

Construction of a Chrome-free Tanning System Based on Highly-oxidized Starch–Zirconium Complexes

by

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Abstract

Chrome-free leather manufacture is one of the major focuses of leather industry. In this work, a chrome-free tanning system based on highly-oxidized starch–zirconium complexes (HOS–Zr) was constructed. Particle size and charge properties analyses revealed that the small size (2.5 nm) and the low cationic species content (45.1%) of HOS–Zr at low pH facilitated its uniform penetration in leather at the initial stage of tanning, and the large size (89–169 nm) and the high cationic species content (77.5%) of HOS–Zr after basification contributed to its stable crosslinking between collagen fibers. A 3% HOS–Zr offer (based on the weight of ZrO₂) imparted wet white with sufficient tanning effect. The physical properties of HOS–Zr crust leather were remarkably better than those of lactic acid–zirconium crust leather and were comparable to those of chrome crust leather. Wastewater in HOS–Zr tanning system showed a reduction in TOC load by 40.0% and higher biodegradability compared with chrome tanning system. As a result, this work provided a practical and sustainable approach to eliminate chrome in leather manufacture.

Introduction

Leather industry is facing an enormous challenge associated with the generation of chrome-containing wastewater and solid wastes that may pose a potential environmental risk.^{1–3} Thus, green and sustainable chrome-free tanning agents and tannages should be developed to eliminate chrome from the source.^{4–6} Owing to the good tanning performance, zirconium salt is regarded as a promising alternative to chrome tanning agent.⁷ However, zirconium salt is easy to undergo hydrolysis and olation to form macromolecular cationic complexes even under low pH conditions,⁸ thereby causing deposition on leather surface and uneven distribution in leather. Consequently, leather tanned with zirconium salt usually shows undesirable organoleptic properties.

Introduction of masking agents (ligands) is a common strategy to promote the penetration of zirconium salt in leather. The reported ligands can be divided into two categories, i.e., small molecular ligands such as lactic acid, citric acid, and tartaric acid,⁹ and

synthetic macromolecule ligands such as multi-carboxyl polymer and sulfonated tetraphenyl calix[4] resorcinarene.^{10,11} Small molecular ligands are effective in strengthening the penetration of Zr complexes, since they can coordinate with zirconium salt and alleviate its surface binding. However, the complexes may be too small to form macromolecule crosslinking networks among collagen fibers.¹² Macromolecule ligands, which have abundant functional groups and wide molecular weight distribution, can improve the tanning performance of complex tanning agents. Nevertheless, these polymer ligands mainly used non-renewable petrochemicals as raw materials. Hence, designing a sustainable ligand is necessary for the development of chrome-free tannage.

We previously developed a type of environment-friendly highly-oxidized starch (HOS) ligand by using H₂O₂ and Cu–Fe catalyst.¹³ The HOS ligand with proper carboxyl content and relatively large molecular size can coordinate with zirconium salt (HOS–Zr) and result in excellent tanning performance. Then research on the modified polysaccharides as ligand of non-chrome metal salts has been an emerging trend.^{14–18} In this study, to further build a satisfactory chrome-free eco-tanning system, the tanning conditions of HOS–Zr were optimized in terms of the shrinkage temperature (T_s) of wet white, and the uptake rate of zirconium and HOS by leather. Then, the particle size and the charge properties of HOS–Zr in tanning liquor were analyzed to reveal its coordination behavior. Finally, HOS–Zr tanning system was systematically compared with conventional lactic acid–zirconium (Lac–Zr) and chrome tanning systems through tanning performance and environmental benefits analyses. This work aims to develop a practical and green chrome-free tanning system for the sustainable leather industry.

Experimental

Materials

Pickled cattle hide for the production of sofa leather was obtained from a local tannery. HOS with carboxyl group of 10.0 mmol/g and Mw of 6.8 kDa was prepared using starch, hydrogen peroxide, and a Cu–Fe catalyst, as described in our previous work.¹³ Lactic acid (Lac), Zr(SO₄)₂·4H₂O, hydrochloric acid, and sodium hydroxide were of

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analytical grade and supplied by Chengdu Kelong Chemical Co., Ltd. (Sichuan, China). Basic chromium sulfate (basicity 33%, Cr₂O₃ 24%) was of industrial grade and supplied by Minfeng Chemical Co., Ltd. (Chongqing, China). The other reagents used for analysis were of analytical grade. The chemicals used for leather processing were of industrial grade.

Optimization of HOS–Zr Tanning System

Pieces of pickled cattle hides (60 cm × 30 cm) were repickled with 80% water (based on weight of limed hide), 7% sodium chloride, and 0.1% sulfuric acid at 25°C for 60 min. Then they were tanned with Zr(SO₄)₂·4H₂O (1%, 2%, 3%, and 4%, based on the weight of ZrO₂) and HOS (the mass ratio of HOS to ZrO₂ was 0.4:1, 0.8:1, 1.2:1) at 25°C for 1, 2, 3, and 4 h, respectively. This duration of tanning before basification was defined as a penetration stage. After the pH of tanning float was basified to 4.0 with magnesium oxide and sodium bicarbonate, 120% hot water (60°C) was added. The drums ran for another 2 h at 40°C, and then stayed overnight. The Zr and total organic carbon (TOC) concentrations of tanning floats before and after processing were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 8000, PerkinElmer, USA) and TOC analyzer (vario TOC, Elementar, Germany), respectively, and the uptake rates of Zr and HOS were calculated.¹⁹ The T_s of the wet white leather was measured using a T_s tester (MSW-YD4, Sunshine Electronic Research Institute, China).

Particle Size Analysis

Particle size measurements of HOS solution (48 g/L) and HOS–Zr solution (containing 48 g/L HOS and 173 g/L Zr(SO₄)₂·4H₂O) were performed at 25°C using particle size analyzer (Omni, Brookhaven, USA). The pH of the solution was adjusted to 0.5 and 3.0 by using HCl solution (1 mol/L) or NaOH solution (1 mol/L) before determination.

Charge Properties Analysis

The contents of anionic, electroneutral, and cationic species in the Zr (3.6 g/L Zr(SO₄)₂·4H₂O), Lac–Zr (containing 1.0 g/L lactic acid and 3.6 g/L Zr(SO₄)₂·4H₂O), and HOS–Zr (containing 1.0 g/L HOS and 3.6 g/L Zr(SO₄)₂·4H₂O) complexes solutions were determined using a precipitation method.^{18,20} One mL of Anionic precipitant (sodium diisobutyl naphthalenesulfonate, Xinrunde Chemical Co. Ltd., Hubei, China) was mixed with 20 mL complexes solution whose pH had been adjusted to 0.5 and 3.0 by using HCl solution (1 mol/L) or NaOH solution (1 mol/L). After centrifuging at 5000 r/min for 5 min, the precipitate was transferred and digested with nitric acid and hydrogen peroxide. The zirconium content in the digestion solution was detected by using ICP-OES and was defined as anionic species content. Likewise, 1 mL of cationic precipitant (a type of cationic polyamine resin, Jogel Industrial Co., Ltd., Shanghai, China) was mixed with 20 mL complexes solution (pH 0.5 and 3.0). Centrifugation, digestion, and ICP-OES detection were performed to obtain the cationic species content. The total zirconium content in complexes solution was determined by using ICP-OES after digestion. The percentage of anionic and cationic complexes were

calculated as formulas (1) and (2), and the rest were defined as the percentage of electroneutral complexes.

$$\text{Anionic complexes percentage \%} = \frac{\text{Anionic species content}}{\text{Total zirconium content}} \times 100 \quad (1)$$

$$\text{Cationic complexes percentage \%} = \frac{\text{Cationic species content}}{\text{Total zirconium content}} \times 100 \quad (2)$$

Tanning Trials

Three pieces of pickled cattle hide (8 kg for each) were used for the tanning trials. The first piece was tanned with Zr(SO₄)₂·4H₂O (3 wt% ZrO₂, based on the weight of limed hide, the same below) and 2.4 wt% Lac ligand to obtain the Lac–Zr tanned leather (Table I). The second piece was tanned with the same dosages of Zr(SO₄)₂·4H₂O and HOS to obtain the HOS–Zr tanned leather (Table I). The last piece was tanned with 7% chrome tanning agent (1.68 wt% Cr₂O₃) to obtain the chrome tanned leather (Table II). After tanning, the T_s of the tanned leathers was measured using a T_s tester. The samples of tanned leather were split into three uniform layers by using a freezing microtome (CM1950, Leica, Germany), and then dried to constant weight at 102°C. The dried samples were digested, and their Zr/Cr contents were determined by using ICP-OES to calculate the ZrO₂/Cr₂O₃ contents (based on the weight of dry leather) in each layer of the tanned leathers. The samples of tanned leathers were cut into pieces (2 cm × 2 cm), dried at 45°C, and ground into particles (diameter less than 2 mm) by using a cutting mill (SM 100, Retsch, Germany), and then their isoelectric points (pI) were determined by using a zeta potential analyzer (MütekTM SZP-10, BTG, Germany).²¹ The samples of tanned leather were lyophilized by using a freeze dryer (LGJ-30F, Xinyi, China), and the grain surface was observed by using a stereo microscope (M205 C, Leica, Germany). The distribution of Zr/Cr on the cross sections of leather was observed by using an energy dispersive x-ray spectroscopy (EDS, INCA X-MAX 50, Oxford, UK), and the cross section of leather was observed by using a scanning electron microscope (SEM, Pro X, Phenom, Netherlands).

The tanned leathers were wrung and shaved to uniform thickness of 1 mm, and then a typical post-tanning process (Table III) was conducted to obtain crust leathers. The crust leathers were conditioned at 20°C and 65% relative humidity for 24 h, and then their physical properties, such as softness, tensile strength, tear strength, bursting strength, elongation at break, compression performance, and resilience performance, were determined.²² Finally, the grain surface was observed by stereo microscope and the cross section was observed by SEM.

Wastewater samples were collected at the end of each tanning and post-tanning process, and the volumes were measured. The Zr/Cr and TOC concentrations in wastewaters were analyzed as mentioned above. The Zr/Cr and TOC loads were calculated and expressed as kg/ton of pickled cattle hide. In addition, biochemical oxygen demand (BOD₅) and chemical oxygen demand (COD_{Cr}) of the wastewater samples were determined.^{23,24}

Table I
La-Zr and HOS-Zr tanning process

Process	Material	Percentage (%) ^a	Temperature (°C)	Time (min)	Remarks
Repickling	Water	80	25		
	Sodium chloride	7			
	Sulfuric acid	0.1		60	
Tanning	Zr(SO ₄) ₂ ·4H ₂ O	8.7	25		3% ZrO ₂
	Lac /HOS	2.8		180	
	Magnesium oxide	1.2	25	30 × 4	
	Sodium bicarbonate	2.4		5 × 20	pH 4.0
	Water	120	40	120	Overnight, drain

Horse up for 24 h →Wet white

^a the percentage of material was based on the weight of limed hide.

Table II
Conventional chrome tanning process

Process	Material	Percentage (%) ^a	Temperature (°C)	Time (min)	Remarks
Repickling	Water	8	25		
	Sodium chloride	7			
	Sulfuric acid	0.1		60	
Tanning	Basic chromium sulfate	7	25	240	
	Sodium formate	1	25	30	
	Sodium bicarbonate	2		6 × 20	pH 4.0
	Water	120	40	120	Overnight, drain

Horse up for 24 h →Wet blue

^a the percentage of material was based on the weight of limed hide.

Table III
Post-tanning process

Process	Material	Percentage (%) ^a	Temperature (°C)	Time (min)	Remarks
Rewetting	Water	400	35		
	Degreasing agent	0.5		40	Drain
Washing	Water	400 × 2	35	10 × 2	Drain
Neutralizing	Water	200	35		
	Neutralization syntan	2			
	Sodium formate	1		30	
	Sodium bicarbonate	0.6 × 2		15 + 60	Drain, pH 6.0
Washing	Water	400 × 2	35	10 × 2	Drain
Retanning	Water	100	35		
	Acrylic resin	3			
	Dispersing syntan	1		30	
	Melamine resin	1			
	Dicyandiamide resin	2			
	Dyestuff	2		30	
	Dispersing syntan	1			
	Mimosa	5		60	
	Formic acid	0.4 × 2		10 + 30	Drain, pH 4.0
	Fatliquoring	Water	150	50	
Phospholipid		5			
Sulfonated fatliquor		1			
Synthetic fatliquor		9			
Dyestuff		0.3		60	
Formic acid		0.5 × 2		15 × 2	Drain, pH 3.8
Washing	Water	200	25	15	Drain

Horse up overnight →Hang drying → Conditioning → Milling → Crust leathers

^a the percentage of material was based on the weight of limed hide.

Results and Discussion

Optimization of HOS–Zr Tanning System

The tanning conditions of HOS–Zr, including mass ratio of HOS to ZrO_2 , HOS–Zr dosage, and penetration time, were optimized to construct a satisfactory chrome-free tanning system. Figures 1 (a) and 1(b) show the effect of mass ratio of HOS to ZrO_2 on HOS–Zr tanning performance. The T_s of wet white reached a peak (89.6°C) when the mass ratio of HOS to ZrO_2 was 0.8:1. Further increase in the mass ratio resulted in a decline of the T_s of wet white because excess HOS with abundant carboxyl groups masked the Zr ion and blocked the binding sites between HOS–Zr and leather collagen fibers. This fact can also be verified by the decrease in the uptake rate of zirconium and HOS. Figures 1 (c) and 1(d) show the effect of HOS–Zr dosage on its tanning performances. High dosage resulted in high T_s of wet white but low uptake rate of zirconium and HOS because of the limited coordination sites on the leather collagen fibers. The T_s of wet white tanned with 3% HOS–Zr was 88.1°C, which met the common requirement for storage, transportation and trade in the leather industry.¹⁹ As shown in Figures 1 (e) and 1(f),

prolonging the penetration favored the uptake of HOS–Zr in leather, and thus enhanced the T_s of wet white. When the penetration time was higher than 3 h, the T_s of wet white and the uptake of HOS–Zr reached a plateau. Thus, the optimized HOS–Zr tanning conditions was summarized as follows. The mass ratio of HOS to ZrO_2 was 0.8:1. The HOS–Zr dosage was 3%. The penetration time was 3 h.

Particle Size of HOS–Zr

Leather collagen fibers possess a hierarchical structure assembled by microfibrils, fibrils, fibers and fiber bundles,²⁵ and its pore size distribution ranges from 7 Å to 150 μm .²⁶ Theoretically, the tanning agents with too large molecular size may be difficult to penetrate into the microfibrils and fibrils (Φ 50–200 nm), whereas those with too small molecular size may be hard to form effective crosslinking bond between fibers (Φ 2–10 μm). Thus, a proper size is an essential factor for a tanning agent to show excellent tanning performance. Here, we performed particle size analysis to verify whether HOS–Zr is suitable for tanning. The particle size distribution of HOS and HOS–Zr solutions at different pH values are shown in Figure 2. When the pH was 0.5, HOS showed two peaks around 1.0 μm and

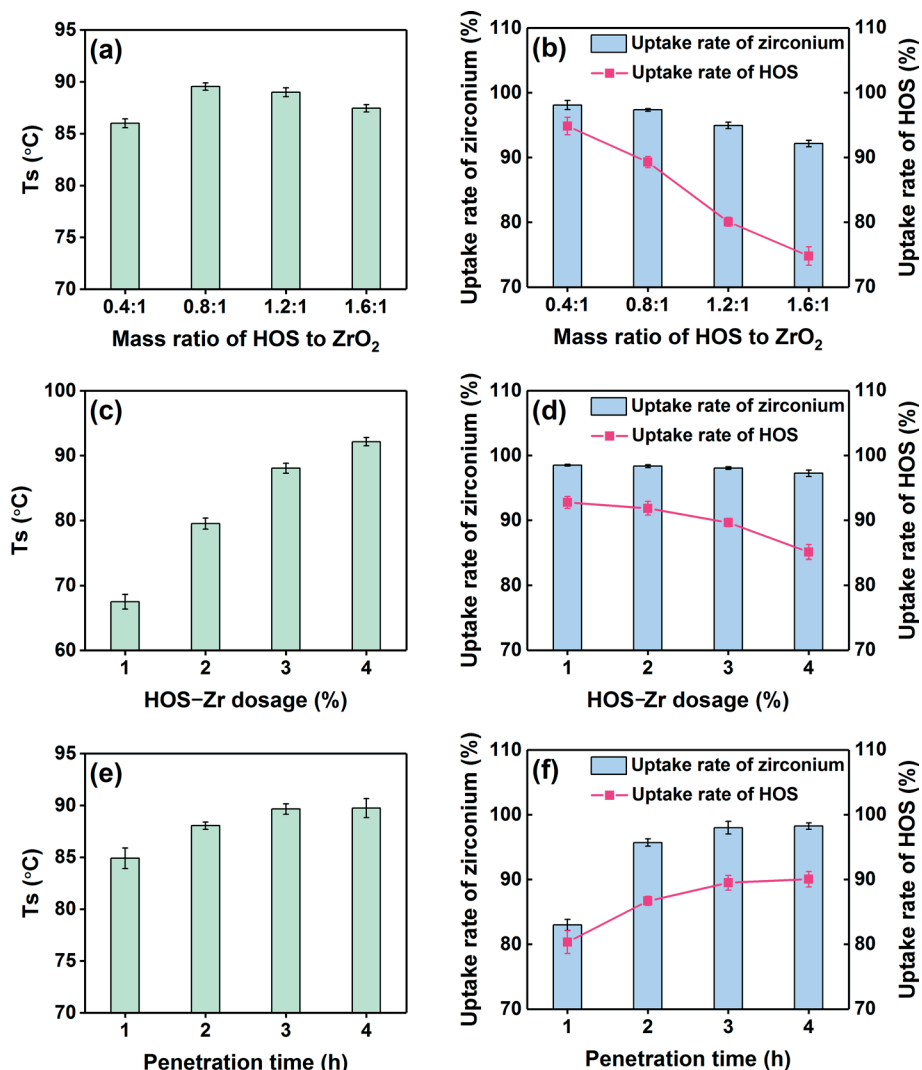


Figure 1. Effects of mass ratio of HOS to ZrO_2 (a, b) (HOS–Zr dosage 3%, penetration time 3 h), HOS–Zr dosage (c, d) (mass ratio of HOS to ZrO_2 0.8:1, penetration time 3 h), penetration time (e, f) (mass ratio of HOS to ZrO_2 0.8:1, HOS–Zr dosage 3%) on T_s of wet white and uptake rate of zirconium and HOS by leather.

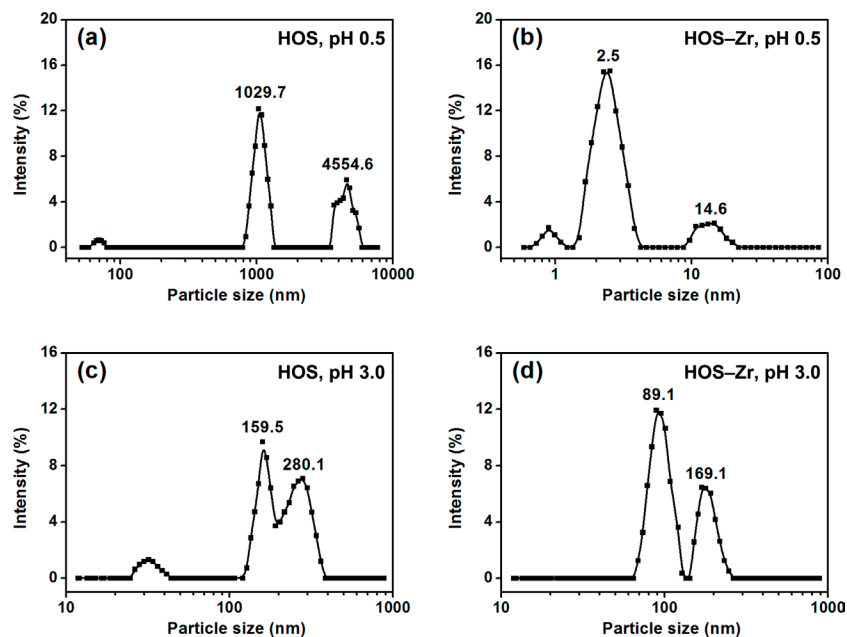


Figure 2. Particle size distribution of HOS and HOS-Zr at pH 0.5 (a, b) and at pH 3.0 (c, d).

4.5 μm (Figure 2a), indicating the formation of serious aggregation structures. However, HOS-Zr exhibited a prominent peak around 2.5 nm (Figure 2b) because the formation of HOS-Zr complexes weakened the hydrogen bonding and van der Waals forces among HOS molecules.²⁷ The small size of HOS-Zr ensured its penetration in the hierarchical structure of collagen fibers at the beginning of tanning (pH 0.5). As the pH increased to 3.0, the partial deprotonation of carboxyl group made the particle size of HOS decreased to 159.5 nm and 280.1 nm (Figure 2c). The hydrolysis and olation of HOS-Zr made its particle size increase to 89.1 nm and 169.1 nm (Figure 2d), which favored its crosslinking among collagen fibers after basification (pH > 3.0). Therefore, HOS-Zr showed a good potential in balancing its penetration and fixation in leather.

Charge Properties of Zr Complexes

The penetration and fixation of a tanning agent in leather is also influenced by its charge properties in tanning float.¹⁸ According to the theory of tanning chemistry, a mineral tanning agent is mainly coordinated with carboxyl anions of collagen through its cationic species. A tanning agent with low cationic species content is easy to penetrate into leather, while that with high cationic species content is prone to bind with collagen.²⁸ Based on this theory, we investigated the charge properties of Zr, Lac-Zr, and HOS-Zr complexes at different pH values, and the results are shown in Figure 3. When the pH was 0.5, the cationic species content in complexes followed the order as HOS-Zr (45.1%) < Lac-Zr (51.7%) < Zr (56.7%). This result indicated that HOS-Zr will be easier to penetrate into the leather

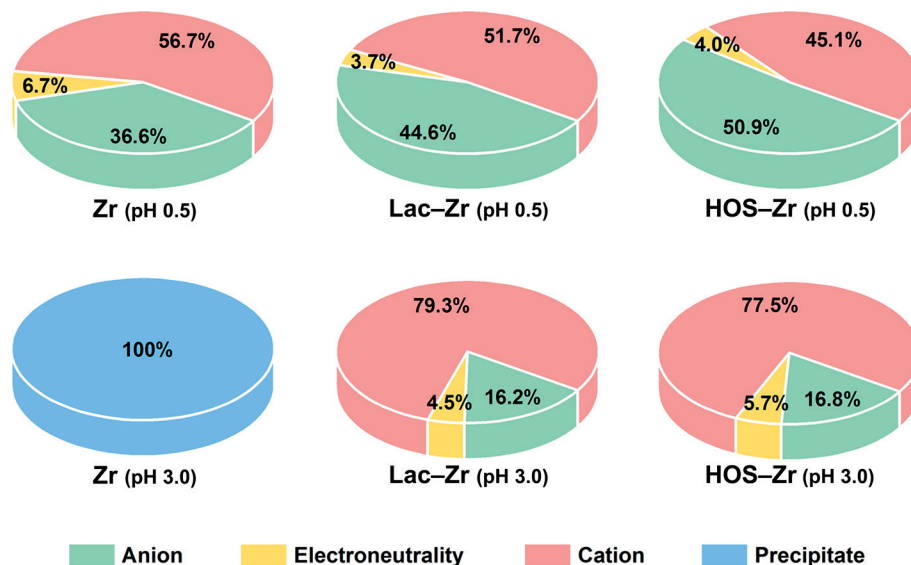


Figure 3. Charge compositions of Zr, Lac-Zr, and HOS-Zr complexes at pH 0.5 and pH 3.0.

in the early stage of tanning (pH 0.5) than Zr and Lac-Zr, which should be attributed to the fact that the introduction of HOS ligand masked the Zr ion more effectively and reduced the electropositivity and reactivity of Zr complexes. When the pH rose to 3.0, pure Zr salt completely precipitated, showing weak stability to alkali. Lac-Zr and HOS-Zr were still in aqueous solution. The cationic species content of HOS-Zr (77.5%) was close to that of Lac-Zr (79.3%), indicating that they had similar binding capacity with collagen fibers after basification (pH > 3.0). Based on the results above, HOS-Zr is expected to have better tanning performance than Lac-Zr and Zr.

Comprehensive Evaluation of the Tanning Performance of HOS-Zr

The tanning performance of HOS-Zr was systematically compared with that of Lac-Zr and chrome to demonstrate its practicability. As shown in Table IV, ZrO₂ distribution uniformity of HOS-Zr tanned leather was obviously higher than that of Lac-Zr tanned leather, which could also be demonstrated by EDS analysis (Figure 4). This result confirmed the speculation of the last section that HOS-Zr complexes can uniformly penetrate and distribute in the leather matrix because of the masking effect of HOS. Accordingly, the T_s (Table IV), the grain surface morphology, and the fiber dispersion degree (Figure 5) of HOS-Zr tanned leather were substantially

better than those of Lac-Zr tanned leather, even close to those of chrome tanned leather. The pI of leather plays an important role in leather processing, since it greatly influences the penetration and the fixation of post-tanning chemicals in leather matrix.²¹ The pI of HOS-Zr tanned leather (7.03, see Table IV) was close to that of chrome tanned leather (7.13), implying an excellent compatibility of the HOS-Zr tanned leather to the existing post-tanning process that was designed for chrome tanned leather.

The properties of HOS-Zr crust leather were further evaluated. Table V shows that all the physical properties of the HOS-Zr crust leather were better than those of Lac-Zr crust leather because of the favorable distribution and fixation of HOS-Zr in leather. Compared with chrome crust leather, HOS-Zr crust leather exhibited higher tensile strength, tear strength, and bursting strength, but lower softness, elongation, compression and resilience performance (Figure 6), probably because of the strengthening effect and strong filling ability of HOS-Zr on collagen fibers. Figure 7 shows that HOS-Zr crust leather presented a finer grain and a looser fiber network than Lac-Zr crust leather, which was similar with those of chrome crust leathers. Therefore, HOS-Zr tanning agent is qualified for leather manufacture because of the reliable physical properties of the resultant leather.

Table IV
Properties of tanned leathers

Sample	ZrO ₂ /Cr ₂ O ₃ (based on dry weight of leather, %)			Ts (°C)	pI
	Grain	Middle	Flesh		
Lac-Zr	8.41 ± 0.03	7.79 ± 0.06	8.32 ± 0.04	81.4 ± 1.3	6.27
HOS-Zr	8.99 ± 0.06	8.67 ± 0.08	8.81 ± 0.03	91.0 ± 0.6	7.03
Chrome	4.91 ± 0.04	4.68 ± 0.03	4.71 ± 0.04	109.9 ± 1.3	7.13

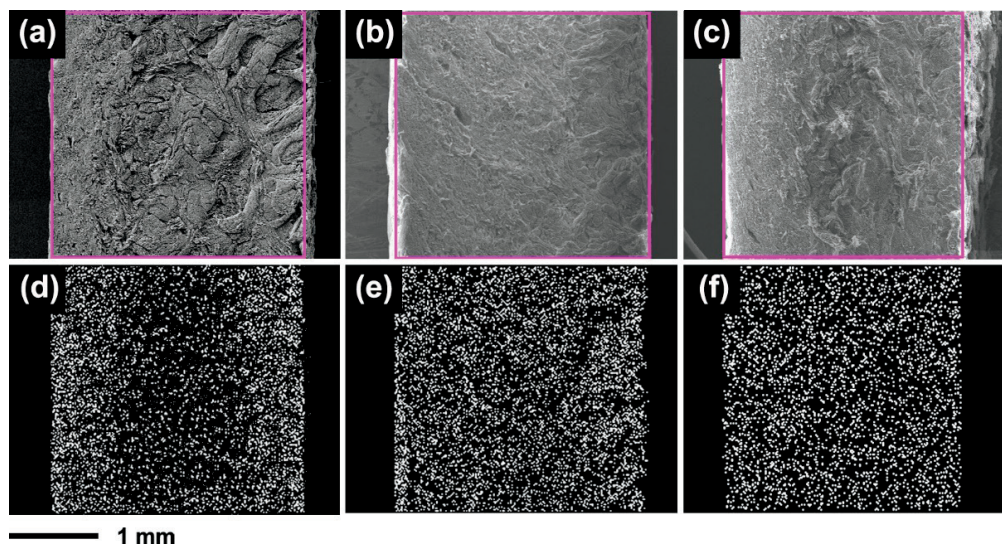


Figure 4. SEM images of cross section of Lac-Zr (a), HOS-Zr (b), and chrome (c) tanned leathers. EDS images of the distribution of zirconium/chromium in cross section of Lac-Zr (d), HOS-Zr (e), and chrome (f) tanned leathers.

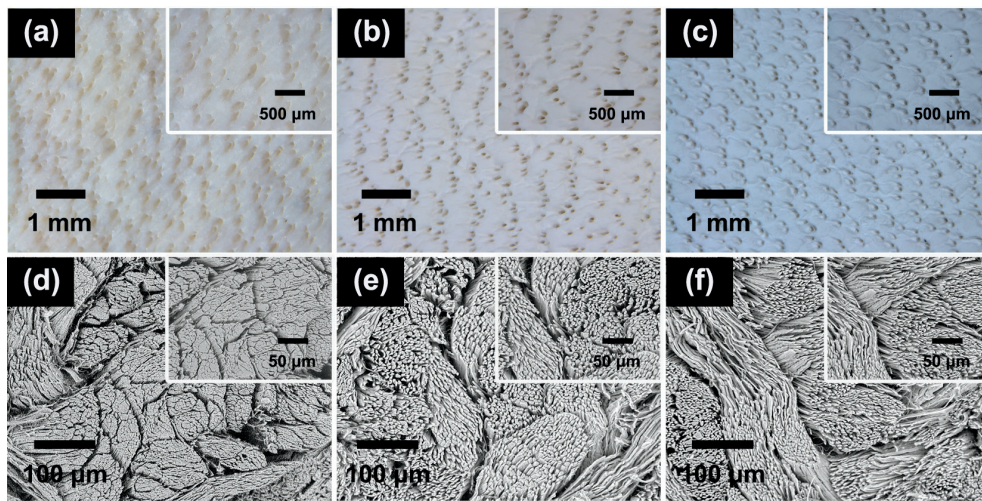


Figure 5. Stereo microscope images of grain surface of Lac-Zr (a), HOS-Zr (b), and chrome (c) tanned leathers. SEM images of cross section of Lac-Zr (d), HOS-Zr (e), and chrome (f) tanned leathers.

Table V
Physical properties of crust leathers

Crust leather sample	Softness(mm)	Tensile strength (N/mm ²)	Tear strength (N/mm)	Bursting strength (N/mm)	Elongation at break (%)
Lac-Zr	7.0 ± 0.2	10.6 ± 1.1	34.3 ± 2.6	275.6 ± 21.5	50.7 ± 3.9
HOS-Zr	8.3 ± 0.1	14.9 ± 1.0	49.8 ± 1.8	342.5 ± 9.7	46.1 ± 4.9
Chrome	8.4 ± 0.1	13.7 ± 0.9	44.8 ± 3.2	289.7 ± 15.2	55.9 ± 6.5

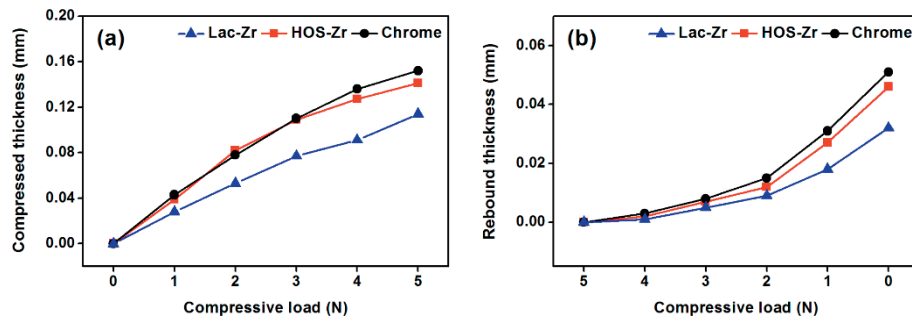


Figure 6. Compression (a) and resilience (b) performance of crust leathers.

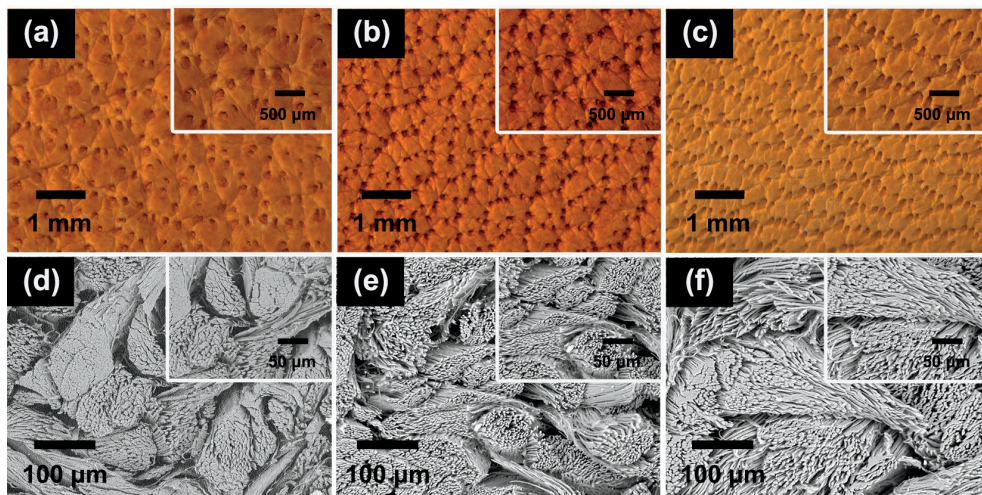


Figure 7. Stereo microscope images of grain surface of Lac-Zr (a), HOS-Zr (b), and chrome (c) crust leathers. SEM images of cross section of Lac-Zr (d), HOS-Zr (e), and chrome (f) crust leathers.

Environmental Impact Assessment

Table VI shows the Zr/Cr and TOC loads in tanning and post-tanning wastewaters. Lac-Zr and HOS-Zr tanning systems did not produce chrome-containing wastewater since no Cr was introduced. Chrome output in conventional chrome tanning system was 7.73 kg/ton of pickled hide. The Zr load in HOS-Zr wastewater (0.29 kg/ton of pickled hide) was dramatically lower than that in Lac-Zr (0.88 kg/ton of pickled hide) wastewater, implying that HOS-Zr was stably fixed on collagen fibers. As for the discharge of organics, the TOC load in HOS-Zr wastewater were reduced by 54.2% and 40.0%, respectively, compared with that in Lac-Zr and chrome wastewaters. The reduction in TOC load was mainly concentrated in retanning and fatliquoring wastewaters, suggesting that HOS-Zr tanned leather exhibited higher uptake for anionic post-tanning chemicals than Lac-Zr and chrome tanned leathers. This finding should be ascribed to the strong electropositivity of HOS-Zr tanned leather, which is consistent with results of our previous study.²¹ Thus, considerable environmental benefits can be achieved by using HOS-Zr tanning system in terms of the reduction in pollution loads.

The ratio of BOD₅/COD_{Cr} is usually used for evaluating the biodegradability of wastewater. A higher ratio means a better biodegradability.²⁹ Table VII shows the biodegradability of tanning and post-tanning wastewaters for the three tanning systems. HOS-Zr tanning wastewater was more biodegradable than Lac-Zr and chrome tanning wastewaters because the ligand, HOS, was originated from natural polysaccharide. Additionally, the BOD₅/COD_{Cr} ratio of HOS-Zr post-tanning wastewater (0.37) was higher

than that of Lac-Zr (0.30) and chrome post-tanning wastewaters (0.24). The reason may be that the low metal ion and organic contents in HOS-Zr post-tanning wastewater were conducive to microorganism growth. Thus, the HOS-Zr wastewater with high biodegradability should be convenient to treat.

Conclusions

A chrome-free eco-tanning system for eliminating chrome discharge has been constructed based on HOS-Zr complexes. The introduction of HOS greatly reduced the electropositivity and reactivity of the Zr complexes, thereby resulting in uniform distribution and effective crosslinking of the complexes in leather. The tanning performance of HOS-Zr was comparable to those of the chrome and was remarkably better than those of Lac-Zr. The HOS-Zr tanning system completely eliminated chrome discharge and reduced TOC load in tanning and post-tanning wastewater by 40% compared with chrome tanning system. Moreover, HOS-Zr wastewater showed preferable biodegradability. Thus, HOS-Zr tanning system is promising to be applied in tanneries due to its reliable leather quality and the environmental benefits.

Acknowledgement

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Table VI
Pollution loads in tanning and post-tanning wastewaters (unit: kg/ton of pickled hide)

Process	Zirconium output		Chromium output	TOC output		
	Lac-Zr	HOS-Zr	Chrome	Lac-Zr	HOS-Zr	Chrome
Tanning	0.51 ± 0.01	0.15 ± 0.00	7.34 ± 0.01	10.23 ± 0.11	8.49 ± 0.05	6.10 ± 0.11
Rewetting*	0.13 ± 0.00	0.07 ± 0.00	0.28 ± 0.01	3.16 ± 0.05	3.02 ± 0.05	1.87 ± 0.01
Neutralizing*	0.14 ± 0.00	0.04 ± 0.00	0.02 ± 0.00	4.52 ± 0.12	3.21 ± 0.18	2.74 ± 0.05
Retanning	0.03 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	9.56 ± 0.12	5.36 ± 0.08	9.49 ± 0.08
Fatliquoring*	0.07 ± 0.00	0.02 ± 0.00	0.08 ± 0.00	52.00 ± 0.55	16.38 ± 0.42	40.55 ± 0.47
Total	0.88 ± 0.02	0.29 ± 0.01	7.73 ± 0.03	79.47 ± 0.93	36.46 ± 0.78	60.75 ± 0.71

*Including the following washing process.

Table VII
Biodegradability of tanning and post-tanning wastewaters

Wastewater sample	COD _{Cr} (g/L)		BOD ₅ (g/L)		BOD ₅ /COD _{Cr}	
	Tanning	Post-tanning	Tanning	Post-tanning	Tanning	Post-tanning
Lac-Zr	3.21 ± 0.07	9.14 ± 0.15	0.75 ± 0.07	2.70 ± 0.21	0.23	0.30
HOS-Zr	2.62 ± 0.05	4.10 ± 0.06	0.85 ± 0.07	1.50 ± 0.14	0.32	0.37
Chrome	1.96 ± 0.04	7.17 ± 0.08	0.25 ± 0.07	1.70 ± 0.14	0.13	0.24

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