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CIRCULAR TECHNOLOGY FOR SHEEPSKIN TANNING

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Abstract: *The circular economy is synonymous with the production of "zero waste" in the context in which valuable resources are lost and the European development agenda aims for a program of smart, sustainable, inclusive growth. At present, finding alternatives to tanning with chromium salts is considered one of the most important objectives of the leather industry.*
The present paper includes original results regarding the formulation, characterization and testing of some organic pre-tanning composites for the processing of sheepskins within the concept of circular technology. The collagen hydrolysate extracted from untanned and organic pre-tanned sheepskins was used to design a new circular technology. Four kinds of pre-tanning agents were formulated based on renewable materials such as collagen hydrolysate, whey and/or vegetable tannins. The characterization of new products by ATR-FTIR spectra showed common wavelength bands of whey and vegetable tannin suggesting a potential interaction and less carboxylic and methyl groups for oxidized pre-tanning agents. The new pre-tanned sheepskin leathers were retanned with a full organic formulation and showed different affinity for anionic chemical auxiliaries due to different chemical functional group activation. Physical-chemical, softness determination and SEM images confirmed the similar morphology with vegetable leathers, with more compact structure of leathers pre-tanned with oxidized products as compared to non oxidized composite products, with a more soft and relaxed aspect. The non oxidized pre-tanning agents were selected for further experiments at pilot level in view of circular technology design with prospect to save 40% sheepskin waste.

Key words: *biotechnology, waste recycling, biodegradable pre-tanning, organic tanning, circular economy, bio-based technology, renewable materials*

1. INTRODUCTION

The circular economy is the economy in which the product is designed to be manufactured and used without generating waste, as an alternative to the linear economy which involves: production, consumption and creation of waste [1].

The circular economy is synonymous with the production of "zero waste" in the context in which valuable resources are lost and the European development agenda aims for a program of smart, sustainable, inclusive growth [2]. European targets include a ban on the storage of recyclable and biodegradable waste until 2025 and even their disposal by 2030 [3].

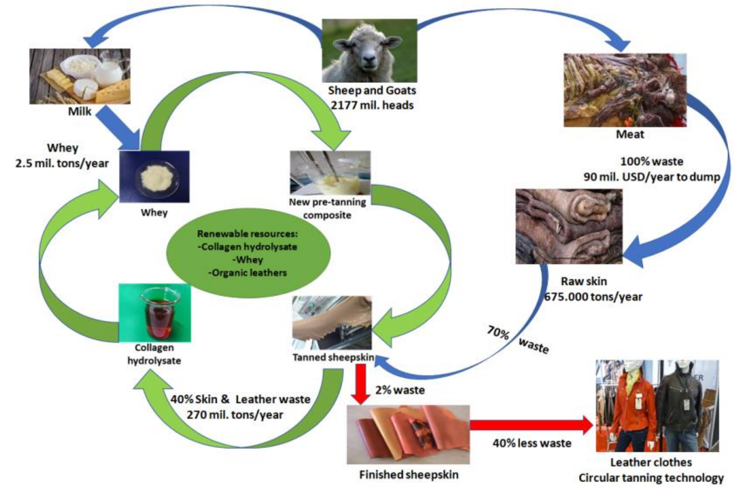
The leather industry represents an intensely globalized economic sector, which capitalizes on a by-product generated by the meat industry. The processing yield of natural leathers is 20-40% [4], leather waste being a valuable, important source of protein. In the last 18 years [5] skin processing has made many advances in terms of environmental impact, water consumption has fallen 2.5 times, energy consumption has fallen 1.96 times, and waste has remained at the same level.

The need to design leather processing technologies to reduce the amount of unused waste is an imperative of the leather industry auxiliary chemicals industry. In this European and global context, the concerns regarding the innovation of leather processing technologies, the recovery and recycling of solid waste represent the main research direction.

At present, finding alternatives to tanning with chromium salts is considered the most important objective of the leather industry [6].There is an increased interest for new plant extracts formulation [7] or for the use of protein resources crosslinked with tannins intented to be used as fillers for leather retanning [8, 9]. All these approaches contribute to leather biodegradability increase and waste circularity improvement.

In this context, the capitalization of the protein resources from the leather as well as the food industry, the finding of new natural sources in the formulation of the agents of ecological processing of the natural skins, represent current topics.

The present paper includes original results regarding the formulation, characterization and testing of some organic pre-tanning composites for the processing of sheepskins within the concept of circular technology in agreement with Scheme 1.



Scheme 1- Circular technology concept for sheepskin processing

2. EXPERIMENTAL

2.1 Pre-tanning materials preparation

Four kinds of pre-tanning agents were prepared by using renewable materials: a) collagen hydrolysate processed from delimed pelt wastes in Leather Research Department by acid hydrolysis, with MW=23000 Da, pH=3; b) whey powder with 12.5% protein and 75% carbohydrates; c) vegetable tanning materials: commercial mimosa extract powder with 65% tannin and tara powder with 38% tannin; $Fe_2SO_4.7H_2O$ and H_2O_2 30% of analytical grade. Pre-tanning TZC and MZC products were prepared by mechanical mixing the collagen hydrolysate, whey and vegetable tanning materials at 40^0C for 4h, when a homogenous paste was obtained. The obtained paste was dehydrated to solid flakes state in an oven with convective air (Caloris SA) at 50^0C. Pre-tanning products ZCox and MZCox were prepared from whey, collagen hydrolysate (ZCox) and mimosa extract, respectively by catalytic oxidation with $Fe_2SO_4.7H_2O$ and H_2O_2 30% for 24 hours, at 50^0C under mechanical stirring [1]. Figure 1 shows the pre-tanning products in paste form and Fig.1 the dried product MZC as flakes or milled powder and leathers pre-tanned with TZC, ZCox, MZC and MZCox new materials.

TZC **ZCox** **MZC** **MZCox**

Fig. 1: *Pre-tanning products prepared from renewable materials*

2.2. Sheepskin pre-tanning and retanning

The technology for skeepskin leather processing was carried out from the pickling stage at a value of pH=2.8-3, and by dosing 15 wt% pre-tanning material in 3 doses every 60 minutes with continuous stirring, for 4 hours in a FA.VE. experimental drum (220 x 500 mm), until the cross section of leather was completely penetrated, followed by a static contact for 24 h. The next day the leathers were stirred for 60 minutes at 40^{0}C, the float was drained and the pre-tanned leathers were deposited for another 24 h when samples were prelevated for shrinkage temperature control analyses. All pre-tanned leathers were neutralized, retanned, dyed, fatliquored and acid fixed together by following an organic formulation for classical chromium tanned soft sheepskin leathers. Figure 2 shows the four leathers processed with new pre-tanning materials and retanned with a fully organic formulation.

Fig. 2*: Pre-tanning materials MZC and sheepskin leathers: TZC, ZCox, MZC, MZCox*

2.3. Pre-tanning materials and leather characterisation

The characterisation of pre-tanning new products was performed by ATR-FTIR (JASCO4200) for specific functional chemical groups identification, by physical-chemical analyses for dry substance, tannin, ash content and pH, using standardized methods: SR EN ISO 4684; SR 1883; SR ISO 4047; SR EN ISO 4045. Crust leathers were analysed for shrinkage temperature, softness, volatile matters, ash, total nitrogen and hide substance, extractible substances, water soluble minerals, pH of aqueous extract by standardized methods: SR EN ISO 3380; SR EN ISO 17235; SR EN ISO 4684; SR ISO 4047; SR EN ISO 5397; SR EN ISO 4048, SR EN ISO 4098 and SR EN ISO 4045. The morphology of collagen fibers was investigated in crust leather cross sections with FEI Quanta 200 Scanning Electron Microscope (FEI, Eindhoven, The Netherlands).

3. RESULTS AND DISCUSSIONS

3.1. Pre-tanning materials characterization

The ATR-FTIR spectra analyses of oxidized and non oxidized pre-tanning agents showed different specific wavelengths of components, especially of whey and vegetable tannin. In figure 2 can be seen the ATR-FTIR spectra of pre-tanning materials with characteristic wavelength for –OH group at 3200-3400 cm^{-1} and a maximum intensity for C=O at 1630-1655 cm^{-1}. The intensity of C=O at 1630-1655 cm^{-1} is higher for ZCox (Figure 3 a) as compared to whey and collagen hydrolysate components (not showed here). TZC product showed more similar chemical functional groups with whey and tara tannin (Figure 3 b), and very similar with product MZC spectra. MZC product has common wavelengths with whey attributed to carbohydrates at 3250-3500 cm^{-1} and at 1500 cm^{-1}, specific for phenolic compounds from mimosa taninng extract, proving the interaction of these materials. By oxidation, MZCox has lost some carboxylic groups (1429-1399 cm^{-1}) and CH_3 group from aromatic compounds (1030 cm^{-1}), as well as some -OH groups from 875 cm^{-1}, as compared to MZC product (Figure 3 c).

The main physical-chemical characteristics of MZC pre-tanning products in paste state were: 40% dry substance, 12% protein, 23% carbohydrates, 2% tannin, 1% ash and pH= 4.

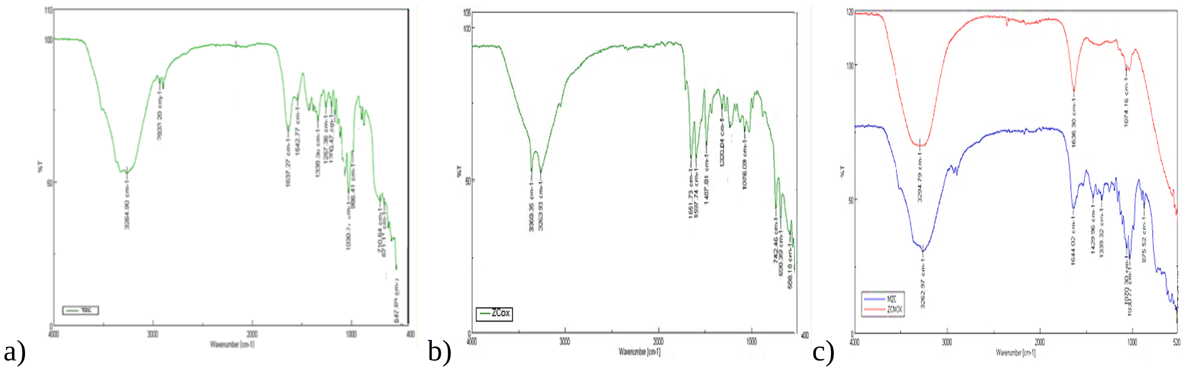


Fig. 3. ATR-FTIR spectra for a) TZC; b) ZCox; c) MZC and MZCox

3.2. Sheepskin leather characterization

The influence of the new pre-tanning compositions on leather characteristics were investigated, starting with collagen crosslinking ability of MZC (an increase of Ts by 22^0C) and lower affinity for the other products (Ts increase by 12^0C), as can be seen in Figure 4a. The interaction of oxidized products (ZCox, MZCox) with sheepskin collagen released more chemical functional groups for retanning materials which crosslinked as much as the pre-tanning materials (an increase of 12 and 9^0C, respectively). Similar behaviour can be observed for TCZ product (an increase of 11^0C).

The influence of new pre-tanning materials on leather softness was distinctly different for oxidized products and not oxidized products, with improved softness and more relaxed surface for MZC and TZC leathers (Fig.4b). The SEM images from Figure 5 show a more compact structure with deposited pre-tanning materials in interfibrilar spaces for leathers pre-tanned with oxidized products and more free spaces for MZC and TZC sheepskin leathers, which is in agreement with softness determinations.

The physical-chemical characteristics of organic sheepskins are presented in Table 1 and show similar properties with vegetable leathers, with 33-40% chemical material deposited inside fibrilar leather matrix or crosslinked with collagen, similar extractible materials content (slightly higher quantity on MZC leather), and pH value in the range of classical processed sheepskins (pH= 4.6-4.8). Low content of water-soluble minerals can be an advantage as compared to chromium tanned sheepskin leathers.

a) b)

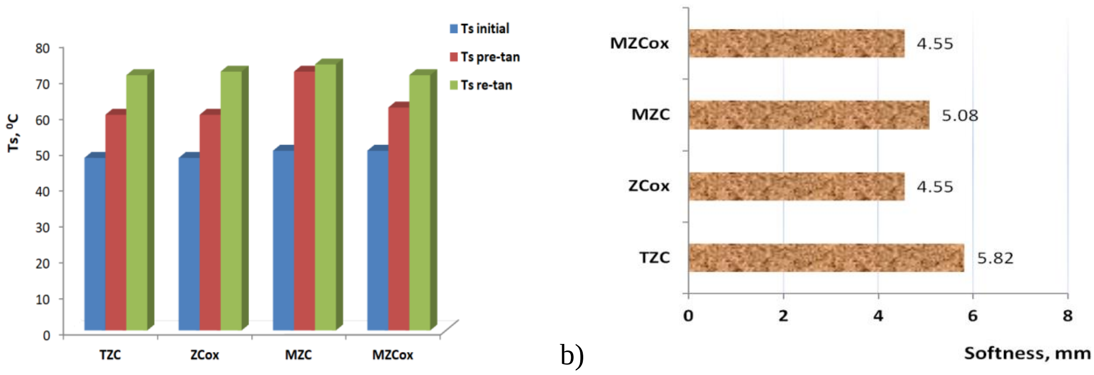


***Fig. 4**. Shrinkage temperature of organic tanned sheepskin (a) and their softness (b)*

a) b) c) d)

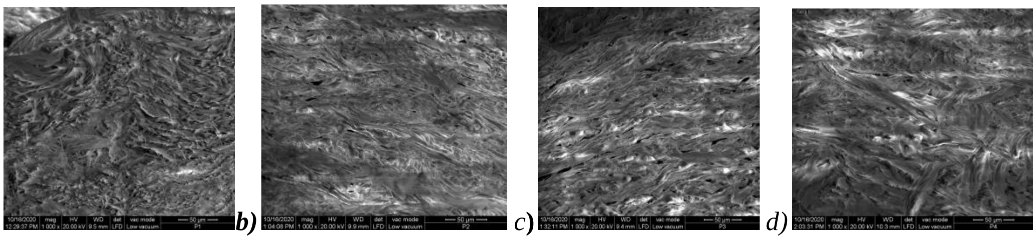


***Fig. 5**. SEM images of leather cross sections: a) TZC, b) ZCox, c) MZC, d) MZCox*

***Table 1.** Physical-chemical characteristics of organic tanned sheepskin leathers*

Characteristcs	TZC	ZCox	MZC	MZCox
Volatile matter,%	9.44	9.43	8.60	8.91
Ash, %	4.05	2.95	3.48	4.29
Total nitrogen, %	11.93	12.06	10.51	11.61
Hide substance, %	67.03	67.76	59.08	65.28
Extractible matters, %	15.15	14.83	16.59	15.08
Water soluble minerals,%	0.41	0.41	0.37	0.44
pH, aqueous extract, pH units	4.75	4.70	4.60	4.60

This research results has demonstrated the potential of renewable materials to be recirculated in sheepskin tanning process. The use of collagen hydrolysate extracted from pre-tanned leathers with MZC/TZC products will enable the design of new pre-tanning composites in a circular technology with prospect to save 40% of waste sheepskin from 70% total waste [10].

4. CONCLUSIONS

Four pre-tanning agents based on renwable materials (whey, collagen hydrolysate, vegetable tannin materials) were prepared for sheepskin leather processing. The collagen hydrolysate extracted from untanned and organic pre-tanned sheepskins was used to design a new circular technology. ATR-FTIR spectra showed common wavelength bands of whey and vegetable tannin for MZC and

TZC agents which suggest a chemical interaction and less carboxylic and methyl groups for oxidized pre-tanning agents, ZCox and MZCox. The new pre-tanned sheepskin leathers were retanned with a full organic formulation and showed different affinity for anionic chemical auxiliaries due to different chemical functional group activation. The product MZC showed the highest affinity for pickled sheepskins and the products TZC, ZCox and MZCox enabled retanning agents to additionally crosslink sheepskin collagen. Physical-chemical, softness determination and SEM images confirmed the similar leather morphology with vegetable leathers, with more compact structure of leathers pre-tanned with oxidized products as compared to TZC and MZC composite products, with a more soft and relaxed aspect. MZC and TZC products were selected for further experiments at pilot level in view of circular technology design with prospect to save 40% sheepskin waste.

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