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Investigations on the general properties of biomass-based aldehyde tanned sheep fur for its selective post-tanning processing

Wei Ding^{1*} , Ya-nan Wang^{2,3}, Jianfei Zhou^{2,3}, Haiteng Liu¹, Xiaoyan Pang¹ and Bi Shi^{2,3*}

Abstract

Dialdehyde sodium alginate (DSA) is an alternative chrome-free tanning material for fur production. To obtain satisfactory resultant fur and provide suggestions for the usage of DSA in fur making, the general properties of DSA tanned sheep fur were systematically investigated. The tanning mechanism of DSA was analyzed and it was verified that DSA was mainly combined with collagen fiber by forming Schiff base covalent bonds while supplemented by a small number of hydrogen bonds and ionic bonds. Due to the acid sensitivity of Schiff base structure, DSA tanned fur had poor resistance to acid rinsing but had excellent resistance to washing and good fatliquoring performance. Also, it had good resistances to yellowing and reductant. After being retanned by chrome tanning agent, the fur was capable of enduring a high-temperature dyeing process (68 °C for 8 h). Overall, DSA tanned sheep fur had favorable properties under appropriate post-tanning processing conditions to manufacture light-colored or dark-colored fur products with desirable physical properties.

Keywords: Sheep fur, Dialdehyde sodium alginate, Stability, Post-tanning, Chrome retanning

1 Introduction

Sheep fur manufacturing is a sustainable industry since it converts raw sheep fur, the byproduct of meat industry, into high value-added products [1]. Sheep fur production generally involves numerous processes. Among them, tanning process is the key one since it determines the hydrothermal stability, dispersion of collagen fiber, and the charge property of tanned fur. These properties will affect the stability of fur under post-tanning processing conditions as well as the uptake and fixation of post-tanning chemicals [2, 3]. Post-tanning processes, including neutralizing, bleaching, retanning, filling, fatliquoring, dyeing et al., are closely related to the physical and organoleptic properties of resultant fur. At present, chrome tanning is the dominant tannage for

sheep fur production because it can endow tanned fur with excellent tanning effect and post-tanning processing properties. However, this conventional tannage is suffering from increasing restriction due to the widespread chrome pollution that is hindering the sustainable development of fur industry [2]. In recent years, new chrome-free tanning agents and clean tanning technologies have been developed to partially replace conventional chrome tannage, such as syntans, biomass-derived aldehyde and chrome-reduced combination tanning technology [4, 5]. As a kind of green and sustainable tanning material, the biomass-derived aldehyde is now arousing more and more interest due to its feasible tanning effect and biodegradability [6–9]. Its industrial use will be significant for the effective control of chrome pollution and the sustainable development of fur industry.

Dialdehyde sodium alginate (DSA) is a sort of special biomass-derived aldehyde with multiple carboxyl groups. It is prepared by periodate oxidation of sodium alginate

* Correspondence: dingwei1368@outlook.com; shibi@scu.edu.cn

¹China Leather and Footwear Research Institute Co. Ltd., Beijing 100015, P.R. China

²College of Biomass Science and Engineering, Sichuan University, Chengdu 610065, China

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

(SA) which is composed of (1–4)- β -D-mannuronic acid (M) units and α -L-guluronic acid (G) units [10, 11]. During the periodate oxidation, the vicinal diols of SA are selectively oxidized to introduce aldehyde groups onto the backbone of DSA along with the decrease of molecular weight [12, 13]. These structural properties enhance the interactions of DSA with the amino groups of collagen/gelatin molecules and the penetrability in collagen fiber matrix [14–16]. This suggests the possibility of DSA as a tanning agent for fur processing. Recently, we developed a kind of DSA with wide molecular weight distribution, which could exhibit a satisfactory tanning effect on sheep fur in terms of high shrinkage temperature (Ts) and well-dispersed collagen fiber network [1]. This DSA tanned fur exhibited the potential to be processed as light-colored fur products. However, the current post-tanning technologies are designed to match up with chrome tanning system and may be not suitable for DSA tannage in consideration of the low isoelectric point of DSA tanned wet-white (less than 5.0) [17]. In addition, as for the production of dark-colored fur, high-temperature dyeing (about 70 °C, 6–8 h) is commonly required for the production of dark-colored sheep fur. The Ts of tanned fur is required to be no lower than 90 °C for preventing fur from shrinkage during high-temperature dyeing [4, 18]. This shows that the DSA tanned fur is not qualified when singly used, and it seems that chrome is essential for making dark-colored sheep fur. Considering that DSA has abundant carboxyl groups to coordinate with Cr (III), chrome-reduced combination tanning based on DSA is a potential approach for dark-colored sheep fur production. However, the current research works about DSA tanning agent mainly focus on its preparation and the relationships between its structure and tanning effect. The general properties of DSA tanned fur under post-tanning processing conditions still remain unclear. In addition, the chrome-reduced combination tanning scheme based on DSA is difficult to be reasonably proposed due to the unclarified interactions between DSA and Cr (III). Thus, it is significant to clarify the general properties of DSA tanned fur under post-tanning processing conditions for the reasonable use of DSA in fur production.

In the present work, the tanning mechanism of DSA was first analyzed and clarified. According to the tanning mechanism and post-tanning processing conditions, the stabilities of DSA tanned fur, e.g., resistances to acid, washing, reductants, yellowing, and the fatliquoring performance were specifically evaluated. Moreover, the interactions between DSA and chrome tanning agents as well as the chrome-reduced combination tanning performances based on DSA were also investigated. Clarification of the general properties of DSA tanned sheep fur under post-tanning processing conditions is expected to

guide the reasonable use of DSA for making satisfactory resultant fur.

2 Experimental

2.1 Materials

Pickled sheep fur was provided by Zhejiang Zhonghui Fur & Leather Co., Ltd. (Tongxiang, China). Dialdehyde sodium alginate was prepared according to the method reported in our previous work [15]. Pickled sheep fur was tanned by 10 g/L DSA (based on the volume of water, the same below) at 25 °C for 4 h and basified with 12 g/L sodium bicarbonate to pH 8.0. Then, the tanning temperature was raised to 40 °C and continuously ran for another 4 h to obtain tanned sheep fur [1]. Gelatin, sodium chloride, sodium carbonate, acetone, urea, sodium pyrosulfite, sodium hydrosulfite and sodium bisulfite, were of analytical grade and purchased from Chengdu Kelong Chemical Co. Ltd. (Chengdu, China). Chrome tanning agent (Cr_2O_3 , 24%) was supplied by Brother Enterprises Holding Co., Ltd. (Haining, China). The other chemicals used in fur processing were of commercial grade. Chemicals used for the analysis of fur were of analytical grade.

2.2 Tanning mechanism analysis of DSA

The tanning mechanism of DSA was analyzed by investigating the effect of rinsing medium on the Ts of rinsed fur and the interactions between DSA and gelatin. Five pieces of DSA tanned fur were respectively added into 500 mL conical flasks containing 200 mL of distilled water, sodium carbonate solution (pH=9.5), urea solution (10 wt%), sodium chloride solution (10 wt%), and acetone aqueous solution (1:1, v/v). After shaking at 30 °C for 12 h, it stood overnight [19]. Then, the treated fur was washed with distilled water and sampled to determine its Ts.

Gelatin solution (20 g/L) and DSA solution (20 g/L) were mixed with equal volume. Then, this mixture was shaken at 30 °C for 4 h. Then, pH of the mixture was adjusted to 7.8–8.0 and continuously shook for another 4 h to obtain their reaction product. The UV-vis spectra of gelatin solution, DSA solution as well as their reaction product were recorded by UV/VIS spectrophotometer (UV-1200, Mapada, Shanghai, China). Besides, the FT-IR spectra of lyophilized gelatin, DSA, and their reaction product were recorded using an FT-IR spectrometer (Nicolet 6700, Thermo Scientific, USA). Samples were pressed as KBr pellet and measured in the range of 400–4000 cm^{-1} at room temperature, using 32 scans and a resolution of 4 cm^{-1} .

In addition, the effect of groups modification on Ts of leather was also investigated to clarify the groups on collagen fiber involved in DSA tanning reaction. Pickled cattle hide was selected for this investigation. It was

modified by de-pickling, blocking carboxyl, deamination, and removing guanidyl [20, 21]. The detailed method was described in supplementary materials.

2.3 Fatliquoring of DSA tanned fur

DSA tanned fur was fatliquored according to the process presented in Table S1. The dosage of fatliquor was 6, 10, 15, and 20 g/L, respectively. After fatliquoring, the fur was sampled for Ts test, and the fatliquoring wastewater was sampled for the analysis of fatliquor uptake rate.

2.4 Interactions between Cr (III) and DSA

Chrome tanning agent solution and DSA solution were mixed with equal volume to control the concentration of chrome tanning agent and DSA was 2 g/L and 10 g/L, respectively. Then, this mixture was shaken at 25 °C for 4 h. The UV-vis spectra of chrome tanning agent solution, DSA solution as well as their fresh mixture and reacted mixture (4 h) were recorded by UV/VIS spectrophotometer (UV-1200, Mapada, Shanghai, China). Besides, the FT-IR spectra of dried DSA and the DSA-Cr (III) complex were recorded using FT-IR spectrometer (Tensor 27, Bruker, Germany). Samples were pressed as KBr pellet and measured in the range of 400–4000 cm^{-1} at room temperature, using 32 scans and a resolution of 4 cm^{-1} .

2.5 Chrome-reduced combination tanning trials

Chrome retanning of DSA tanned sheep fur was performed in a drum with 800% water (based on the weight of tanned sheep fur, similarly hereinafter). First, a certain amount of formic acid (10 wt%) was added to adjust the pH of tanning liquor to 2.8–3.0, and then a certain amount of chrome tanning agent (1, 2, 3, 4 g/L, respectively) was added. After running at room temperature for 4 h, the pH of tanning liquor was raised to 4.0–4.2 by adding sodium bicarbonate. Then the temperature was increased to 40 °C. After continuously running for 4 h, the chrome retanned sheep fur was washed for 5 min and piled for 24 h for further analysis. This tanning scheme was set as Scheme A. Other two tanning schemes were conducted for performance comparisons, which were defined as Scheme B and Scheme C, respectively. The detailed tanning processes were presented in Table S1 and Table S2. The combination tanned fur prepared from the optimal tanning scheme was dyed at 68 °C according to the process reported by our previous work [4].

2.6 Analytical methods

2.6.1 Shrinkage temperature and area yield of fur

Shrinkage temperature (Ts) is commonly used to characterize the hydrothermal stability of leather/fur. The Ts of fur was measured and recorded using digital

leather shrinkage temperature tester (MSW-YD4, Shaanxi University of Science and Technology, China). The rate of heating was set to 2 °C/min. Pickled and tanned furs were wrung to control its moisture content around 65%. Then, the area of fur was measured by using the grid counting method (1 cm^2 /(grid unit)). The area yield of fur was the ratio between the area of tanned/post-tanned fur and pickled fur.

2.6.2 Resistance to acid rinsing and washing

20 g DSA tanned fur and 160 g water were added into the drum and then ran at 30 °C for 20 min. Then, a certain amount of formic acid aqueous solution (10 wt%) was added to adjust the float pH as 6.0, 5.0, 4.0, 3.0, and 2.0, respectively, and continuously ran for 1, 2, 3, 4 h. After that, the Ts of rinsed fur was determined for the analysis of resistance to acid rinsing. DSA tanned fur was washed with distilled water at 40 °C for 1, 2, 4, 6, 8, 10, 12 h, respectively. The Ts of washed fur was tested for the analysis of resistance to washing.

2.6.3 Resistance to reductants

20 g DSA tanned fur and 160 g water were added into the drum and ran for 5 min at room temperature, and then a certain amount (0.5, 1.0, 1.5, 2.0 wt%) of sodium pyrosulfite (SP), sodium hydrosulfite (SH) and sodium bisulfite (SB) were respectively added into the drum. After that, the drum ran at 30 °C for 60 min, and then the treated fur was sampled to test its Ts for the analysis of resistance to reductants.

2.6.4 UV-irradiation

DSA tanned fur and conventional formaldehyde tanned fur were air-conditioned for 24 h according to standard methods. Then, the air-conditioned furs were irradiated using a UV light ($\lambda=365$ nm, 8 W) for 0, 3, 6, 12, 24 h, respectively. The color parameters (L, a, b) of irradiated furs were recorded using a color measurement instrument (Color reader CR-13, Konica Minolt, Japan). The total color difference (ΔE) was calculated by eq. (1).

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \quad (1)$$

ΔE represents the overall color difference; ΔL is the lightness difference; Δa and Δb stand for the difference of a and b values. ΔL , Δa and Δb were calculated by subtracting the corresponding values for standard white ($L=93.8$, $a=-0.5$, $b=3.6$).

2.6.5 Chrome content in sheep fur and wastewater

The chrome content in sheep fur and wastewater was determined according to the method reported in our previous work [4]. Sheep fur was completely shaved and cut into small particles. After drying to a constant

weight, the fur samples were digested using concentrated nitric acid and hydrogen peroxide (2:1, v/v). The digestion liquor was filtered and then diluted with deionized water. The concentration of chrome was determined by ICP-OES (Optima 8000, PerkinElmer, USA). The chrome content of fur was calculated by eq. (2).

$$\begin{aligned} &\text{Chrome content in tanned fur} \\ &= \frac{\text{Weight of Cr}_2\text{O}_3}{\text{Weight of dried fur}} \times 100\% \end{aligned} \quad (2)$$

10 mL tanning or dyeing wastewater was digested using a certain amount of concentrated nitric acid and hydrogen peroxide (2:1, v/v) at first, and then the chrome concentration was determined as above. The uptake rate of chrome was calculated by eq. (3).

$$\text{Uptake rate of chrome} = \frac{\text{Cr}_0 - \text{Cr}_1}{\text{Cr}_0} \times 100\% \quad (3)$$

Cr_0 : the initial additive amount of chrome; Cr_1 : the concentration of chrome in tanning wastewater multiplied by the volume of tanning wastewater.

2.6.6 Uptake rate of fatliquor

The uptake rate of fatliquor was determined according to the method reported in our previous work [22]. The raw fatliquor solution and fatliquoring wastewater were diluted by a certain multiple, and then 200 μL diluted solution was added into COD_{Cr} reagent tube. After being heated at 150 $^{\circ}\text{C}$ for 2 h, the COD_{Cr} value was recorded using HI99109COD spectrophotometer (HANNA, Italy). The uptake rate of fatliquor was calculated according to eq. (4):

$$\text{Uptake rate of fatliquor} = \frac{F_0 - F_1}{F_0} \times 100\% \quad (4)$$

F_0 : COD_{Cr} value of diluted raw fatliquor solution multiplied by the dilution multiple; F_1 : COD_{Cr} value of diluted fatliquoring wastewater multiplied by the dilution multiple.

2.6.7 Physical properties

Fatliquored fur with shaved wool was first air-conditioned for 48 h at 20 $^{\circ}\text{C}$ and 65% RH, and then its tensile and tear strengths, as well as elongation at specified load (5 N/mm²), were determined according to IUP test methods [23, 24]. The softness of fur was tested using a standard leather softness tester (GT-303, designed based on IUP standard [25], Gotech Testing Machines Inc., China) with a reading range from 0.1 mm to 10 mm. The aperture was 20 \pm 0.1 mm for the measurement of softer apparel furs.

3 Results and discussion

3.1 Tanning mechanism of DSA

Fig. 1a shows the effect of rinsing medium on Ts of rinsed fur. After being rinsed with distilled water, there was no significant change in Ts, indicating that the combination of DSA and collagen fibers was relatively stable. After being rinsed with sodium chloride solution, the Ts of fur decreased by 0.3 $^{\circ}\text{C}$, indicating that there was a small amount of ionic bonding between DSA and collagen fibers. After being rinsed with sodium carbonate solution, the Ts of fur did not change, implying that DSA and collagen fibers were mainly covalently bonded, and DSA tanned fur had strong resistance to alkali rinsing. After being rinsed with acetone and urea solutions, the Ts of fur decreased by 1.2 $^{\circ}\text{C}$ and 2.2 $^{\circ}\text{C}$, respectively, suggesting that there was hydrogen bonding between DSA and collagen fibers. Collagen molecules contain many carboxyl, amino and guanidyl groups, which can participate in tanning reaction. Fig. 1b illustrates the effect of groups modification on Ts of leather. After DSA tanning, the Ts of carboxyl-blocked leather increased by 21.6 $^{\circ}\text{C}$ to 85.1 $^{\circ}\text{C}$, and the Ts of de-pickled leather without group modification increased by 20.7 $^{\circ}\text{C}$ to 85.4 $^{\circ}\text{C}$. This shows that DSA exhibited tanning effect not by crosslinking the carboxyl groups of collagen molecules. However, the Ts of DSA tanned leather only increased by 3.5 $^{\circ}\text{C}$ and 10.5 $^{\circ}\text{C}$ to 56.4 $^{\circ}\text{C}$ and 72.8 $^{\circ}\text{C}$, respectively when the amino and guanidyl groups of collagen molecule were removed. The above results indicate that DSA mainly crosslinked with the amino groups on collagen molecules to form a covalent bond to exhibit tanning effect. Meanwhile, DSA could also form partial covalent crosslinks with the guanidyl group on the side chain on collagen molecule to enhance the tanning effect.

Fig. 1c shows the FT-IR spectra of gelatin, DSA, and DSA crosslinked gelatin. DSA has a symmetric vibration of aldehyde group around 1735 cm^{-1} [26], but it disappears on the spectrum of DSA crosslinked gelatin. This indicated that the aldehyde group of DSA had reacted with gelatin. As reported, the characteristic absorption peak of C=N bond usually appears around 1623 cm^{-1} [27]. The absorption band around 1630 cm^{-1} is generally assigned to the amide I of gelatin [28]. However, after overlapping with the characteristic peak of gelatin amide bond at 1630 cm^{-1} , there is a significantly enhanced absorption peak at 1626 cm^{-1} . The appearance of this peak proves the existence of C=N structure in DSA crosslinked gelatin. Moreover, the characteristic band of gelatin at 1543 cm^{-1} assigned to amide II is completely absent in the spectrum of crosslinked gelatin, proving the involvement of this group in the crosslinking reaction [26]. The results above indicated that the aldehyde groups on DSA and the amino groups on gelatin formed

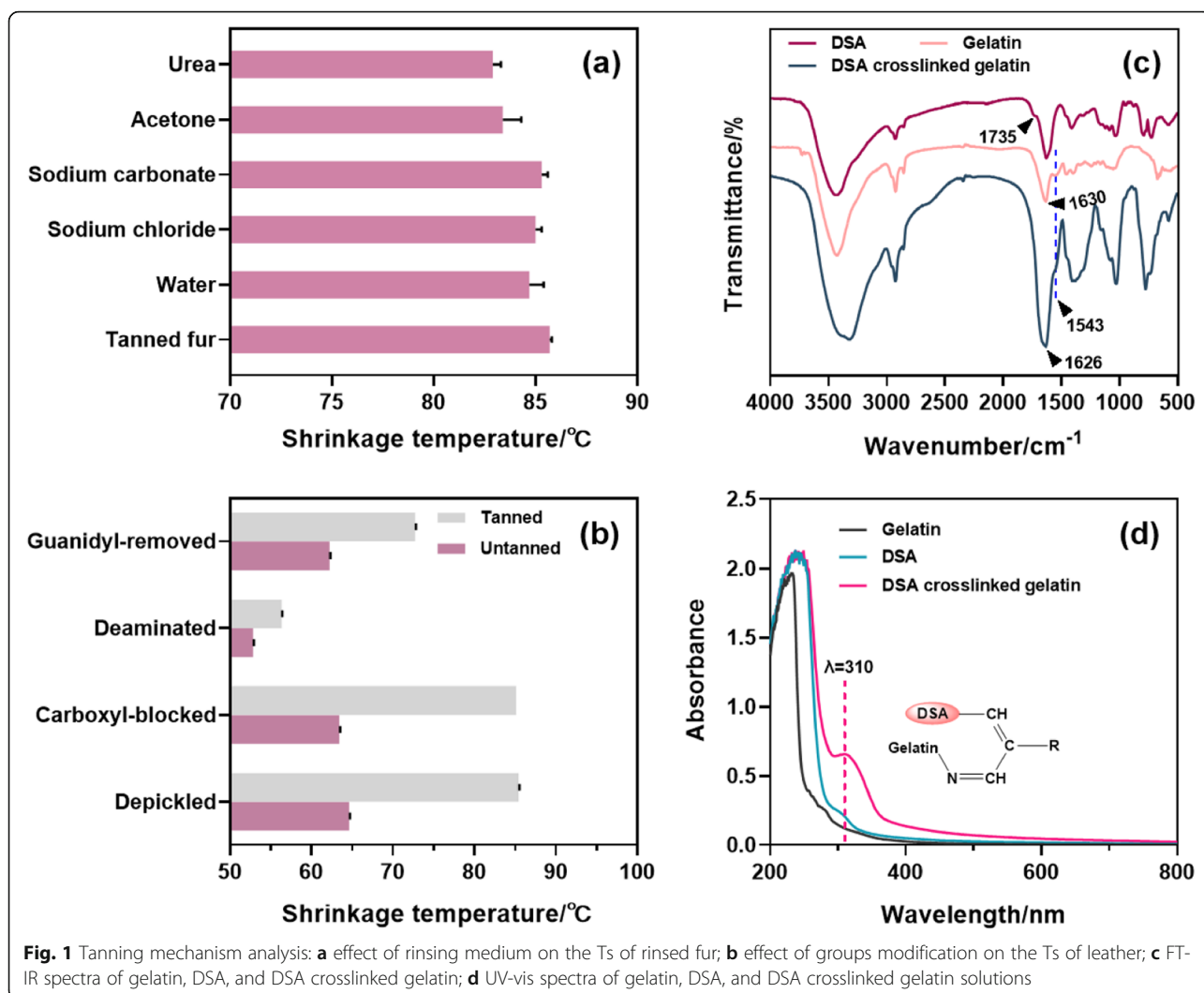


Fig. 1 Tanning mechanism analysis: **a** effect of rinsing medium on the Ts of rinsed fur; **b** effect of groups modification on the Ts of leather; **c** FT-IR spectra of gelatin, DSA, and DSA crosslinked gelatin; **d** UV-vis spectra of gelatin, DSA, and DSA crosslinked gelatin solutions

Schiff base structures. Fig. 1d illustrates that a new absorption peak at 310 nm occurs in the spectrum of DSA crosslinked gelatin. This is because DSA may partially undergo β -elimination reaction to form $-\text{C}=\text{C}-$ structure under alkaline crosslinking conditions (around 8.0). The combination of $-\text{C}=\text{C}-$ structure with Schiff base structure may lead to the formation of a new conjugated structure [29, 30]. These results demonstrated that DSA and gelatin did undergo Schiff base reactions to crosslink each other.

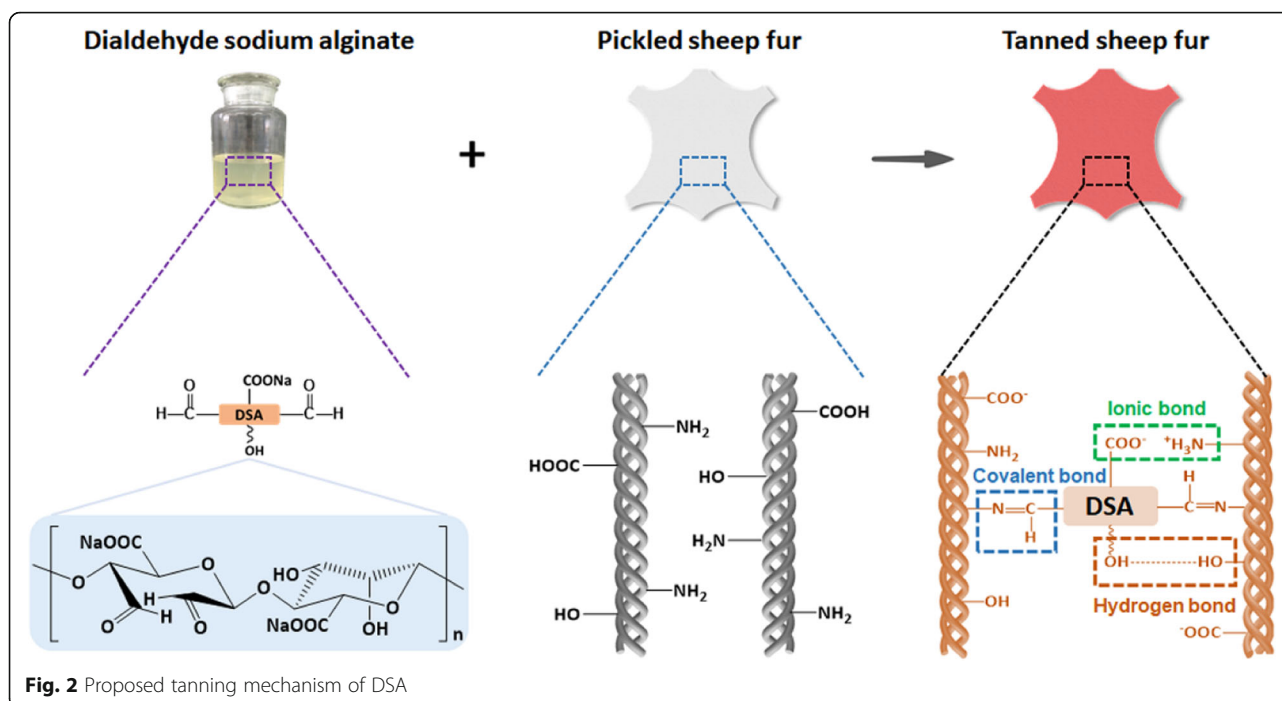
In summary, DSA was mainly combined with collagen fiber by forming Schiff base covalent bonds between aldehyde groups and amino/guanidyl groups while supplemented by a small number of hydrogen bonds and ionic bonds. The tanning mechanism of DSA was proposed and illustrated in Fig. 2, which was similar to the traditional aldehyde tanning mechanism [19]. Based on the tanning mechanism, the processing properties of DSA tanned sheep fur should be further investigated to guide

the practical application of sustainable DSA tanning agent in the future.

3.2 Stability of DSA tanned sheep fur

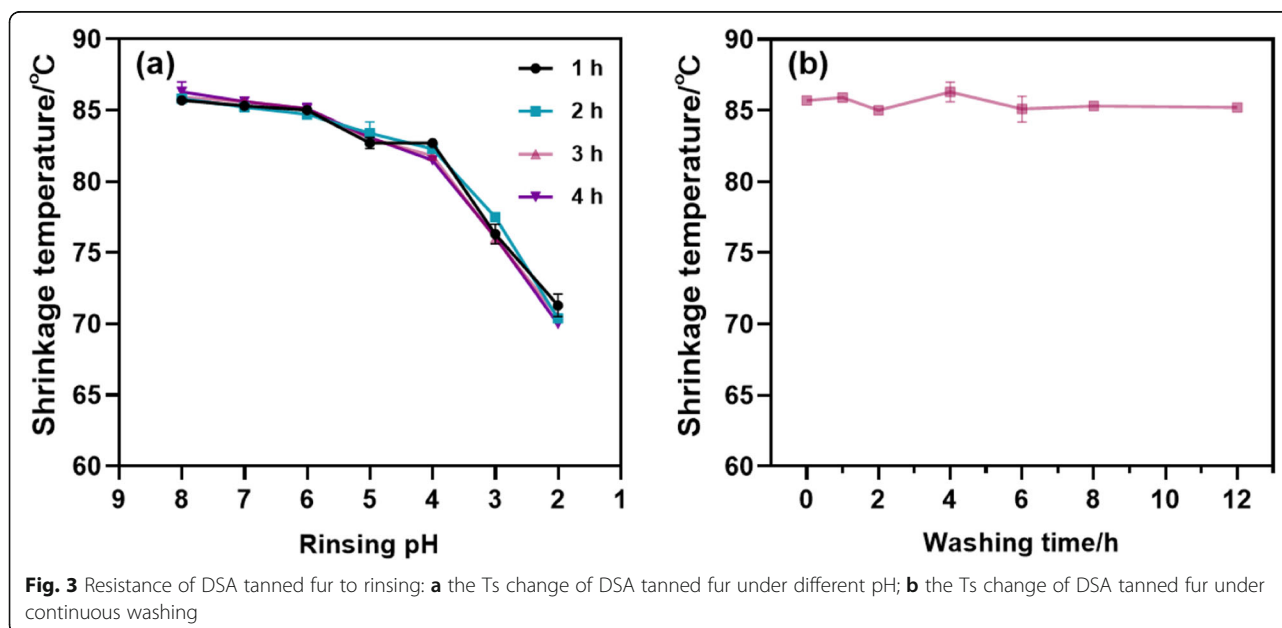
3.2.1 Resistance to acid rinsing

As is well acknowledged, the Schiff base is a dynamic covalent bond, which is less stable under acidic conditions than in basic conditions [31]. At present, the conventional post-tanning process of fur is generally conducted under acidic conditions. For instance, the fixation of dyestuff and fatliquor should be under an acidic condition with pH 3.8 to 4.0. Fig. 3 shows the Ts change of DSA tanned fur under different pH (a) and continuous washing (b). It can be found that the Ts of DSA tanned fur began to decrease when the float pH was lower than 6.0, and it would decrease dramatically when the float pH was lower than 4.0. This indicated that the reversible reaction proceeded and resulted in the cleavage of Schiff base crosslinks between DSA and collagen fiber.



Whereas, the Ts of DSA tanned fur did not change significantly with the prolonging of duration under different acidic conditions. The above results indicate that the stability of Schiff base crosslinks between DSA and collagen fiber is dominated by the acidity of float. These crosslinks are relatively stable and not easily affected by the rinsing duration when the float acidity is fixed. It is worth noting that under the experimental conditions,

the Ts of DSA tanned fur roughly remained at 82 °C when the float pH decreased to 4.0, even though the rinsing duration was up to 4 h. Fig. 3b illustrates that the Ts of DSA tanned fur tended to be stable with prolonging the washing time. This indicated that the covalent crosslinks between the DSA and collagen fiber were relatively stable to washing, which was in agreement with the results shown in Fig. 1a. To sum up, DSA tanned fur



has undesirable resistance to acid but has favorable resistance to washing.

3.2.2 Resistance to reductants

In the post-processing of tanned fur, the fur may be bleached to remove the stains and pigment on the fur by some reductants. The effect of commonly used reductive bleaching agents, including sodium pyrosulfite (SP), sodium hydrosulfite (SH) and sodium bisulfite (SB), on the Ts of DSA tanned fur herein was investigated to evaluate the resistance to reductants. As can be seen from Fig. 4, the Ts of the tanned fur did not change obviously after the treatments with different reductants at a dosage of 0.5 wt%. The Ts of treated fur tended to slightly decrease as the dosage of reductants continuously increased. When the dosage of reductant was up to 2 wt%, the Ts of treated fur remained above 82 °C. According to the float pH presented in Fig. 4b, it can be inferred that the decrease of Ts might be due to the reversible reaction of Schiff base crosslinking caused by the increase of acidity of bleaching float. This shows that DSA tanned fur has good resistance to the commonly used reductive bleaching agents.

3.2.3 Resistance to yellowing

Resistance to yellowing is an important property for fur, which is generally evaluated according to the color change under UV irradiation. Thus, DSA tanned fur was treated by UV-irradiation to evaluate its resistance to yellowing. Formaldehyde (FA) tanned fur has a high resistance to yellowing, so it was treated in the same way for comparison. The ΔE value of irradiated fur was calculated by subtracting the corresponding values for

standard white to characterize the whiteness of irradiated fur, and lower ΔE value generally means higher resistance to yellowing [17]. Moreover, the color change is slightly observable to human eyes when the ΔE value is no higher than 1.5 [32]. Table 1 shows that the chromatic values of FA tanned fur had no obvious change, indicating that its whiteness was stable under UV irradiation and it had high resistance to yellowing. As illustrated in Fig. 5a, the ΔE value of flesh side of DSA tanned fur was 2.24 when the UV irradiation time was prolonged to 12 h, which would further increase as the irradiation time was continuously prolonged. However, it can be found from Table 1 that the L value of flesh side of DSA tanned fur increased and b value decreased as the irradiation time prolonged. This indicated that the flesh side of DSA tanned fur gradually became whiter under UV irradiation. Table 1 also shows that the L value of wool of DSA tanned fur slightly decreased and b value increased as the irradiation time prolonged. This implied that the wool of DSA tanned fur slightly yellowed under UV irradiation. However, the wool of DSA tanned fur had slightly higher ΔE value compared with the wool of FA tanned fur (Fig. 5b). Overall, it can be deemed that DSA tanned fur has good resistance to yellowing.

3.3 Fatliquoring performance

Fatliquoring is an essential process for fur manufacturing to enable the resultant fur product with desirable softness. In general, the fatliquoring process of fur is conducted at 50 °C, and the fixation of fatliquor was under the acidity with a pH around 4.0. Thus, in consideration of the acid-sensitivity and reversibility of Schiff

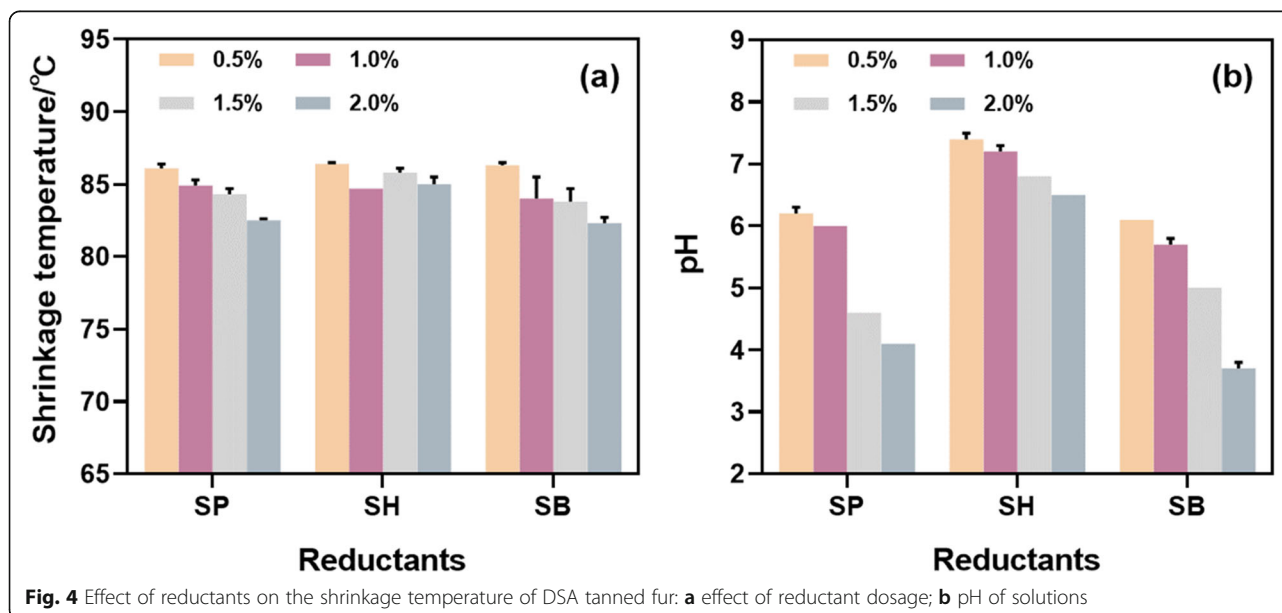


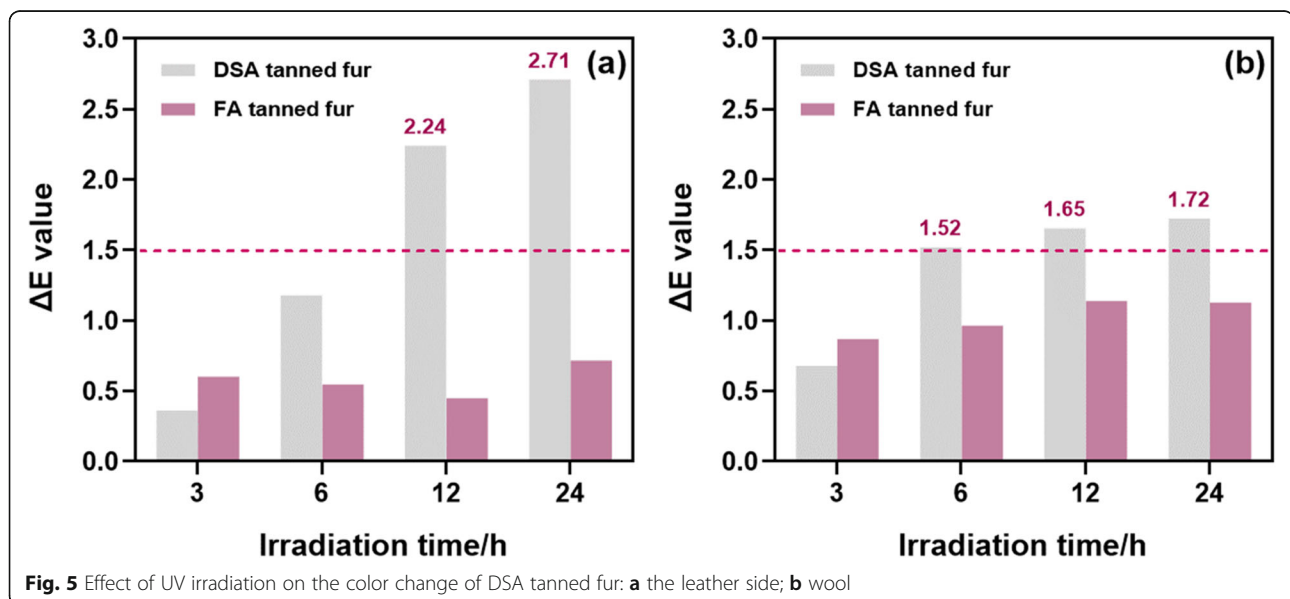
Table 1 Effect of UV-irradiation on the chrominance of tanned sheep fur

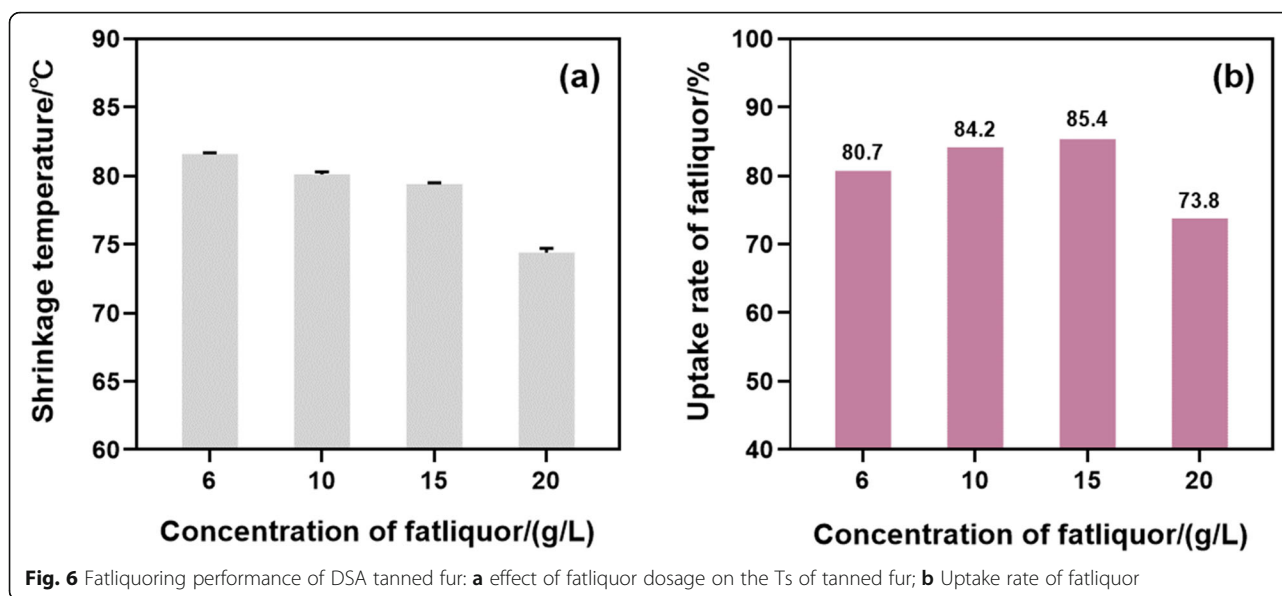
Irradiation time/h	Flesh side						Wool					
	DSA tanned fur			FA tanned fur			DSA tanned fur			FA tanned fur		
	L	a	b	L	a	b	L	a	b	L	a	b
0	86.9	0.4	16.5	85.9	1.1	10.1	82.7	0.2	12.9	79.4	0.1	11.9
3	86.8	0.8	15.7	85.3	1.4	10.4	82.2	0.6	13.8	78.6	0.5	11.9
6	86.5	1.2	15.7	85.4	1.4	10.3	81.7	0.8	13.8	78.7	0.6	12.3
12	87.1	1.1	14.4	85.7	1.4	10.4	81.5	1.1	13.5	78.5	0.7	11.8
24	87.2	1.2	14.0	85.4	1.5	10.5	81.6	1.2	13.6	78.6	0.8	11.7

base crosslinks, the fatliquoring performance of DSA tanned sheep fur was investigated. Fig. 6a illustrates that the T_s of fatliquored fur decreased slightly as the fatliquor concentration raised from 6 g/L to 20 g/L. After fatliquoring, the T_s of fur decreased by 4.1 °C to 11.3 °C in comparison with the T_s of DSA tanned fur (Fig. 3b). This might be due to the cleavage of Schiff base crosslinks between DSA and collagen fiber under acidic conditions, which could be verified by the resistance to acid of DSA tanned fur (Fig. 3a). In addition, the fatliquor accumulated between the collagen fibers to increase the chain spacing between collagen molecules, thereby weakening the interaction degree between collagen fibers [33]. Higher dosage of fatliquor could result in a stronger weakening effect, thus the T_s of fatliquored tanned fur gradually decreased with the increase of fatliquor dosage.

DSA tanning will consume the amino groups on collagen fiber and introduce carboxyl groups onto the collagen fiber, thus reducing the positive charge of tanned fur [17]. This will be negative for the uptake and fixation

of conventional fatliquor [31, 34]. As shown in Fig. 6b, the uptake rate of fatliquor for DSA tanned fur gradually increased with the increase of fatliquor concentration, which could reach to 85.4% when the fatliquor concentration was raised to 15 g/L. However, the uptake rate of fatliquor began to decrease with continuously increasing the dosage of fatliquor. This was mainly due to the limited capability of DSA tanned fur to absorb and combine fatliquor. Table 2 shows the physical properties of fatliquored DSA tanned fur after being air-dried, softened, and air-conditioned. The mechanical strengths, softness and extensibility of fatliquored fur gradually improved with the increase of fatliquor dosage. This was mainly because the surface of collagen fibers was covered by fatliquor to form a lubricating layer between collagen fibers, thus reducing the sliding friction between collagen fibers. Therefore, the softness, tear and tensile strengths of fatliquored fur were improved. As shown in Fig. 6a, the DSA tanned fur was severely de-tanned under these conditions, thereby greatly reducing the crosslinking density between collagen fibers. This performed negative





impacts on the above-mentioned properties of fatliquored fur. Thus, the physical properties of fatliquored fur began to decrease when the fatliquor concentration was higher than 15 g/L. The dosage of fatliquor needs to be reasonably controlled to obtain desirable resultant fur products when the DSA tanned fur undergoes the fatliquoring process. To sum up, DSA tanned fur has good fatliquoring performance when an appropriate amount of fatliquor is used, which can meet the requirements for making light-colored sheep fur products without high-temperature dyeing.

3.4 Chrome-reduced combination tanning performance based on DSA

3.4.1 Interactions between DSA and chrome tanning agent

In practice, in addition to the aforementioned light-colored sheep fur, the wool of sheep fur often needs to be dyed to manufacture dark-colored sheep fur products for meeting the market demands. Wool dyeing is generally carried out by using acid dyes in the temperature range of 65 °C to 85 °C. Under such severe conditions, high hydrothermal stability of sheep fur is required to prevent the fur from shrinking, and our previous studies have shown that the Ts of fur generally needs to be

higher than 90 °C [4]. It can be seen that the Ts of DSA tanned sheep fur (around 85 °C) did not meet this requirement and should be further improved. Chrome-reduced combination tanning of sheep fur has been proven to be an alternative strategy [4, 35]. Considering that DSA contains multifunctional groups, e.g., carboxyl group, hydroxyl group and aldehyde group, it has the potential to interact with Cr (III) to form a more robust crosslinking network in the collagen fiber matrix of fur. Fig. 7a shows the UV-vis spectra of the complex of DSA and Cr (III). The fresh chrome tanning agent solution (2 g/L) had two absorption peaks assigned to Cr (III) at λ_1 –430 nm and λ_2 –595 nm, and DSA (10 g/L) had no absorption peaks here. In the fresh mixture of chrome tanning agent and DSA, the two absorption peaks of Cr (III) shifted to λ_1 –420 nm and λ_2 –592 nm, respectively. This indicated that the DSA molecule was coordinated with Cr (III). After reaction for 4 h, the two absorption peaks of Cr (III) continuously shifted to λ_1 –408 nm and λ_2 –575 nm, respectively. This suggested that Cr (III) was further coordinated with the carboxyl and/or hydroxyl groups on DSA molecules. The blue shift of the two absorption peaks demonstrates that there was an obvious steric hindrance effect of the DSA–Cr (III) complex [36],

Table 2 Physical properties of fatliquored DSA tanned sheep fur

Dosage of fatliquor/(g/L)	Tensile strength/(N/mm ²)	Tear strength/(N/mm)	Elongation at a load of 5 N/%	Softness/mm
6	15.93±0.54	38.32±5.60	33.14±1.76	8.02±0.30
10	17.79±1.32	49.91±4.51	36.24±8.96	8.11±0.24
15	22.12±2.73	62.77±10.05	42.50±6.99	8.15±0.13
20	15.89±0.26	42.62±1.84	31.14±7.53	8.13±0.45

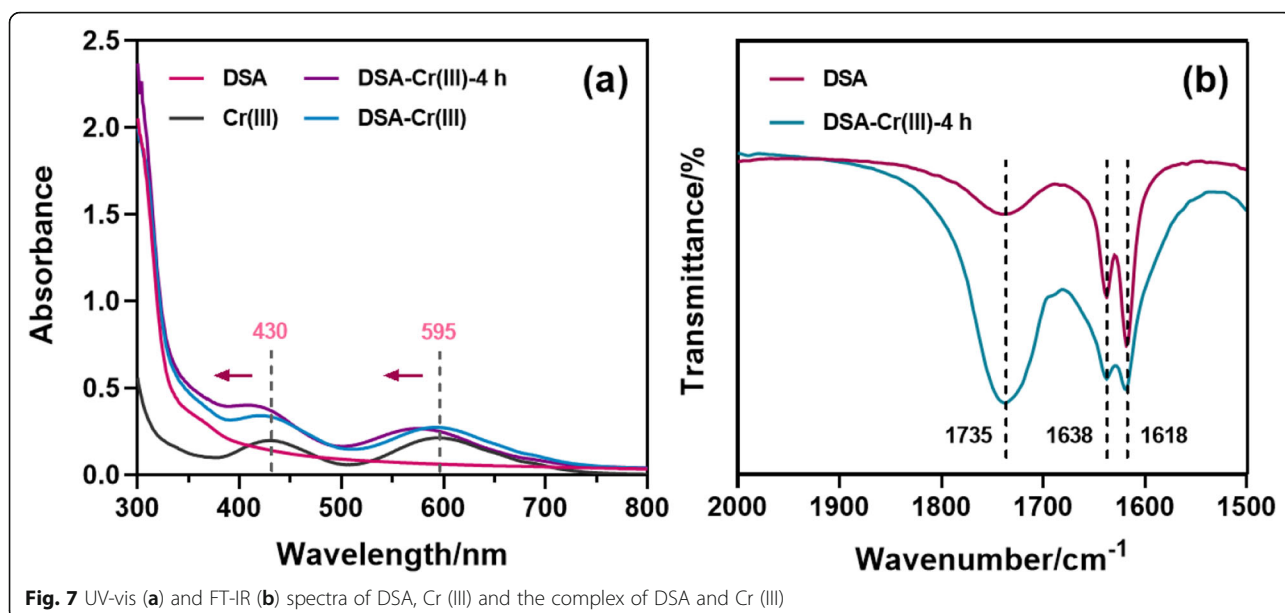


Fig. 7 UV-vis (a) and FT-IR (b) spectra of DSA, Cr (III) and the complex of DSA and Cr (III)

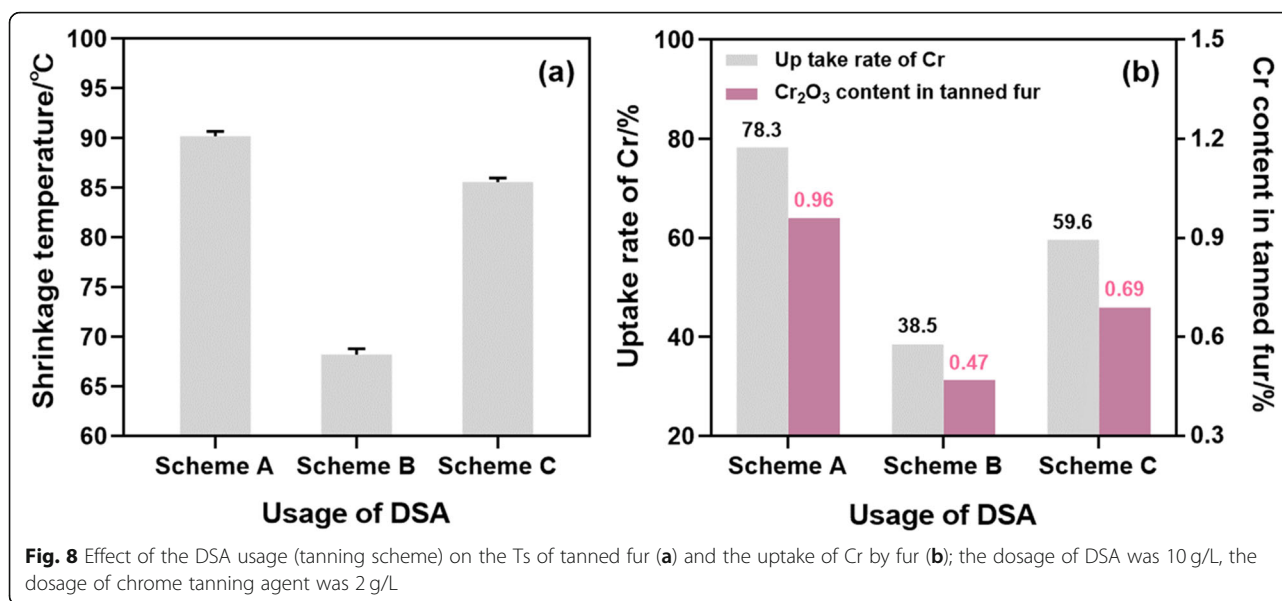
which might be caused by the macromolecular characteristics of DSA. Moreover, the ratio of absorbances at λ_1 –408 nm (0.4014) and λ_2 –575 nm (0.2659) was 1.51, indicating that DSA was coordinated with Cr (III) in terms of bridge bonding or cyclic coordination bonding [37].

The FT-IR spectra of the complex of DSA and Cr (III) is shown in Fig. 7b. The absorption bands at 1638 cm^{-1} and 1618 cm^{-1} were assigned to the antisymmetric stretching and symmetrical vibrations of carboxylate ions on DSA. The absorption band at 1735 cm^{-1} was assigned to symmetric vibration of aldehyde group. After coordinating with Cr (III), the vibration intensity of the absorption band assigned to carboxylate ion was obviously decreased. The new absorption band assigned to the carboxylate combined with Cr (III) was overlapped by the absorption band assigned to the carboxylate on excessive DSA. Whereas, it can be also inferred that the difference between the antisymmetric and symmetrical vibration frequencies of carboxylate was lower than 100 cm^{-1} , indicating DSA and Cr (III) might be coordinated in a chelated form [37]. The above results demonstrate that DSA can be complexed with Cr (III), providing the feasibility of chrome-reduced combination tanning of sheep fur based on DSA.

3.4.2 General tanning performance

According to the interactions between DSA and Cr (III), DSA tanning of sheep fur combined with reduced chrome tanning agent was proposed. As illustrated in Fig. 8, three tanning schemes were designed, including “DSA tanning first and then chrome retanning” (Scheme A), “DSA and chrome tanning in the same bath”

(Scheme B), and “chrome tanning first and then DSA retanning” (Scheme C). The Ts of fur tanned by Scheme A was improved to 90.2°C , which met the Ts requirement of high-temperature dyeing. When the fur was tanned by Scheme B, the Ts of tanned fur was only 68.2°C , which was 10.7°C lower than that of fur only tanned by 2 g/L chrome tanning agent (78.9°C) [38]. The Ts of fur tanned by Scheme C was 85.6°C , which was not further improved and comparable to that of fur only tanned by 10 g/L DSA (85.7°C). Fig. 8b shows that the uptake rate of chrome tanning agent and the Cr content of fur tanned by different schemes were rather different. Our previous work showed that the Cr content of sheep fur tanned only by 2 g/L chrome tanning agent was 0.73% (calculated as Cr_2O_3 , similarly hereinafter) [38]. The Cr content of fur tanned by Scheme A was 0.96%, which was obviously higher than that of fur tanned by the same dosage of chrome tanning agent. This shows that DSA tanning could promote the subsequent penetration and fixation of chrome tanning agent in the collagen fiber matrix of fur. When tanning Scheme B was employed, the Cr content of tanned fur was the lowest (only 0.47%), which was significantly lower than that of fur only tanned by 2 g/L chrome tanning agent. This indicates that DSA will prevent the penetration of chrome tanning agent into the collagen fiber matrix of fur, thus DSA and chrome tanning agent cannot be used in the same tanning bath. When the fur was tanned using Scheme C, the Cr content of tanned fur was 0.69%, which was slightly lower than that of fur only tanned by 2 g/L chrome tanning agent. This might be attributed to the release of small amount of chrome from tanned fur during the later DSA tanning process.



The reason for the difference in tanning performances of the three tanning schemes can be explained by the strong binding interaction between DSA and Cr (III). Since Cr (III) had been fully coordinated with the carboxyl groups on collagen fiber, few Cr (III) could combine with the carboxyl groups on DSA molecules to further strengthen the tanning effect. Compared with fur only tanned by DSA, the Ts of fur tanned by Scheme A had no obvious increase, and tanning Scheme C should not be suggested. Based on the results presented in Fig. 7, Cr (III) could form stable coordination bonds with the carboxyl and/or hydroxyl groups on macromolecular DSA, making DSA molecules become larger. Thus, the DSA-Cr (III) complex was difficult to penetrate into the collagen fiber matrix of fur. Meanwhile, Cr (III) also lost partial capability to coordinate with carboxyl groups on collagen fiber, so the Ts of tanned fur was the lowest, and tanning Scheme B should not be adopted. As for tanning Scheme A, DSA was fixed in the collagen fiber matrix of fur in advance by forming Schiff base cross-links, resulting in the dispersion of collagen fibers to expand the penetration channel for subsequent chrome tanning agent. When Cr (III) penetrated into the

collagen fiber matrix of fur, it could not only combine with the carboxyl groups on collagen fiber, but also coordinate with the carboxyl groups on DSA molecules. Finally, the absorption and fixation of Cr (III) was improved, thereby increasing the effective crosslinking between collagen fibers and improving the Ts of tanned fur. As a result, the tanning Scheme A endowed tanned fur with the highest Ts, thus it should be recommended for the production of dark-colored sheep fur.

3.4.3 High-temperature dyeing performance and physical properties

The effects of high-temperature dyeing on Cr release, Ts, and area yield of the combination tanned fur were investigated. As shown in Table 3, the released Cr from the fur during high-temperature dyeing was lower than the discharge standard of total Cr in tannery wastewater from workshop outlet (1.5 mg/L, in China) [1], which was less than that from the conventional chrome tanned fur under the same offer of chrome tanning agent [4]. This means that the combination tanning using DSA enhanced the fixation of Cr since more carboxyl groups were introduced onto collagen fibers. Table 3 also shows

Table 3 High-temperature dyeing performance of chrome-reduced combination tanned sheep fur

Tanning scheme	Cr conc. in dyeing wastewater/ (mg/L)	Ts/°C		Area yield/%	
		Before dyeing	After dyeing	Before dyeing	After dyeing
DSA + 1Cr ^a	0.88±0.01	86.0±0.5	80.0±1.2	119.9±0.5	107.5±0.0
DSA + 2Cr	1.18±0.01	91.0±0.3	83.1±1.1	131.4±0.0	131.4±0.0
DSA + 3Cr	1.24±0.02	93.6±0.3	88.7±0.2	125.4±0.0	125.4±0.0
DSA + 4Cr	1.46±0.01	97.2±0.1	89.8±0.9	117.1±0.0	117.1±0.0

^aPickled sheep fur was tanned by 10 g/L DSA and then retanned by 2 g/L chrome tanning agent, similarly hereinafter

Table 4 Physical properties of fatliquored sheep fur made from chrome-reduced combination tanning based on DSA

Tanning scheme	Tensile strength/(N/mm ²)	Tear strength/(N/mm)	Elongation at a load of 5 N/%	Softness/mm
DSA + 1Cr	11.06±2.70	39.20±3.37	22.83±2.94	6.76±0.18
DSA + 2Cr	16.27±2.61	54.19±5.15	23.58±1.97	7.44±0.10
DSA + 3Cr	17.86±0.07	58.37±12.65	24.46±0.08	7.94±0.18
DSA + 4Cr	18.00±0.17	62.77±2.98	25.90±2.12	8.28±0.14

that the Ts decreased after high-temperature dyeing. This might be due to the partial cleavage of Schiff base crosslinks between DSA and collagen fiber under severe acidic conditions (around pH 4.0, 50 °C). Even so, the area yields of the fur did not decrease except the fur tanned by 10 g/L DSA and 1 g/L chrome tanning agent. These results suggest that the chrome-reduced combination tanned fur based on DSA is capable of enduring the high-temperature dyeing process.

Physical properties of resultant fur determine its processing performance for fur products manufacturing. As our previous work reported, the tensile and tear strengths of fur made by conventional chrome tanning using 16 g/L chrome tanning agent were 13.27 N/mm² and 49.67 N/mm, respectively [4]. Table 4 shows that mechanical strengths of the combination tanned dyed fur were higher than those of conventional chrome tanned fur when the chrome tanning agent used in the combination tanning was no lower than 2 g/L. The elongation at a specified load (5 N) and softness of resultant fur increased as the concentration of chrome tanning agent was raised. This was mainly due to the improved uptake of post-tanning chemicals [4]. Based on the results above, chrome-reduced retanning of DSA tanned sheep fur can be proposed as a feasible strategy to make dark-colored fur products that need high-temperature dyeing.

4 Conclusions

Sustainable dialdehyde sodium alginate (DSA) can be used as an organic tanning agent for the tanning of sheep fur. DSA was mainly combined with collagen fiber by forming Schiff base covalent bonds between the aldehyde groups and amino/guanidyl groups while supplemented by a small number of hydrogen bonds and ionic bonds. As a new tanned sheep fur, DSA tanned fur had poor resistance to acid rinsing due to the acid sensitivity of Schiff base structure, but it had excellent resistance to washing and good fatliquoring performance as well as good resistances to yellowing and reductant. Considering that macromolecular DSA can highly coordinate with Cr (III), DSA and chrome tanning agent cannot be used in the same tanning bath. Tanning of sheep fur using DSA first and then retanning by chrome tanning agent is the optimal combination tanning scheme, which can make the tanned fur meet the needs of high-temperature

dyeing processing. The use of DSA brings about high fixation of chrome in the collagen fiber matrix of fur, thus this strategy can not only largely reduce the dosage of chrome tanning agent, but also produce dark-colored fur with favorable area yield and physical properties. Overall, the sheep fur tanned by sustainable DSA has favorable properties under appropriate post-tanning processing conditions to produce satisfactory resultant light-colored or dark-colored fur.

5 Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1186/s42825-020-00047-8>.

Additional file 1: Table S1. Fatliquoring process of DSA tanned fur; **Table S2.** Process for DSA and chrome tanning in the same bath (Tanning Scheme B); **Table S3.** Process for chrome-reduced tanning and DSA retanning (Tanning Scheme C).

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Authors' contributions

WD designed and performed all the experiments, and drafted the manuscript. YW provided suggestions for the experiments and analyzed the results. JZ provided suggestions for the design of tanning trials. HL prepared the samples for FT-IR analysis and conducted the FT-IR determinations. XP provided resources for the FT-IR determinations. BS supervised the project and reviewed the manuscript. The authors read and approved the final manuscript.

Availability of data and materials

All data generated or analyzed during this study are included in this manuscript and the additional file. The authors declare that the data in this article is reliable.

Competing interests

The authors declare that they have no competing interests.

Author details

¹China Leather and Footwear Research Institute Co. Ltd., Beijing 100015, P.R. China. ²College of Biomass Science and Engineering, Sichuan University, Chengdu 610065, China. ³Key Laboratory of Leather Chemistry and Engineering of Ministry of Education, Sichuan University, Chengdu 610065, P.R. China.

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