

A Novel Non-Pickling Combination Tanning for Chrome-free Leather Based on Reactive Benzenesulphonate and Tannic acid

by

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Abstract

A non-pickling combination tanning based on reactive benzenesulphonate (rBS) and Tannic acid (TA) has been developed for the chrome-free leather manufacturing. By optimizing the tanning process, the two-bath combination tanning with 4% rBS and 10% TA at the final pH 3.0-3.5 can raise the shrinkage temperature (T_s) of goatskins to $\sim 86^\circ\text{C}$. Morphological analysis results reveal that the chrome-free leather exhibits a clear even grain surface and isolated collagen fiber network structure. The novel combination tanning approach not only improves light fastness, but also confers high physical and mechanical properties to the chrome-free leather which can meet the Chinese standard requirements for furniture leather and shoe upper leather. The non-pickling tanning without use of salt or acid is also benefit to clean leather-making production.

Introduction

Chrome tanning remains the most widely used tannage in world leather industry due to excellent comprehensive properties of the resultant leather.¹ However, the utilization of chromium in conventional chrome tanning procedure is only 60-70%, which not only causes serious waste of chromium resources, but also brings about negative effects on the environment because of large quantities of chromium-containing sludge² and leather waste.³ Trivalent chromium salts used in tanning systems are potentially oxidized to hexavalent chromium in the presence of alkali, UV radiation and high temperature, as well as post-tanning materials such as fatliquoring agents containing unsaturated bonds.⁴ Since Cr(VI) is considered as highly allergenic,⁵ carcinogenic⁶ and genotoxic⁷ to animals and humans, the chrome-tanning solid waste has been listed in National Hazardous Waste list (HW21) in China since 2008. Moreover, increasingly strict restrictions on the Cr(VI) level in leather articles have been issued in succession.⁵ In addition, high concentration of salt contamination is introduced in conventional pickling-chrome tanning process.⁸ The Cl⁻ content in effluents from leather plants must be below 3000 mg/L before

discharge to the environment as required by Mandatory National Standard GB 30486-2013, China.⁹ Therefore, exploring of eco-friendly chrome-free tanning agent and green tanning process is becoming highly desirable for the sustainable development of the leather industry.¹⁰

At present, chrome-free tanning agents mainly include non-chrome mineral tanning agents (aluminum, titanium and zirconium) and organic tanning agents such as vegetables, aldehydes and syntan etc.¹¹ And the combination tanning¹² is always applied due to the relatively poor tanning property of those agents by solo tanning. Among them, the chrome-free combination tanning based on vegetable tannins has drawn great attention because of its natural origin, suitable molecular weight and appropriate tanning properties.¹³ So far, combination tannages by tannic acid-zinc sulfate or sodium silicate,¹⁴ tannic acid-aluminum-silica¹⁵ and tannic acid-organophosphorus¹⁶ have been reported. However, the potential environmental and health risks from metal salts (Al³⁺) and free formaldehyde in some syntans cannot be neglected. The newly developed combination tannage based on TA and nano-clay shows that the improvement in leather physical performances and environmental impact can be achieved by the appropriate combination of the two tanning agents with cooperation effect.^{17,18}

In addition, some novel chrome-free tanning materials have been developed and commercialized. We noticed a novel amphoteric organic compound syntan, reactive benzenesulphonate (Figure 1). The reactivity of the two chlorine groups (-Cl) in the benzenesulphonate molecule are temperature-dependent. The first one (marked in red in the structure, Figure 1) can react with amino group of collagen at 30-50°C; while the reaction temperature for the second one needs to be above 80°C. And its sulfonate groups (-SO₃⁻) and secondary amine can also interact with -NH₃⁺ and -COO⁻ on collagen under certain conditions.¹⁹ Its tanning effect can be simply performed at initial pH 7 and produce light color leather. Nevertheless, the tanned leather has some shortcomings such as low shrinkage temperature and poor storage resistance.

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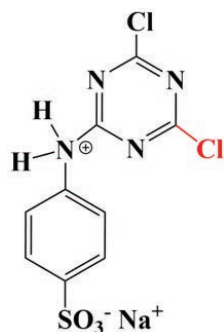


Figure 1. The structure representation of reactive benzenesulphonate

In the present work, we have developed a combination tannage based on reactive benzenesulphonate and TA in order to overcome the negative aspects of solo tanning and avoid potential metal and neutral salt pollution. The parameters of the tanning process have been optimized and the characteristics of the obtained leather have been investigated. Our aim is to develop a novel non-pickling combination tanning technology for chrome-free leather.

Experiments

Materials

The limed goatskin pelts with an average area of 4~5 square meters were taken as raw materials for leather processing. The dosages of the chemicals were all based on the weight of limed pelts. Reactive benzenesulphonate (denoted as rBS hereafter), sodium p-[(4,6-dichloro-1,3,5-triazin-2-yl)amino]benzenesulphonate (CAS: 4156-21-2), is from Granofin® Easy F-90 liq with 20~25 wt% active component, courtesy of Stahl Company. Tannic acid (TA, tannins content: 81 wt%) was purchased from Institute of Chemical Industry of Nanjing Forest Products, China. All the chemicals used in leather processing were of commercial grade.

Particle size determination of TA and rBS

0.1 g/L TA and rBS aqueous dispersions were prepared respectively before measurement and then measured at 25°C using a nanoparticle size and Zeta potentiometer (Zetasizer NanoZS, Malvern, England). Each value reported is an average of three parallel test data.

Tanning process

Table I gives the combination tanning process recipe for chrome-free leather. The limed goat pelts were delimed, bated and washed before tanning. For two-bath combination tanning, the pelts were first tanned with 1~10 wt% rBS for 8 h without pickling,²⁰ then rinsed and tanned by TA with varied amounts from 5~15 wt% for another 3 h. The final pH of tanning floats was adjusted to 3.0~5.0 with an interval of 0.5 by NaHCO₃. The obtained chrome-free leathers were piled overnight. In order to compare the tanning effect, first adding TA and then rBS (TA-rBS) in separate baths was also studied. In addition, rBS-TA tanning in the same float, namely one-bath combination tanning was carried out as well to explore the tanning mechanism. Solo rBS tanning was performed under the same conditions (Table I) as control. The dosages of tanning materials were optimized by the measurement of the shrinkage temperature (T_s) of the crust leathers and the uptake of TA in the tanned float.

Determination of shrinkage temperature

The shrinkage temperature of crust leather was determined by a shrinkage tester using the ASTM method.²⁰ A 10 mm 60 mm sample was cut out from the tanned leather and hung vertically in water. The rate of heating was kept at 2°C per minute. The temperature at the first definite sign of shrinking of the samples was taken as T_s . Each experimental result was obtained from average of three samples.

Measurement of the uptake of TA

The standard curve of TA concentration against the maximum absorbance value was measured and plotted ($R^2 = 0.9990$) by using UV-visible spectrophotometer (UV3600, Shimadzu, Japan) according to previously reported method.²¹ Then, 10 mL spent liquor from solo TA tanning and experimental tanning processes were collected and centrifuged at 2500 rpm for 5 min to remove suspended solids. The TA concentration in the spent liquor was analyzed by UV-visible spectrophotometer and the uptake of TA was calculated by the formulation as follow.

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

Where C_o is the concentration of TA offered and C_s is the concentration of TA in the spent liquor.

Table I
rBS-TA combination tanning Process

Process	Material	Dosage (%)	Time (h)	Temperature	pH
Limed goats were weighed, delimed, bated and washed as conventional process.					
Tanning	Water	40		35 °C	~7.8
	rBS	1~10	2		~6.0
	Water (55-65°C)	30	2	40 °C	~5.6
	Water (55-65°C)	30	4	45 °C	~5.0
Draining, and washing					
	Water	100		25 °C	5.0
	TA	5~15	3		
	HCOOH	0~0.5	1	35 °C	3.0~5.0
Check the final pH, stay overnight and measure T_s .					

Zeta potential measurements

10 g chrome-free leather samples were pulverized into powder particles and dispersed in 400 mL deionized water to form suspension. The pH of the suspension was adjusted to 2.5~6.0 with an appropriate amount of 0.1 mol/L HCl or NaOH solution, respectively, and then stirred at 150 rpm, 30°C for 30 min. The Zeta potential of the suspension was measured using a flow potential analyzer (Mütek™ SZP-10, BTG, Germany). Each experimental result is obtained from average of three parallel test data. The zero point indicates the isoelectric point (IEP) of leather.²²

SEM analysis

After lyophilized at -50°C in a freeze dryer for 24 h, experimental crust leather samples were cut into specimens with uniform thickness (~1 cm × 1 cm) by a microtome (CM1900, Leica, Germany), respectively. The cross-section images of samples at low and high magnification levels were obtained by a scanning electron microscope (JSM-7500F, JEOL, Japan). The accelerating voltage was set as 15 KV.

Determination of color difference

The control and experimental crust leather were irradiated by 15 W ultraviolet lamp at room temperature for different times before measurement.²³ Then the color parameters of the irradiated crust leather were measured by Chromaticity analyzer at the spectral detection wavelength of 400~700 nm. Color measurement of lightness-darkness (L^*), redness-greenness (a^*) and yellowness-blueness (b^*) were recorded, and the color difference (ΔE) was calculated using the following equations:

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (2)$$

Where ΔL^* , Δa^* and Δb^* represent the lightness, redness-greenness and yellowness-blueness differences between irradiated and unirradiated crust leather, respectively, and ΔE represents the total color difference.

Physical and mechanical properties measurements

The control and experimental leather specimens of standard dimensions for various physical tests were obtained according to IULTCS methods.²⁴ The specimens were first conditioned at 20 ± 2°C in a suitable environment (RH = 65 ± 2 %) for 48 h. Then physical and mechanical properties, such as tensile strength, elongation at break,²⁵ tear strength²⁶ and bursting strength²⁷ were measured as per standard procedures. Each value is an average of three samples.

Results and Discussion

Optimization of rBS and TA combination tanning

Combination tanning methods

Figure 2 shows the T_s of the crust leathers obtained by different tanning methods. It is clear that the adding order of tanning agents has significant effect on the T_s . First tanning with rBS and then TA (rBS-TA) results in higher hydrothermal stability of crust leathers

than that of TA-rBS. This is reasonable because the underlying tanning mechanisms of TA and rBS are different. Vegetable tannin like TA reacts with collagen primarily via hydrogen bonding and has a strong filling effect within the collagen fiber structure.²⁸ Whereas rBS can form covalent bonds with the amino groups of collagen and exhibit tanning effect. In the case of TA-rBS tanning, the smaller TA particles (Figure 3) initially penetrate into collagen fibers, then fix to polar side chains of collagen with available carboxyl, amino or hydroxyl groups (depending on pH). Especially, the possible interaction of the polyphenols with amino sidechains is unfavorable to the covalent bonding between rBS and the amino groups of collagen. Thus, adding of TA before rBS may block the diffusion paths and hinder the penetration and bonding of the larger-sized rBS molecules.

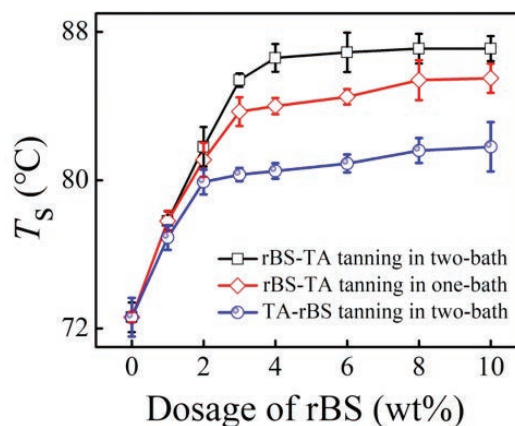


Figure 2. T_s of crust leathers obtained by varied tanning methods. The dosage of TA was kept at 10% based on the weight of limed pelts.

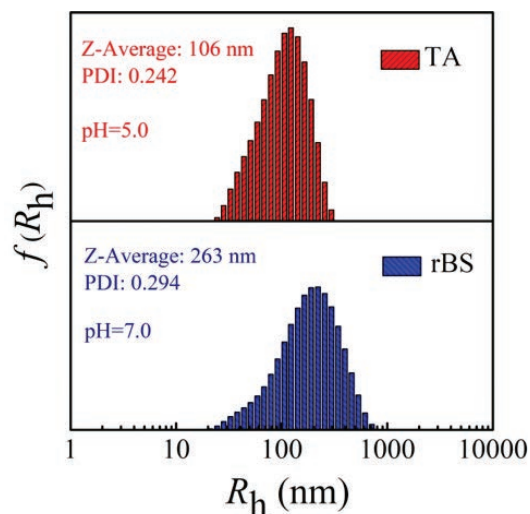


Figure 3. Hydrodynamic radius distributions $f(R_h)$ of TA and rBS at 25 °C.

Furthermore, Figure 2 also shows that for rBS-TA combination tanning, two-bath method is better than one-bath, as reflected in higher T_s . In other words, it is necessary to rinse the rBS-tanned leather before shifting to TA tanning float, because the higher temperature (~45°C) and residual benzenesulphonate in rBS pre-tanned float may facilitate the formation of TA-based aggregates in the outer layer of the pelt. Such insufficient combination tanning can

only cause limited increase of T_s to the leather with the increasing of rBS. Therefore, rBS-TA two-bath combination tanning is the optimal tanning system, and it is used for further experiments.

The dosage of rBS and TA

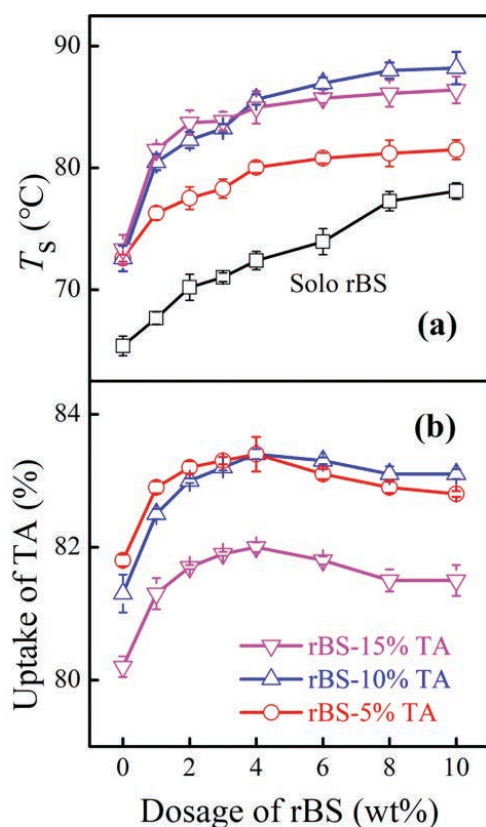


Figure 4. T_s of crust leather (a) and the uptake of TA (b) as a function of rBS dosage

Figure 4a shows the T_s of rBS-TA combination tanned crust leather. Note that the solo TA tanning with 5~15% dosage can raise the T_s of bated goatskins by 6~8°C. The solo rBS tanning with 1~10% dosage gives an increase in T_s of 3~12°C. In contrast, the T_s of rBS-TA combination tanned leather reaches ~85°C. Namely, the rise in T_s is much higher than that of solo TA and rBS tanning at the same dosage, showing the synergistic tanning effect of rBS and TA. Moreover, the uptake of TA significantly increases in comparison to solo TA tanning, indicating that rBS can facilitate the fixation of TA in crust leather (Figure 4b). When rBS is above 4%, the T_s values plateaus, whereas the corresponding uptakes of TA decrease slightly. It can be related to the blockage of available bonding sites of collagen fibers by rBS and TA at certain concentrations. On the whole, the use of 4% rBS and 10% TA for the combination tanning can be both efficient and economical compared with the reported 10% benzenesulphonate solo tanning.¹⁹

Final pH

It is known that for both collagen and tanning agents, the availability of reactive groups depend on the float pH, which in turn has a substantial influence on the tanning reactivity.²⁹ Figure 5 shows the effect of final pH in the tanning float on the T_s of crust leather. When

the pH is adjusted to 3.3~3.5, the T_s reaches the peak. The reason can be that at the pH close to the precipitation point of TA (pH = 2.5), TA particles tend to aggregate and deposit onto collagen fibers,¹⁸ promoting the synergistic interaction between rBS and TA. However, further lowering pH, the efficient binding of tanning materials and collagen fibers may decrease instead in view of the T_s . Therefore, the final pH in the combination tannage is optimized as 3.3~3.5.

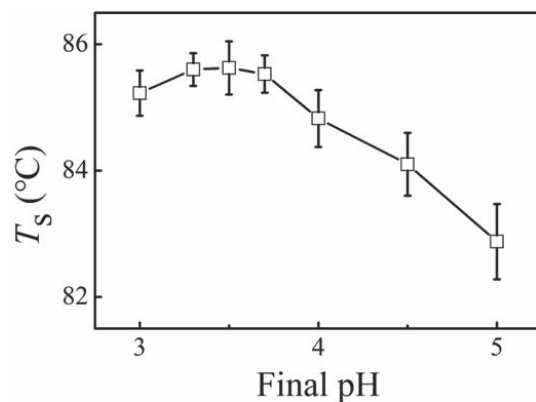


Figure 5. T_s of crust leather as a function of final pH.

Zeta potential analysis

The isoelectric point (IEP) of collagen and its changes during leather making can indicate the state of hide substance and help to understand the bonding between tanning agents and the groups on the collagen molecule, revealing the tanning mechanism.³⁰ As given in Figure 6, IEP of solo rBS tanned leather is at pH ~4.81, lower than that of bated goatskins (~5.2). It is because the surface positive charge of leather (NH_3^+) is blocked by rBS. After the introduction of TA, IEP of the chrome-free leather decreased to pH ~3.66, showing some kind of characteristics of vegetable tanned leather (IEP 3.2~4.0).²⁹ Moreover, the float pH 4.5~5.0 in the later rBS tanning is basically consistent with the initial pH of TA tanning, which is beneficial to the penetration of TA into collagen fibers. Therefore, non-pickling tanning is reasonably feasible to the present combination tanning system, so that the salt pollution from conventional chrome tannage can be eliminated.

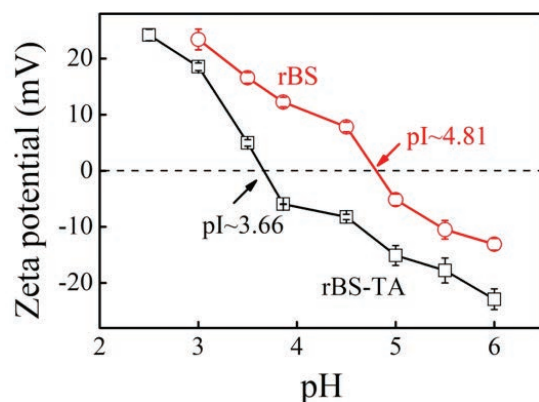


Figure 6. Zeta potentials of solo rBS and rBS-TA combination tanned leathers at different pH.

3.3 Morphological analysis

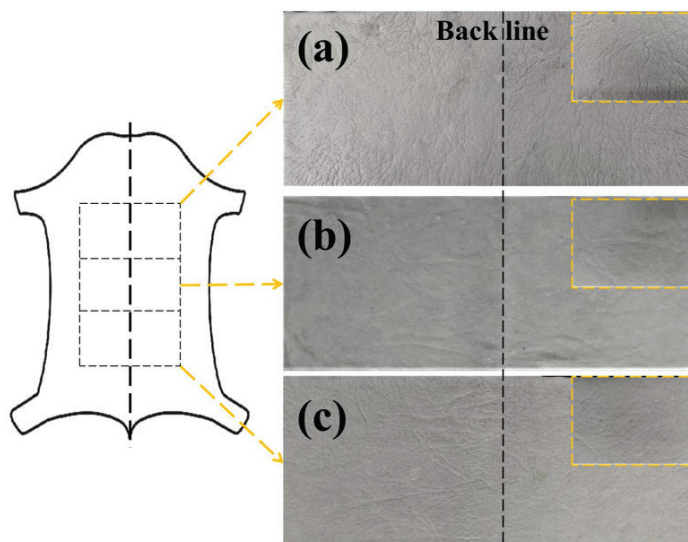


Figure 7. The photos of solo TA tanned (a), solo rBS tanned (b) and rBS-TA combination tanned (c) crust leathers.

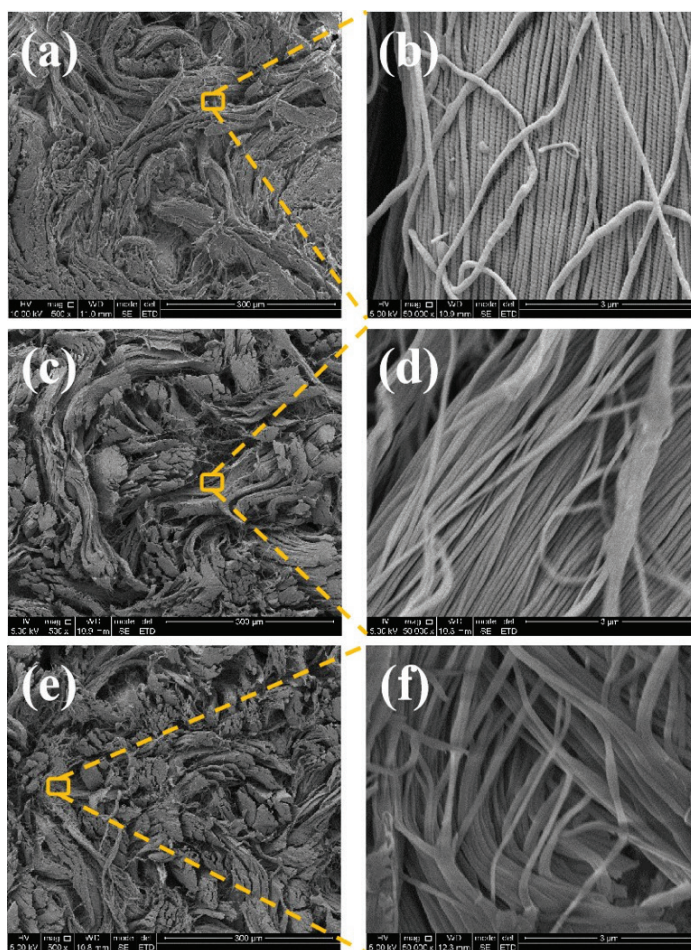


Figure 8. SEM morphologies of cross sections of solo TA tanned leather (a and b), solo rBS tanned leather (c and d) and rBS-TA combination tanned leather (e and f).

Figure 7 shows the photos of solo TA, solo rBS and rBS-TA combination tanned crust leathers. The presence of TA confers the crusts (Figure 7a and c) tight and clear grain surface, mainly attributed to the filling and astringent nature of TA. In contrast, the solo rBS tanned leather (Figure 7b) exhibits fine and even grain, and the rBS-TA tanned leather (Figure 7c) does combine the features of both, showing clear and fine grain surface with fullness, elasticity and foam hand-feel.

SEM observations (Figure 8) further indicate that solo TA tanned leather exhibits tight and thick collagen fiber bundles (Figure 8a and b). Whereas, the collagen fibers of solo rBS tanned and the combination tanned leathers seem loosened and isolated to some degree (Figure 8c-8f). The results suggest the advantages of rBS-TA combination tannage.

The synergistic tanning mechanism of rBS and TA

Figure 9 shows the synergistic tanning mechanism of rBS and TA. It is generally accepted that Type I collagen plays a key role in the manufacture of leather and in determining the properties of leather. The content of acidic (7.82%) and basic (8.61%) amino acids, amino acids containing hydroxyl groups (15.24%) and peptide groups is decisive for the reactivity of the collagen.²⁹ As to rBS tanning in an aqueous solution, reactive chlorine on benzenesulphonate molecule is hydrolyzed to hydroxyl first, then reacts with side-chain aminos of Lys, Hyl and Arg residues by C–N covalent bonding. The covalent crosslinking is regarded as the predominant reaction in rBS tanning. Meanwhile, the released H⁺ can automatically reduce the pH of the tanning float, promoting the formation of –NH₃⁺ on collagen and its subsequent bonding with sulfonate groups (–SO₃[−]) of the benzenesulphonate by electrostatic salt linkage.¹⁹ Phenolic hydroxyl groups of TA can not only form hydrogen bonding with hydroxyl groups of Hyp, Hyl, Ser and Tyr residues or peptide groups in the fundamental chain,³¹ but also can interact with secondary amine of benzenesulphonate molecules by hydrogen bonding. Thus, the synergistic crosslinking within collagen fibers can be formed, which substantially contributes to the enhanced hydrothermal stability of the chrome-free leather.

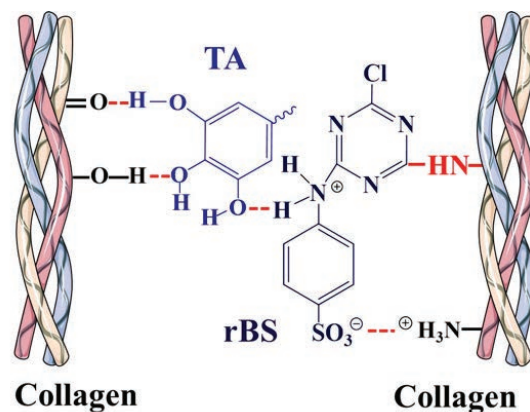


Figure 9. Schematic representation showing synergistic interactions of rBS and TA with collagen in the combination tannage

Color difference analysis

Light fastness is assessed by the exposure of the crust leathers in UV irradiation.³² As shown in Figure 10a, the color difference (ΔE) of rBS-TA combination tanned leather is lower than that of solo rBS tanning under different irradiation time, illustrating that the introduction of TA improves the light fastness of crust leather. The enhanced resistance to UV irradiation can be due to the UV absorption capacity and antioxidant ability of TA.³³ In addition, the introduction of TA slightly reduces L^* value of the combination tanned leather (Figure 10b) due to the darkness effect of TA. Nevertheless, rBS-TA combination tanned leather still gives a light shade (Figure 7).

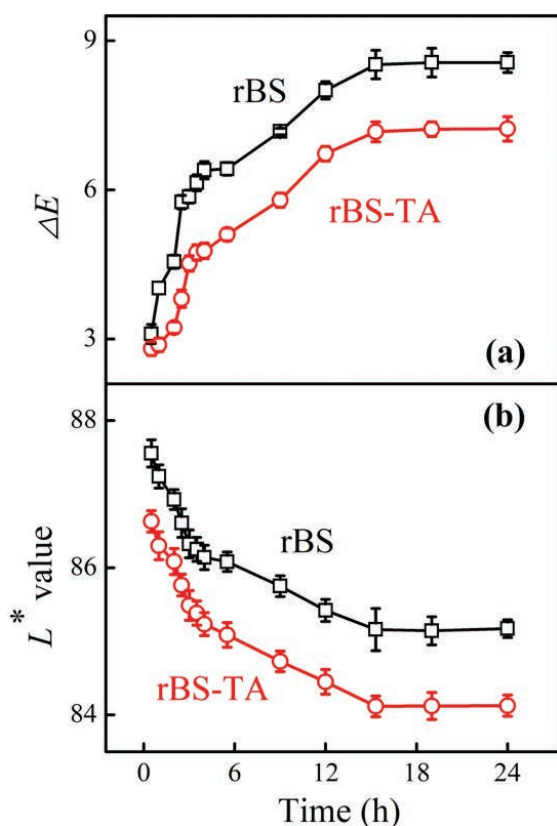


Figure 10. ΔE (a) and L^* value (b) of crust leathers under UV irradiation for 24 h.

Physical and mechanical properties measurements

The physical and mechanical properties of crust leathers including tensile strength, tear strength, elongation at 10N, elongation at break, bursting strength and T_s are shown in Table II. Note that all of the physical properties of rBS-TA combination tanned leather are better than that of solo rBS tanned leather. This is consistent with the increased hydrothermal stability owing to synergistic tanning effect of rBS and TA. Moreover, all of the physical properties can meet the Chinese standard requirements for furniture leather³⁴ and shoe upper leather³⁵. Therefore, the rBS-TA non-pickling combination tannage is promising for the manufacture of furniture leather and shoe upper leather.

Table II

Physical and mechanical properties of crust leathers

Parameters	rBS	rBS-TA	furniture leather	shoe upper leather
$T_s / ^\circ\text{C}$	77.3 \pm 0.8	86.5 \pm 0.7	/	\geq 80
Tensile strength/ MPa	13.8 \pm 2.4	20.4 \pm 2.1	/	/
Tearing load / N	48.8 \pm 3.1	52.2 \pm 4.4	\geq 40	\geq 20
Tear strength / N \cdot mm ⁻¹	43.5 \pm 3.9	45.4 \pm 3.3		
Elongation at 10N / %	21.8 \pm 3.2	26.2 \pm 4.1	/	\leq 40
Elongation at break / %	44.3 \pm 2.1	58.3 \pm 2.4	35~60	/
Bursting strength / N \cdot mm ⁻¹	182.3 \pm 3.2	259.7 \pm 3.6	/	\geq 200

Conclusions

A novel non-pickling combination tanning for chrome-free leather based on reactive benzenesulphonate and tannic acid has been developed in this work. Compared with TA and rBS solo tanned leathers, the hydrothermal stability of the rBS-TA tanned leather increases significantly due to the presence of synergistic effect between rBS and TA. The optimized combination tanning, i.e. 4% rBS and 10% tannic acid at the final pH 3.0-3.5 in two-bath process, can confer the leather with a T_s of above 86 $^\circ\text{C}$. And the obtained leather has fine isolated collagen fiber network structures. Moreover, the introduction of TA improves physical properties and light fastness of leather. The non-pickling combination tannage can not only completely eliminate the risks of chromium salts and free formaldehyde, but also reduce the neutral salts used in conventional pickling process, most beneficial to clean leather production.

Acknowledgements

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