu, V. Deselnicu, D.C. Deselnicu, L. Albu, “Valorization of titanium metal wastes as tanning agent used in leather industry”, *Waste Manag.*, vol. 34, pp. 1806–1814, 2014.
- [5] E. Zuriaga-Agustí, M.V. Galiana-Aleixandre, A. Bes-Pia, J.A. Mendoza-Roca, V. Risueno-Puchades, V. Segarra, “Pollution reduction in an eco-friendly chrome-free tanning and evaluation of the biodegradation by composting of the tanned leather wastes”, *J. Clean. Product.*, vol. 87, pp. 874–881, 2015.
- [6] W. Kangjian, X. Shiwei, L. Meng, “Chrome-free tanning: a nonpickle process using a Zr–Al–Ti complex tanning agent”, *J. Soc. Leather. Technol. Chem.*, vol. 96, pp. 141–147, 2012.

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