

RESEARCH

Open Access



Sustainable metal-free leather manufacture via synergistic effects of triazine derivative and vegetable tannins

Yuanhang Xiao¹, Jiajing Zhou^{1,2}, Chunhua Wang¹, Jinwei Zhang¹, Vera D. Radnaeva³ and Wei Lin^{1,4*} 

Abstract

Restrictions on heavy metals, especially chromium, have encouraged alternative tanning systems that can reduce environmental and human health risks from conventional chrome-based tanning. In this work, metal-free combination tanning was developed by using vegetable tannins and a triazine-based syntan containing active chlorine groups (SACC). Specifically, the relationship between leather performance (e.g., hydrothermal stability and organoleptic properties) and technical protocols (e.g., types and dose of tannins) was systematically established. The optimized protocol involving a unique procedure (i.e., 10% SACC pre-tanning, shaving, and 25% wattle tanning) endowed the leather with high shrinkage temperature (~92 °C) and met the Chinese standards for shoe upper leather (QB/T 1873-2010). Our method not only produces zero chrome-containing solid wastes, but also uses ~75% less tannin for leather manufacture. The excellent leather performance was ascribed to the synergistic effects, where SACC and wattle diffused into collagen fibrils and may bind to collagen via covalent, hydrogen and ionic bonding, locking the hierarchical structure of collagen from microfibrils to fiber bundles. Moreover, we summarized these findings and proposed a diffusion-binding-locking mechanism, providing new insights for current tanning theory. Together with the biodegradable spent tanning liquor, this approach will underpin the development of sustainable leather manufacture.

Keywords Metal-free tanning, Triazine derivative, Vegetable tannins, Synergistic effect, Eco-friendly leather

*Correspondence:

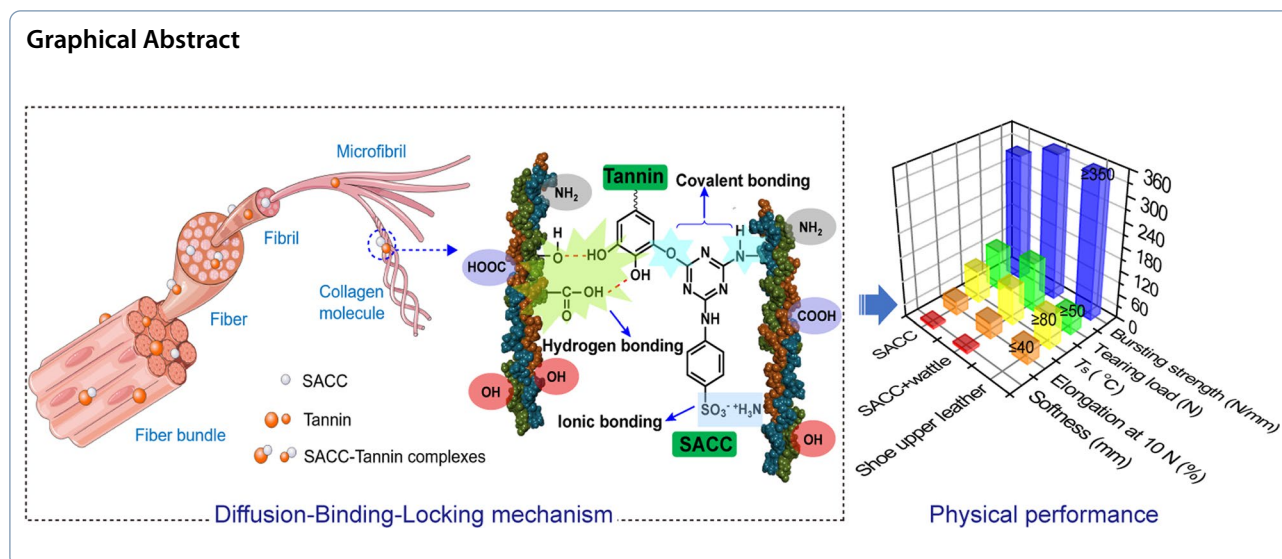
Wei Lin

wlin@scu.edu.cn

Full list of author information is available at the end of the article



© The Author(s) 2023. **Open Access** This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.



1 Introduction

Tanning is the critical process in leather industry through which animal hides and skins are converted into leathers that are resistant to heat and microbial attack. Chrome tanned leather has been dominant in the tanning industry because of their excellent comprehensive properties, such as good hydrothermal stability, reliable mechanical behavior, etc. [1]. However, conventional chrome tanning generates substantial non-renewable chrome-containing wastewater [2] and solid wastes [3, 4]. These unfixed Cr(III) in leather and wastewater may be oxidized to carcinogenic Cr(VI) [5, 6], which seriously threatens human health and environment. Therefore, various countries or regions have released stringent restrictions regarding the Cr discharge. In 2008, chrome-containing solid wastes have been listed in the “National Hazardous Waste Inventory” in China, which limits the production and circulation of chrome tanned leather. More recently, the European Union has limited the content of Cr(VI) in leather products to 3 mg/kg in 2014 (Annex XVII of REACH regulation) [7, 8].

The utilization of non-chrome metal materials (e.g., Al^{3+} , Zr^{4+} and Ti^{4+}) as tanning agents has been reported to coordinate and crosslink collagen fibers, but their binding strength is weaker than chrome, leading to poor leather performance [9]. Moreover, many countries also have restricted the content of metals in leather and textiles, such as Leather Standard by Oeko-Tex (2021 version) [10]. To this end, the development of metal-free tanning materials and cleaner tanning systems is imperative [11]. This also requires a deeper understanding of the physicochemical interactions between tanning agents and collagen at the molecular and structural levels—the crosslinking effect of tanning

agents is not only related to their reactivity [12], but also relevant to the collagen structure, size of tanning agents, and their diffusion capacity in leather matrix [13, 14].

The tanning system using environmentally friendly organic tanning agents is considered as an alternative tanning approach [15]. One typical bio-based material is vegetable tannins from plant leaves, fruits, seeds and barks, which have molecular weights of 500–3000 Da and are classified into ester derived hydrolysable tannins (e.g., chestnut) and flavonoid derived condensed tannins (e.g., mimosa) [16, 17]. They can penetrate and bind with collagen in multiple levels [18, 19] via hydrogen and hydrophobic bonds [20] to endow the leather with good fullness, human skin compatibility and environmental friendliness. More recently, triazine derivatives as tanning agents for chrome-free leather has attracted immense interest [7, 11, 21, 22]. It mainly reacts with the side-chain amino groups of collagens to form strong covalent bonds, thus enhancing hydrothermal stability of leather [22]. Compared with other organic tanning agents (e.g., aldehydes and syntan), triazine derivatives can effectively mitigate the health risks due to their biocompatibility [23, 24]. Meanwhile, the released H^+ in tanning process (Additional file 1: Fig. S1) can simultaneously reduce the tanning liquor pH from ~ 7.8 to ~ 5.0 , which facilitates the tanning process (e.g., dispense with pickling) and reduces the discharge of neutral salts [25]. In our previous work, the combination tanning system using tannic acid and triazine derivative (i.e., Granofin® Easy F-90) has been studied to overcome the poor thermal stability and storage stability of solo tanned leather [26]. However, the restricted leather performance of such

combination tannages and relatively expensive tannic acid limited their practical application. Moreover, the tanning mechanism underneath this approach lacks clear understanding from molecular level to collagen structure level.

Here we reported a sustainable metal-free leather processing for eco-leather manufacture involving triazine derivative pre-tanning, shaving and vegetable tannins tanning. The types of tannins including hydrolysable tannins (i.e., chestnut, valonea and tara extracts) and flavonoid derived condensed tannins (i.e., wattle, quebracho and bayberry extracts) in this method were systematically optimized (Additional file 1: Fig. S2). The characteristics and environmental performance of the tanning process were also investigated. This work not only revealed the synergistic effects of triazine derivative and tannins on leather matrix, but also established a reliable novel tannage to endow the leather with required organoleptic properties and physical performance. We envisaged this method would produce zero chrome-containing solid wastes (i.e., eliminating the risks of heavy metals to human health and environment) and emerge as a cost-effective tanning strategy, which contributes to the cleaner production towards a sustainable development of leather manufacture.

2 Experimental sections

2.1 Materials

Bated cattle hide from our laboratory were used as raw materials for leather processing. Sodium p-[(4,6-dichloro-1,3,5-triazin-2-yl) amino] benzenesulphonate (Granofin® Easy F-90 liquid with 20–25 wt% active chlorine groups, courtesy of Stahl Company) is a syntan denoted as SACC (Additional file 1: Fig. S1), which was synthesized by reacting sulphanilic acid (SA) with cyanuric chloride (CC). The wattle (tannins content: ~72.5 wt%) and tara (tannins content: ≥ 48 wt%) were purchased from Seta S.A. (Brazil). The extracts of quebracho (tannins content: 72 ± 1.5 wt%) and chestnut (tannins content: 72 ± 1.0 wt%) were sourced from SilvaTeam S.p.a. (Italy). The bayberry (tannins content: 68–70 wt%) and valonea (tannins content: ~32 wt%) extracts were received from Guangxi Wuming tannin extract factory (China). Disodium EDTA, NaHCO_3 , HCOOH , urea and *n*-propanol were purchased from Chengdu Chron Chemicals Co. LTD (China). All the chemicals used for leather processing were of commercial grade.

2.2 Leather tanning process

The solo SACC tanning process (Additional file 1: Table S1, above the dotted line) was conducted according to a previously reported method [26]. Specifically, the bated cattle pelt samples from back part (30 cm \times 30 cm)

were first immersed in 70 wt% water at 25 °C and tanned with 10 wt% SACC for 2 h at 25 rpm/min in a stainless-steel temperature-controlled drum (GSD, Wuxi Xinda Light Industrial Machinery Co., LTD, China) to give a complete penetration. Then 50 wt% hot water (55–65 °C) was added to the drum twice, and the drum temperature was raised to 40 °C for 2 h and 45 °C for 4 h, respectively, to facilitate the binding between SACC and collagen. Meantime, the pH of the tanning system spontaneously reduced from ~7.8 (bating pH) to ~5.0. The obtained SACC-tanned leather was washed and piled overnight.

As for the combination tanning for metal-free leather (Additional file 1: Table S1), the above obtained SACC-tanned leather was shaved, weighed (baseline of material dosage) and washed. Then, 0.5 wt% oxalic acid and 0.3 wt% disodium EDTA were used for rewetting and deferrization, preventing the tannin extract from darkening with iron. Subsequently, the leather was neutralized to pH 4.5–4.7 with 0.5 wt% NaHCO_3 solution and tanned with 10–30 wt% different tannin extracts (i.e., wattle, quebracho, bayberry, chestnut, tara, valonea). After tanning for 3 h, pH of the floats was adjusted to ~3.5 with 0.5 wt% HCOOH solution. The resulting SACC-tannins combination tanned leather was washed and piled for 24 h.

Post-tanning processing (Additional file 1: Table S2) was performed according to common procedures including retanning (e.g., acrylic resins, amino resins, syntan), dyeing and fatliquoring. The obtained leather was termed as crust leather.

2.3 Characterization

2.3.1 Measurement of shrinkage temperature

The shrinkage temperature (T_s) of SACC-tanned leather and SACC-tannins combination tanned leather were measured by a shrinkage tester (Sunshine electronic institute, Shaanxi University of Science & Technology) according to the ASTM method [15]. The leather samples (10 mm \times 60 mm) were suspended vertically in water and the heating rate was maintained at 2 °C/min. The temperature at which samples shrink was recorded as T_s . Each reported value was an average of three experiments.

2.3.2 Determination of the uptake of tannin extract

The maximum absorbance and standard curves of six tannin extracts were measured by an UV–visible spectrophotometer (UV3600, Shimadzu, Japan) according to the previously reported method [27]. Specifically, 10 mL of tanning spent liquor was collected and centrifuged at 5000 rpm for 30 min to remove suspended solids. The UV spectra of different tanning spent liquors were determined to obtain their maximum absorption peak (Wattle and Bayberry: 276 nm, Quebracho: 274 nm, Valonea:

270 nm, Chestnut: 278 nm, Tara: 265 nm) (Additional file 1: Fig. S3). Then 1.00 g/L standard solutions of different tannins were prepared and diluted to concentrations of 5, 10, 15, 20, 25, 30 and 35 mg/L. The absorbance values were measured with water as blank at maximum absorption peak and plotted against the concentration values as standard curves (Additional file 1: Fig. S3). Finally, the concentration of tannin extract in the spent liquor was acquired by the standard curves, and the absorptivity of tannin extract was calculated by the following formula:

$$\text{Uptake of tannin extract(\%)} = [(C_o - C_t) / C_o] \times 100 \quad (1)$$

where C_o and C_t are the concentration of tannin extracts in tanning spent liquor before and after the tanning process, respectively.

2.3.3 Chemical resistance stability measurements

The SACC tanned leather and SACC-tannins combination tanned leather samples (5 cm × 5 cm) were incubated with distilled water, 10% urea solution, 0.5% Na_2CO_3 solution, 10% *n*-propanol solution or HCOOH solution (pH 2.5) in conical flask, respectively. The incubation was carried out at room temperature for 12 h in a water bath thermostatic oscillator. Each of them was piled overnight. The T_s of the leather samples was then measured before and after washing.

2.3.4 Amino acids analysis

The bated pelt and SACC-tanned leather samples were first crushed into powder. Then, 0.2 g samples were hydrolyzed in 20 mL of 6 mol/L HCl at 110 °C for 10 h. The hydrolysates were dried to remove HCl, the obtained residues were dissolved and diluted with deionized water. After filtered through a 0.22 μm filter syringe, the solution was measured by using an amino acid analyzer (A300, MembraPure GmbH, Germany) to analyze the content of amino acids [28]. The detection wavelength was 570 nm and the injection volume was 20 μL.

2.3.5 Fourier transform infrared spectroscopy (FTIR) studies

The SACC tanned leather and SACC-tannins combination tanned leather samples after freeze drying for 24 h were tested by a Fourier transform infrared spectroscopy (FTIR, Nicolet iS10, Thermo Fisher Scientific Inc., USA) in the range of 400–4000 cm^{-1} .

2.3.6 Raman spectral measurements

The SACC tanned leather and SACC-tannins combination tanned leather samples after freeze drying were measured on a confocal Raman spectrometer (Horiba Labra HR, France) excited by a laser at 785 nm. The

Raman shifts were carefully calibrated using Si plate with an uncertainty of 0.5 cm^{-1} . The scanning was in the range of 700–1800 cm^{-1} .

2.3.7 Scanning electron microscopy (SEM) observation

After freeze drying at −45 °C in a freeze dryer (Alpha 1–2 LD, Christ, Germany) for 24 h, the bated pelt, SACC tanned leather and SACC-wattle combination tanned leather samples were cut into defined specimens with uniform thickness (~1 cm × 1 cm) by a freezing microtome (CM1900, Leica, Germany) at −20 °C. Then the samples were sputter-coated with Au before SEM observation. The SEM images for the cross section were obtained by operating a scanning electron microscope (JSM-7500F, JEOL, Japan) at an accelerating voltage of 15 kV.

2.3.8 Pore structure measurement

The bated pelt, SACC tanned leather and SACC-wattle combination tanned leather samples were freeze dried at −45 °C for 24 h. Then the pore structures of leather samples were measured using a mercury intrusion porosimetry (MIP, AutoPore IV 9500, Micromeritics, USA) [29]. The porosity, total pore area and average pore diameter were given by this instrument.

2.3.9 Organoleptic property assessment

The quality and grade of the leathers largely depend on its organoleptic properties, such as softness, fullness, grain smoothness, grain compactness and color shade. Thereinto, softness is defined as an integration of the thickness, compressibility, smooth handle, bend-ability, and extensibility of leather. Fullness is defined as a feeling of compressibility and smoothness to the touch when the leather is deformed under an external force [30]. Grain smoothness and compactness are related to the area of leather, and grain smoothness will reduce and compactness will increase as the leather shrinks [31]. Color shade of leather is influenced by the color of tannins. These organoleptic properties were assessed by hand and visual examination. The crust leathers were evaluated on score from 1 to 10 points for each property by three experienced tanners [32].

2.3.10 Determination of physical properties

The crust leather samples were first conditioned for 48 h at 20 ± 2 °C with a relative humidity of 65 ± 2%. Then physical properties of the samples were examined using the standard IULTCS methods [33]. Specifically, tear load, elongation at 10 N, bursting strength and

softness were measured as per standard procedures. Each reported value was an average of four samples (2 along the backbone, 2 across the backbone).

2.4 The environmental impact assessment (EIA) of metal-free tanning process

2.4.1 Extractable metal content measurement of crust leather

In order to simulate the scenario where leather products contact human skin, the crust leather samples were first extracted with acidic artificial sweat, filtered and acidified using international standard ISO 17072-1:2019 method [34]. Then the common metal concentration (i.e., Cr, Al, Zr, Ti, Fe) in the extracts were measured by inductively coupled plasma-optical emission spectrometer (ICP-OES, IRIS Intrepid II, Thermofisher, USA).

2.4.2 Pollution load assessment of metal-free tanning system

The total dissolved solids (TDS) in the tanning spent liquor was tested according to the standard method of the American Wastewater Association (AWWA) [35]. The

tanning effluent after vacuum filtration was dried in a drying oven at 102 °C until reaching a constant residual weight, and the ratio of the dried solid mass to the volume of the spent liquor was calculated as the TDS content (g/L). The chloride ion (Cl^-) content, chemical oxygen demand (COD_{Cr}) and biological oxygen demand (BOD_5) in spent tanning liquor were measured by ion chromatograph (CIC-D160, Shenghan Chromatograph, Qingdao), COD_{Cr} analyzer (DR1010, Hach, USA) and BOD_5 analyzer (TrakII, Hach, USA), respectively. COD_{Cr} refers to chemical oxygen demand measured with potassium dichromate as the oxidant. BOD_5 represents the amount of oxygen required for 5 days of microbial biodegradation.

3 Results and discussions

3.1 Optimizations of metal-free combination leather tannage

We first investigated the effect of various tannin extracts and SACC on the T_s of tanned leathers in a solo tanning method. The pickled pelts were tanned by using conventional vegetable tannage and the dosages of

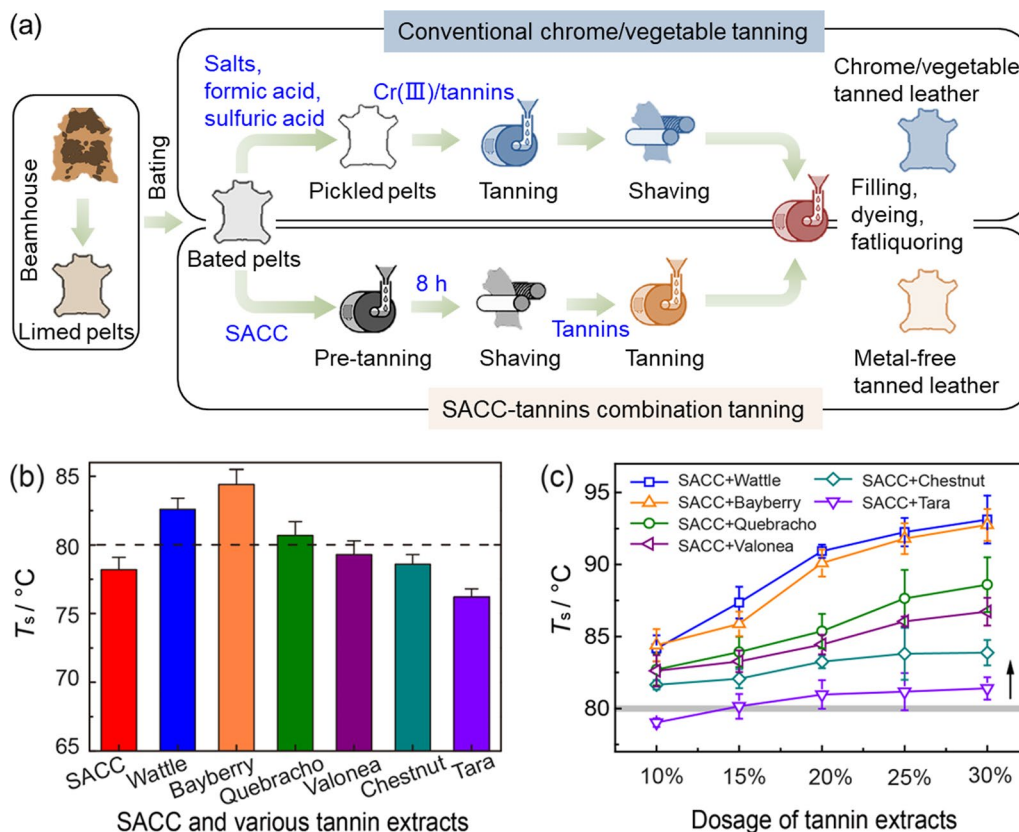


Fig. 1 a Route diagram of conventional chrome/vegetable tanning process and SACC-tannins combination tanning process. b T_s of tanned leathers produced by SACC (10%) or various tannin extracts (25%) in solo tanning. c T_s of tanned leathers produced by combination tanning systems (10% SACC + various dose of tannin extracts). The error bars represent standard deviations (n = 3)

chemicals were applied based on the weight of limed pelts (a piece of limed pelt ~30 kg) (Fig. 1a). Six types of tannins including wattle, quebracho, bayberry, tara, chestnut, and valonea were chosen as the representative tannins, covering both condensed and hydrolysable tannins (Additional file 1: Fig. S2). The dosage of tannin extracts was kept at 25% based on the weight of pickled pelts. The T_s of leather tanned by condensed tannins (80–85 °C) was much higher than that of hydrolysable tannins (75–80 °C), which is mainly due to the stronger astringency of condensed tannins (i.e., possible covalent reaction between the basic amino groups of collagen and aromatic carbon in the condensed tannin molecules via quinoid structures) than hydrolysable tannins (Fig. 1b) [19, 36]. In contrast, solo SACC tanning gave the leather an increased T_s (~78 °C) compared to the bated pelts (~60 °C), owing to the covalent bonding between the active chlorines of SACC and amino groups of collagen [26]. Notably, the T_s of SACC tanned leather can meet the requirement of shaving ($T_s > 75$ °C).

The unique combination tanning strategy by using SACC and tannins was then studied for better performance of the leather products. Specifically, bated pelts were first treated by 10% SACC for 8 h, then these pre-tanned leathers were shaved before the tanning with

different tannins (*Note*: the dosages of the tanning chemicals applied were based on the weight of shaved leather; a piece of shaved leather ~7 kg) (Fig. 1a). This method produces no chrome-containing solid waste and reduces the dosages of tannins by ~75% compared to conventional vegetable tanning (Additional file 1: Table S3). It is notable that SACC-condensed tannin system conferred the leather an increased T_s (>87 °C), much higher than solo SACC or tannins tanning (Fig. 1c), implying the presence of synergistic interactions of SACC and tannins. For example, the T_s of combination tanning leather (10 wt% SACC and 25 wt% wattle) can reach ~92 °C. Moreover, although the introduction of hydrolysable tannins (even up to 30 wt%) into combination tanning system gave the leather a limited increase (4–6 °C) in T_s , which is still above the critical T_s standard (80 °C) of the qualified shoe upper leather products (QB/T 1873-2010).

The uptake efficiency of tannins in the different combination protocols was then determined. Generally, the spent liquor after tanning with condensed tannins was clearer than that of the hydrolysable tannins (Fig. 2). For example, the spent liquor from 20–25 wt% wattle was clear, while the spent liquor from 10–15 wt% tara was still turbid. The uptake efficiency of condensed tannins is significantly higher than that of hydrolysable

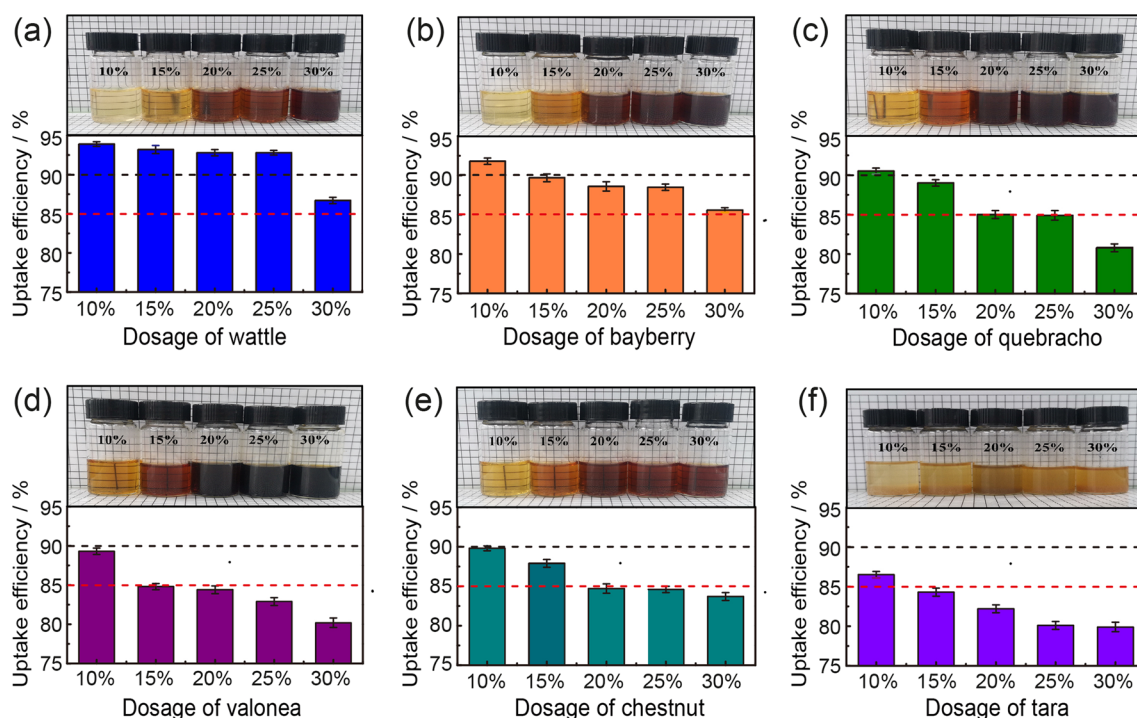


Fig. 2 The photos of tanning spent liquor and uptake efficiency of tannins in different SACC-tannin combination tanning: **a** wattle, **b** bayberry, **c** quebracho, **d** valonea, **e** chestnut, and **f** tara. The concentration of SACC was fixed at 10% and the concentration of tannins varied from 10 to 30 wt%

tannins (85–90% vs. <85%) based on absorbance measured by UV–vis spectroscopy. Especially, the uptake of wattle tannin could reach ~92% (Fig. 2a). The uptake of tannins in combination tanning is as follows: Wattle > Bayberry > Quebracho > Chestnut > Valonea > Tara. Therefore, the combination tanning with 20–25 wt% wattle tannins was applied in the following assessment based on tanning effects and economic benefits.

3.2 Molecular mechanisms in the combination tanning system

We next explore the dominant stabilizing interactions in the leather matrix. The chemical interactions, e.g., ionic bonding, hydrogen bonding and hydrophobic bonding between the tanning agent and collagen can be disrupted by washing with certain chemical reagents, which in turn leads to the change of T_s of the leather. This provides us a clue to infer the key interaction after the combination tanning [37]. For example, distilled water can wash out tannins that are free or weakly adsorbed in the leather; Urea and n-propanol are hydrogen bond and hydrophobic bond breaking reagents, respectively [38, 39].

The solo SACC tanned leather showed no obvious change (<1.0 °C) in T_s after washing with water, urea, n-propanol and sodium carbonate solution (Fig. 3a). This is mainly due to the formation of robust covalent interaction between active chlorine and the side-chain amino groups of Lys, Arg, His and Hyl in collagen [26]. In contrast, a minor decrease (2.9 °C) in T_s was observed after formic acid treatment. This may be attributed to the instability of the covalent interaction between SACC and collagen amino groups in acidic environment (i.e., formic acid) [40–42]. The ΔT_s of SACC-tannins combination tanning leathers was further investigated (Fig. 3a). A slightly reduced T_s was observed after washing with distilled water and formic acid solution (2.0–2.5 °C and 2.5–3.5 °C, respectively). This indicated that compared with solo SACC tanning, SACC-tannin combination tanning had a multi-modal tanning effect on collagen fibers. All the leather products remain a relatively high T_s (>80 °C), implying the good water and acid resistance for post-tanning procedures (e.g., filling, dyeing and fatliquoring). It is notable that the urea solution and n-propyl alcohol brought about a decrease of T_s (3.6–4.2 °C and 4.2–4.7 °C, respectively) via breaking hydrogen and hydrophobic bonds. Moreover, sodium carbonate solution generated an obvious decrease of T_s (6.2–7.7 °C), which is probably because of the deprotonation of tannins (i.e., defloculating) at high pH leading to the reduced multi-point interaction (e.g., hydrogen bonding) with collagen [43]. Overall, this suggested the SACC and tannin can form hydrogen bonds, hydrophobic bonds, and covalent bonds between collagen molecules.

To understand the collagen structure and tanning mechanism after this combination tanning process. Firstly, the amino acids content of bated pelt and SACC-tanned leather were analyzed. The content of Lys, His and Arg in leather fiber is reduced by 27–30% after SACC tanning (Fig. 3b). This may be due to the covalent interaction of active chlorine on SACC with collagen amino groups. Then, the FT-IR spectra and Raman spectra of leather samples before and after different tannins tanning were collected. Type I collagen is known to possess a special triple-helix conformation which has a backbone structure with a high proportion of amide and imide groups. The absorption peaks of leather at 3410 cm^{-1} and 3084 cm^{-1} (N–H stretching of amides A and B), 1642 cm^{-1} (peptide chain C=O stretching of amide I), 1532 cm^{-1} (couple of N–H bending and C–N stretching of amide II) and 1240 cm^{-1} (–CH₂ wagging, C–N stretching and N–H bending of amide III) indicated the presence of collagen backbone (Fig. 3c) [44]. Moreover, no obvious shift of the amide I band absorption peak was observed, showing that the triple-helix structure of collagen largely remained after the introduction of SACC and tannins [45]. The increased intensity of amide A band can be attributed to the formation of hydrogen bond between phenolic hydroxyl groups of tannins and side-chain amino groups of collagen [46]. In addition, the appearance in absorption peaks of C–O–C and C–N in the Raman spectra (Fig. 3d) may be attributed to the covalent interaction of active chlorine with side-chain amino groups of collagens and phenolic hydroxyl groups of tannins [26].

Based on these results, the synergistic mechanism of SACC and tannin in the metal-free tanning system was summarized in Fig. 3e. Active chlorine groups on SACC molecules can not only interact with the amino groups on the collagen fibers via covalent bonding, but also bind to the phenolic hydroxyl groups on the tannin molecules, exerting robust crosslinking effects [47]. In addition, –SO₃[–] of SACC molecules can form ionic bonding with –NH₃⁺ of collagen [48], and the phenolic hydroxyl groups on the tannin molecules can interact with amino, hydroxyl or carboxyl groups of collagen by hydrogen bonds and/or hydrophobic bonds [49]. Collectively, the synergistic interactions within collagen fibers are formed, which substantially contribute to the enhanced hydrothermal stability of the metal-free leather.

3.3 Morphologies and porous structures of leather

The microstructures of collagen after tanning processes and the distribution of SACC-tannin in leather matrix were then analyzed. SEM showed the morphologies of bated pelt, solo SACC tanned leather and SACC-tannin combination tanned leather (Fig. 4a–f). Bating pelt

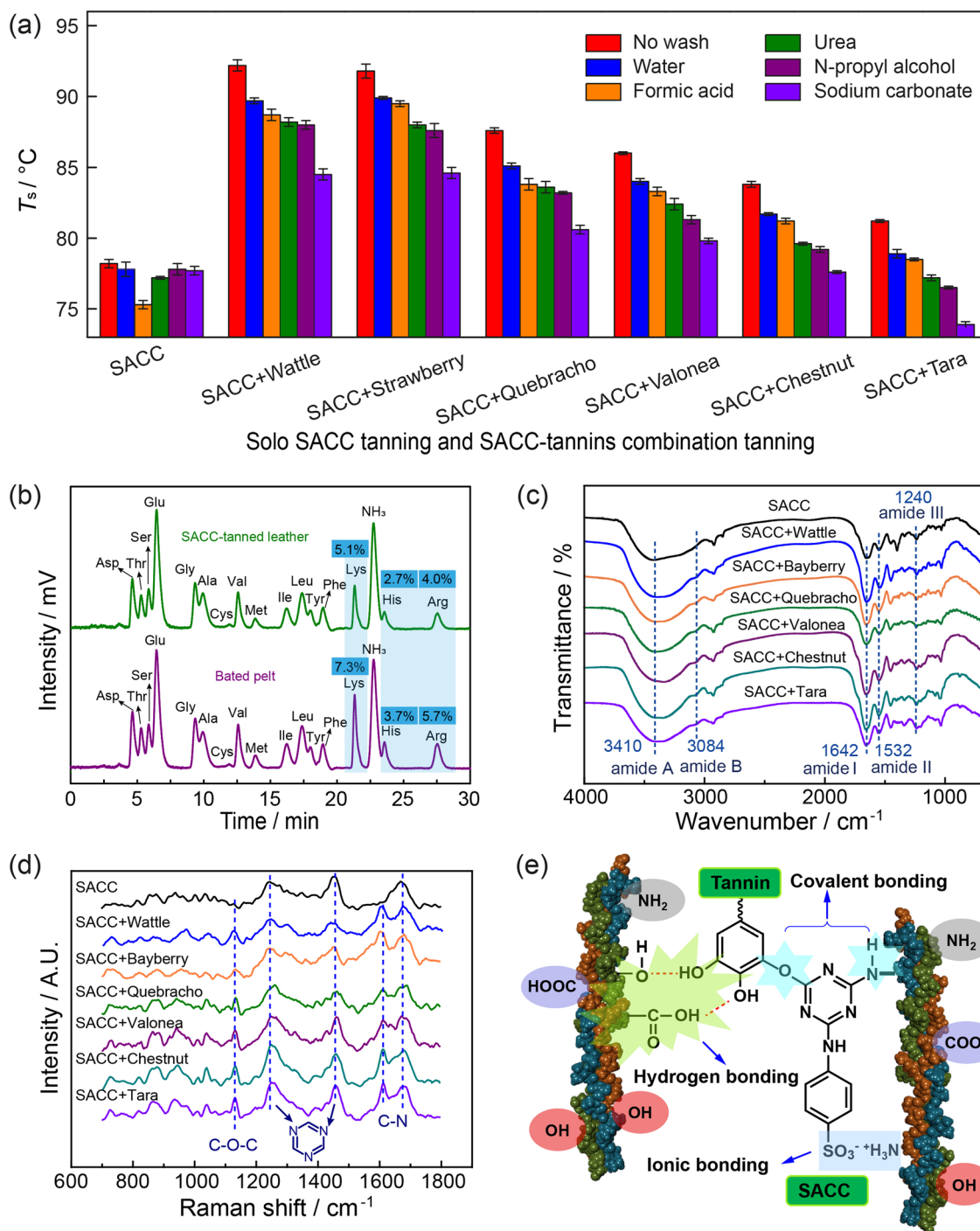


Fig. 3 a T_g of produced leather after washing with different chemical media. b The chromatograms of amino acids in bated pelt and SACC-tanned leather. c FT-IR spectra and d Raman spectra of samples. e Schematic illustration showing synergistic interactions of SACC and tannins with collagen in the combination tanning

exhibited sticky, tight and thick collagen fiber bundles (Fig. 4a). In contrast, the collagen fibers after the combination tanning became loose and isolated. Moreover, the larger SACC-tannin complexes with micron

dimensions were well deposited between fiber strands to form the crosslinked network structure (Fig. 4c) [14]. Magnified SEM image confirmed that the collagen fibrils in all groups exhibited the quarter-stagger structure

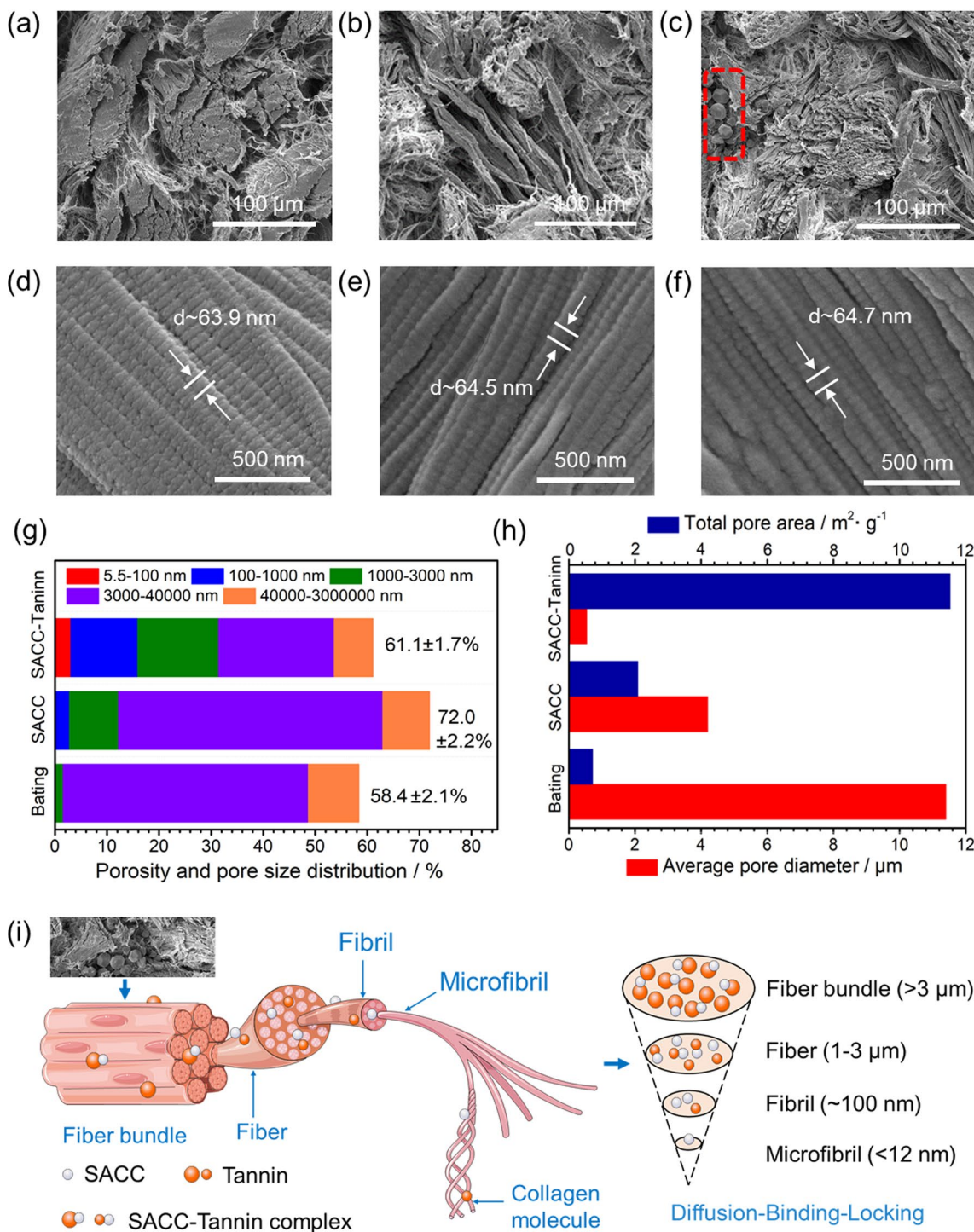


Fig. 4 Cross-section SEM of bating pelt (a and d), solo SACC tanned leather (b and e) and SACC-wattle combination tanned leather (c and f). Red dash frame in c indicates the SACC-tannin complexes. g Porosity and pore size distribution of tanned leathers. h Total pore area and average pore diameter of tanned leathers. i Schematic diagram of diffusion-binding-locking mechanism proposed in this combination tanning. The distribution of SACC-tannins in collagen was highlighted in multiple levels from collagen molecule to fiber bundle

(Fig. 4d–f), which was the typical collagen banding pattern of grooves and ridges [50]. Specifically, the collagen fibrils maintained native D-periodic banding patterns

with a longitudinal repeat of ~ 64 nm with SACC and tannin dispersed between the fibrils [51]. The intact D-periodic pattern indicated that the collagen molecules were

still stacked together in order, retaining their native conformation [52]. Therefore, we concluded that the complexes were incorporated into the fibrillar structure of collagen without disrupting their primary and conformational structures.

The pore size distribution of leather matrix including microfibrils (<12 nm), fibrils (~100 nm), elementary fibers (1–3 μm) and fiber bundles (>3 μm) was categorized by using a theoretical model [53]. Measurements based on the MIP confirmed that the pore size of bated pelt was mainly from 3.0 to 40 μm (Fig. 4g), which indicated that bating pelts were woven at the fiber bundle level. In contrast, after the introduction of SACC, the percentage of pore size (<3.0 μm) increased from 1.6 to 12.2%, indicating that the SACC molecules were able to diffuse into the collagen fiber network and form bindings between the microfibril, fibril and elementary fiber. Whereas the pores in the range of 3.0–40 μm were almost unaffected. Thus, the SACC tanning led to the increased total porosity from 58.4 to 72.0%. Notably, SACC-tannin combination tanned leather exhibited a higher proportion in the range of 5.5 nm–3.0 μm and a lower proportion in the range of 3.0–40 μm. This gave rise to a decreased total porosity of leather (61.1%), and indicated the larger SACC-tannin complexes mainly distributed in space among collagen fiber bundles and bound to these bundles. Overall, SACC-tannin played a role in “locking” the multi-level structure of collagen to form a network structure. Moreover, the average pore diameters of leather decreased and the total pore areas increased after this combination tanning (Fig. 4h). We reasoned that the deposition of SACC and tannin in the collagen fibers can increase the small pore size (5.5 nm–3.0 μm) and form dense intertwining networks in the leather matrix. Therefore, we proposed a diffusion-binding-locking mechanism for this combination tanning (Fig. 4i), where SACC-tannins diffused into the hierarchical leather matrix and interacted with collagen molecules. The multiple levels of interaction

prevented fibers from collapsing into the interstices, reduced the ability of collagen to shrink, and eventually improved the denaturation temperature [54].

3.4 Organoleptic properties and physical performance of the leathers

The organoleptic properties (i.e., softness, fullness, grain smoothness, grain compactness and color shade) determine the quality of leather products, which can be evaluated through haptic and visual feedback. The performance comparison was summarized in Fig. 5a, b. Condensed tannins outperformed hydrolyzed tannins in terms of fullness and grain compactness of tanned leathers. This is because condensed tannins have larger molecular weights and stronger astringency, and therefore are more effectively deposited in collagen fibrils to form hierarchical network structure [31]. Particularly, the flavanol polycondensation structure and strong tanning ability of wattle tannin endowed the leather with excellent softness and grain smoothness. Notably, the color shade of the leathers are as follows: Valonea>Bayberry>Quebracho>Chestnut>Wattle>Tara. Therefore, choosing tannins in this metal-free tanning systems can selectively meet the market requirements. For example, metal-free tanning system based on the combination of 10 wt% SACC and 25 wt% wattle can be optimized for manufacturing light-colored or bright-colored leather.

We further evaluated the potential of the obtained leather for market requirements. As given in Table 1, the dispersing effect of wattle tannin on collagen fibers increased the softness of leather by ~1.1 mm. The combination tanned metal-free leather exhibited enhanced physical and mechanical properties (tearing load, elongation at 10 N, T_s and bursting strength) compared to solo SACC tanned leather. For example, the introduction of wattle tannin increased the T_s of leather from ~79 to ~92 °C, and the tearing load from ~102 to ~122 N. Furthermore, all the physical properties (elongation

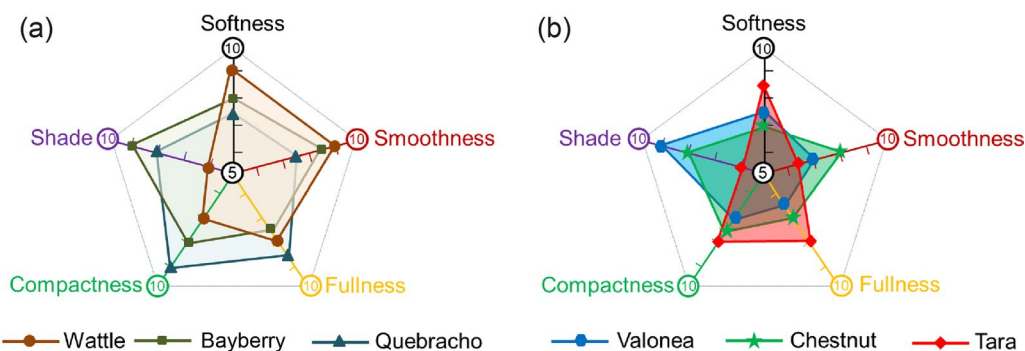


Fig. 5 The organoleptic properties of leather products from different combination tanning. **a** SACC + condensed tannins combination tanning leather. **b** SACC + hydrolyzed tannins combination tanning leather

Table 1 The physical properties of the leathers. The value on the shoe upper leather suggests the Chinese standard requirements (QB/T 1873-2010)

Parameters	SACC	SACC + wattle	Shoe upper leather
Softness (mm)	4.3 ± 0.2	5.4 ± 0.1	—
Elongation at 10 N (%)	33.2 ± 2.9	37.9 ± 3.5	≤ 40
T_s (°C)	79.2 ± 1.2	91.9 ± 1.0	≥ 80
Tearing load (N)	101.5 ± 8.0	122.4 ± 7.2	≥ 50
Bursting strength (N/mm)	315.2 ± 4.2	358.4 ± 5.5	≥ 350

Table 2 The content of extractable metals in the metal-free finished leather

Metal species	Detected concentration	Quantification limit
Cr (mg/kg)	ND	10
Al (mg/kg)	ND	100
Zr (mg/kg)	ND	10
Ti (mg/kg)	ND	10
Fe (mg/kg)	0.48	25

ND = not detected, Quantification limit: quantification limit possible with ICP-OES, from EN ISO 17072-1-2019

at 10 N: 38%; T_s : 92 °C; tearing load: 122 N; bursting strength: 358 N/mm) of the metal-free leather met the Chinese standard requirements for shoe upper leather (QB/T 1873-2010), indicating that the proposed metal-free leather tannage is promising for manufacturing shoe upper leather.

3.5 Environmental assessment and cost analysis of our method

Heavy metals in leather are harmful to the ecological environment, and the metal ions commonly involved in leather tanning include Cr^{3+} , Al^{3+} , Zr^{4+} , Ti^{4+} , and Fe^{3+} . Table 2 revealed the extractable metals from the leather products in the scenario where leather products contact human skins. It showed that Cr^{3+} , Al^{3+} , Zr^{4+} and Ti^{4+} were not detected in the acidic artificial sweat. Trace amount of Fe^{3+} (0.48 mg/kg) was detected in leather, which may be caused by the leached Fe^{3+} from the stainless-steel drum.

The conventional chrome tanning process not only has the risk of toxic Cr ions, but also produces substantial wastewater containing neutral salts, which harms the aquatic environment. Compared with the wastewater from chrome tanning process, the Cl^- content of the waste liquor produced by the SACC-tannin

Table 3 Environmental assessment index of tanning spent liquor

Tanning system	$\text{Cl}^-/\text{g L}^{-1}$	$\text{TDS}/\text{g L}^{-1}$	$\text{COD}_{\text{Cr}}/\text{g L}^{-1}$	$\text{BOD}_5/\text{g L}^{-1}$	$\text{BOD}_5/\text{COD}_{\text{Cr}}$
SACC-Tannin	~3.2	~8.5	~13.2	~4.6	0.35
Cr	~11.3	~13.5	~19.7	~3.8	0.19

Table 4 The cost of main chemicals used in the SACC-tannin acid and SACC-wattle combination tanning

Cost content	Average cost	SACC-tannin acid		SACC-wattle	
		Amount ⁽¹⁾	Cost/\$	Amount ⁽¹⁾	Cost/\$
SACC	2.7 \$/kg	40.0 kg	108.0	100.0 kg	270.0
Tannin acid	7.4 \$/kg	100.0 kg	740.0	Amount ⁽²⁾	Cost
Wattle	3.0 \$/kg	—	—	62.5 kg	187.5
HCOOH	1.3 \$/kg	5.0 kg	6.5	1.25 kg	1.6
Composite cost		854.5		459.1	

⁽¹⁾ The amount was calculated according to the weight 1000 kg limed cowhide.

⁽²⁾ The amount was calculated according to the weight 250 kg shaving leather

combination tanning process was significantly lower by 71.7% (Table 3). This is because no NaCl was used for the pickling process in our metal-free tanning system. Moreover, the reduced amount of Cr^{3+} and Cl^- also led to a lower TDS content in the waste of combination system. For example, $\text{BOD}_5/\text{COD}_{\text{Cr}}$ is the index of biochemical degradation of wastewater. When the ratio of $\text{BOD}_5/\text{COD}_{\text{Cr}}$ is higher than 0.3, the biodegradability of organic pollutants in wastewater can be classified as good [55]. $\text{BOD}_5/\text{COD}_{\text{Cr}}$ value of wastewater in our combination tanning system was 0.35, suggesting the improved biodegradability. Therefore, the SACC-tannin combination tanning process is environmentally friendly, and the leather products can meet the development demands of metal-free leather.

We then evaluate the market viability of this tanning process including commercial value, cost effectiveness and sustainability [22]. In a case of 1000 kg limed cowhide, the total cost of chemicals for the SACC-tannin acid combination tanning and this tanning method (i.e., SACC pre-tanning, shaving and wattle tanning) are given in Table 4. Our tanning method exhibited a total chemical cost of ~459.1 \$, which is 46.3% lower than that of the SACC-tannin acid process (~854.5 \$) [26]. Together with the environmental assessment, the significant improvement of cost suggests our reported method as an attractive option for sustainable leather manufacture.

4 Conclusion

We reported a sustainable metal-free leather processing based on SACC and vegetable tannins. The results demonstrated that a unique combination tanning (i.e., SACC pre-tanning, shaving and wattle tanning) can significantly enhance the hydrothermal stability of the leather ($T_s \sim 92$ °C). We revealed that SACC and wattle can evenly diffuse into the collagen fibrils, and bind to the collagen via synergistic effects including covalent, hydrogen and ionic bonding. We also revealed that SACC-wattle complexes can “lock” the multi-level structure of leather matrix without destabilizing the conformational structure of collagen. Therefore, we proposed a diffusion-binding-locking mechanism, which provided new insights of tanning mechanisms. This novel eco-friendly metal-free tanning system can not only improve the organoleptic properties and physical performance of the leather products, but also can reduce environmental risks of chrome-containing wastes and improve biodegradability of tanning spent liquor. Of particular interest is that these leather products meet current Chinese standard requirements for shoe upper leather (QB/T 1873-2010), validating it as an attractive translational technology. We envision that this work is beneficial to the sustainable development of eco-leather manufacturing.

Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1186/s42825-022-00108-0>.

Additional file 1. Fig. S1. Schematic diagram of structure and hydrolysis of SACC. **Fig. S2.** Structural representation of condensed tannins (a: wattle, b: quebracho, c: bayberry) and hydrolysable tannins (d: chestnut, e: valonea, f: tara). **Fig. S3.** The UV spectra of different tanning spent liquors and standard curves of six tannin extracts (a: wattle, b: bayberry, c: quebracho, d: valonea, e: chestnut, f: tara). The insets show the standard curves of six tannin extracts. **Table S1.** The combination tanning process of SACC and tannins. **Table S2.** The posttanning process of tanned leathers. **Table S3.** The solo tanning process of the vegetable tannins.

Acknowledgements

The authors would like to thank Zhonghui Wang from Sichuan University for her help in FT-IR measurement and characterization.

Author contributions

YX performed the experiments, analyzed the data, and drafted the manuscript. JZ visualized the results and revised the manuscript. CW analyzed and validated the data. VR made contributions to conception of this research. JZ performed the experiment on the organoleptic properties of leather. WL conceived the idea, supervised the project, and revised the manuscript. All authors read and approved the final manuscript.

Funding

The financial support of National Natural Science Foundation of China (21978177, 22178230) is gratefully acknowledged.

Availability of data and materials

All data generated or analysed during this study are included in this published article and the supplementary information files.

Declarations

Competing interests

The authors declare that they have no competing interests.

Author details

¹Department of Biomass and Leather Engineering, Key Laboratory of Leather Chemistry and Engineering of Ministry of Education, Sichuan University, Chengdu 610065, China. ²Department of NanoEngineering, University of California San Diego, 9500 Gilman Drive, La Jolla, CA 92093, USA. ³Department of Leather and Fur Technology Water Resources and Commodity Research, East Siberia State University of Technology and Management, Ulan-Ude, Buryatia, Russia 670013. ⁴National Engineering Research Center of Clean Technology in Leather Industry, Sichuan University, Chengdu 610065, China.

Received: 16 September 2022 Revised: 18 November 2022 Accepted: 3 December 2022

Published online: 05 January 2023

References

- Gao DG, Wang PP, Shi JB, Li F, Li WB, Lyu B, Ma JZ. A green chemistry approach to leather tanning process: cage-like octa(aminosilsesquioxane) combined with Tetrakis(hydroxymethyl) phosphonium sulfate. *J Clean Prod.* 2019;229:1102–11. <https://doi.org/10.1016/j.jclepro.2019.05.008>.
- Pradhan D, Sukla LB, Sawyer M, Rahman PKSM. Recent bioreduction of hexavalent chromium in wastewater treatment: a review. *J Ind Eng Chem.* 2017;55:1–20. <https://doi.org/10.1016/j.jiec.2017.06.040>.
- Jiang HY, Liu JS, Han W. The status and developments of leather solid waste treatment: a mini-review. *Waste Manag Res.* 2016;34(5):399–408. <https://doi.org/10.1177/0734242x16633772>.
- Pradeep S, Sathish M, Sreeram KJ, Rao JR. Melamine-based polymeric crosslinker for cleaner leather production. *ACS Omega.* 2021;6(20):12965–76. <https://doi.org/10.1021/acsomega.0c05668>.
- Moretto A. Hexavalent and trivalent chromium in leather: what should be done? *Regul Toxicol Pharm.* 2015;73(2):681–6. <https://doi.org/10.1016/j.yrtph.2015.09.007>.
- Yu Y, Lin YR, Zeng YH, Wang YN, Zhang WH, Zhou JF, Shi B. Life cycle assessment for chrome tanning, chrome-free metal tanning, and metal-free tanning systems. *ACS Sustain Chem Eng.* 2021;9(19):6720–31. <https://doi.org/10.1021/acssuschemeng.1c00753>.
- Cui L, Qiang XH. Clean production for chrome free leather by using a novel triazine compound. *J Renew Mater.* 2019;7(1):57–71. <https://doi.org/10.32604/jrm.2019.00118>.
- Fontaine M, Clement Y, Blanc N, Demesmay C. Hexavalent chromium release from leather over time natural ageing vs accelerated ageing according to a multivariate approach. *J Hazard Mater.* 2019;368:811–8. <https://doi.org/10.1016/j.jhazmat.2018.12.112>.
- Covington AD, Wise WR. Current trends in leather science. *J Leather Sci Eng.* 2020;2:28. <https://doi.org/10.1186/s42825-020-00041-0>.
- OEKO-TEX. Leather standard by OEKO-TEX (2021). 2021.
- Beghetto V, Agostinis L, Gatto V, Samiolo R, Scrivanti A. Sustainable use of 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride as metal free tanning agent. *J Clean Prod.* 2019;220:864–72. <https://doi.org/10.1016/j.jclepro.2019.02.034>.
- Covington AD. Modern tanning chemistry. *Chem Soc Rev.* 1997;26(2):111–26. <https://doi.org/10.1039/cs9972600111>.
- Covington AD, Lampard GS, Hancock RA, Ioannidis IA. Studies on the origin of hydrothermal stability: a new theory of tanning. *J Am Leather Chem Assoc.* 1998;93(4):107–20.
- Reich G. From collagen to leather—the theoretical background. *Basf, Ludwigshafen*; 2008. p. 1–329.
- Shi JB, Zhang RZ, Mi ZY, Lyu SQ, Ma JZ. Engineering a sustainable chrome-free leather processing based on novel lightfast wet-white tanning system towards eco-leather manufacture. *J Clean Prod.* 2021;282:124504. <https://doi.org/10.1016/j.jclepro.2020.124504>.
- Das AK, Islam MN, Faruk MO, Ashaduzzaman M, Dungani R. Review on tannins: extraction processes, applications and possibilities. *S Afr J Bot.* 2020;135:58–70. <https://doi.org/10.1016/j.sajb.2020.08.008>.

17. Sebestyen Z, Jakab E, Badea E, Barta-Rajnai E, Sendrea C, Czegeny Z. Thermal degradation study of vegetable tannins and vegetable tanned leathers. *J Anal Appl Pyrol.* 2019;138:178–87. <https://doi.org/10.1016/j.jaap.2018.12.022>.
18. Kanth SV, Venba R, Madhan B, Chandrababu NK, Sadulla S. Cleaner tanning practices for tannery pollution abatement: Role of enzymes in eco-friendly vegetable tanning. *J Clean Prod.* 2009;17(5):507–15. <https://doi.org/10.1016/j.jclepro.2008.08.021>.
19. Falcao L, Araujo MEM. Vegetable tannins used in the manufacture of historic leathers. *Molecules.* 2018;23(5):1081. <https://doi.org/10.3390/molecules23051081>.
20. Teng B, Wu JC, Chen WY. Penetration of the polyflavonoids and simple phenolics: a mechanistic investigation of vegetable tanning. *J Am Leather Chem Assoc.* 2017;112(12):420–7.
21. Zou XL, Fang Q, Chai YY, Li ZY, Ren BL. Tanning properties of 4-((4,6-dichloro-1,3,5-triazin-2-yl) amino) benzene sulfonic acid. *J Soc Leather Technol Chem.* 2019;103(5):268–71.
22. Yu LD, Qiang XH, Cui L, Chen B, Wang XK, Wu XH. Preparation of a syntan containing active chlorine groups for chrome-free tanned leather. *J Clean Prod.* 2020;270:122351. <https://doi.org/10.1016/j.jclepro.2020.122351>.
23. Jiang HF, Zhang Q, Zhang Y, Feng HX, Jiang H, Pu F, Yu RL, Zhong Z, Wang CM, Fung YME, Blasco P, Li YX, Jiang T, Li XC. Triazine-pyridine chemistry for protein labelling on tyrosine. *Chem Commun.* 2022;58(50):7066–9. <https://doi.org/10.1039/d2cc01528e>.
24. Mikolaichuk OV, Sharoyko VV, Popova EA, Protas AV, Fonin AV, Vasina LV, Anufrikov YA, Luttsev MD, Nashchekina IA, Malkova AM, Tochilnikov GV, Ageev SV, Semenov KN. Biocompatibility and bioactivity study of a cyto-static drug belonging to the group of alkylating agents of the triazine derivative class. *J Mol Liq.* 2021;343:117630. <https://doi.org/10.1016/j.molliq.2021.117630>.
25. Cui L, Qiang XH, Yu L, Wei X, Li CT. A cleaner method for low-chrome tanning with no-salt pickling. *J Soc Leather Technol Chem.* 2017;101(5):219–26.
26. Xiao YH, Wang CH, Sang J, Lin W. A novel non-pickling combination tanning for chrome-free leather based on reactive benzenesulphonate and tannic acid. *J Am Leather Chem Assoc.* 2020;115(1):16–22.
27. Shi JB, Ren KS, Wang CH, Wang J, Lin W. A novel approach for wet-white leather manufacture based on tannic acid-laponite nanoclay combination tannage. *J Soc Leather Technol Chem.* 2016;100(1):25–30.
28. Zhang X, Gao MC, Zhang CX, Chattha SA, Peng BY. A rapid method for measuring elastin degradation and its application in leather manufacturing. *J Am Leather Chem Assoc.* 2020;115(8):294–300.
29. He X, Wang YN, Zhou JF, Wang HB, Ding W, Shi B. Suitability of pore measurement methods for characterizing the hierarchical pore structure of leather. *J Am Leather Chem Assoc.* 2019;114(2):41–7.
30. Peng WL, Zhang XL, Chen SR. The principle and method of testing leather fullness and softness. *J Soc Leather Technol Chem.* 2006;90(3):117–22.
31. Ren BL, Fang Q, Chai YY, Lan YJ, Zou XL. The relationship between the organoleptic properties of leather and the aggregate structure of collagen fibres. *J Soc Leather Technol Chem.* 2018;102(6):289–92.
32. Musa AE, Gasmelseed GA. Combination tanning system for manufacture of shoe upper leathers: cleaner tanning process. *J Soc Leather Technol Chem.* 2012;96(6):239–45.
33. Williams JMV. IULTCS (IUP) test methods—introduction. *J Soc Leather Technol Chem.* 2000;84(7):301.
34. IX-ISO. ISO 17072-1:2019 Leather—chemical determination of metal content—part 1: extractable metals. 2019.
35. Jia L, Ma JZ, Gao DG, Lyu B, Zhang J. Application of an amphoteric polymer for leather pickling to obtain a less total dissolved solids residual process. *J Clean Prod.* 2016;139:788–95. <https://doi.org/10.1016/j.jclepro.2016.08.097>.
36. Endres H. Theory of interaction of vegetable tannins with collagen. *Leather Sci.* 1964;11:455–62.
37. Liu XH, Wang YY, Wang XC, Han TF, Wang WN, Jiang HE. A salt-free pickling and chrome-free tanning technology: a sustainable approach for cleaner leather manufacturing. *Green Chem.* 2022;24(5):2179–92. <https://doi.org/10.1039/d1gc04105c>.
38. Usha R, Ramasami T. The effects of urea and n-propanol on collagen denaturation: using DSC, circular dichroism and viscosity. *Thermochim Acta.* 2004;409(2):201–6. [https://doi.org/10.1016/s0040-6031\(03\)00335-6](https://doi.org/10.1016/s0040-6031(03)00335-6).
39. Han YY, Lin ZX, Zhou JJ, Yun G, Guo R, Richardson JJ, Caruso F. Polypeptide-mediated assembly of proteins for engineering functional materials. *Angew Chem Int Ed.* 2020;59(36):15618–25. <https://doi.org/10.1002/anie.202002089>.
40. Chakarska I, Goshev I, Idakieva K, Todinova S, Apostolovi G. Cross-linking phosphoric acid hydrolysates of collagen with cyanuric chloride. *J Soc Leather Technol Chem.* 2008;92(2):81–4.
41. Yan Z, Xue WL, Zeng ZX, Gu MR. Kinetics of cyanuric chloride hydrolysis in aqueous solution. *Ind Eng Chem Res.* 2008;47(15):5318–22. <https://doi.org/10.1021/ie071289x>.
42. Xin Y, Yuan J. Schiff's base as a stimuli-responsive linker in polymer chemistry. *Polym Chem.* 2012;3(11):3045–55. <https://doi.org/10.1039/c2py20290e>.
43. Du Y, Brumaud C, Winnefeld F, Lai YH, Habert G. Mechanisms for efficient clay dispersing effect with tannins and sodium hydroxide. *Colloid Surf A.* 2021;630:127589. <https://doi.org/10.1016/j.colsurfa.2021.127589>.
44. He LR, Mu CD, Shi JB, Zhang QA, Shi B, Lin W. Modification of collagen with a natural cross-linker, procyanidin. *Int J Biol Macromol.* 2011;48(2):354–9. <https://doi.org/10.1016/j.ijbiomac.2010.12.012>.
45. Payne KJ, Veis A. Fourier transform IR spectroscopy of collagen and gelatin solutions: deconvolution of the amide I band for conformational studies. *Biopolymers.* 1988;27(11):1749–60. <https://doi.org/10.1002/bip.360271105>.
46. Chen JJ, Ahn T, Colon-Bernal ID, Kim J, Holl MMB. The relationship of collagen structural and compositional heterogeneity to tissue mechanical properties: a chemical perspective. *ACS Nano.* 2017;11(11):10665–71. <https://doi.org/10.1021/acsnano.7b06826>.
47. Russomanno P, Assoni G, Amato J, D'Amore VM, Scaglia R, Brancaccio D, Pedrini M, Polcaro G, La Pietra V, Orlando P, Falzoni M, Cerofolini L, Giuntini S, Fragai M, Pagano B, Donati G, Novellino E, Quintavalle C, Condorelli G, Sabbatino F, Seneci P, Arosio D, Pepe S, Marinelli L. Interfering with the tumor-immune interface: making way for triazine-based small molecules as novel PD-L1 inhibitors. *J Med Chem.* 2021;64(21):16020–45. <https://doi.org/10.1021/acs.jmedchem.1c01409>.
48. Zhang J, Wang CH, Zhang FT, Lin W. Anionic surfactant sulfate dodecyl sodium (SDS)-induced thermodynamics and conformational changes of collagen by ultrasensitive microcalorimetry. *J Leather Sci Eng.* 2021;3:21. <https://doi.org/10.1186/s42825-021-00063-2>.
49. Lu ZB, Liao XP, Shi B. The reaction of vegetable tannin-aldehyde-collagen: a further understanding of vegetable tannin-aldehyde combination tannage. *J Soc Leather Technol Chem.* 2003;87(5):173–8.
50. Okuyama K. Revisiting the molecular structure of collagen. *Connect Tissue Res.* 2008;49(5):299–310. <https://doi.org/10.1080/03008200802325110>.
51. Shi JB, Wang CH, Ngai T, Lin W. Diffusion and binding of laponite clay nanoparticles into collagen fibers for the formation of leather matrix. *Langmuir.* 2018;34(25):7379–85. <https://doi.org/10.1021/acs.langmuir.8b00923>.
52. Wu B, Mu CD, Zhang GZ, Lin W. Effects of Cr³⁺ on the structure of collagen fiber. *Langmuir.* 2009;25(19):11905–10. <https://doi.org/10.1021/la901577j>.
53. He X, Ding W, Zeng YH, Yu Y, Zhou JF, Shi B. Insight into the correlations between fiber dispersion and physical properties of chrome tanned leather. *J Am Leather Chem Assoc.* 2020;115(1):23–9.
54. Covington AD, Song L, Suparno O, Koon HEC, Collins MJ. Link-lock: an explanation of the chemical stabilisation of collagen. *J Soc Leather Technol Chem.* 2008;92(1):1–7.
55. Ramesh RR, Ponnuel M, Ramalingam S, Rathinam A. Compact glyoxal tanning system: a chrome-free sustainable and green approach towards tanning-cum-upgradation of low-grade raw materials in leather processing. *Environ Sci Pollut Res.* 2022;29(23):35382–95. <https://doi.org/10.1007/s11356-022-18660-x>.

Publisher's Note

Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.