Effect of Calcium in Delimed Hide on Leather Quality

by

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Abstract

The efficient removal of calcium from delimed hide is essential to leather quality, but few reports have elaborated on how residual calcium in delimed hide affects leather quality. In this study, four delimed hides containing different calcium content were first prepared by using ammonium sulfate and sodium gluconate. Energy dispersive X-ray spectrometry results showed that the atomic percentages of calcium on the grain surfaces of the four delimed hides were 8.17%, 4.82%, 2.34%, and 0.25%, respectively. The bating, chrome tanning, and post-tanning performances of the four delimed hides were then analyzed to evaluate the effect of calcium in delimed hide on leather quality. Results showed that the removal efficiency of non-collagenous protein from hide in enzymatic bating, the evenness of chromium distribution, the shrinkage temperature of wet blue, and the physical properties of crust leather all increased as the calcium content of delimed hide decreased. Furthermore, efficient calcium removal from the grain surface of delimed hide played a key role in the color brightness and uniformity of wet blue and crust leather. The results draw our attention to the importance of considering the effectual removal of calcium from delimed hide for obtaining high-quality leather.

Introduction

Leather quality is always attracting considerable attention from consumers and is vital to the price and sales of leather products. High leather quality is closely related to each process of leather manufacture, including soaking, liming, deliming, bating, pickling, tanning, post-tanning, dyeing, fatliquoring, and finishing.[1,2] The conventional liming process aims to remove hair and epidermis from the hide or skin and open up collagen fibers in the raw material using sodium sulfide or hydrosulfide and lime (calcium hydroxide) and is considered the most important process in the beamhouse, as it plays a key role in preparing for the tanning process.[3,4] The liming process increases the pH of the hide to more than 12 and introduces high amounts of calcium into the hide. The high pH and calcium content of limed hide are not suitable for the subsequent bating, pickling, and tanning.[5,6] Therefore, the deliming process is performed to decrease the pH of limed hide to 8–9 and remove calcium from the hide before the bating process.[7]

Existing deliming agents include ammonium salts,[8] boric acid,[9] organic acids,[10,11] and esters.[12] The extent of calcium removal from limed hide using these deliming agents is 50–80%. Sometimes, small amounts of ammonium salt or other weakly acidic substances are also used in the bating process to further remove the residual calcium in the delimed hide for maintaining the proteolysis activity of trypsin.[13] In addition, tanners have found that the insufficient removal of calcium from the hide probably increases the color difference of wet blue and crust leather. The efficient removal of calcium from limed hide is essential to leather quality. However, to the authors' knowledge, few reports have elaborated on how residual calcium in delimed hide affects leather quality.[13] Obviously, a clear understanding of the relationship between calcium in the hide and leather quality has a substantial implication for developing better deliming agents and technologies and ensuring leather quality.

This study focuses on how residual calcium in delimed hide affects the performances of the bating, tanning, and post-tanning processes and the organoleptic and physical properties of leather. Ammonium salts, such as ammonium sulfate and ammonium chloride, are usually used to perform the deliming owing to their high pH-buffering capacity, rapid penetration in the limed hide, and low cost.[14] However, the extent of calcium removal from hide is limited by ammonium salts. Sodium gluconate is applicable for the efficient removal of calcium from limed hide based on our previous work.[15] Therefore, different amounts of sodium gluconate were used with ammonium sulfate in the deliming to prepare delimed hides with different calcium content. The effects of residual calcium in delimed hide on the removal efficiency of non-collagenous protein from bated hide, chromium distribution, shrinkage temperature (T_s) and color of wet blue, and the color and physical properties of crust leather were analyzed in order to establish how the calcium content affects leather quality.

Experimental

Materials

Relimed cattle hide (pH 12.54) prepared by conventional soaking, liming (3% sodium sulfide and 8% lime, based on the weight of fleshed hide), splitting, and reliming (4% lime, based on the weight of limed grain split) processes was used in deliming, bating, pickling, chrome tanning, and post-tanning experiments. The sodium gluconate

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Manuscript received August 13, 2022, accepted for publication October 2, 2022.

used for removing calcium from the limed hide was of analytical grade and purchased from Chron Chemicals Co., Ltd. (Chengdu, China). Trypsin from bovine pancreas was purchased from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). The chemicals used for analyses were of analytical grade. Lime, ammonium sulfate, chrome tanning agent, dye, and other chemicals used for leather processing were of commercial grade.

Deliming experiments and evaluation of deliming performance

Four pieces of relimed hides labeled SG-0%, SG-0.4%, SG-0.8%, and SG-1.2% were used for the four groups of deliming experiments. Each deliming experiment was performed in a drum with 2.0% ammonium sulfate, *X*% sodium gluconate (*X*=0, 0.4, 0.8, 1.2), and 100% water (based on the weight of relimed hide) at 32°C for 60 min. During the deliming process, the float pH values were measured using a precise pH meter (FE28-Standard, Mettler-Toledo, Switzerland), where the hides were delimed for 5, 10, 20, 40, and 60 min. After deliming for 20 min, the hides were cut with a scalpel, checked using a phenolphthalein indicator, and observed using a stereomicroscope (M205C, Leica, Germany) to determine the penetration of the deliming agents. After deliming for 60 min, the hydroxyproline (Hyp) concentrations of the deliming effluents were measured to assess collagen damage.[16] The measurement was repeated thrice to obtain the average values and standard deviation. The delimed hides were sampled to analyze the morphology and calcium content of grain surfaces by scanning electron microscopy (SEM; JSM-7500F, JEOL, Japan) and energy dispersive X-ray spectrometry (EDX; INCA X-MAX 50, Oxford, UK), respectively. EDX can be used to determine which chemical elements are present in a sample and estimate their relative abundance (semi-quantitative content).[17] In addition, the calcium contents of relimed and delimed hides were determined by inductively coupled plasma–atomic emission spectrometry (ICP–AES; Optima 8000DV, PerkinElmer, USA) after ashing and acid digestion of the hides as described in the literature,[9] and the measurement was repeated thrice to obtain the average values and standard deviation. The extents of calcium removal from the hides calculated using Formula (1):

$$\%\text{ extent of calcium removal} = \frac{(C_1 - C_2)}{C_1} \times 100 \qquad (1)$$

where C_1 is the calcium content of relimed hide (mg/g), and C_2 is the calcium content of delimed hide (mg/g).

Bating experiments and evaluation of bating performance

The four delimed hides were subsequently bated in a drum with 0.1% trypsin and 100% water (based on the weight of relimed hide) at 32°C for 40 min. The bating effluents were collected and centrifuged at 8000 rpm for 6 min. The total protein concentrations of the supernatants were measured according to the method described in the document.[8] In addition, the Hyp concentrations of the bating effluents were analyzed.[16] The measurements of the total protein and Hyp concentrations were repeated thrice to obtain the average values and standard deviation. The non-collagenous protein concentrations of the bating effluents were calculated using Formula (2):[18]

$$\text{Non-collagenous protein concentration (mg/L)} = P - H \times 7.4 \qquad (2)$$

where P is the total protein concentration of the bating effluent (mg/L), H is the Hyp concentration of the bating effluent (mg/L), and 7.4 is the conversion factor from Hyp to collagen.

Tanning experiments and evaluation of tanning performance

The four bated hides were pickled and chrome tanned using conventional processes.[7] After chrome tanning, the T_s of wet blue was measured using a shrinkage temperature tester (MSW-YD4, Sunshine Electronic Research Institute, China). The measurement was repeated thrice to obtain the average values and standard deviation. Then, the wet blue after horsing up for 48 h was sampled for the following tests. The sample was divided into the grain, middle, and flesh layers, and each layer was dried to constant weight and digested as reported previously.[19] After cooling, the chromium concentration of the digestion solution was determined by ICP–AES. The measurement was repeated thrice to obtain the average values and standard deviation. The Cr_2O_3 content of each layer was calculated using Formula (3):

$$Cr_2O_3\text{ content (\%)} = \frac{M(Cr_2O_3) \times c \times V}{2 \times M\text{ (Cr)} \times w} \qquad (3)$$

where $M(Cr_2O_3)$ is the molar mass of Cr_2O_3 (152 g/mol), c is the chromium concentration of the digestion solution (mg/L), V is the volume of the digestion solution (L), M(Cr) is the molar mass of Cr (52 g/mol), and w is the dry weight of wet blue (mg).

Moreover, the sample was freeze-dried to analyze the morphology and elemental (carbon, calcium, and chromium) distributions of cross-sections using SEM and EDX, respectively. The grain surface of the sample was directly observed using a digital camera, and their color parameters (L^*, a^*, and b^*) were recorded using a colorimeter (CR-13, Konica Minolta, Japan) by testing 10 different points in each sample.[20] The color difference (ΔE) was calculated using Formula (4):

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \qquad (4)$$

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.

Post-tanning experiments and evaluation of crust leather performance

The wet blue was treated by conventional shaving, rewetting, neutralization, retanning, dyeing, fatliquoring, horsing up, samming, and milling, and four crust leathers with a thickness of 1.0 mm were prepared. The grain surface of the crust leathers were observed using a stereomicroscope. The color parameters (L^*, a^*, and b^*) of the grain surfaces were recorded using a colorimeter by testing 10 different

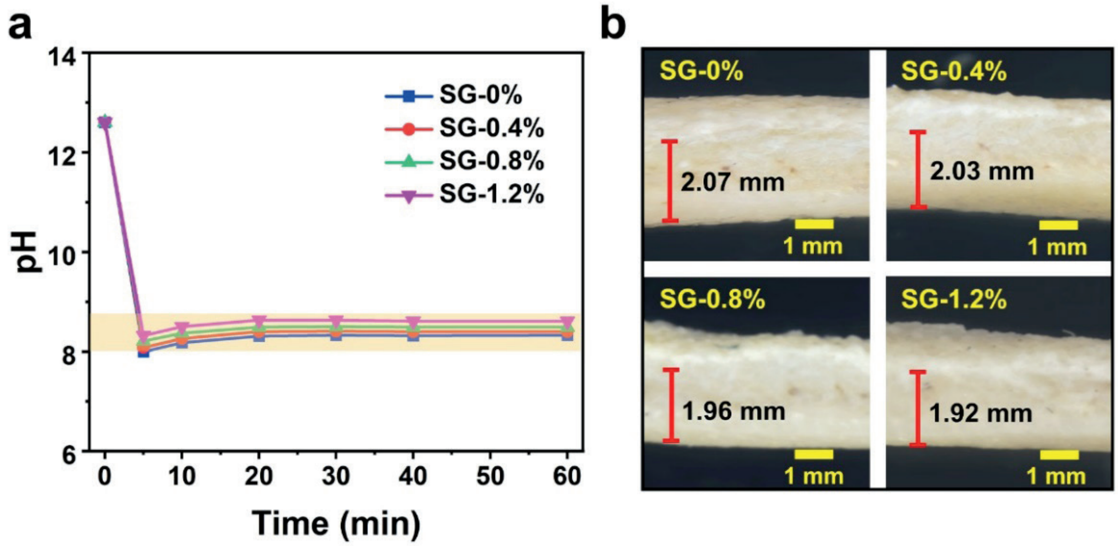

Figure 1. **(a)** Float pH during deliming process (The reliming float pH of 12.60 was recorded as the initial pH of deliming float) and **(b)** stereomicrographs of hide vertical sections after deliming for 20 min and checking with phenolphthalein.

points in each sample,[20] and ΔE was calculated using Formula (4) above. Besides, the four crust leathers were sampled and conditioned at 20°C and 65% relative humidity for 24 h (ISO 2418:2002), and their physical properties, including tensile strength (ISO 3376:2011), tear strength (ISO 3377-2:2002), bursting strength (ISO 3379:2015), and softness (ISO 17235:2015), were measured.

Results and Discussion

Preparation of delimed hides with different calcium contents

The main purposes of deliming are to reduce the pH of limed/relimed hide from 12–13 to 8–9 and remove calcium from the limed/relimed hide.[7] The effects of percentage of sodium gluconate (X% = 0, 0.4, 0.8,

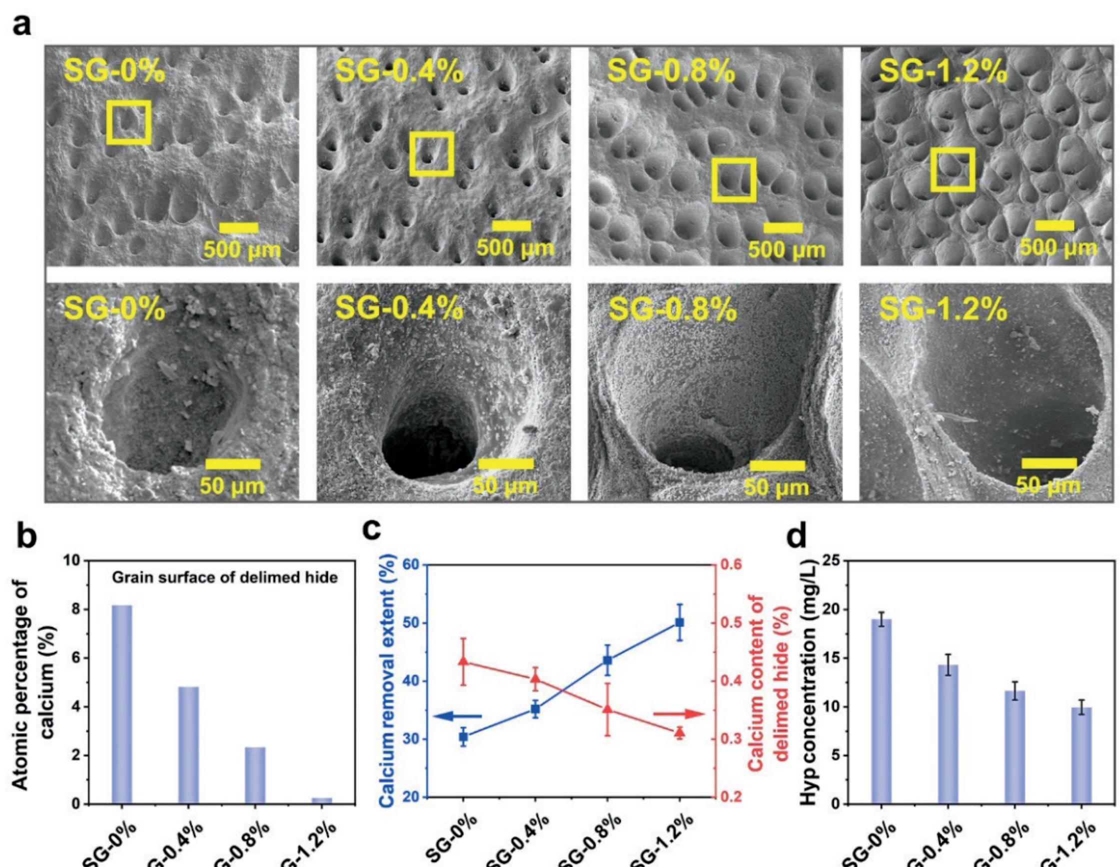

Figure 2. **(a)** SEM micrograph of the grain surface of delimed hide; **(b)** atomic percentage of calcium on the grain surface of delimed hide; **(c)** extent of calcium removal and calcium content of delimed hide (based on the dry weight of hide); **(d)** Hyp concentration of the deliming effluent.

1.2) on the pH of deliming float, the penetration of deliming agent, the calcium content of hide, and the damage to hide collagen are shown in Figures 1 and 2. The deliming float pH increased slightly with increasing sodium gluconate but was maintained in the range of 8.0–8.6 because of the high pH-buffering capacity of ammonium sulfate (Figure 1a). The four hides were all colorless after deliming for 20 min and checking with phenolphthalein (Figure 1b), which indicated that deliming agents SG-0%, SG-0.4%, SG-0.8%, and SG-1.2% penetrated the relimed hide rapidly.

The SEM observation of the grain surfaces of the delimed hides showed that the grain surface became smoother with more sodium gluconate (Figure 2a). The EDX data indicated that the atomic percentage of calcium on the surface decreased sharply with increasing sodium gluconate (Figure 2b). The SEM and EDX results revealed that the calcium precipitates on the surface could be converted into soluble calcium salts and removed using sodium gluconate.[15] The total extent of calcium removal from the hide also increased with the increase in sodium gluconate (Figure 2c). The results proved that delimed hides with different calcium content were obtained using different amounts of sodium gluconate. Specifically, the atomic percentages of calcium on the grain surfaces of delimed hides SG-0%, SG-0.4%, SG-0.8%, and SG-1.2% were 8.17%, 4.82%, 2.34%, and 0.25%, respectively (Figure 2b), and the calcium contents of the delimed hides SG-0%, SG-0.4%, SG-0.8%, and SG-1.2% were 0.43±0.04%, 0.40±0.02%, 0.35±0.05%, and 0.31±0.01% (based on the dry weight of hide), respectively (Figure 2c).

Moreover, the Hyp concentration of the deliming effluent decreased with increasing sodium gluconate (Figure 2d), indicating that deliming with sodium gluconate was useful in reducing collagen damage. The smooth surface (few calcium precipitates on the grain surface) caused by sodium gluconate could be the reason for the reduction in collagen damage.

Effect of calcium in delimed hide on bating performance

The effect of residual calcium in the delimed hide on the bating performance was investigated in this section. The aim of bating is mainly to soften the hide by removing non-collagenous protein from the hide and improve the smoothness of the grain.[6,21] Therefore, bating performance was evaluated by analyzing the concentration of non-collagenous protein in the bating effluent and the smoothness of the grain. As shown in Figure 3a, the non-collagenous protein concentration of the bating effluent increased as the calcium content of the delimed hide decreased. The results indicated that calcium removal from delimed hide was beneficial to remove non-collagenous protein and disperse collagen fibers. Additionally, we found that the grain surface with lower calcium content was smoother. But it is worth noting that the decrease in calcium content was also accompanied by an increase in the Hyp concentration of the bating effluent (Figure 3b), which implies that extreme calcium removal during deliming may damage the hide collagen. The results in Figure 3 imply that hide protein is easier to be hydrolyzed by trypsin than calcium-bound hide protein.

Effect of calcium in delimed hide on chrome tanning performance

Tanning is the key process of converting hide into leather, and chrome tanning is the most commonly used form of tannage because of its ability to produce soft and lightweight leathers with high hydrothermal stability.[22] In this section, the effect of residual calcium in the hide on the chrome tanning performance was investigated by analyzing the changes in the T_s and color of wet blue with different calcium content.

The data in Figure 4a show that the T_s of wet blue followed the order: SG-0% (92.3±1.3°C) < SG-0.4% (95.6±2.1°C) < SG-0.8% (101.2±1.4°C) < SG-1.2% (102.5±1.7°C). The main reason for this order is probably because the hide with a lower calcium content was bated more effectively and achieved a more uniform distribution of chrome tanning agent. The Cr_2O_3 content of each layer of wet blue

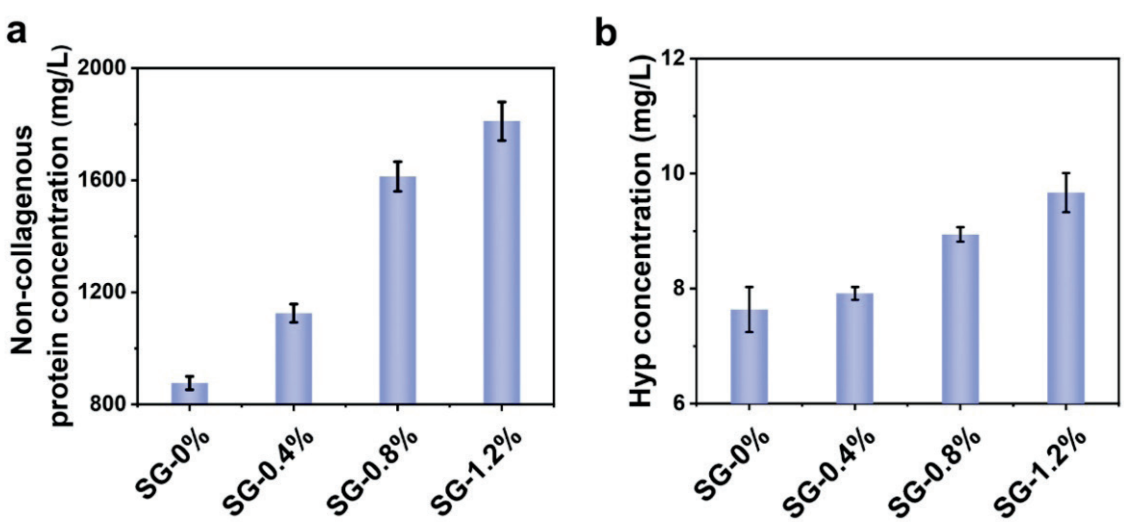

Figure 3. Concentrations of non-collagenous protein **(a)** and Hyp **(b)** in bating effluents.

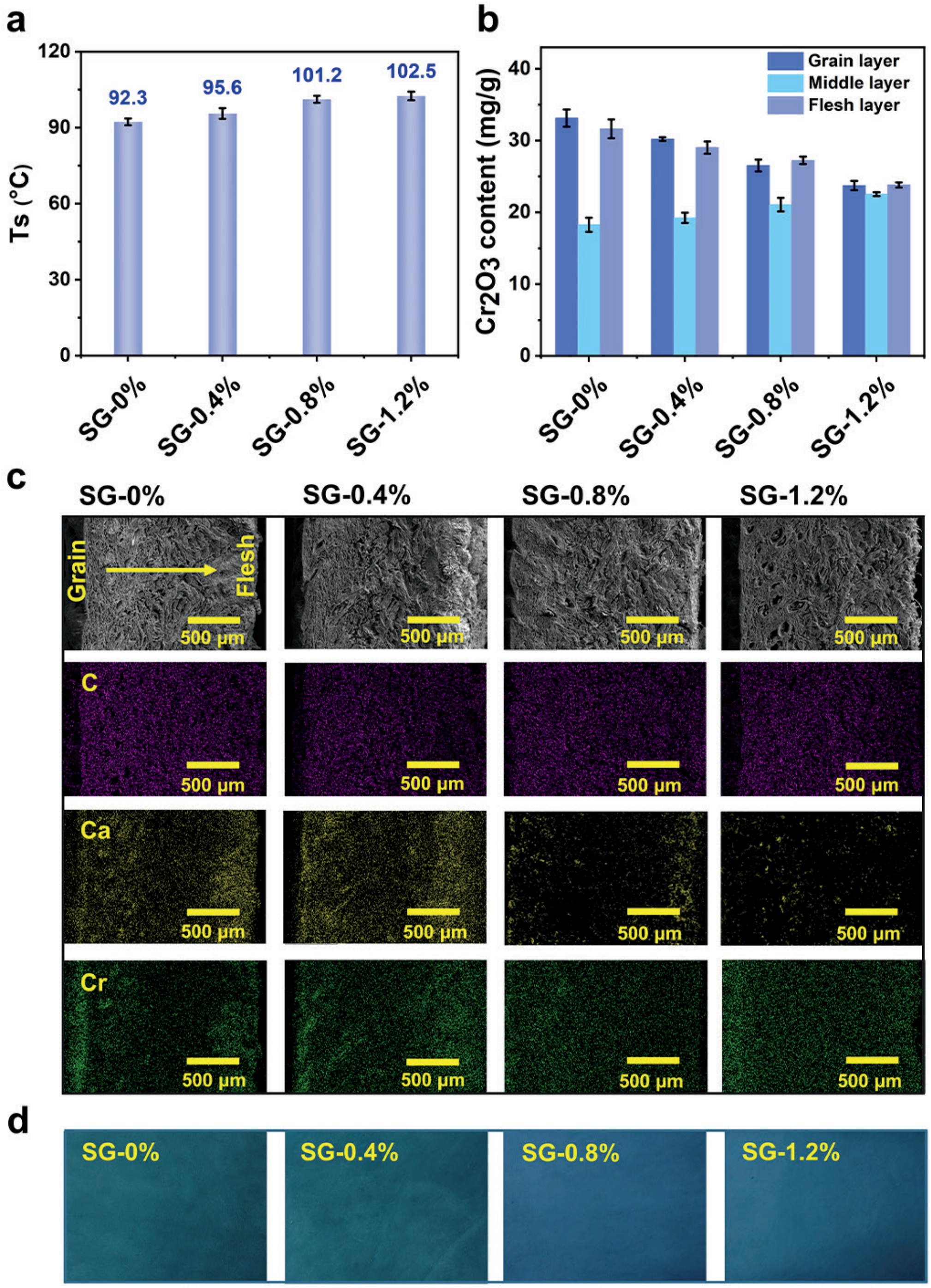

Figure 4. **(a)** T_s of wet blue; **(b)** Cr_2O_3 content of each layer of wet blue; **(c)** SEM micrograph and EDX elemental mapping images of C, Ca, and Cr distributions of the cross-section of wet blue; and **(d)** digital photo of wet blue.

in Figure 4b and the EDX results of wet blue in Figure 4c proved this point. The chromium content of the surface layers decreased and that of the middle layer increased with decreasing calcium content (Figure 4b), and the distribution of chromium in wet blue was more uniform when the hide had less calcium (Figure 4c). These phenomena supported the view that a low calcium content of the hide favors the uniform distribution of chromium in wet blue. Another reason may be that the calcium in the delimed hide would form calcium sulfate in the pickled hide and negatively affect the penetration of chrome tanning agent and its reaction with collagen fiber.[23]

In addition, the photos in Figure 4d and the *a** and *b** values in Table I show that the wet blue SG-0% and SG-0.4% were greener and darker compared with the wet blue SG-0.8% and SG-1.2% (lake blue).[24] The obvious differences in the ΔE_1 values of the four wet blue (Table

Table I

Color parameters of the wet blue

Sample	**L***	**a***	**b***	**ΔE_1 [a]**	**ΔE_2 [b]**
SG-0%	46.84 ± 1.01	-8.68 ± 0.71	-3.06 ± 0.50	11.47 ± 0.94	2.41 ± 0.72
SG-0.4%	45.56 ± 1.00	-7.85 ± 0.80	-4.28 ± 0.40	10.15 ± 1.03	1.43 ± 0.65
SG-0.8%	46.62 ± 0.76	-5.23 ± 0.47	-5.36 ± 0.58	7.08 ± 0.67	1.24 ± 0.61
SG-1.2%	46.81 ± 0.54	-4.04 ± 0.38	-5.79 ± 0.42	0	1.22 ± 0.37

[a]ΔE_1 reflects the color difference among the four wet blue. The wet blue SG-1.2% was used as the calibration board.

[b]ΔE_2 reflects the color difference among various points in a single wet blue. One of the points on the wet blue was used as the calibration board.

I) show that the calcium content of hide greatly affects the color of wet blue. The ΔE_2 values of wet blue decreased with decreasing atomic percentage of calcium on the grain surface, indicating that an efficient calcium removal from the hide surface can improve the color uniformity of wet blue.

Effect of calcium in delimed hide properties of crust leather

The color and physical properties of leather directly affect the consumer experience and market sales.[25,26] High-quality leather requires a uniform color and excellent physical properties. Hence, the effect of residual calcium in delimed hide on the crust leather was investigated by analyzing the color and physical properties of crust leathers. The stereomicrographs in Figure 5 and the L^*, a^*, and b^* values in Table II indicate that the crust leather became brighter and yellower as the atomic percentage of calcium on the grain surface decreased. The change trend of the crust leather color was consistent with that of the wet blue color. The ΔE_1 values of the four crust leathers had great differences, showing that the calcium content of the hide is an important factor affecting the color of crust leather. The ΔE_2 values of crust leathers followed the order: SG-0% > SG-0.4% > SG-0.8% > SG-1.2%. This finding is likely because the calcium on the grain surface made the dye form a precipitate.[27,28] This finding indicates that an effectual calcium removal from the hide surface is important for the color uniformity of crust leather.

As shown in Table III, the tensile strength, tear strength, bursting strength, and softness of crust leathers followed the order, SG-0% < SG-0.4% < SG-0.8% < SG-1.2%, which is consistent with the removal extent of calcium from the delimed hide. The delimed hide with lower residual calcium content produced a crust leather with better

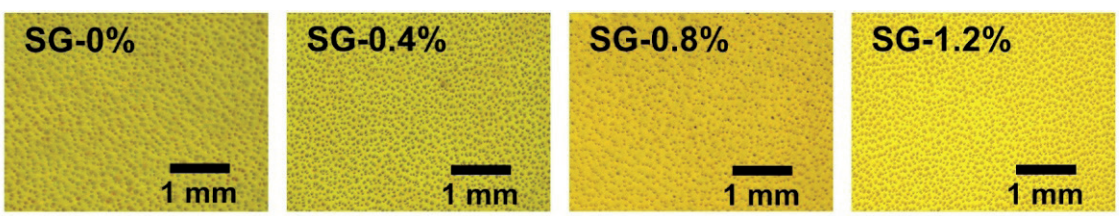

Figure 5. Stereomicrograph of the crust leather.

Table II

Color parameters of the crust leathers

Sample	L^*	a^*	b^*	**ΔE_1 [a]**	**ΔE_2 [b]**
SG-0%	57.43 ± 3.60	3.58 ±1.70	48.45 ± 4.24	23.24 ± 3.41	7.57 ± 3.07
SG-0.4%	53.29 ± 3.06	2.97 ± 1.63	59.42 ± 3.60	14.58 ± 4.01	5.80 ± 2.80
SG-0.8%	56.96 ± 1.41	2.38 ± 1.06	68.11 ± 2.04	5.77 ± 1.69	3.88 ± 1.54
SG-1.2%	56.06 ± 1.11	1.94 ± 0.88	73.38 ± 1.69	0	2.24 ± 0.78

[a]ΔE_1 reflects the color difference among the four crust leathers. The crust leather SG-1.2% was used as the calibration board.

[b]ΔE_2 reflects the color difference among various points in a single crust leather. One of the points on the crust leather was used as the calibration board.

Table III

Physical properties of the crust leathers

Sample	Tensile strength (N/mm^2)	Tear strength (N/mm)	Bursting strength (N/mm)	Softness (mm)
SG-0%	8.0 ± 1.0	54.6 ± 2.9	266.7 ± 11.2	4.6 ± 0.1
SG-0.4%	8.4 ± 0.8	58.1 ± 2.3	276.6 ± 10.9	5.0 ± 0.2
SG-0.8%	11.6 ± 1.4	69.4 ± 3.2	335.3 ± 11.6	6.2 ± 0.2
SG-1.2%	12.3 ± 1.0	71.9 ± 2.8	336.1 ± 15.1	6.6 ± 0.1

Values are means ± standard deviations of six determinations.

physical properties, probably because better bating and chrome tanning performances were obtained and promoted the penetration and fixation of post-tanning agents and fatliquors.

Conclusion

Calcium removal from delimed hide greatly affects the bating, chrome tanning, and post-tanning performances. Efficient calcium removal from delimed hide is beneficial to improve the enzymatic bating effectiveness, the uniform distribution of chrome tanning agent in wet blue, the color brightness and uniformity of wet blue and crust leather, and the physical properties of crust leather. Therefore, the ability of deliming agent to remove calcium and the extent of calcium removal from delimed hide should be considered to be important indicators to guarantee the high quality of leather.

Acknowledgement

This work was supported by the National Natural Science Foundation of China (21878193). We thank Jinwei Zhang for technical assistance in fleshing, splitting, samming, and shaving operations.

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