Effect of Pickling Materials on Leather Quality from a Hide Surface Charge Perspective

by

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Abstract

Salt-free pickling technology has recently received increased attention because it produces much lower salt pollution than the conventional pickling technology using formic acid, sulfuric acid, and sodium chloride. However, the existing salt-free pickling materials, for instance, aromatic sulfonic acids (ASAs), lead to reduced leather quality and the reason behind this phenomenon is unclear. In this study, we explored how ASAs affect the properties of tanned leather. Results showed that typical ASAs, such as 5-sulfosalicylic acid, 1,5-naphthalenedisulfonic acid, and 2-naphthalenesulfonic acid, penetrated cattle hide more slowly compared with formic and sulfuric acids because of their large molecular weight and strong intermolecular interactions with hide collagen. ASAs decreased the positive charge of the pickled hide via interactions with their sulfonic acid groups, resulting in the increased adsorption rate of chrome tanning agent to the hide surface. Rapid tanning agent adsorption could impede the deep penetration and uniform distribution of the agent in the ASA-pickled hide. Thus, the properties of wet blues and crust leathers pickled with ASAs are inferior to those of wet blue and crust leather pickled using conventional pickling materials. Our results indicate that a strongly positive charge of the pickled hide is vital to obtaining high-quality leather and provide insights into salt-free pickling materials from a hide surface charge perspective.

Introduction

Tanning is an important leather-making procedure because it converts hides/skins into leathers with good resistance to acids, alkalis, microbes and heat.[1,2] The most popular tannage is chrome tannage.[3] Pickling is performed prior to chrome tanning to enhance the penetration of the chrome tanning agent into the hide and obtain high-quality leather.[4] The pickling procedure reduces the float pH to 2.8–3.0 by using formic and sulfuric acids to inhibit the hydrolysis of chrome complexes and achieve small-sized chrome tanning agent that could easily penetrate hide.[5] However, a large amount of sodium chloride (6%–7% of the limed hide weight) is needed in the pickling procedure to prevent the hide collagen from acid swelling.[6] Indeed, tanneries around the world use approximately 300,000 tons of salt each year for pickling and generate massive amounts of high-salinity wastewater, which is harmful to the environment.[7] Thus, pickling effluents with high salinity are a serious challenge in the leather industry.[8]

Salt-free pickling materials, such as sulfosalicylic acid,[9,10] phenol sulfonic acid,[11] naphthalene sulfonic acid,[9,11] and naphthol sulfonic acid,[12] have been developed to reduce the salt pollution generated by the tanning industry. These aromatic sulfonic acids (ASAs) can bind with the side chains of hide collagen via electrostatic interactions and hydrogen bonds (Figures 1[a], 1[b], and 1[c]),[13] thereby avoiding the acid swelling of the hide. ASAs are believed to be suitable replacements for sodium chloride in pickling. Unfortunately, ASAs are not widely used in the leather industry because the comprehensive properties of leather pickled with ASA are inferior to those of conventional leather.[7,11] Why ASA pickling results in leather of relatively low quality remains unclear. Undoubtedly, this knowledge gap hinders further developments in salt-free pickling materials and technologies and undermines efforts to reduce salt pollution in the tanning industry.

Interactions between hide collagen and chemicals, including covalent bonding, coordination, electrostatic interaction, hydrogen bonding, van der Waals interaction, and hydrophobic interaction, affect the penetration and fixation of chemicals in hide/leather.[14-16] Because long-range electrostatic interaction is a major factor influencing the penetration of leather chemicals, this type of interaction has gained extensive attention in leather manufacturing.[17-19] Good penetration and uniform distribution of chrome tanning agent in hide is essential to obtaining high-quality leather. The chrome tanning agent tends to coordinate with the carboxyl group of collagen side chains, which allows the easy binding of the chrome tanning agent but impedes its penetration into the hide.[20-21] The hide collagen is positively charged at a pickling pH of approximately 3, and electrostatic repulsion between hide collagen and the chrome tanning agent could help slow down their surface binding.[7] That is to say, electrostatic repulsion plays an important role in ensuring the penetration depth of chrome tanning agent. ASAs have sulfonic acid groups that can combine with the amino groups of hide collagen and reduce the positive charge of pickled hide,[6] thereby inhibiting the deep penetration and uniform distribution of chrome tanning

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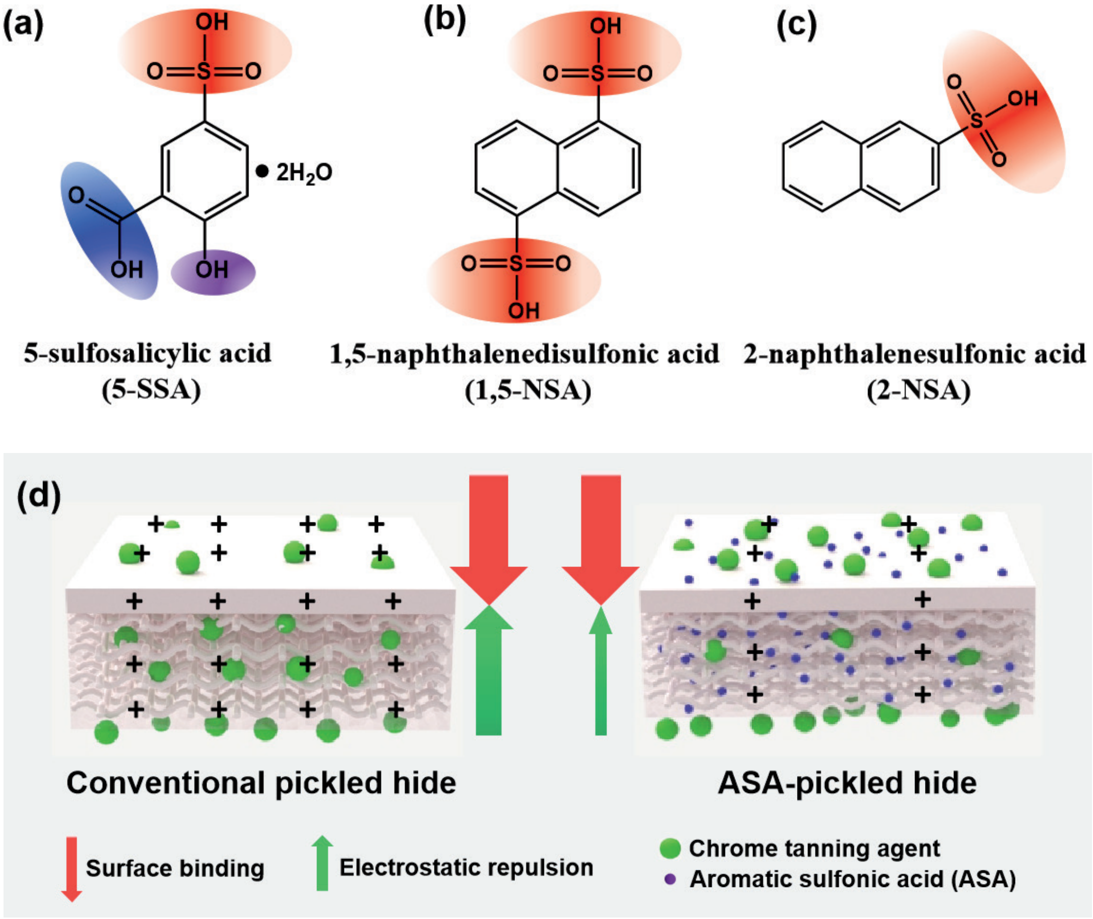

Figure 1. **(a-c)** Structures of aromatic sulfonic acids. **(d)** Schematic diagram of effect of the surface charge of pickled hide on chrome penetration.

agent (Figure 1[d]). This mechanism may explain why ASA pickling reduces the quality of leather.

In the present study, conventional pickling materials (i.e., formic and sulfuric acids, and sodium chloride) and typical salt-free pickling materials, such as 5-sulfosalicylic acid (5-SSA), 1,5-naphthalenedisulfonic acid (1,5-NSA), and 2-naphthalenesulfonic acid (2-NSA), were used to pickle cattle hides. The pickling and chrome tanning performance of the materials and the properties of the crust leather were then compared. The effects of the pickling materials on the surface charge of the pickled hides, as well as penetration and uptake of the chrome tanning agent, were further analyzed to explain how pickling materials affect leather quality and provide new insights into pickling materials.

Experimental

Materials

Limed cattle hide with a thickness of 2.2 nm was prepared by conventional presoaking, soaking, liming, and splitting. Analytical grade sodium chloride, concentrated sulfuric acid, and formic acid were purchased from Chron Chemicals Co., Ltd. (Chengdu, China). 5-SSA, 1,5-NSA, and 2-NSA were purchased from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Chrome tanning agent (Cr_2O_3 content, 25%; basicity, 33%) was provided by Brother Chemical Co., Ltd. (Haining, China). All other chemicals used for leather processing were of commercial grade, while those used for analyses were of analytical grade.

Pickling experiments

Four limed hides, each weighing approximately 2 kg, were delimed, bated, and washed as shown in Table I. Number 1 bated hide (control) was treated with 7% sodium chloride for 10 min and then pickled with 0.6% formic acid and 0.6% sulfuric acid. Numbers 2, 3, and 4 bated hides were treated with 3% sodium chloride for 10 min and then pickled with 1.4% 5-SSA, 1.2% 1,5-NSA, and 1.0% 2-NSA, respectively. The required final pH of the pickling float (i.e., 2.8) determined the dosages of sulfuric acid, 5-SSA, 1,5-NSA, and 2-NSA used for pickling. After pickling, the four hides were chrome-tanned, as shown in Table I, and then retanned, dyed, and fatliquored according to conventional procedures for crust leathers.

Table I

Pickling and chrome tanning processes

Procedure		Temperature (°C)	Chemical	Dosage (%)[a]	Remark
Pickling	**Control**	22	water	50	Run 10 min.
			sodium chloride	7	
			formic acid	0.6	Run 30 min.
			sulfuric acid	0.2	Run 20 min.
			sulfuric acid	0.2	Run 20 min.
			sulfuric acid	0.2	Run 20 min; pH 2.8; run 120 min; still overnight. Next day, run 30 min.
	Experimental	22	water	50	Run 10 min.
			sodium chloride	3	
			5-SSA/1,5-NSA /2-NSA	1.4/1.2/1.0	Run 90 min; pH 2.8; run 120 min; still overnight. Next day, run 30 min.
Chrome tanning		22	Chrome powder	3	Run 240 min.
			Sodium acetate	1	Run 30 min.
			Sodium hydrogen carbonate	0.2	Run 20 min.
			Sodium hydrogen carbonate	0.2	Run 20 min; pH 4.0; run 60 min.
		40	Water	150	Run 120 min; still overnight. Next day, run 30 min.
Horse up for 48 h, sammy, and shave for a thickness of 1.0 mm.					

[a] Percentage of chemicals is based on weight of limed hide.

Analyses of pickling performance

The pickled hides were cut 5, 10, 20, 30, 40, 60, 90, 120, and 180 min after the addition of formic acid, 5-SSA, 1,5-NSA, and 2-NSA. The hide incisions were checked with methyl red indicator and then observed using a stereo microscope (M205C, Leica, Germany) to determine the penetration depth of the acid. The penetration rate of the acid into the pickled hide was calculated using Formula (1).

$$\text{Penetration rate (\%)} = \frac{T_r}{T} \times 100\% \tag{1}$$

where T_r is the thickness of red stained part of the pickled hide, and T is the total thickness of the pickled hide.

The zeta potentials of pickled hides at pH ranging from 3 to 7 were determined using a zeta potential analyzer (Mütek SZP-10, BTG, Germany) according to the method reported in the literature.[22] The zeta potentials of 5-SSA, 1,5-NSA, and 2-NSA aqueous solutions were also measured using a zeta potential analyzer (Nano Brook Omni, Brookhaven, USA) after equilibration at 25 °C for 3 min. Based on their dosages used for the pickling experiments, the concentrations of 5-SSA, 1,5-NSA, and 2-NSA solutions were 1.4, 1.2, and 1.0 g/L, respectively.

The shrinkage temperature (T_s) of the pickled hides was measured using a digital leather shrinkage temperature instrument (MSW-YD4, Shaanxi University of Science and Technology, China). The pickled hides were lyophilized using a vacuum freeze dryer (LGJ-30F, XinYi, China), after which their pore structures were analyzed using a mercury intrusion porosimeter (AutoPore IV 9500, Micromeritics, USA) as described in the literature.[23]

Analyses of chrome tanning performance

The four hides were sampled 5, 10, 20, 30, 40, 60, 90, 120, 180, and 240 min after the addition of chrome powder. The samples were divided into three layers, including the upper, middle, and lower layers, by using a freezing microtome (CM1950, Leica, Germany) and then dried at 100°C for 8 h. A total of 0.5 g of dried sample was digested with a mixture of 5 mL of nitric acid and 5 mL of H_2O_2 solution

(30wt%) by using a microwave digestion instrument (Multiwave 3000, Anton Paar, Austria). The concentration of chrome in the digestion solution was determined by inductively coupled plasma–atomic emission spectrometry (Optima 8000DV, PerkinElmer, USA). The chrome content of the hide was calculated using Formula (2).

$$\text{Chrome content (\%)} = \frac{c \times V \times 152}{104 \times w} \quad (2)$$

where c is the chrome concentration of the digestion solution (mg/L), V is the volume of the digestion solution (L), w is the dry weight of the hide (mg), 152 is the molar mass of Cr_2O_3 (g/mol), and 104 is the molar mass of Cr in Cr_2O_3 (g/mol).

The T_s and pore structure of wet blue were analyzed as described previously. The cross section of lyophilized wet blue was observed using a scanning electron microscope (SEM, Phenom Pro, Phenom, The Netherlands). The surface of wet blue was also directly observed using a stereo microscope. Color parameters were recorded using a colorimeter (CR-13, Konica Minolta, Japan) by testing 10 different points in each sample. The color difference (ΔE) was calculated using Formula (3).

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \quad (3)$$

where L is the brightness and describes the color in the range from black to white, a is the red/green value, and b is the yellow/blue value.

Determination of the physical properties of crust leather

The crust leathers were sampled and conditioned at 20°C and 65% relative humidity for 24 h (ISO 2418:2002). Their physical properties, such as softness, tensile strength, tear strength, and bursting strength, were then measured according to the standards ISO 17235:2015, ISO 3376:2011, ISO 3377-2:2002, and ISO 3379:2015, respectively.

Results and Discussion

Penetration of various acids into hide

The penetration of traditional pickling materials (formic and sulfuric acids) and typical ASAs (5-SSA, 1,5-NSA, and 2-NSA) into the hides was compared by detecting color changes in the pickled hides after treatment with methyl red. The hide micrographs observed by stereo microscopy (Figure 2(a)) and the penetration rates of acids into the hide (Figure 2(b)) show that the pickling materials are all transferred slowly into the cattle hide. The inorganic acids completely penetrated the hide within 120 min, whereas the ASAs required more time to penetrate the hide fully. This finding may be explained by the fact that acid radical ions with negative charges are prone to bind electrostatically to the hide surface, which features positive charges (the pI of delimed hide is above 6, and the pH of pickling float is below 3), thus exerting a negative effect on the penetration of acids into the inner layers of the hide. Compared with formic and sulfuric acids, ASAs penetrated the hides more slowly because they have large molecular weights and could form strong intermolecular forces, such as hydrogen bonds, hydrophobic interactions and van der Waals force, with the collagen.[7]

Surface charge properties of hides pickled with various acids

The surface charge of pickled hide greatly affects the penetration, distribution, and fixation of tanning agents in the leather matrix.[20,24] Therefore, the effect of the pickling materials on the surface charge of pickled hide was evaluated. As shown in Figure 3(a), the zeta potentials of the three ASA solutions are below zero in the pH range of 3–7 and decrease with increasing pH, which means the three ASAs have negative charges during pickling. Figure 3(b) shows that the pI values of the ASA-pickled hides are lower than that of the control pickled hide, likely because sulfonic acid groups in the ASAs can combine with the amino groups of hide collagen. The zeta potentials

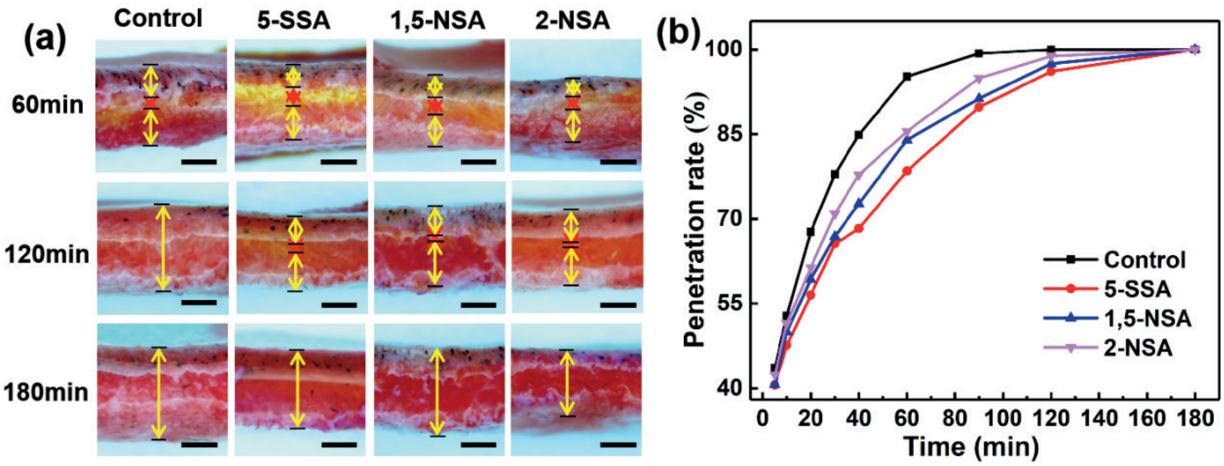

Figure 2. **(a)** Micrographs of vertical sections of different pickled hides (scale bar, 1 mm). **(b)** Penetration rates of different acids into the hides over time.

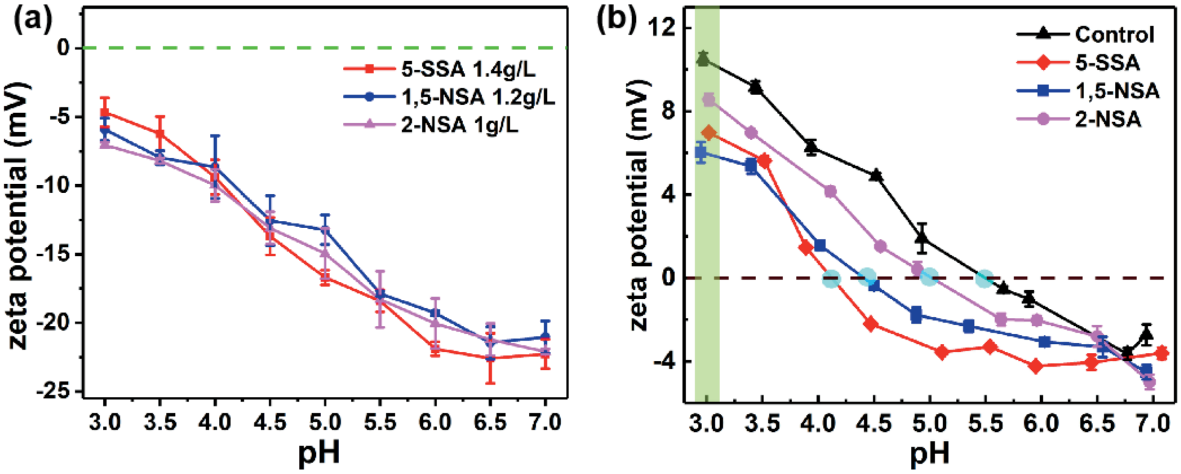

Figure 3. **(a)** Zeta potentials of 5-SSA, 1,5-NSA, and 2-NSA aqueous solutions. **(b)** Zeta potentials of different pickled hides.

of the experimental pickled hides at pH 3 were also lower than that of the control hide because of the introduction of sulfonic acid groups to the hide collagen. However, as mentioned in the Introduction, such interaction may not be beneficial to the penetration of chrome tanning agent.

Hydrothermal stability and fiber dispersion of hides pickled with various acids

The effects of the pickling materials on the hydrothermal stability and fiber dispersion of pickled hide were evaluated by measuring the T_s and pore size distribution of the hides. The data in Figure 4 show that the T_s, porosity, and percentage of small pores (sizes ranging from 0 μm to 5 μm) of the experimental pickled hides are slightly higher than those of the control hide. These results indicate that the hydrothermal stability and fiber dispersion degree of the ASA-pickled hides are greater than those of the control hide, which is related to the weak tanning property of ASAs.[25] Among the hide specimens, the 5-SSA-pickled hide had the greatest T_s and fiber dispersion because 5-SSA bears hydroxyl and carboxyl groups, which can form more hydrogen bonds with hide collagen compared with 1,5-NSA and 2-NSA.

Effect of pickling materials on chrome tanning performance

Penetration and uptake of the chrome tanning agent

The penetration and uptake of chrome tanning agent in different pickled hides were evaluated by analyzing the adsorption kinetics of the chrome to hide. In the initial stage of chrome tanning (within 60 min), the adsorption of chrome to the four pickled hides occurred quickly and in a similar manner (Figures 5(a)–5(d)). As chrome tanning progressed, adsorption equilibrium was achieved within approximately 120 min. The adsorption kinetic data were further analyzed using the pseudo-first-order (4) and the pseudo-second-order (5) kinetic models as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{4}$$

$$\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{k_2 q_e^2} \tag{5}$$

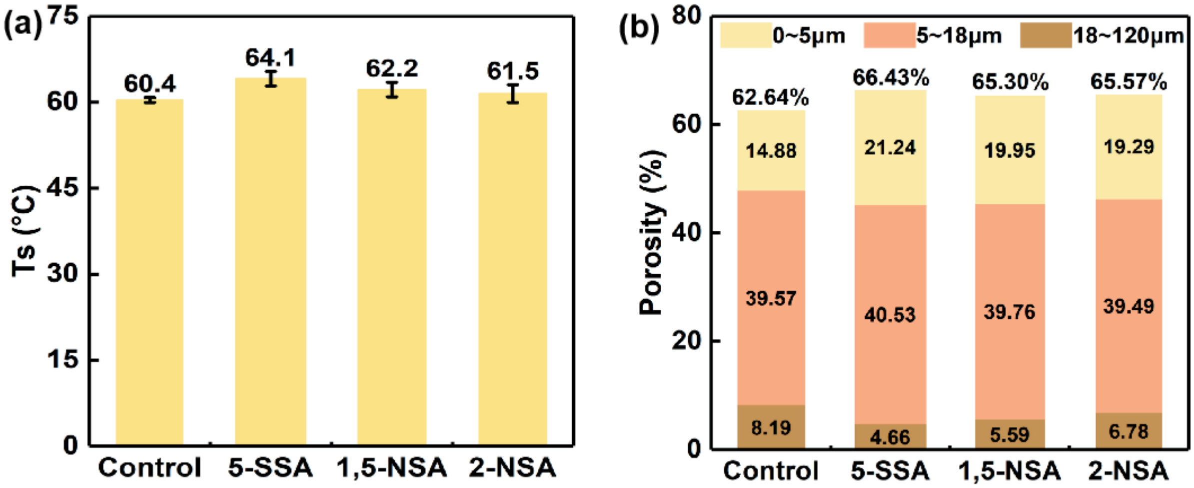

Figure 4. **(a)** Shrinkage temperatures of the pickled hides. **(b)** Pore size distributions of the pickled hides.

where q_t and q_e are the amounts of chrome adsorbed (mg/g) onto the hides at t min and equilibrium, respectively, and k_1 and k_2 are the pseudo-first-order (min^{-1}) and the pseudo-second-order (g/(mg·min)) rate constants, respectively.[26]

Table II compares the pseudo-first-order and pseudo-second-order kinetic parameters of the hides for chrome adsorption. The correlation coefficients (R^2) obtained from the pseudo-second-order kinetic model were consistently higher than 0.99. Moreover, the adsorption amounts at equilibrium calculated by the pseudo-second-order kinetic model were much closer to those determined from the experiments (Error < 6%) than those calculated by the pseudo-first-order kinetic model (Error > 24%). These results indicate that the adsorption of chrome to the four pickled hides follows pseudo-second-order kinetics rather than pseudo-first-order kinetics. Moreover, the adsorption of the chrome tanning agent to hide was controlled by chemisorption.[27] The higher rate constants (k) in the experimental groups compared with that in the control group indicate that the experimental pickled hides have more rapid adsorption rates for chrome than the control pickled hide.[28] This finding should be attributed to the less positive charge and the lower resistance to chrome bonding of the ASA-pickled hides.

The data in Figure 5(f) show that the amount of chrome adsorbed by the control pickled hide is higher than those adsorbed by the ASA-pickled hides. In particular, the chrome tanning agent is distributed more evenly in the control hide than in the experimental hides, likely because the rapid adsorption of chrome to the experimental

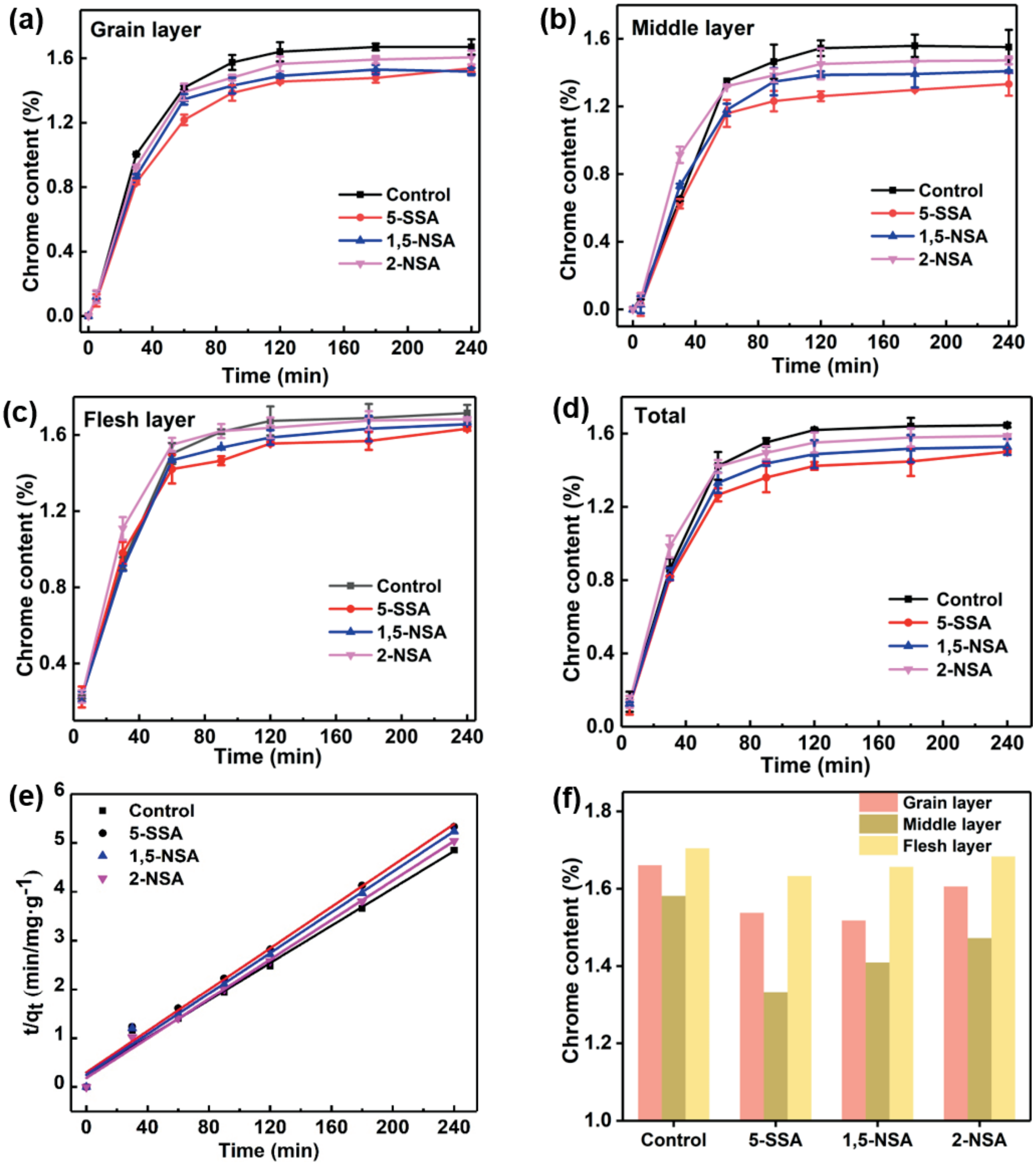

Figure 5. **(a-d)** Chrome contents of the grain **(a)**, middle **(b)**, flesh **(c)**, and total **(d)** layers of wet blue. **(e)** Adsorption kinetics of chrome to hide fitted using the pseudo-second-order kinetic model. **(f)** Chrome distributions of wet blue.

Table II

Pseudo-first-order and pseudo-second-order kinetic parameters for chrome adsorption

		Pseudo-first-order kinetic model				Pseudo-second-order kinetic model			
Group	q_e *exp* (mg/g)	k_1 (min^{-1})	R^2	q_e *cal* (mg/g)	Error (%)	k_2 (g/(mg·min))	R^2	q_e *cal* (mg/g)	Error (%)
Control	49.47	0.02567	0.9720	37.13	24.94	0.00147	0.9984	52.33	-5.78
5-SSA	45.03	0.01679	0.9440	28.55	36.60	0.00151	0.9906	47.17	-4.75
1,5-NSA	45.84	0.02278	0.9749	31.99	30.21	0.00172	0.9909	48.12	-4.97
2-NSA	47.61	0.02675	0.9864	34.39	27.77	0.00163	0.9951	49.46	-3.89

q_e *exp*: determined by experiments.
q_e *cal*: calculated by the pseudo-first-order or the pseudo-second-order kinetic model.
Error (%) = $(q_{e\,exp} - q_{e\,cal})/q_{e\,exp} \times 100$.
R^2: correlation coefficient.

hide surface impedes its deeper penetration. By contrast, the chrome tanning agent slowly binds to the control hide surface, thereby facilitating the uniform distribution of the tanning agent. These experimental results validate our hypothesis shown in Figure 1.

Hydrothermal stability, fiber dispersion, and color of wet blues

Figure 6(a) shows that the T_s of the control wet blue is higher than those of the experimental wet blues. Figures 6(b) and 6(c) show that the collagen fibers of the control wet blue are more disperse than those of the experimental groups. These findings are mainly attributed to the deeper penetration and higher uptake of chrome tanning agent in the control pickled hide, which features more positive surface charges than the experimental hides. As shown in Figure 7(a), the control wet blue is lake blue, while the experimental wet blues, especially the wet blue pickled with 5-SSA, are teal. The color difference among the hides was obvious when observed with the naked eye. In addition, the wet blue pickled with 2-NSA has a rougher grain surface compared with the other wet blues because of the strong astringency of 2-NSA. A larger ΔE_a means a greater color difference between the control and experimental wet blues.[29] The ΔE_a values of the three experimental wet blues showed the order 5-SSA > 2-NSA > 1,5-NSA (Figure 7(b)), which is consistent with the results in Figure 7(a). The color uniformity of the wet blues was evaluated by calculating their ΔE_b. The results show that the control

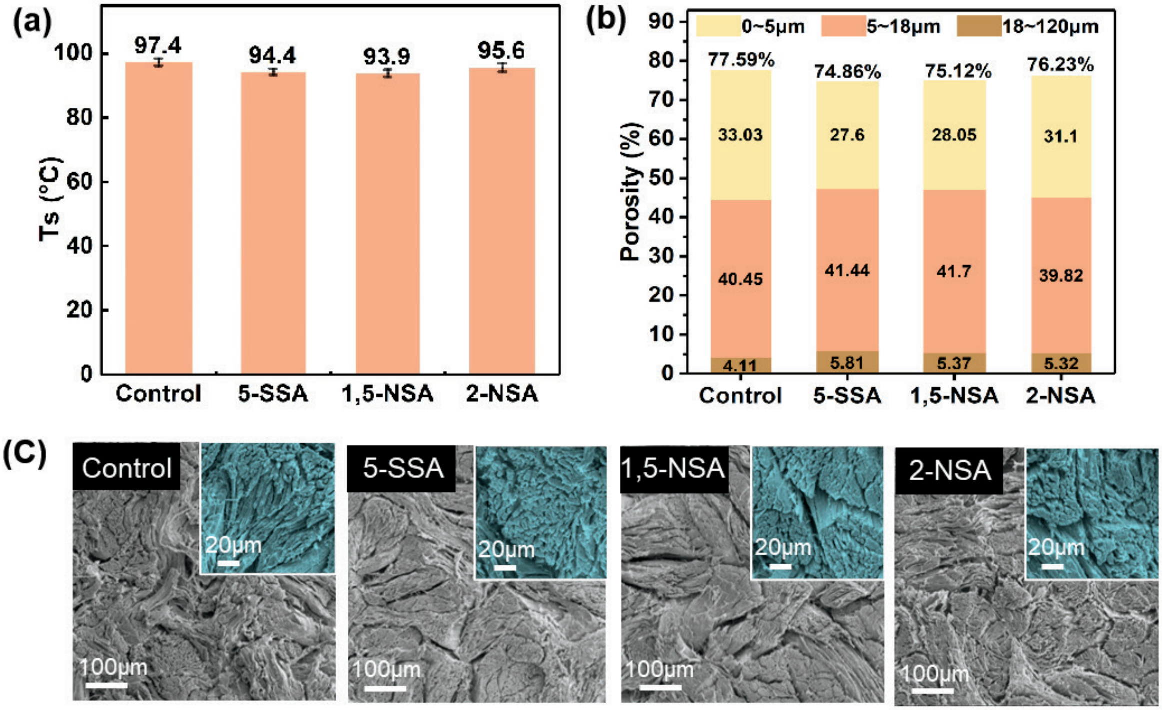

Figure 6. **(a)** Shrinkage temperatures of wet blues. **(b)** Pore size distributions of wet blues. **(c)** SEM images of cross sections of the wet blues.

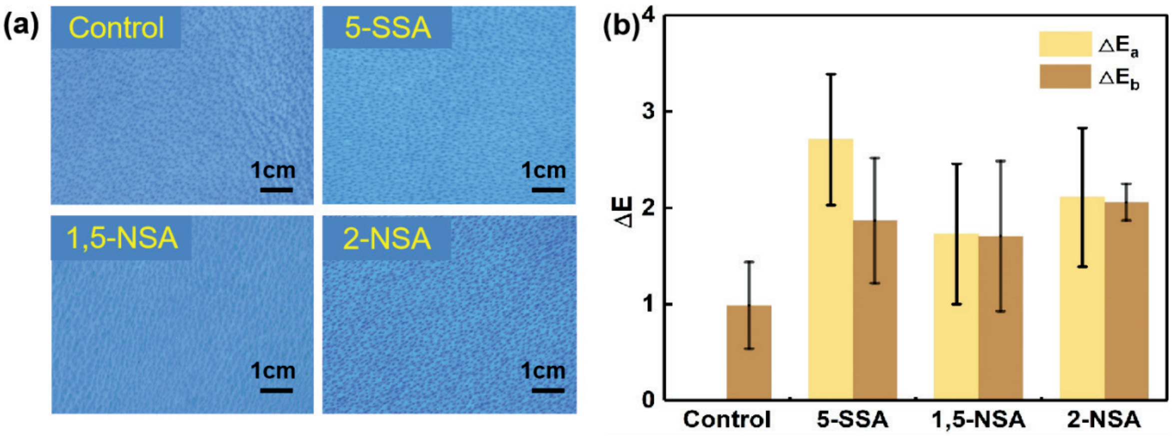

Figure 7. **(a)** Colors of different wet blue surfaces. **(b)** ΔE values of different wet blue surfaces. ΔEa reflects the color difference between the control and experimental wet blues. Here, the control wet blue is used as the calibration board. ΔEb reflects the color difference among various points in a single wet blue. Here, one of the points on the wet blue was used as the calibration board.

wet blue has a smaller ΔE_b than the experimental wet blues, thereby indicating that the color of the former is more uniform than that of the latter (Figure 7(b)). These results are closely correlated with the adsorption/bonding rate of the chrome tanning agent to the hide surface.

Effect of pickling materials on the physical properties of crust leathers

The physical properties of the control and experimental crust leathers, such as their softness, tensile strength, tear strength, and bursting strength, were determined and compared in Table III. The physical properties of the control crust leather were better than those of the experimental leathers mainly because the extensive and uniform distribution of chrome in the control wet blue could promote the penetration and fixation of post-tanning agents and fatliquors. These results suggest that a strongly positive charge of the pickled hide is important to obtain high-quality wet blue and crust leather. Developing salt-free pickling materials with fewer anionic groups or pretreating salt-free pickled hides with cationic oil may help improve the performance of salt-free pickling agents.

Conclusion

In the pickling pH range 2.8–3.0, the ASA-pickled hides had fewer positive charges than the conventional pickled hide because the sulfonic acid groups of ASAs are introduced to the hide collagen. This phenomenon resulted in the increased adsorption/bonding rate of the chrome tanning agent to the ASA-pickled hide surface. Therefore, the penetration depth and distribution uniformity of chrome in the ASA-pickled hide were inferior to those in the conventionally pickled hide. These findings could explain why the properties of wet blue and crust leather pickled with ASA are poorer than those of conventional wet blue and crust leather. The results suggest that the influence of salt-free pickling on the surface charge of hide should be seriously considered in future work.

Acknowledgements

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Table III

Physical properties of crust leathers

Group	Softness (mm)	Tensile strength (N/mm^2)	Tear strength (N/mm)	Bursting strength (N/mm)
Control	7.38 ± 0.45	14.12 ± 1.20	14.13 ± 1.69	730.21 ± 8.42
5-SSA	6.86 ± 0.74	13.08 ± 0.98	11.12 ± 2.52	613.98 ± 9.34
1,5-NSA	7.11 ± 0.33	12.44 ± 2.02	12.08 ± 1.88	622.79 ± 9.55
2-NSA	7.39 ± 1.01	14.13 ± 2.45	13.44 ± 2.22	685.03 ± 14.62

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