Zero chemical treatment of leather waste for highly performing, circular and sustainable finishings

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Abstract

Many strategies have been adopted, in recent years, in order to minimize the impact of tannery waste, mainly made up of solid waste, such as sewage sludge, shavings, trimmings, splits and more. On the other hand, tanning waste recovery processes already identified are a virtuous application case of the circular bioeconomy for the use of waste tanning biomass, as secondary raw materials in the production of other industrial sectors. Currently, the main challenges are focalized on finding solutions for the transformation and valorization of tanned waste, characterized by a significant and variable chemical complexity; moreover, the growing use of innovative tanning systems, makes the search for solutions for the treatment of waste more challenging.

In the present work, which originates from a Research and Development Project, co-financed by the Italian Ministry of Economic Development, the use of mechanical pre-treatments using ball milling technologies has been identified as a particularly sustainable, promising and transversal approach, for obtaining leather micro and nano-fibers, to be used as a reinforcement and replacement component in finishing, through conservative processes of the collagen structure, according to the PMW (Principle Minimal Wrecking) and PMS (principle of massive separation) principles.

The obtained micro and nano-fibers have been finely characterized, by multiple techniques including X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Attenuated Total Reflection infrared spectroscopy (ATR-IR); then, water dispersions of the fibers have been used in finishing formulations, in addiction or substitution of polyurethane and polyacrylate based chemicals. The obtained films have been applied on leather samples, both on laboratorial and industrial scale. The performances of the obtained films and of the treated leather samples have been tested in terms of mechanical, chemical-physical properties, mereological features and sustainability impact, through multiple techniques, including Thermogravimetric/Derivative Thermogravimetric analysis (TG/DTG), Attenuated Total Reflection infrared spectroscopy (ATR-IR); Gas chromatography–mass spectrometry (GC-MS) - Purge & Trap equipped.

Finally, the studies carried out allowed to verify the applicability of the strategy to different sectors, with reference to the production of leather for footwear, leather goods and the automotive industry, determining the impacts in terms of economic and environmental impacts, which highlighted the feasibility of the

approach for obtaining finishes with increased performance, biodegradability and sustainability.

Keywords: Leather Waste, Zero Chemical, Mechanical Treatments, Ball Milling, Nanotechnologies, Circular Finishing

1. Introduction

Remarkable efforts have been made in recent years to ensure a solid process of valorisation of waste, with a view to making the production context increasingly circular. The tanning industry, in fact, while representing a sector that is progressively increasingly sensitive to environmental sustainability issues, and while constituting a solid example of circular economy, mainly dealing with the transformation and valorisation of waste from the food industry, nonetheless envisages a series of complex chemical and mechanical operations, following which further waste is generated.

The chemical, physical, mechanical and eco-toxicological characteristics of such waste will depend not only on the type of animal of origin, but also on the processing stage following which the waste was produced and on the type of processing carried out. Consequently, the approaches for the valorisation of waste and the possibility of reusing the products obtained from their transformation will also be influenced by these factors.

The transformation and valorisation operations of solid waste mainly concern untanned waste; examples in this sense are the activities aimed at obtaining protein hydrolysates (collagen, keratins), for their use in the production of fertilizers and biostimulants; another example is the use of these products for the production of animal gelatine for food use.

On the other hand, the recovery of already tanned waste is more complex, due to the greater complexity of the matrix and the potential presence of substances with an impact on the eco-toxicological level; it is therefore on these types of waste that the main challenges of the sector are currently focalised, aimed at identifying new frontiers for the treatment of matrices and for the production of novel generations of products, to be introduced in market segments not yet explored on a large scale.

In this sense, methods have been proposed to extract proteins from solid leather waste by alkaline [1] or acid [2] hydrolysis. Enzymatic hydrolysis has also been suggested as an alternative for obtaining products and raw materials through more sustainable processes [3,4]. However, these processes involve a waste of products which is not always compensated by the use of transformation products. Physical-mechanical treatments, on the other hand, are promising in terms of responding to the different needs connected to the treatment of solid waste, through processes that do not involve significant economic and environmental costs [5].

On the other hand, traditional leather finishing processes may cause a potential impact deriving from the use of synthetic polymers produced from non-renewable resources.

In response to these needs for minimizing sector impacts, the present study allowed to explore challenging and promising solutions for obtaining novel generations of finishings achieved through the use of micro and nano powders of tanned waste, obtained from ball milling.

2. Materials and Methods

2.1 Materials:

Samples of tanning waste: shavings and trimmings deriving from chrome, chrome-free and metal-free processing of sheep and goat skins for footwear and leather goods and bovine hides for the automotive industry

Finishing chemicals: Water-based polyacrylates and polyurethanes

Leathers: sheep and goat crast leathers for footwear and leather goods and bovine skins for automotive

2.2 Procedures for waste treatment:

The waste was treated using an ultracentrifugal miller (Retsch ZM-200) for 15 minutes at a speed of 12000 rpm; micro and nano-powders from shaving and trimming have been dispersed in finishing chemicals, and sonicated for 5 minutes using an ultrasonic tip at 100% power (model Hielscher UP400S); the finishing films with the addition of waste nano-powders were characterized and applied to bovine leather for automotive and sheep and goat leather for footwear and leather goods.

2.3 Characterization equipment:

X-ray diffraction (XRD) measurements were obtained with a Bruker D2 PHASER X-ray diffractometer instrument.

Scanning electron microscope (SEM) images were obtained using a TESCAN FIB SEM microscope and Zeiss EVO MA10 Scanning Electron Microscope (SEM)-INCA X-act detector.

The optical microscope images were obtained using Wild Heerbrugg Stereoscope equipped with OPTIKA Room B3 Digital Camera.

The infrared spectra were obtained using Perkin Elmer ATR-IR - Spectrum ONE - Spectrophotometer. And through Nicolet I50 from ThermoFisher.

The thermogravimetric analysis (TG-DTG) was conducted using a Mettler Toledo thermobalance from room temperature up to 1000°C (10 °C/min) in air flow.

The mechanical measurements were obtained using an Instron mod. 5967.

3. Results and Discussion

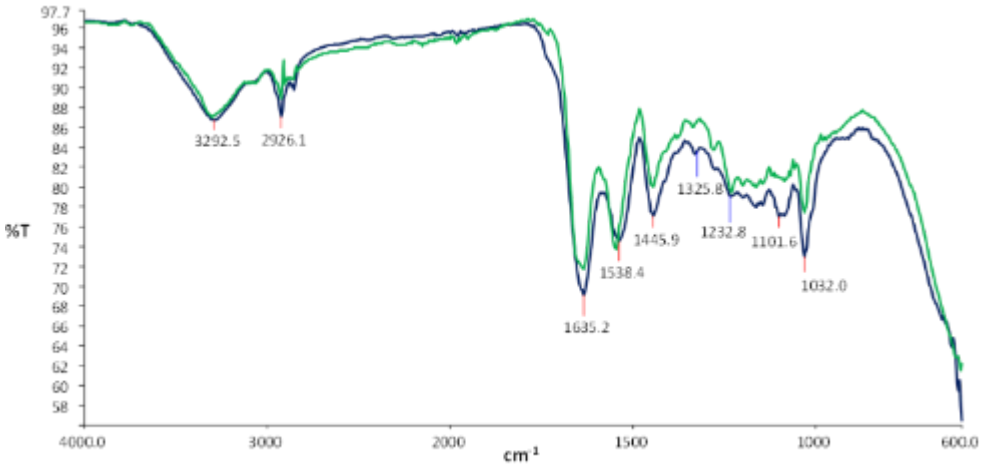
3.1 Waste treatment and characterization

The waste samples described in the previous session were treated for reduction into micro and nano-powders: the shavings starting from in the natural state; the trimmings after reduction into smaller pieces (squares of 2 cm per side) using a blade; all samples were then ground using an ultracentrifugal mill (Retsch ZM-200) for 15 minutes at a speed of 12000 rpm (Figure 1).



Fig.1: waste in original state and post miling treatment

The comparative analysis between original and milled samples, using ATR-IR analysis (Figure 2), highlighted a substantial conservation of the relative intensity ratios of the peaks characterizing the collagen structure. Particular attention, in this comparison, was dedicated to the analysis of specific signals: raw collagen normally shows a ratio between the amide III peak (1,240 cm^{-1}) and the peak at 1,450 cm^{-1} which is very close to 1.0, demonstrating the presence of the triple helix structure which is characteristic of collagen. The band close to 1,240 cm^{-1} is sensitive, in fact, to changes in the secondary structure of the tropocollagen (triple helix), while the band at 1,450 cm^{-1} corresponds to vibrations of the pyrrolidine rings of proline and hydroxyproline [6]. The substantial conservation of the relative intensity ratios of the peaks characterizing the collagen structure, suggesting a possible use of the obtained micro and nano-fibers to



provide properties of high added value to the surface of the leather.

Fig.2: overlap of ATR-IR spectra of treted (green) and native (blue) leather wastes

The TG-DTG profiles for the original waste and for the trated powders are showed in Figure 3. The TGA profiles of the obtained treated powders are generally similar to the profiles obtained for the original waste. Thermogravimetric profiles show different weight losses. In particular, the first weight loss between 30°C and 120°C can be attributed to the evaporation of water and small molecular substances. The temperature of denaturation and contraction of collagen can also be found in this temperature range. The two weight losses between 120°C and 380°C and between 380°C and 500°C can be associated with the decomposition of peptide bonds [7,8], as well as other organic-fatty fractions). For samples after milling, the water content is reduced for all samples by approximately 2%. This decrease is attributable to the volatilization of small molecular substances, water and volatile substances, etc.

Fig.3: TG-DTG profiles of ovine leather waste, before (left) and after miller (right) treatment

The morphology of the leather powders was examined by SEM analysis, as shown in Figure 4. The images highlight that the leathers, following the milling treatment, present morphologies similar to fibers and rods of variable length and with a diameter between 50 nm-5 μm.

Fig.4: SEM analysis of ovine leather waste, before (left) and after miller (right) treatment

3.2 Utilization of treated leather waste in finishing processing

The milled waste obtained was dispersed within the water-based finishing chemicals, at different concentrations (in the range from 1 to 100 mg/ml) and sonicated for 5 minutes using an ultrasonic tip at 100% power (model Hielscher UP400S). The visual examination suggested the excellent dispersion of the milled waste within the finishing chemical products, without requiring subsequent compatibility treatments, regardless of the type of waste used (animal origin and kind of tanning) (Figure 5).

The comparative examination of the spectroscopic profiles acquired by ATR-IR analysis of the samples highlights the presence, in the treated sample, beside of the chemical product, found to be based on polyacrylonitrile, also of signals relating to leather waste powder, with excellent repeatability, confirming optimal dispersion (Figure 6).

Fig.5: example of milled waste dispersion in a finishing chemical

Fig.6: overlap of the spectroscopic profiles (ATR-IR) of an acrylic-based finishing product (blue) and of the finishing with added nanopowder of leather waste (green)

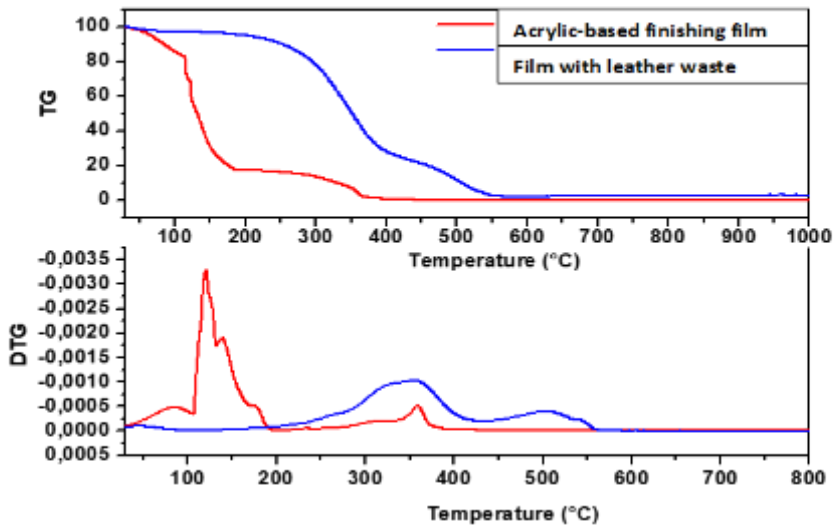


Figure 7 shows the TG-DTG profiles of the film carried out by evaporation of the solvent from the acrylic-based finishing chemical and of the film loaded with milled ovine leather waste (70 mg/ml); the first shows a weight loss up to 120 °C of approximately 80 wt.% attributable to physically absorbed water, and a second weight loss up to 350 °C with a residue of 0%; the second profile, relating to the product loaded with milled waste from a chrome free ovine leather, has a lower tendency to adsorb water and shows superior thermal stability compared to the original product, both at low and high temperatures. In this case the residue resulted to be 3%. Similar results have been obtained from other samples of waste used.

Fig.7: comparative TG-DTG profiles of finishing films

The mechanical strength of films obtained by adding different types of waste to the finishing products, was also evaluated, using an Instron dynamometer mod. 5967 (Table 1).

Sample Tipology	**Average values of Young E modulus [N/m^2]**
1 - Reference film – polyacrylate based finishing film (without waste added)	0.12
2 - Finishing film reinforced with waste from chrome-tanned leathers	1.83
3 - Finishing film reinforced with waste from chrome/zeolite-tanned leathers	2.19

Table.1: Average values of Young modulus for different kind of leather films

The presence of milled powders provides, in general, a substantial increase in the mechanical properties of the finishing, as expected, thanks to the optimal dispersion of powders obtained through the adoption of ball milling [6,9], suggesting the use of this approach in the direction of a circular economy aimed at determining an upgrading of materials for leather production. The following figures show, by way of example, the mechanical tests carried out on the reference film and, for comparison, on the film loaded with milled leather waste of the third type (mixed chrome-zeolite tanning with sheep waste, with reduced content of chrome) (Figure 8).

Fig.8: mechanical tests on the reference film and on the film reinforced with milled leather waste

3.3 Application of finishing reinforced with milled leather waste to leather samples

The finishing films thus obtained were then applied on samples of bovine leather for automotive and sheep and goat leather for footwear and leather goods, first on a laboratory scale, through the use of an airbrush, then on an industrial scale, in spray booths, using reinforced finishes, such as basecoat finishes, in order to verify the effectiveness of the approach studied in order to verify: the ability of the novel finishing films to fit uniformly to the leather surface, without modifying its aesthetic, product and sensorial properties; the ability of the novel circular finishing films to provide to leather greater mechanical resistance, macroscopically verifiable through industry standards.

By way of example, examining the section of one of the samples under an optical microscope highlights the ability of the composite material to form thin films (of the order of 20 microns) well fit to the surface of the leather (figure 9); regarding the features provided to the surface, as can be highlighted from figure 10, the finishes containing nano-powders were found to be able to preserve the product aspect, qualifying the natural surface, with evidence of all the typical morphological characteristics of the grain, comparable to those relating to untreated products (evidence of hair follicles, structure of the grain, etc.).

Furthermore, resistance tests to 1600 cycles of dry abrasion, according to the UNI EN ISO 17704 standard, have highlighted the ability of the composite finishes, with the addition of waste nano-fibres, to preserve the surface from evident signs of abrasion, which instead are visible on the sample treated with the polyacrylonitrile-based finishing polymer alone (figure 11).



Fig.9: section of a leather sample finished with the acrylic product with the addition of nano powder of leather waste

A

B

C

Fig.10: MO 16x - A: unfinished leather; B: leather sample finished with the acrylic-based product only; C: leather sample finished with the acrylic product with the of nano powder of leather waste

This evidence was confirmed by the experimentation of processes on an industrial scale, where the performance of leather for automotive, footwear and leather goods was tested, and where companies found the possibility of reducing the use of traditional chemical products (to the extent of 5 % to 20%, depending on the type of article and the amount of waste added), guaranteeing and improving at the same time the performance of the products up to 100%, in terms of abrasion resistance.

Fig.11: B1 and B2: optical microscope examination at 16x and 40x magnifications of the leather sample finished with the acrylic-based product only and subjected to 1600 abrasion cycles; C1 and C2: optical microscope examination at 16x and 40x magnifications of the leather finished with the acrylic product added with nano powder of leather waste and subjected to 1600 abrasion cycles

B1

B2

C1

C2

The minimization of chemical products has also led to a consequent reduction of volatile substances, with positive repercussions in eco-toxicological and environmental terms, as was found in the example in figure 12, concerning the comparative analysis of the VOCs of a sample with a traditional finishing, compared to one containing waste, with finishing of the same thickness, where in the example showed a reduction in VOCs of about 14% was highlighted.

A

B

Fig.12: Comparative VOCs analysis of a standard leather sample (A) and of a sample finished with the addition of leather wastes (B)

4. Conclusion

The study highlighted the effectiveness of the milling treatment for obtaining micro and nano-fibres from leather waste, characterized by excellent dispersion capabilities in common finishing products. The finishing films with waste additives showed improved mechanical and thermal properties. The application of these formulations containing waste to leather, for the development of novel generations of circular finishings allowed to develop sustainable and improved products in terms of performance, especially in terms of abrasion resistance. The industrial application of finishing has highlighted tangible effects, both in terms of savings in chemical products (of the order of 5%-20%), and in product sustainability, fostering the green and circular evolution of the *automotive*, footwear and leather goods sectors.

5. Acknowledgements

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