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High performance leathers finishing through zero waste and metal-free leather wastes valorization

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A contemporaneous functionalization of leathers and valorization of metal-free tannery waste was performed by reducing the waste into fine powders through mechanical grinding. The morphology of the milled wastes constited of fibers with diameters of a few microns (1–3 µm) and below. XRD analysis of leather powders confirms that even after the milling treatment, the leathers maintain retains its helical structure. The fibers were added to a finishing ink, and the resulting materials were characterized from different perspectives. The fibers containing finishing allows for better surface preservation, due to well-dispersed nanofibers filling the micropores of the coating, thus reducing the density of defects in the coating itself and improving the rubbing fastness. It should be noted that the presence of milled leather can impart color to the finished leather without requiring additional dyes. This approach results in cost-saving, and, more importantly, has positive environmental and ethical impacts.

Keywords Nanofibers, Leather waste valorization, Mechanical properties, Aesthetic/morphological aspect

Leather is a unique consumer material with numerous properties[1,2], including flexibility, softness[3,4], permeability to air and water vapor[5], excellent hygroscopicity and wearability, coupled with genuine and unique beauty, etc. Furthermore, it boasts the benefits characteristic of biomass materials, including biodegradability and exceptional biocompatibility. The manufacturing of leather, which is one of the oldest examples of circular economy, has been, indeed, one of the earliest activities of mankind, dating back to the Neolithic period[1,6,7]. Reports indicate that global leather production reached more than 20 billion square feet in 2020, underlining the significant potential of the leather industry[8–11]. On the other hand, with increased impetus on environmental protection worldwide, wastewater, sludge, and solid waste (up to 30% of processed leathers with a high content of chemicals) from tanneries have gradually become the three technological bottlenecks for the sustainable development of the leather industry[12–14]. Furthermore, the production cost of leather increases significantly, when addressing these eco-environmental issues, making traditional leather manufacturing more challenging. Although the developments in science and technology have made leather processing cleaner and more eco-friendly[15,16], it is key for leather manufacturing to enhance the value of the products with more competitive and performing properties along with cost preservation and reduction of wastes and environmental impacts[17–19]. Therefore, developing a green and easily implementable technology that can allow the recycling of waste products, typically rich in a lot of different chemicals, together with the introduction of new and fascinating properties, is a fundamental challenge with the potential to generate significant impacts[20]. The leather industry goes through many stages of processing before taking to the leathers the final form. Finishing, which is the last stage of leather processing[21], defines the leather's organoleptic dimension. Some characteristics such as softness, mechanical strength[22], and color[23–26] are established during tanning, re-tanning, and dyeing. However, it is during the finishing process that the look and function of the leather are defined, and its surface is both protected and refined. During chemical finishing, polymeric resins, caseins, waxes, pigments, and dyes are applied to the

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grain of the leather to impart the desired color, give brilliance, texture, and other organoleptic, physical, and commercial characteristics[27]. In general, finishing is a process aimed at improving surface resistance through some physical properties, fastness to abrasion, resistance to light and heat, etc. of leather products (such as bags, shoes, jackets, and upholstery leather). In particular, during this process, a homogeneous thin film, often polymeric, is formed on the leather surface. All these aspects make it a delicate and important phase, requiring thorough investigation, especially in terms of sustainable research and innovation.

Because of their resistance to hydrolysis, hardness, good adhesion, effective film-forming properties, and cost-effectiveness, acrylates are as the predominant commercial binders used in the leather industry[28,29]. These acrylic emulsion binders are mainly thermoplastic, characterized by a low glass transition temperature (Tg), which ensures optimal flexibility during use, along with strong pigment-binding capability[30]. Although they fulfil essential requirements such as resistance to abrasion, chemicals, water, and heat, they still exhibit relatively low adhesion and only moderate mechanical properties.

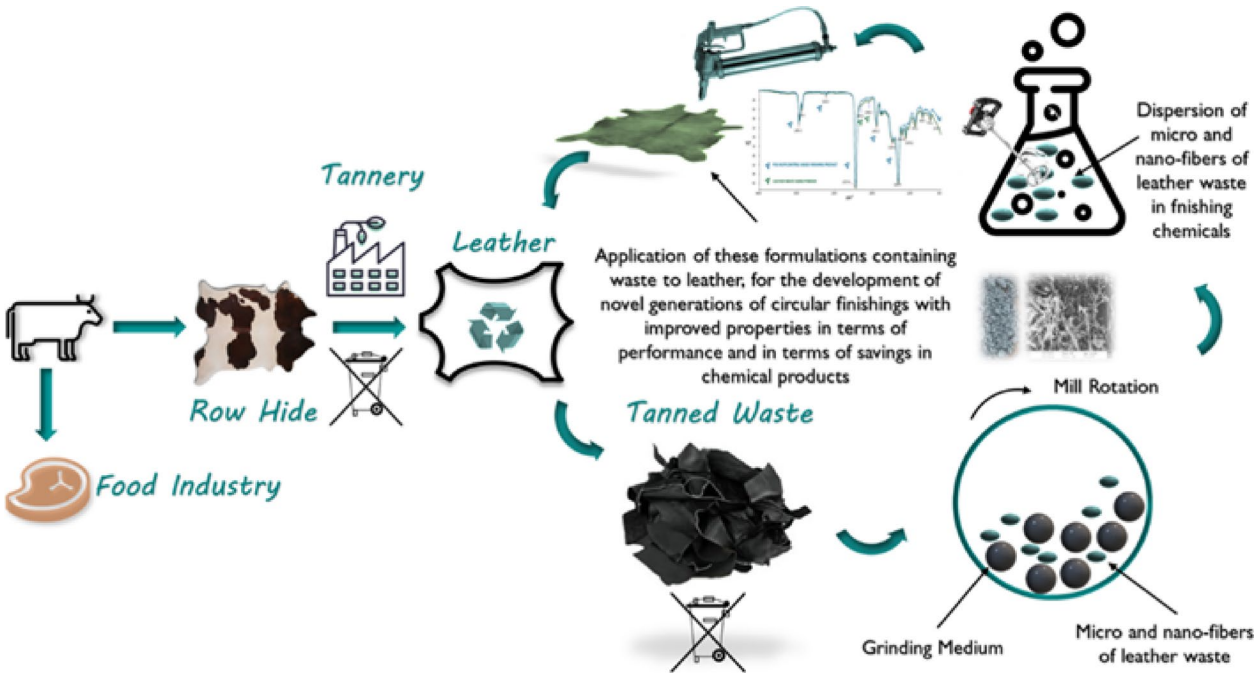
Leathers consist of collagen-rich tissues arranged in five hierarchical structures: the primary structure of amino acids, organized in an α-helix secondary structure, and in triple helix tertiary structure to form fibers (quaternary structure), in turn, to constitute a supramolecular aggregation[8]. One of the most explored and promising approaches to leather waste recycling consists of their use as composite fillers, following the model used for plant fibers[14,31,32]. In these cases, the main challenge lies the compatibilization of the fibers[31]. On the other hand, considering the fibrous nature of leather, another approach may consist in reducing it into fine fibers, as close as possible to nanometric dimensions, in order to exploit the properties of one-dimensional (1D) nanomaterials fibers whose length is significantly greater than their diameter. These structures exhibit a high surface-to-volume ratio, which is advantageous for integration into the finishing polymer. Proper homogenization can enable for conferring new properties, e.g. improved mechanical performance. Furthermore, this approach can be implemented directly within the tannery in a practical and sustainable manner, promoting zero-waste production and effective waste valorization (see Scheme 1). The resulting materials were then characterized from multiple perspectives, and an economic evaluation was also conducted to assess the impact of the proposed recycling strategy.

Experimental

Materials and methods

This paper describes the activities carried out toward innovative and eco-sustainable processes for the functionalization of leather and the valorization of waste materials. For this purpose, metal-free tannery waste was reduced to powder by mechanical grinding, avoiding the use of additional chemicals and complex procedures, and was easily dispersed in water-based finishing ink solutions.

Metal-free tanned leathers were selected not only due to their growing interest and usage in the leather industry but also for their compatibility with water-based polymer inks. Indeed, the molecules involved in metal-free tanning, during their interaction with collagen and subsequent polymerization, expose hydrophilic groups[33]. The same procedure can also be applied to chrome-tanned leathers, either through direct dispersion in hydrophobic media or following appropriate functionalization steps.



Scheme 1. Sustainable reuse of tanned leather waste for circular finishing applications.

The resulting nanofibres were thoroughly characterized from a chemical and physical standpoint, and, for comparison, they were also combined with previously studied and developed nanoparticles, as reported in Fierro et al.[34].

Materials

Leather wastes and polymer inks RP806/19 were used as received by the DMD tanning industry (Solofra, Italy). The water-based ink RP806/19 is a commercial leather finishing product containing an acrylic polymer binder. It is transparent and flexible, with good film-forming properties and excellent compatibility with hydrophilic components such as metal-free leather powder. Further details on the formulation are proprietary.

For the synthesis of the flower-like (FL) nanoparticles (NPs), the following reagents were used: deionized water, methanol, silver nitrate ($AgNO_3$, Sigma Aldrich > 99), titanium isopropoxide (Sigma Aldrich ≥ 99.9), tetraethyl orthosilicate (TEOS, Sigma Aldrich > 99%), (3-Aminopropyl)triethoxysilane (APTES), cyclohexane, ammonia hydroxide, oleic acid, 1,2 hexadecanediol, benzyl ether, ethanol, and other chemicals, which were acquired from Sigma Aldrich. All chemicals were of analytical grade.

The metal-free tanned dyed crust leathers used in this study are characterized by the presence of hydrophilic functional groups, such as carboxyl and hydroxyl groups, introduced during the synthetic tanning process. These functionalities enhance compatibility with water-based systems and facilitate fiber dispersion within the polymer ink.

Although the majority of leather production waste derives from chrome tanning, we specifically selected metal-free tanned leather waste due to its increasing use in sustainable tanning practices and its compatibility with water-based polymer systems. The hydrophilic functional groups exposed by the synthetic tanning agents facilitate direct dispersion into the finishing ink without the need for additional treatments.

Methods

Methods of preparation

Preparation of the leather fibers The leather waste, provided by DMD Solofra, was first cut into small pieces of useful dimensions by a blade (5–10 cm in length and 2–3 cm in width). Subsequently, the pieces were frozen in liquid nitrogen and ground using an ultracentrifugal miller (Retsch ZM-200) for 15 min at a speed of 12,000 rpm.

Flower-like nanoparticles Flower-shaped NPs, where "pistil" and "petals" give distinct functions, were prepared, as reported in[34], to take advantage of the different NP properties but also enhancement/amplification of these properties due to the heterojunctions between nanoparticles.

Preparation of polymer ink films and polymer ink films containing fibers The obtained milled leathers were dispersed into the water-based finishing ink RP806/19, which contains an acrylic polymer binder based on polyacrylonitrile, at a concentration ranging from 10 to 70 mg/mL. The dispersion was carried out under sonication for 5 min with an ultrasonic tip at 100% power (Hielscher UP400S model). The resulting mixtures were then used to prepare cast films.

Preparation of polymer inks and finishing procedure The resulting milled leather powders were dispersed into the water-based ink RP806/19 at concentrations ranging from 10 to 70 mg/mL, using an ultrasonic tip (Hielscher UP400S model) operated at 100% power for 5 min. A paint spray gun (5 atm), loaded with 10 ml of the finishing mixture, was used to apply the coating to the leather, ensuring complete surface coverage. The operation was carried out by a specialized operator, moving the jet on the sample with first horizontal and then vertical movements until the entire areas were covered. This process involved alternating between spray and drying cycles for a total of four spray passes.

The finishing coat formulation consisted of the water-based acrylic ink RP806/19, into which milled leather powders (sample D2) were dispersed at concentrations between 10 and 70 mg/mL. 5 mg/mL of flower-like nanoparticles were added in selected formulations to enhance aesthetic and functional properties. No additional additives or compatibilizers were necessary.

Characterization

A Hunter colorimeter was used for color measurements (Hunter Lab Color Flex CFLX 45 – 2). The color of the film was expressed as lightness (L*), redness (a*) and yellowness (b*) values. A standard white color plate was used as a reference to calculate the color difference (ΔE).

Dry abrasion resistance tests were performed for 1600 cycles, in accordance with the UNI EN ISO 17,704 and ISO 17,076 standards.

Mechanical tests were performed with a PCE-FB TW (PCE Instruments).

For structural and morphological characterization, the following techniques were used: X-ray diffraction (XRD) measurements were carried out using a Bruker D2 X-ray diffractometer with CuKα radiation. Scanning Electron Microscope (SEM) images were obtained with a TESCAN-VEGA LMH (230 V), coupled with an Energy Dispersive X-ray Spectroscopy (EDS) probe. The samples, without any pre-treatment, were covered with a 50 Å thick chromium film using a sputter coater (QUORUM 150 T). For the thermogravimetric studies (TG-DTG), a TGA 2 (METTLER TOLEDO) was used under an air flow at a rate of 10 °C/min.

FT-IR spectra were obtained using a Nicolet iS50 FT-IR spectrometer operating in ATR mode. Samples were placed on a diamond ATR crystal and data were collected in transmittance mode (%T), with a resolution of 4 cm^{-1} and 32 scans, over the spectral range of 4000–400 cm^{-1}.

Results and discussion

Waste and fiber characterization

The as-received samples are shown in Fig. 1. These are waste from leather processing. Among them, samples D1, D2, and D3, which were metal-free tanned at different processing stages (as tanned, after color consolidation and after finishing treatment), were selected for further study. The procedure for powder reduction is illustrated in Fig. 2, which also includes photographs of the powders obtained after the milling process.

The morphology of the milled D1, D2, and D3 was analyzed by scanning electron microscopy (SEM), as shown in Fig. 3. The samples consist of fibers organized in bundles, from which straighter segments emerge, allowing the measurement of diameters in a range of a few microns (1–3 μm) and below. Figure 4 presents the thermal characterization of leather samples before and after milling. The TGA profiles of the leather powders are generally comparable to those of the corresponding raw wastes. The thermogravimetric curves reveal distinct stages of weight loss. In particular, the initial weight loss, occurring between 30 °C and 120 °C, is attributed to the evaporation of water and the release of low molecular weight substances. The two subsequent weight losses, observed between 120 °C and 380 °C and between 380 °C and 550 °C, correspond to the decomposition of peptide bonds[35,36]. As shown in Fig. 4a, the weight loss associated with absorbed water, bound water, and small

Code	Origin/Stage
D1	free metal tanning
D2	free metal tanning + dyed retanning
D3	free metal tanning + finished

Fig. 1. Photograph of processing wastes as received from the tannery, at the top. Photos of the distinct classified materials, at the bottom.

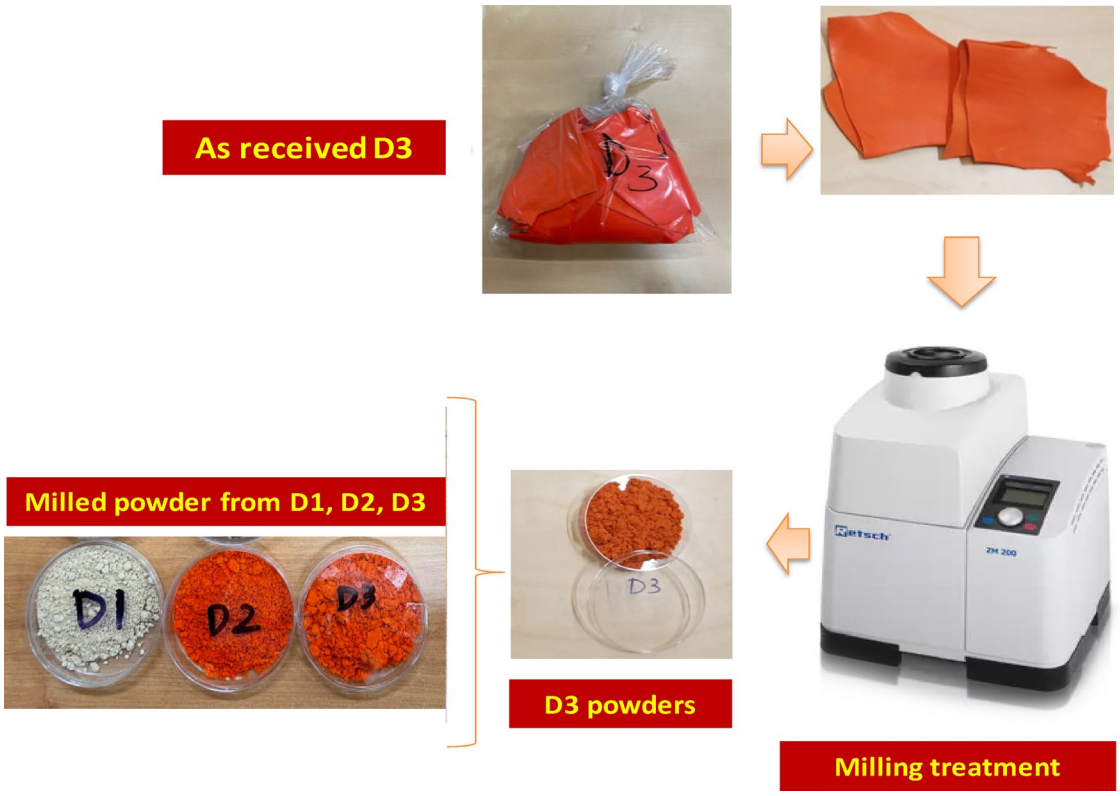


Fig. 2. Leather powders preparation procedure.

molecular substances is approximately 8% for the D1, D2, and D3 samples. For the milled samples (Fig. 4b), this value decreases by around 2%, likely due to the volatilization of small molecules and water, as well as partial degradation of polar functional groups during the grinding process. Notably, the thermogravimetric analysis revealed a differentiated thermal response between the tanned (D1) and retanned (D2) leather samples, both before and after milling. In the case of the metal-free tanned leather (D1), the untreated (whole) sample exhibited higher thermal stability than the corresponding milled form. This decrease in stability can be ascribed to the greater exposure of collagen fibers to thermal degradation following mechanical disruption, which facilitates the loss of volatile components and the cleavage of weaker chemical bonds. Conversely, for the retanned leather (D2), the milled sample displayed enhanced thermal stability compared to its whole counterpart. This improved stability is likely a result of the higher degree of chemical crosslinking introduced during the retanning process, which leads to a denser, more thermally resistant molecular network. Furthermore, during milling, the loss of polar volatile groups and the increased relative content of thermally stable carbonaceous components[37], further contributing to the enhanced thermal behavior.

Figure 5 shows the FTIR spectra of the as-received samples, and after the milling treatment. The FT-IR spectra of the leathers, in Fig. 5a, showed vibrational bands around 3295 cm^{-1}, probably due to the combined effect of the N–H and O–H groups. Furthermore, bands at 2922 cm^{-1} and 2850 cm^{-1} are observed, corresponding to the asymmetric and symmetric stretching vibrations of C-H groups. The characteristic amide I and II vibrations are present at 1623 cm^{-1} and 1556 cm^{-1}, respectively. After the milling treatment, the leather powders exhibit slightly shifted vibrational bands compared to the raw leather. FT-IR of the powders, shown in Fig. 5b, reveals bands at 3300 cm^{-1}, 2926 cm^{-1}, 2851 cm^{-1}, 1625 cm^{-1}, and 1551 cm^{-1}, indicating that the primary molecular structure of the powders, attributable to collagen, remains intact. Moreover, no new bands were detected in the spectra of the powders, suggesting that the milling process does not induce chemical modification. The observed shift from 3295 cm^{-1} to 3300 cm^{-1} can be attributed to the transformation of strong hydrogen bonds into weaker ones, as induced by the mechanical stress of the milling process[38,39].

Leathers are characterized by collagen fibers, which contain triple-helical structures with good orientation and high crystallinity. The XRD analysis of leather powders after the tanning and finishing processes is shown in Fig. 6. In XRD spectra, typical features include a peak at 22°, corresponding to the distance between the peptide chain of the collagen fibers, and a weaker peak around 28°. The presence of these peaks confirms that even after the triple-helical collagen structure is preserved even after the milling process.

Polymer ink films and polymer ink films containing fiber characterization

Figure 7a, on the left, shows a photo of the "ink + milled D2" (30 mg/mL), as cast and prior to drying, which highlights the excellent dispersion of the milled leathers within the ink, without the need for additional compatibilization treatments. The central image (Fig. 7b) shows the cast films obtained using the ink alone

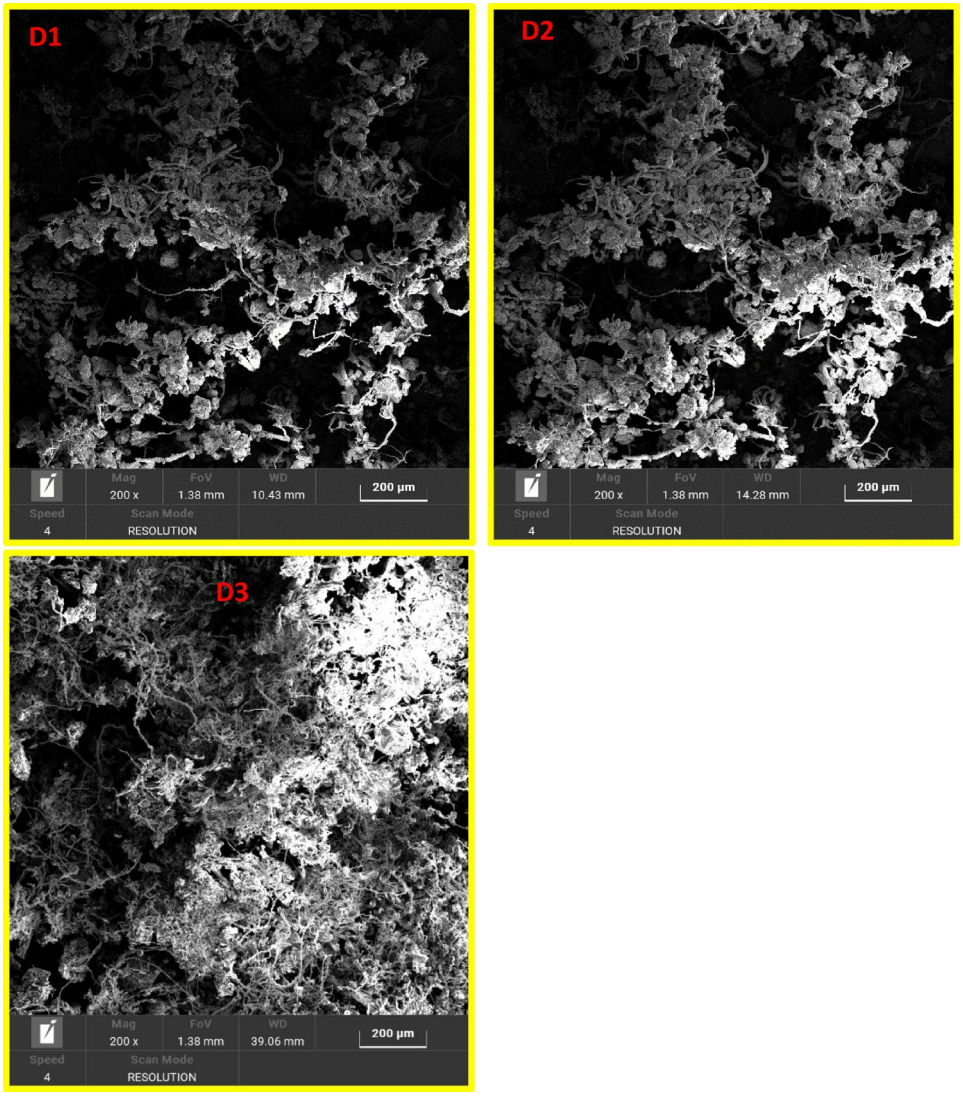


Fig. 3. SEM images of D1, D2 and D3 after milling.

and the ink loaded with D2 milled powders at a concentration of 70 mg/mL. On the right, Fig. 7c presents a comparison between leather finished with RP806/19 ink containing dyes (sample D2) and white leather finished with RP806/19 ink loaded with milled D2 powders (70 mg/mL). It is worth noting that the presence of milled leather can impart color to the finished leather without the need for additional dyes (see also Table 1). In contrast, the use of uncolored ground wastes does not confer additional coloration to the finishing ink. The red coloration visible in Fig. 7b (right) and Fig. 7c results from the use of red-dyed leather waste (sample D2) and pre-dyed substrate.

Mechanical tests

Additionally, the mechanical properties of the finishing films were evaluated following the incorporation of D2 fibers. To determine the longitudinal elasticity of each sample, Young's modulus (E) was calculated based on the tension (S) and deformation (ε) values experienced by the material, as shown in Table 2. Table 2 reveals a notable increase in the E modulus after the fibers were incorporated, indicating an overall improvement in mechanical performance. The observed improvement in mechanical properties, despite the low fiber loading (10–30 mg/mL), can be attributed to the fine dispersion and high specific surface area of the milled leather fibers. These fibers interact effectively with the polymer matrix, reinforcing the film structure by filling micropores and reducing defect density.

TG-DTG characterization

Figure 8 shows the TG-DTG profiles of RP806/19 polymer film and RP806/19 polymer ink film containing milled D2 powders. The RP806/19 profile exhibits an initial weight loss of approximately 80 wt% before 200 °C, attributed to the evaporation of absorbed water. This is followed by a second weight loss, with an endset at 410 °C and a residue of about 0%. The profile of RP806/19 film containing milled D2 fibers shows a lower water

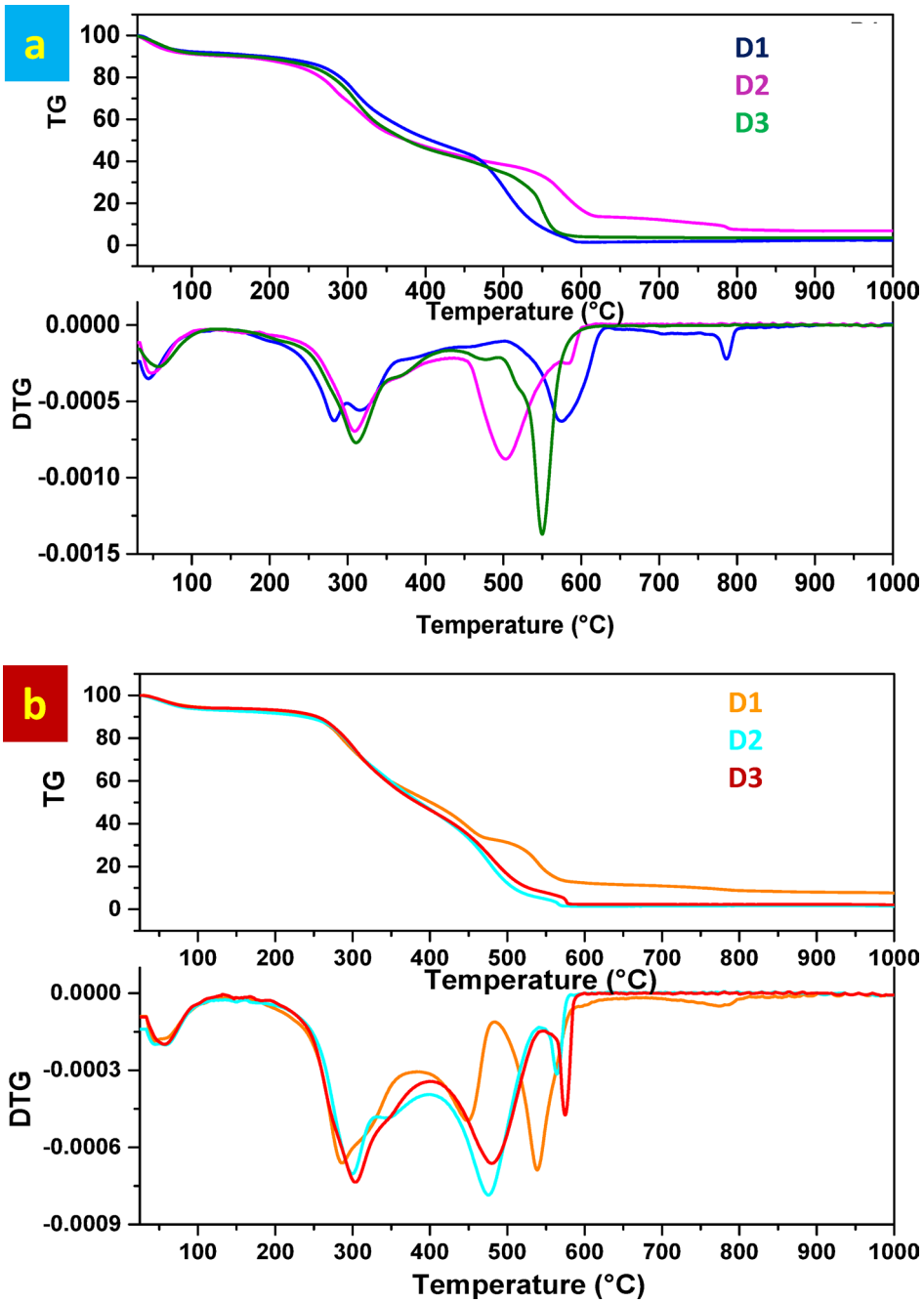


Fig. 4. TG-DTG analysis of leathers before (**a**) and after (**b**) the leather milling.

content and enhanced thermal stability, as indicated by the shifted endset temperature of the main degradation step, occurring between 200 °C and 430 °C. An additional weight loss is observed at higher temperatures, likely due to the presence of the added fibers. The final residue, about 2%, observed in the TGA analysis of the film containing D2 fibers, is attributed to residual inorganic components present in the D2 leather powders. These may originate from industrial additives or pigments used during the wet-finishing or dyeing processes, despite the leather being metal-free tanned.

Analysis of the product characteristics and performance of the finished leather

The comparative analysis of the spectroscopic profiles acquired by ATR-IR of a leather sample finished with the acrylic-based product RP 806/19 only (blue profile) and a sample finished with RP 806/19 containing D2 powders (10 mg/ml) (green profile) highlights the presence, in the latter, not only of the characteristic polyacrylonitrile-based signals but also of additional bands associated with the D2 leather powders (Fig. 9).

The comparative examination of the sections from goat leather finished with RP 806/19 and with RP 806/19 containing D2 powders (10 mg/ml), carried out via optical microscopy, demonstrates the ability of the

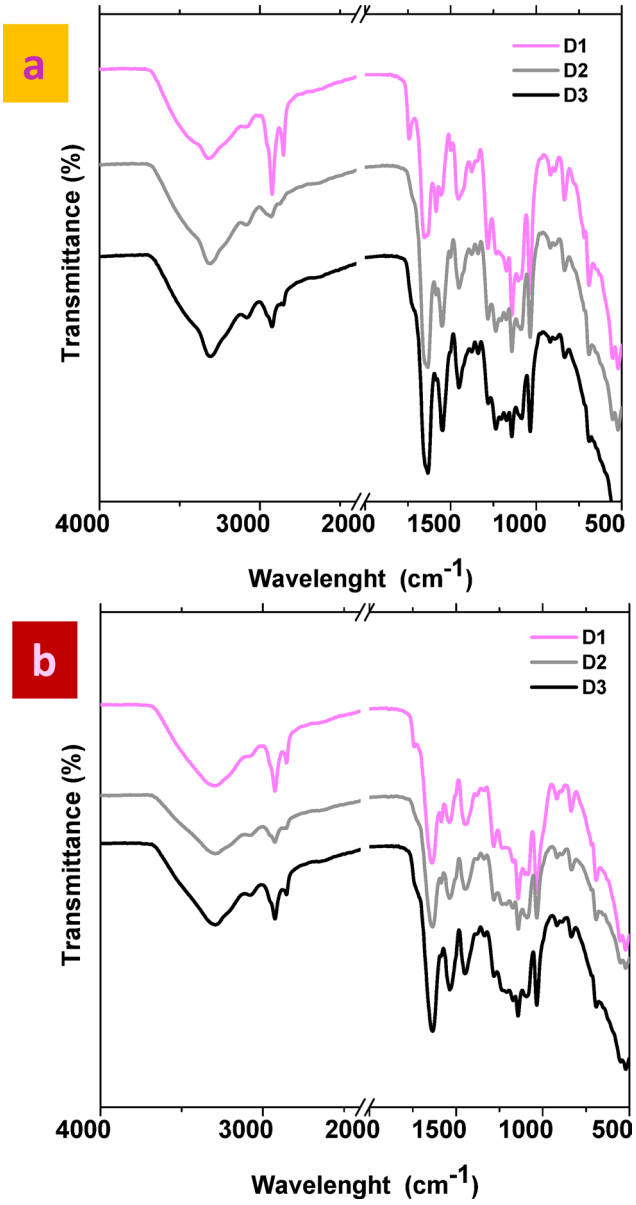


Fig. 5. FT-IR of D1, D2, D3 before (**a**) and after (**b**) milling.

composite system to form thin films with an average thickness of approximately 20 µm (ranging from 18 to 22 µm), well adhered to the leather surface (Fig. 10). As shown in Fig. 11, the presence of waste powders in the finishing formulation contributes to preserving the natural appearance of the leather surface, maintaining all typical morphological features of the grain. This is evident in Fig. 11a and c (first row), and 11d (first row). In particular, the surface treated with D2 fibers appears more homogeneous and glossy, while still retaining the original texture, such as visible hair follicles and the natural grain structure. Lastly, dry abrasion resistance tests (1600 cycles) according to UNI EN ISO 17,704 standard show that the finishing layer containing waste fibers helps preserve the surface integrity. Leather samples finished without D2 (Fig. 11c, second row) exhibit large abraded areas at 16X magnification, which are not present in samples treated with D2 powders (Fig. 11d, second row). Further magnified images (third row, Fig. 11c and d) reveal more pronounced abrasion marks on the polymer-only samples. These improvements are likely due to the presence of well-dispersed nanofibers within the finishing layer, which fill the micropores of the polymer coating, reduce defect density, and improve rubbing fastness.

Figure 11b shows an image of a leather surface finished with RP 806/19 containing both D2 fibers and flower-like nanoparticles[34]. The surface appears even more refined in terms of morphology and aesthetics, likely due to the LSPR (localized surface plasmon resonance) effect of the NPs, which may also benefit from the other properties, given by these particles, as described in the experimental section. The top coat appeared homogeneous and brilliant, as confirmed by optical microscopy (Fig. 11) and visual inspection. This enhanced surface quality was also supported by the organoleptic evaluation (Table 3), where samples finished with fiber-

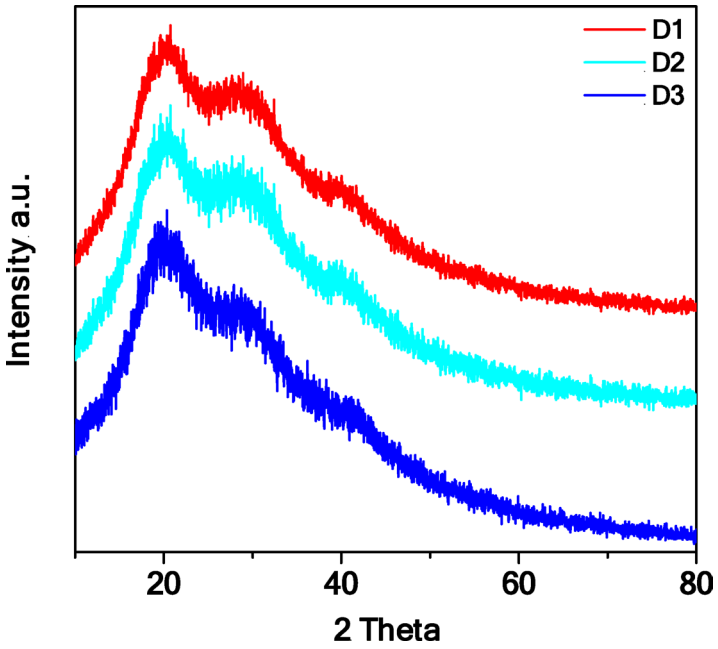


Fig. 6. XRD spectra of the D1, D2, and D3 after milling.

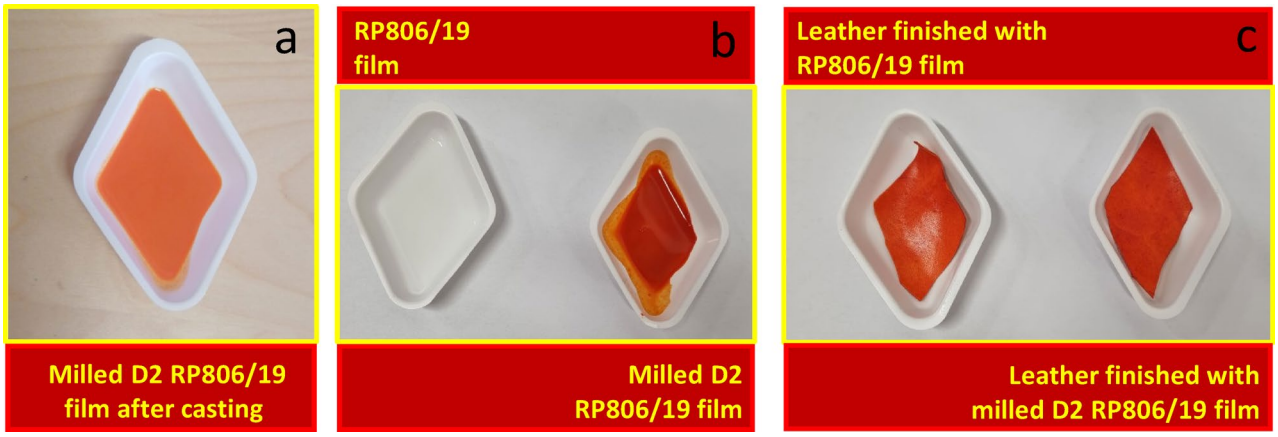


Fig. 7. Photos of: as casted milled D2 in RP806/19 solution (**a**); film of polymer ink RP 806/19 and polymer ink containing milled D2 powders (**b**); a leather finished with RP806/19 and with milled D2 in RP806/19 (**c**).

Samples	L*	a*	B*	ΔE
As-received D2	61.4 ± 0.15	7.2 ± 0.07	9.72 ± 0.16	3.08 ± 0.85
White leather finished with milled D2 RP806/19	60.7 ± 0.15	5.9 ± 0.11	9.12 ± 0.16	3.01 ± 0.42

Table 1. Films color comparison: traditional finishing and fibres contained finishing. The asterisk serves to distinguish these chromatic axes from ordinary letters, highlighting that they are standardizedvalues in a specific color space. It does not have a mathematical value, but is a typographic convention used toindicate that these are Lab coordinates, rather than generic ones.

containing formulations received higher scores in terms of overall appearance and uniformity. This, ultimately, suggests considering the addition of well-dispersible organic, including waste, and eventually small quantities of inorganic materials with specific properties, in finishing polymers, for innovative products capable of supporting the competitiveness of the tanning industry. To complement the analytical and morphological characterizations, a qualitative organoleptic evaluation was carried out by five experienced tanners. The assessment focused on four key parameters: texture, flexibility, fullness, and overall appearance, with scores assigned on a scale from

Samples	S_y (Pa)	ε_y (%)	S_b (Pa)	ε_b (%)	$E = \sigma/\varepsilon$ (GPa)
Polymer film	8.18E + 07	9.09 ± 1.9	1.81E + 08	> 100	0.91 ± 0.19
Polymer film containing D2 (10 mg/mL)	1.30E + 08	6.90 ± 0.3	2.97E + 08	> 100	1.89 ± 0.19
Polymer film containing D2 (30 mg/mL)	2.06E + 08	5.10 ± 0.4	12.99E + 08	> 100	4.05 ± 0.32

Table 2. Mechanical properties of the films.

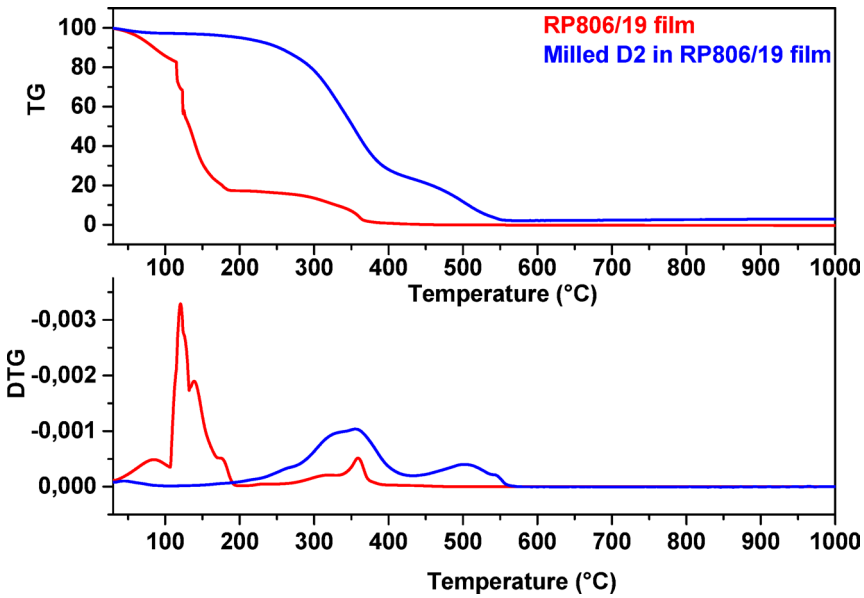


Fig. 8. TG-DTG analysis of RP 806/19 polymer film and RP806/19 polymer ink containing milled D2 powders.

1 (poor) to 5 (excellent). The results, averaged across all evaluators, are presented in Table 3. This evaluation confirms that the leathers finished with D2 fibers show enhanced tactile and visual quality compared to the control. In particular, the treated samples were perceived as more uniform in appearance, fuller, and softer, which are highly desirable characteristics in commercial leather products.

Furthermore, abrasion resistance tests in accordance with ISO 17,076 were carried out (Table 4), confirming that the incorporation of D2 fibers improves the mechanical resistance of the finishing layer, as shown by smaller differences in grey scale values. An analysis was also carried out to evaluate the possibility of finishing film thickness reduction at the same performances, observing that it is possible to reduce the thickness by 20% without compromising the durability and quality of the finish, compared to that obtained with the ink alone.

Analysis and economic evaluation

An economic evaluation was also carried out, not because the cost of waste disposal is particularly significant, as the impact is mainly environmental and ethical, but rather to assess the impact of the proposed recycling, which involves freezing/grinding and sonication steps.

For example, Table 5 presents data on the quantity of leather waste produced by a tannery processing 900,000 leathers annually (year 2022, DMD-Solofra Italy). In particular, the analysis aimed at a quantitative assessment of waste reuse in the finishing phase. Based on the data reported in the middle rows of Table 5, the amount of waste that can be reused for finishing all the produced leathers was calculated. As a result, the entire annual waste could therefore be completely reused, in accordance with the principles of the circular economy, thus avoiding solid waste disposal.

An economic comparison between waste recovery and disposal was also performed. Assuming a working year of 220 days and 8-hour shifts, the total annual disposal cost was estimated (Table 5, lower row). On the other hand, Table 6 provide an evaluation of the costs related to the milling and sonication operations, to which the cost of liquid nitrogen must be added. Based on experimental data and time requirements, an average amount of 0.1 L of nitrogen per kg of waste would be needed, resulting in 834 L per year. At a cost of 0.61 €/L, this corresponds to 509 €/year. Moreover, as highlighted in the last column of Table 6, this advantageous economic evaluation is further supported by the possibility of reducing the thickness of the finishing layer, thanks to improved mechanical performance, which leads to additional savings in finishing chemical products.

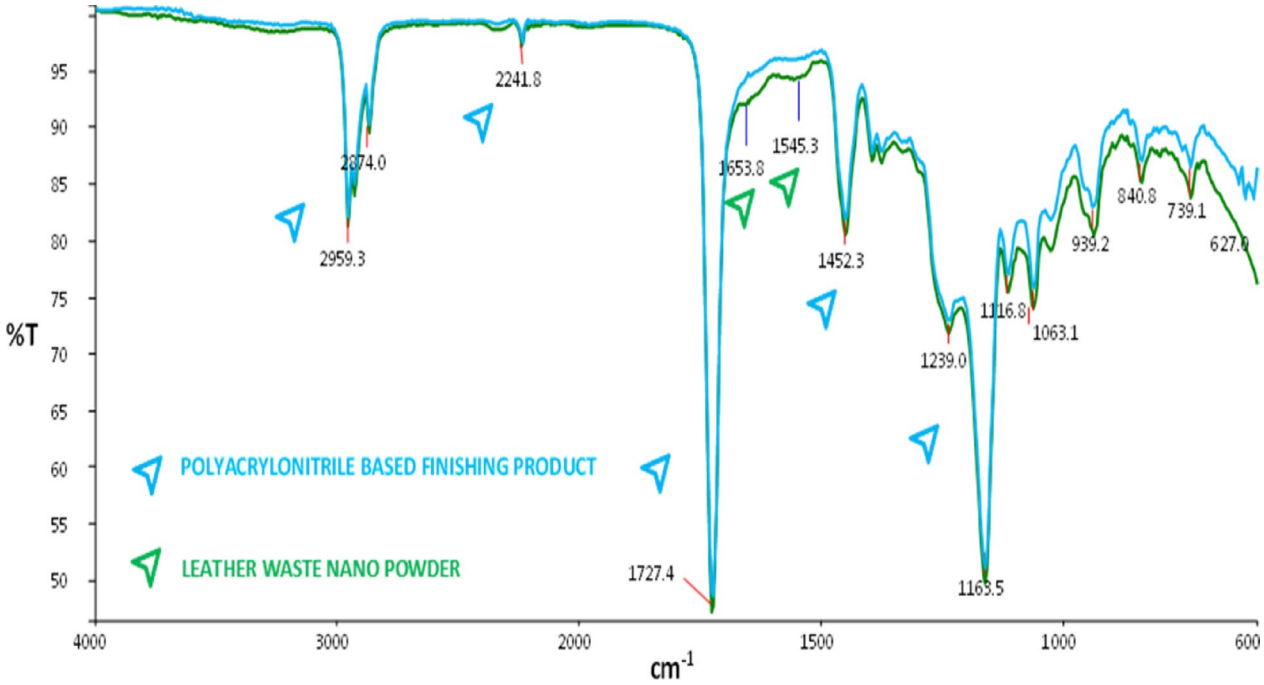


Fig. 9. Overlay of the spectroscopic profiles (ATR-IR) of a leather sample finished with the acrylic-based product RP 806/19 only (blue profile); and, of a sample finished with RP 806/19 containing D2 powders (10 mg/ml) (green profile).

Conclusion

Leather waste was characterized before and after milling. The ultracentrifugal milling technique, as a mechanical treatment, does not require the use of chemical reagents and allows the leather to be reduced into powdered fibers. This approach avoids time-consuming and costly separation and purification steps. The chemical/physical characterization of the powdered fibers highlights the preservation of the collagen structure after milling. The fibers, whose size ranges between a few microns and a few hundred nanometers, according to SEM characterization, can be easily dispersed in water-based finishing inks without further modifications, thanks to residual hydrophilic functional groups present on the collagen fibers following metal-free tanning. The easy dispersion of the fibers in finishing inks is confirmed by the formation of homogeneous polymer films, which exihibit improved mechanical and thermal properties, as well as interesting color characteristics. The comparative examination of finishing performed with ink alone and fibers-loaded ink highlights the ability of the composite material to form thin, continuous films in close contact with the leather surface. The addition of fibers during the finishing phase further enhanced the aesthetic and morphological quality of the surfaces, which were found to be more homogeneous and brilliant, while retaining all the original characteristics of the natural leather grain, commonly known as the "flower" in the leather industry, such as visible hair follicles and the original dermal texture. Leathers finished with ink alone, already at 16X magnification, show evident large abraded areas, which are absent in sample finished in presence of the fibers. The economic evaluation results are advantageous, especially considering the possibility of reducing the finishing thickness, due to the improved mechanical performance, which implies a reduction in the cost of chemicals used in finishing.

Overall, our findings suggest considering the addition of well-dispersible organic materials, including waste, and small quantities of inorganic materials with specific properties, into finishing polymers, to develop innovative products capable of enhancing the competitiveness of the tanning industry.

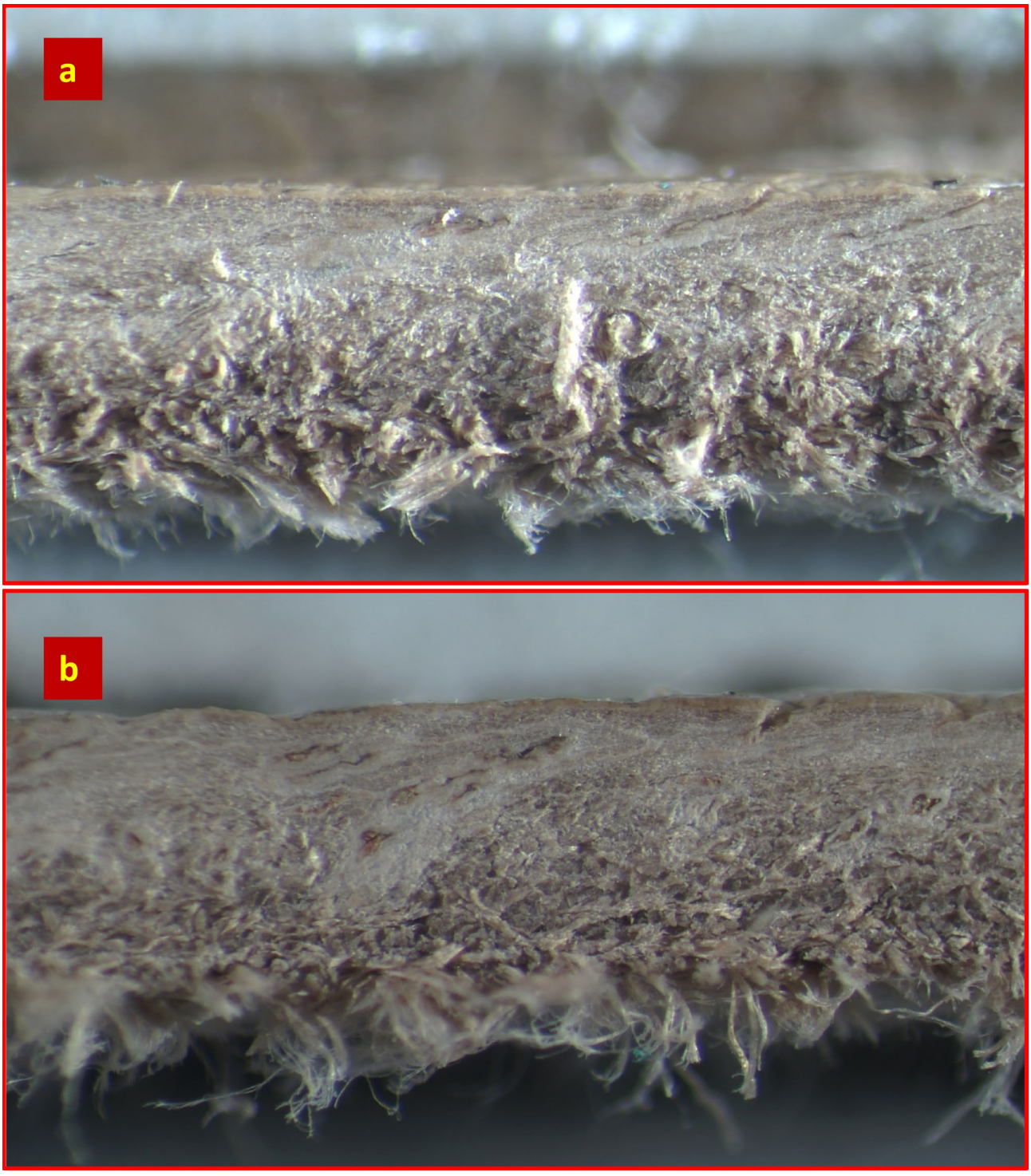


Fig. 10. Sections of a goat skin finished with RP 806/19 (**a**), and with RP 806/19 containing D2 powders (10 mg/ml) (**b**).

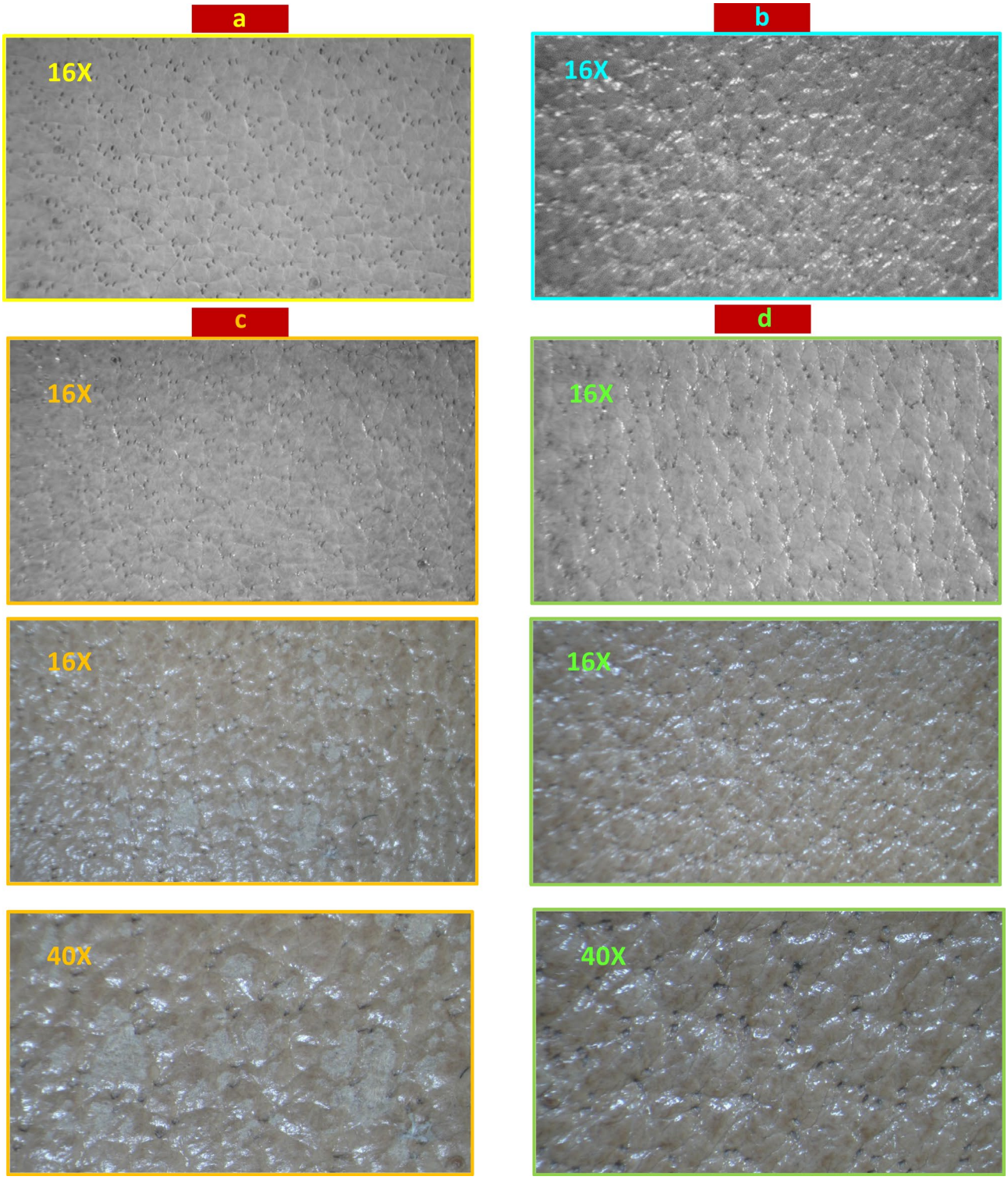


Fig. 11. Leather before finishing (**a**); finished leather with RP 806/19 containing D2 (10 mg/mL) and FL nanoparticles (5 mg/mL) (**b**); finished leather with RP 806/19 before (1st line at 16X) and after (2nd line at 16X and 3th line 40X) 1600 abrasion cycles (**c**); finished leather with RP 806/19 containing D2 (10 mg/mL), before (1st line at 16X) and after (2nd line at 16X and 3th line 40X) 1600 abrasion cycles (**d**).

Sample	Texture (1–5)	Flexibility (1–5)	Fullness (1–5)	Overall appearance (1–5)
Control (RP806/19 only)	3.6 ± 0.5	3.4 ± 0.6	3.2 ± 0.4	3.5 ± 0.5
Treated (RP806/19 + D2 fibers)	4.4 ± 0.4	4.2 ± 0.5	4.3 ± 0.3	4.6 ± 0.4

Table 3. Organoleptic assessment of leather samples (average ± standard deviation, $n = 5$). Scale: 1 (poor) to 5 (excellent).

Sample	Gray scale chromatic difference between the various grey pairs at time 0 and after 100 cycles*
RP 806/19	3
RP 806/19 containing D2 powders (10 mg/ml)	4

Table 4. Abrasion resistance tests (ISO 17076). *1 = significant variation (worst rating) and 5 = no variation (best rating).

Type of waste	Description	(kg/year)	(€/kg) for disposal
CER 04.01.08	Leather scraps: crust + simple finishing	8340	1.85

Product: number of leathers	900,000
Surface area of one leather	0.54 m^2
Square meter of leathers produced in 2022	486,000 m^2

Leather waste in 500 ml[§], [mg/mL]	Leather waste for finishing of a one leather surface, (g)	Leather waste for finishing of one year production (kg)
10	5	4500
50	25	22,500
70	35	31,500
100	50	90,000

Leather waste, (Kg/year)	Leather waste, (kg/day)	(€/kg) Average	Disposal costs, (€,year)
8340	38	1.85	1,5429.00

Table 5. Leather waste referring to the year 2022. Disposal cost evaluation, year 2022. [§]250 mL water and 250 mL finishing ink

Miller consumption, (KW)	Gross cost of electricity[@], [€/kWh]	Electricity cost, (€/h)	Electricity cost per day, (€) (4 h)	Waste/day, (kg)	(€, year)
1.3	0.3273	0.42	1.3	100	283.00

Sonication consumption, (KW)	Gross cost of electricity[@], (€/kWh)	Electricity cost, (€/h)	Electricity cost per day, (€)	(€, year)
0.4	0.3273	0.13	1.04	228.00

Table 6. Ultracentrifugal miller costs (Retsch ZM 200). Sonication dispersion costs. [@]https://luce-gas.it/business/offerte/costo-kwh-aziende.

Data availability

The datasets used and/or analysed during the current study available from the corresponding author on reasonable request.

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References

1. Wegene, J. D. & Thanikaivelan, P. Conducting leathers for smart product applications. *Ind. Eng. Chem. Res.* **53**, 18209–18215 (2014).
2. Gautieri, A., Vesentini, S., Redaelli, A. & Buehler, M. J. Hierarchical structure and nanomechanics of collagen microfibrils from the atomistic scale up. *Nano Lett.* **11**, 757–766 (2011).
3. Alexe C.A. et al. Multifunctional leather surfaces coated with nanocomposites through conventional and unconventional methods. *Mater. Today: Proc.* **54**(Part 1), 44–49 (2022).
4. Velmurugan, P., Lee, S. M., Cho, M., Park, J. H. & Oh, B. T. Antibacterial activity of silver nanoparticle-coated fabric and leather against odor and skin infection causing bacteria. *Appl. Microbiol. Biotechnol.* **98**, 8179–8189 (2014).
5. Akalović, J., Skenderi, Z., Rogale, S. F. & Zdraveva, E. Water vapor permeability of bovine leather for making professional footwear. *Leather Footwear* **67**, 12–17 (2018).

6. Falcão, L. & Araújo, M. E. M. Vegetable tannins used in the manufacture of historic leathers. *Molecules* **23**, 1081 (2018).
7. Muthukrishnan, L. Nanotechnology for cleaner leather production: a review. *Environ. Chem. Lett.* **19**, 2527–2549 (2021).
8. Wang, Y. et al. Advanced collagen nanofibers-based functional bio-composites for high-value utilization of leather: A review. *J. Science: Adv. Mater. Devices*. **6**, 153–166 (2021).
9. Chojnacka, K. et al. Progress in sustainable technologies of leather wastes valorization as solutions for the circular economy. *J. Clean. Prod.* **313**, 127902 (2021).
10. Muralidharan, V., Palanivel, S. & Balaraman, M. Turning problem into possibility: A comprehensive review on leather solid waste intra-valorization attempts for leather processing. *J. Clean. Prod.* **367**, 133021 (2022).
11. China, C. R. et al. Alternative tanning technologies and their suitability in curbing environmental pollution from the leather industry: A comprehensive review. *Chemosphere* **254**, 126804 (2020).
12. Dang, X., Yuan, H. & Shan, Z. An eco-friendly material based on graft copolymer of gelatin extracted from leather solid waste for potential application in chemical sand-fixation. *J. Clean. Prod.* **188**, 416–424 (2018).
13. Venkatesan, N., Krishna, A., Nishad, N. & Fathima Leather solid waste derived activated carbon as a potential material for various applications: A review. *J. Anal. Appl. Pyrol.* **176**, 106249 (2023).
14. Senthil, R. et al. Recycling of finished leather wastes: A novel approach. *Clean Technol. Environ. Policy***17**, 187–197 (2015).
15. Hu, W. & Deng Application of supercritical carbon dioxide for leather processing. *J. Clean. Prod.* **113**, 931–946 (2016).
16. Kanagaraj, J., Senthilvelan, T., Panda, R. C. & Kavitha, S. Eco-friendly waste management strategies for greener environment towards sustainable development in leather industry: A comprehensive review. *J. Clean. Prod.* **89**, 1–17 (2015).
17. Selvaraj, S., Ramalingam, S., Parida, S. & Raghava Rao, J. Fathima Nishter, chromium containing leather trimmings valorization: Sustainable sound absorber from collagen hydrolysate intercalated electrospun nanofibers. *J. Hazard. Mater.* **405**, 124231 (2021).
18. Teklay, A., Gebeyehu, G., Getachew, T., Yaynshet, T. & Sastry, T. P. Conversion of finished leather waste incorporated with plant fibers into value added consumer products—an effort to minimize solid waste in Ethiopia. *Waste Manag.* **68**, 45–55 (2017).
19. Ozgunay, H., Colak, S., Mutlu, M. M. & Akyuz, F. Characterization of leather industry wastes. *Pol. J. Environ. Stud.* **16**, 867–873 (2007).
20. Liu, X., Xie, Y. & Sheng, H. Green waste characteristics and sustainable recycling options. *Resour. Environ. Sustain.* **11**, 100098 (2023).
21. Gargano, M., Bacardit, A., Sannia, G. & Lettera, V. *From Leather Wastes Back To Leather Manufacturing: the Development of New Bio-Based Finishing Systems* 13775 (Coatings, 2023).
22. Ramasami, T. Approach towards a unified theory for tanning: Wilson's dream. *J. Am. Leather Chem. Assoc.* **96**, 290–304 (2001).
23. Elsayed, H. et al. Preparation of polyurethane silicon oxide nanomaterials as a binder in leather finishing. *Fibers Polym.* **19**, 832–842 (2018).
24. Thorstensen, T. C. *Practical Leather Technology* 4th edn 300–320 (Shoe Trade Publishing, 1993).
25. Sarkar, K. T. Modern Practice in Retanning, Dyeing and Finishing of Leather (Sarkar, K. T. ed), 1st edn 70–90, (Madras, India, 1996).
26. Mohamed, O., Moustafa, A., Mehawed, M. & ElSayed, N. Styrene and butyl methacrylate copolymers and their application in leather finishing. *J. Appl. Polym. Sci.* **111**, 1488–1495 (2009).
27. Ebabu, W. et al. Exploration of functional polymers for cleaner leather industry. *J. Inorg. Organomet. Polym Mater.* **31**, 1–14 (2021).
28. Yılmaz, O. & Cheaburu-Yılmaz, C. N. Synthesis and application of a low emulsifier content composite polyacrylic latex for leather finishing. *J. Polytechnic*. **21**, 19–25 (2018).
29. Schindler, F. Properties distinguishing acrylic polymers as binders for basecoats on leather. *J. Am. Leather Chem. Assoc.* **98**, 97–100 (2003).
30. Yılmaz, O., Cheaburu-Yılmaz, C. N., Gülümser, G. & Vasile, C. Rheological behaviour of acrylate/montmorillonite nanocomposite latexes and their application in leather finishing as binders. *Prog. Org. Coat.* **70**, 52–58 (2011).
31. Santos, R. J., Agostini, D. L. S., Cabrera, F. C., Budemberg, E. R. & Job, A. E. Recycling leather waste: Preparing and studying on the microstructure, mechanical, and rheological properties of leather waste/rubber composite. *Polym. Compos.* **36**, 2275–2281 (2015).
32. Sumathi, V. & Senthil, R. Physico-chemical properties of reconstituted fibers composite prepared from leather waste. *Int. J. Pharma Bio Sci.* **7**, P105–P110 (2016).
33. Lu, Z. B., Liao, X. P., Sun, D. H. & Shi, B. Reaction of vegetable tannin-aldehyde-collagen–a further Understanding on vegetable tannin-aldehyde combination tannage. *Chem. Indus. For. Prod.* **24**, 7–11 (2004).
34. Fierro, F. et al. Multifunctional leather finishing vs. applications, through the addition of well-dispersed flower-like nanoparticles. *Sci. Rep.* **14**, 2163 (2024).
35. Xu, W., Cui, W., Li, W. & Guo, W. Development and characterizations of super-fine wool powder. *Powder Technol.* **140**, 136–140 (2004).
36. Xia, L. et al. Protective bleaching of camel hair in a neutral ethanol-water system. *Polymers* **10**, 730 (2018).
37. Xia, L. et al. Utilization of waste leather powders for highly effective removal of dyes from water. *Polymers* **11**(11), 1786. https://doi.org/10.3390/polym11111786 (2019).
38. Zhu, L., Xu, W., Ma, M. & Zhou, H. Effect of plasma treatment of silk fibroin powder on the properties of silk fibroin powder/polyurethane blend film. *Polym. Eng. Sci.* **50**, 1705–1712 (2010).
39. Chen, X., Li, W., Zhong, W., Lu, Y. & Yu, T. pH sensitivity and ion sensitivity of hydrogels based on complex-forming chitosan/silk fibroin interpenetrating polymer network. *J. Appl. Polym. Sci.* **65**, 2257–2262 (1997).

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Declarations

Competing interests

The authors declare no competing interests.

Additional information

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