Biomass-based Tanning Agent for Sustainable Leather Manufacture via Cyanuric Chloride Modified Chitooligosaccharide

by

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Abstract

Developing alternative tanning agents to avoid the potential environmental and human health risks from the conventional chrome tanning is essential for the leather industry. In this work, we prepared an eco-friendly biomass-based tanning agent dichlorotriazinyl chitooligosaccharide (DTCS) by modifying chitooligosaccharide (COS) with cyanuric chloride (CC) for chrome-free leather manufacture. The synthesis of such biomass-based tanning agent was systematically optimized to obtain the target product with high grafting degree of 67% and weight-average molecular weight (M_w) of 1465 g/mol. The non-pickling tanning procedure using DTCS was investigated, and the interactions between DTCS and collagen fibers were studied. Our results showed that the hydrothermal stability of the tanned leather was significantly increased, i.e., the shrinkage temperature (T_s) exceeding 82.0 °C, and the mechanical properties were improved. Moreover, the organoleptic properties of leather (e.g., fullness, softness and grain tightness) exhibited obvious improvement. This research not only offers a reliable approach for cleaner leather manufacturing while addressing the underlying ecological pressure, but also highlights the emerging use of biomass materials in the leather industry.

1. Introduction

Chrome tannage has catalyzed the advance of modern leather industry for more than 120 years.[1] These Cr(III) salts endow the leather with high hydrothermal stability, light resistance and versatile performance, which are virtually suitable for various types of leather products. However, Cr(III)-containing sludges and solid wastes from chrome tanning processing may pose potential environmental burdens and have been listed in the "Directory of National Hazardous Wastes (Version 2021)" in China.[2,3] Moreover, possible conversion of Cr(III) into hazardous and carcinogenic Cr(VI) under certain conditions has drawn public health concern worldwide.[4,5] Several regulations have been published to strictly limit the content of Cr(VI) in leather articles.[6] The European Commission requires the content of Cr(VI) in leather products in contact with skin to be below 3 mg/kg (Annex XVII of REACH regulation). Therefore, the development of chrome-free tanning agents has become a critical research topic in the leather industry.

Currently, chrome-free tanning techniques can be mainly categorized into non-chrome metal tanning (e.g., aluminum tanning and zirconium tanning) and organic tanning (e.g., aldehyde tanning and vegetable tanning).[7] However, the weak coordination stability of non-chrome metal tanning agents endows the tanned leather with poor properties[8]. Besides, the content of metal in metal-free leather has been restricted by international standards (i.e. Leather Standard by OEKO-TEX)[9], which promotes the development of metal-free tanning agents. The common metal-free agents, including modified glutaraldehyde, oxazolidine and organic phosphine), are derived from non-renewable petrochemicals and have been restricted owing to the release of formaldehyde during their preparation and leather production.[10-12] Therefore, efficient and eco-friendly metal-free tanning agents are still rare.

Polysaccharides such as starch, cellulose and sodium alginate have received extensive interest to produce green chemicals due to their versatile chemistry, biocompatibility, and biodegradability.[13-15] Chemical modification of polysaccharides has allowed the introduction of active groups (e.g., aldehyde groups, hydroxyl groups and alkenyl groups) for leather tanning.[16-18] However, the oxidative modification of polysaccharides may involve free formaldehyde during the process.[19] Moreover, the low isoelectric point of the obtained leather leads to the poor absorption and fixing efficiency of subsequent anionic materials (e.g., anionic dyes and fatliquors).[10]

Chitooligosaccharide (COS) is the degradation product of chitosan with the degree of polymerization (DP) less than 20.[20] The relatively low molecular weight, less chain entanglement and steric hindrance of COS lead to good water solubility and diffusion kinetics.[21,22] Recently, triazine moiety has emerged as an attractive crosslinker alternative for metal-, formaldehyde-, and phenol-based moieties in leather manufacture due to its biocompatible nature.[23] For example, Granofin® Easy F-90 liquid (F-90) is a commercialized triazine tanning agent, which can produce the light colored leather via the efficient

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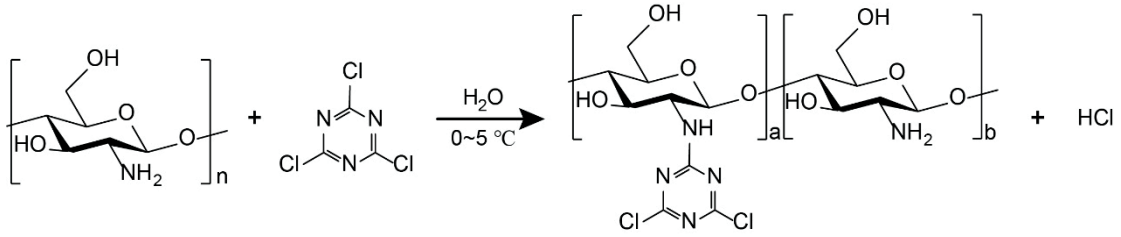

Scheme 1. The preparation of DTCS from chitooligosaccharide and cyanuric chloride.

crosslinking between active chlorines in the benzenesulphonate and the amino groups in collagen.[24] This tanning process can start from bated pelt without the pickling process, thus reducing the pollution of neutral salts[25] and simplifying the tanning process. However, F-90-tanned leather suffers from low shrinkage temperature, poor softness and undesirable fullness. Therefore, we hypothesize that novel tanning materials can be obtained by combining the advantage of cationic COS and biocompatible triazine to exert a synergistic effect, which can contribute to sustainable and reliable leather manufacture.

In this work, we developed a biomass-based chrome-free tanning agent by modifying COS with CC and evaluated its performance. The biomass-based tanning agent (i.e., dichlorotriazinyl chitooligosaccharide, DTCS) possesses active chlorines which serve as the active sites to crosslink collagen fibers, while the adequate molecular weight endows the tanned leather with satisfactory organoleptic properties such as fullness and softness. The synthesis of DTCS was optimized to provide sufficient reactive chlorines and the chemical structure of DTCS was characterized in detail. The important parameters affecting the tanning effect (e.g., tanning temperature, tanning pH, tanning time and the dosage of DTCS) were evaluated in the non-pickling tanning process. This work provides a theoretical and practical reference for clean production of leather using COS-based tanning agent, demonstrating the immense potential of biomass-based materials for sustainable development.

2. Materials and Methods

2.1 Materials

Wet salted cattle hides used for preparation of pickled and bated pelt were supplied by Zhangpu Zhiyuan Leather Co., Ltd, and the average weight of the raw materials was about 33 kg. Chitooligosaccharide (COS) was purchased from Xi'an Benfeng Biotechnology Co., Ltd. Cyanuric chloride (CC) was obtained from Aladdin Reagent Co., Ltd. The reagents used for synthesis were of analytical grade, and the other chemicals used for leather processing were commercial products.

2.2 Synthesis of DTCS

Cyanuric chloride and deionized water were first added into a three-necked flask reactor and stirred for 10 min to fully dispersion. Then COS was dissolved in deionized water, and the solution was added dropwise into reaction system over 30 min. The mass ratio of CC to COS (i.e., 0.1, 0.2, 0.3, 0.4, 0.5, 0.6) was regulated, and the reaction took placed at 2 °C for 10 h under stirring. Meanwhile, different amounts of sodium carbonate aqueous solution (20wt%) (i.e., the mass ratio of sodium carbonate to CC at 0, 0.1, 0.2, 0.3 and 0.4) was continuously added dropwise to neutralize hydrogen chloride generated in the reaction system over 10 h. Finally, the biomass-based tanning agent dichlorotriazinyl chitooligosaccharide (DTCS) was obtained through freeze drying of the supernatant for 48 h. The reaction formula is depicted in Scheme 1.

2.3 Determination of grafting degree (GD) of DTCS

O-phthaldialdehyde (OPA) spectrophotometric assay, where o-phthaldiadehyde and β-mercaptoethanol react with primary amine to form adduct with strong absorption at 340 nm,[26] was adopted to determine the grafting degree (GD) of DTCS. Specifically, the OPA reagent was prepared by combining the following solutions and diluting to a final volume of 50 mL with deionized water: 0.1 M sodium tetraborate (25 mL), 20wt% SDS (2.5 mL), 40 mg OPA (dissolved in 1 mL of methanol) and 100 μL of β-mercaptoethanol. 0.1 g/L COS/DTCS aqueous solution (5 mL) was mixed with OPA reagent (5 mL) and the mixture was incubated for 10 min at ambient temperature. Then the absorbance values at 340 nm were measured by UV-visible spectrometer (Hitachi U-3900H, Japan). The absorbance-concentration curve of glucosamine hydrochloride was plotted as calibration curve to obtain the amino content of the samples. The GD of DTCS was calculated by the following formula (1):

$$GD = \frac{(C_0 - C_S)}{C_S} \times 100\% \quad (1)$$

Where C_0 and C_s represent the amino concentration of the COS and DTCS solution, respectively.

2.4 Characterization of DTCS

2.4.1 Fourier transform infrared (FT-IR) spectroscopy

The CC, COS and DTCS samples were collected and mixed with potassium bromide. FT-IR spectra of the samples were recorded in the range from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} on a Nicolet IS10 infrared spectrometer.

2.4.2 Nuclear magnetic resonance (NMR) spectroscopy

^{13}C-NMR spectra of CC, COS and DTCS were recorded on a 400 MHz Brucker ARX400 NMR spectrometer (Bruker, Switzerland) using $CDCl_3$, D_2O and D_2O as solvent at a concentration of 50

mg/mL, respectively. Tetramethylsilane (TMS) was adopted as an internal reference.

2.4.3 X-ray diffraction (XRD) measurement

The crystallinity of COS and DTCS was analyzed by an X-ray diffractometer (Rigaku Ultima IV, Japan) with a voltage of 40 kV and a current of 40 mA at Cu-Kα irradiation. The samples were scanned in the diffraction angle (2θ) ranging from 5° to 55° with a scanning rate of 5°/min.

2.4.4 X-ray photoelectron spectroscopy (XPS)

The elements composition and molecular structure on the surface of COS and DTCS samples were analyzed using X-ray photoelectron spectrometer (ThermoFischer, ESCALAB 250Xi, USA) with Al Kα ray as the excitation source under a vacuum degree of 8×10^{-10} Pa.

2.4.5 Gel permeation chromatography (GPC) analysis

The average molecular weight and corresponding polydispersity indexes of COS and DTCS were determined by GPC equipped with refractive index detector (Shimadzu Rid-20A, Japan), $TSK_{gel}GMPW_{XL}$ chromatographic column (Tosoh Bioscience, Japan) and high-performance liquid chromatography (HPLC) pump (Shimadzu LC20, Japan). The COS and DTCS aqueous solution (20 mg/mL) were filtered to eliminate the influence of the dust particles before injection. A solution of 0.1 M $NaNO_3$ was used as mobile phase and the flow rate was 0.6 mL/min with elution temperature at 40 °C.

2.5 DTCS tanning trials

The bated cattle hides were prepared according to the conventional process.[27] The bated cattle hide samples from back part (30 cm × 30 cm) were first immersed in 100wt% water, and then 5, 10, 15, 20, 25 and 30wt% of DTCS was added as tanning agent. The pH of the tanning bath was adjusted to 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0, respectively. The tanning system was operating at 25, 30, 35, 40, 45 and 50 °C for different periods (i.e., 1, 2, 3, 4, 5, 6, 7 and 8 h). The tanned leather was washed and piled overnight. The dosage of chemical materials in the tanning process were based on the weight of limed pelt. The specific process recipe is given in Table I.

The commercially available active chlorine tanning agent (i.e., Granofin® Easy F-90 liquid from Stahl Company, abbreviation as F-90) and conventional chrome tanning agent were used to treat leather as control groups. The tanning process of F-90 is shown in Table II and chrome tanning process was carried out according to the conventional process.

The fatliquoring process of tanned leather was performed by introducing natural+synthetic fatliquor combination (3%), lecithin fatliquor (3%), synthetic fatliquor (3%), lanolin fatliquor (1%) and synthetic neatsfoot oil (1%). The fatliquored leather was dried and softened at room temperature to prepare crust leather for further evaluation.

2.6 Leather properties analysis

2.6.1 Determination of shrinkage temperature

Shrinkage temperature (T_s) of tanned leather was measured by a shrinkage temperature tester (Sunshine electronic institute, Shaanxi University of Science & Technology) according to the ASTM

Table I

Tanning process for DTCS.

Process	Chemical	Dosage/%	Temperature/°C	Time/min	Remarks
Wash	Water	400	25	5	
Tanning	DTCS	0-30	25-50		
	Water	100		0-480	pH 3-8
Wash	Water	400	25	20	Overnight
Horse up					

Table II

Tanning process for F-90.

Process	Chemical	Dosage/%	Temperature/°C	Time/min	Remarks
Wash	Water	400	25	5	
Tanning	Water	40			
	F-90	15		120	
	Water	30	35	120	
	Water	30	45	240	Overnight
Wash	Water	400	25	20	
Horse up					

method.[28] Samples (60 mm × 3 mm) were cut out from tanned leather and suspended vertically in water. The heating rate was kept at 2 °C/min. The temperature when samples shrink was recorded as T_s of tanned leather.

2.6.2 Morphology observation

The microstructure of the cross section of lyophilized leather samples was observed to analyze the dispersion of collagen fibers using a scanning electron microscope (SEM, Thermo scientific Apreo 2C, USA) with an accelerating voltage of 15 kV. The grain surface morphologies of lyophilized leather samples were observed to analyze the gain flatness by a stereomicroscope (M205 C, LEICA, Germany).

2.6.3 Determination of thickening rate

Thickening rate of tanned leather (i.e., DTCS, F-90 and Cr(III)-tanned leather) was determined by a thickness gauge (PEACOCK, Japan) according to the standard recommended by International Union of Leather Technologists and Chemists Societies.[29] The thickening rate could be calculated according to the following formula (2), in which the T (mm) is the thickness of tanned leather and the T_0 (mm) is the thickness of the pelt prepared for tanning.

$$\textit{Thickening rate}\ (\%) = \frac{(T-T_0)}{T_0} \times 100\% \quad (2)$$

2.6.4 Physical and organoleptic properties measurement

Physical properties of crust leather were measured according to the official standards recommended by International Union of Leather Technologists and Chemists Societies. Test items include tensile strength and elongation at break,[30] tear strength,[31] burst strength[32] and softness.[33]

3. Results and Discussion

3.1 Optimization of DTCS synthesis condition

The nucleophilic substitution reaction rate of CC onto COS is mainly related to the concentration of CC and the available nucleophile at different pH.[34] Therefore, effects of the CC dosage and sodium carbonate dosage on the GD of DTCS were explored.

The effect of different mass ratio of sodium carbonate to CC on the GD of DTCS was first investigated (Figure 1a). When maintaining the mass ratio of CC to COS at 0.5, the GD of DTCS increased first and then decreased with the increase of the mass ratio of sodium carbonate to CC. It reached the maximum (i.e., ~64%) when the mass ratio was 0.3. Sodium carbonate was continuously added to neutralize the hydrogen chloride generated along with the nucleophilic substitution reaction between COS and CC, which promoted the forward reaction. However, continuous addition of excess sodium carbonate caused the enhancement of the alkalinity of the reaction system, which intensified the hydrolysis reaction of cyanuric chloride, leading to the decline of the GD of DTCS. Therefore, the optimal mass ratio of sodium carbonate to CC is 0.3.

Keeping the mass ratio of sodium carbonate to CC at 0.3, the effect of different mass ratio of COS to CC on the GD of DTCS was studied (Figure 1b). The GD of DTCS increased when the mass ratio of CC to COS increased from 0.1 to 0.5, and the maximum GD was obtained (i.e., ~67%). This was attributed to the fact that the increase of CC dosage in the reaction system was conducive to the occurrence of nucleophilic substitution reaction between CC and COS. However, if the mass ratio of CC to COS exceeded 0.5, the GD of DTCS decreased. We speculated that the increase of CC dosage also promoted the hydrolysis of CC, which led to the generation of excessive HCl, thus leading to the decline of the GD of DTCS.[34] Therefore, the optimal mass ratio of CC to COS is 0.5.

3.2 Characterization of DTCS

FT-IR, ^{13}C NMR, and UV-vis analyses were performed to confirm the formation of DTCS. In the FT-IR spectrum of DTCS (Figure 2a), the broad absorption peaks between 3650 cm^{-1} and 3100 cm^{-1} were assigned to the stretching vibration of –NH_2 and –OH groups, while the relatively weak peak between 3000 cm^{-1} and 2800 cm^{-1} was attributed to C–H band stretching vibration. This indicated that the basic structural unit of COS existed in DTCS. Besides, the characteristic absorption bands of CC also appeared in DTCS, where the C=N and C–N stretching vibration of triazine ring were at around 1544 cm^{-1} and 1326 cm^{-1}, and the stretching vibration of

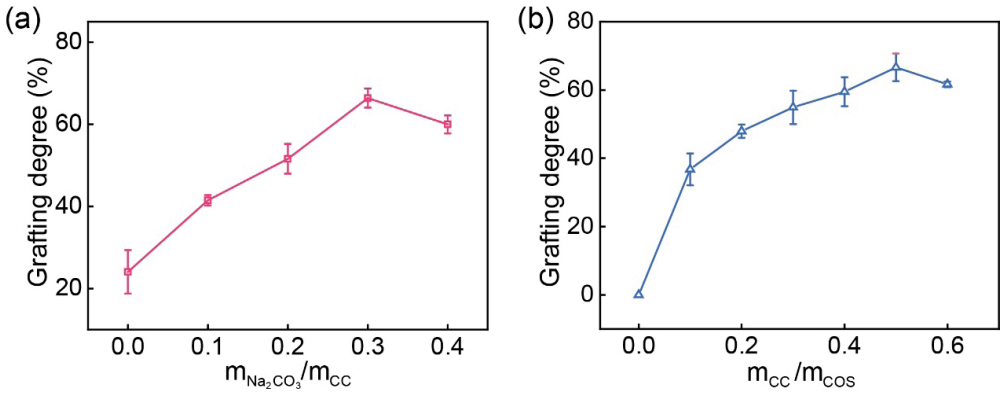

Figure 1. The GD of DTCS under **(a)** different mass ratio of sodium carbonate to CC and **(b)** different mass ratio of CC to COS.

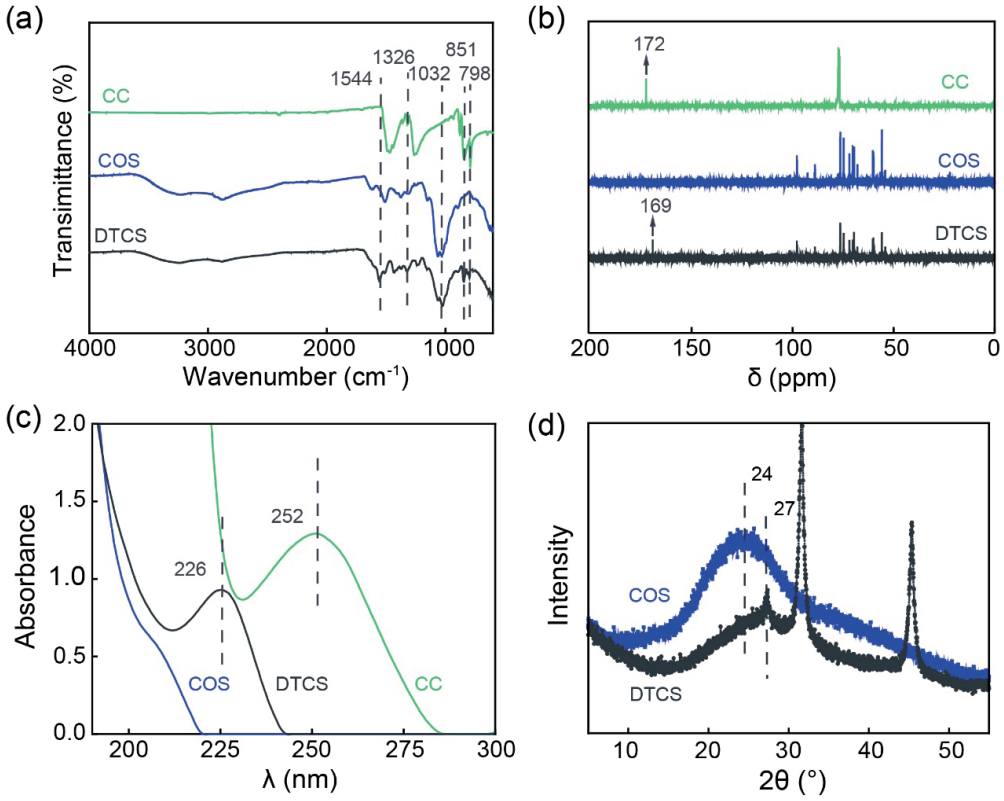

Figure 2. FT-IR spectra **(a)**, ^{13}C NMR spectra **(b)**, UV-vis absorption spectra **(c)** of CC, COS and DTCS; XRD spectra of COS and DTCS **(d)**.

C–Cl bond was at 851 cm^{-1} and 798 cm^{-1}. Collectively, FT-IR spectra indicated that CC could react with COS.

^{13}C-NMR spectra of CC, COS and DTCS were then obtained (Figure 2b). In the spectrum of CC, the carbon signal appearing at δ=172 ppm was ascribed to triazine ring. The signals of C1 (98.1 ppm), C2 (55.9 ppm), C3 (70.0 ppm), C4 (88.8 ppm), C5 (76.4 ppm), C6 (60.0 ppm) were observed in the spectrum of COS.[35,36] These peaks remained after the formation of DTCS, where the typical carbon signal of CC appeared at 169 ppm. Therefore, ^{13}C-NMR spectra confirmed that the substitution reaction of CC occurred successfully.

The UV-vis absorption spectra of CC, COS and DTCS were also collected (Figure 2c). There was no maximum absorption peak in the range of 200 nm to 400 nm for COS. The maximum absorption peaks of DTCS and CC were located in 226 nm and 252 nm, respectively. The difference was attributed to the inductive effect of imine on triazine ring which caused the λ_{max} of DTCS to move towards the shorter wavelength (i.e., blue shift). These results also demonstrated the presence of the triazine structure in DTCS.

The crystal structures of COS and DTCS were characterized (Figure 2d). XRD patterns exhibited well crystallinity of COS with a distinct 2θ peak at 24°, associated with the intermolecular and intra-molecular hydrogen bonding.[37] In contrast, the broad peak at 27° weakened significantly, owing to the introduction of dichlorotriazinyl and breakdown of hydrogen bonds, while the peaks at 31° and 45° were assigned to residual sodium chloride after the modification process. These also indicated that DTCS was more amorphous than COS, which can promote water solubility as well as penetration in tanning process.

The XPS spectra were also performed to determine the surface element composition of COS and DTCS (Figure 3). The XPS survey spectra of COS (Figure 3a) and DTCS (Figure 3d) both contained carbon, nitrogen and oxygen elements. Two obvious signal peaks of sodium and chlorine elements appeared in the spectrum of DTCS, related to the introduction of sodium chloride and dichlorotriazinyl in the modification process. Spectra of C 1s and N 1s were fitted to further estimate the functional groups on the surface of COS and DTCS. The C 1s peaks of COS (Figure 3b) were attributed to the contribution of C–C/C–H, C–O/C–N and O–C–O bonds, corresponding to the peak positions at 284.8 eV, 286.3 eV and 287.8 eV. In contrast, the C 1s of DTCS (Figure 3e) showed two additional peaks at 288.7 eV and 289.8 eV, assigned to C=N and C–Cl bonds, respectively.[38] Besides, the N 1s spectrum of COS (Figure 3c) was decomposed into two component peaks at 399.3 eV and 401.6 eV, corresponding to free amino groups and protonated amino groups.[39] In contrast, the two peaks in the N 1s spectrum of DTCS (Figure 3f) (389.9 eV and 400.6 eV) were attributed to C–N and C=N.[38]

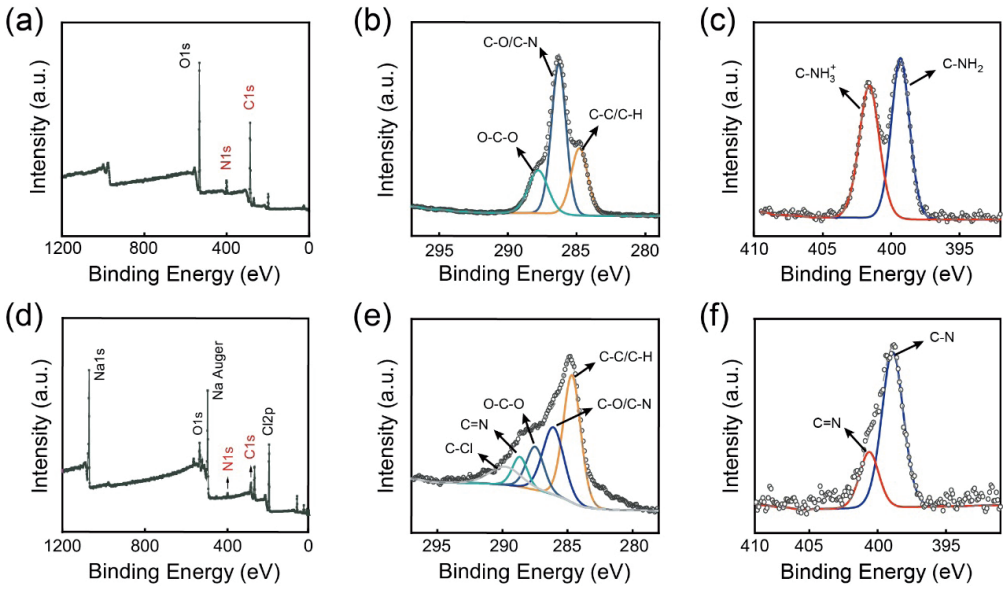

Figure 3. The wide scan XPS survey spectra of COS **(a)** and DTCS **(d)**, and the corresponding XPS spectra of C 1s and N 1s of COS **(b, c)** and DTCS **(e, f)**.

Therefore, the results of XPS analysis could further confirm the successful synthesis of DTCS.

The tanning properties of tanning agent are closely related to the size of the tanning agent molecule In order to ensure the penetration of tanning agent molecule into the inner structure of three-dimensional leather matrix and effective crosslinking with collagen fibers, the molecular weight distribution of tanning agents is generally controlled in the range of 500-3000 Da.[40] The molecular weight and the distribution of COS and DTCS were determined (Table III) using GPC. The molecular weight of DTCS was higher than COS and the M_w increased from 1077 g/mol to 1465 g/mol, which indicated the successful grafting of CC onto COS. Besides, the polydispersity (M_w/M_n) increased from ~1.4 to ~1.9. This data indicated that DTCS has suitable molecular weight and broad molecular weight distribution, which can penetrate into the collagen fibers for tanning process.

3.3 Optimization of DTCS tanning process

Tanning processes have great influence on the properties of tanned leather. We investigated the effects of the different factors (e.g., temperature, pH, time and dosage of tanning agent) on tanning properties by evaluating the hydrothermal stability of the tanned leather, which is the critical criterion for leather products.

3.3.1 Tanning temperature

The substitution of active chlorine on CC is largely controlled by temperature.[41] For example, the di-substitution of chloride occurs while the temperature exceeds 25 °C. Hence, the effect of temperature on the tanning property of DTCS was explored at different temperatures (i.e., 25 °C, 30 °C, 35 °C, 40 °C, 45 °C and 50 °C) (Figure 4a). When the tanning temperature was adjusted to 25 °C, 30 °C and 35 °C, the T_s of tanned leather was close to 75.5 °C. The highest T_s (i.e., 78.5 °C) was obtained at 40 °C. However, there was no significant contribution to the T_s by further increasing the tanning temperature. These results demonstrated that the efficient binding of DTCS and collagen fibers had already happened at 25 °C, and could be strengthened at 40 °C.

3.3.2 Tanning pH

The pH of reaction system is related to the availability of reactive groups from collagen and tanning agents, which has a significant influence on the tanning reactivity. We revealed the effect of pH on the T_s of tanned leather (Figure 4b). The T_s of tanned leather increased along with the increase of pH and achieved the highest value (~81.2 °C) when the pH was controlled at ~6.0, while it decreased slightly by further raising the pH of the reaction system. The increase of tanning pH facilitated the covalent interaction between C–Cl and $-NH_2$ under acidic conditions (i.e., pH<6.0), while the alkaline conditions (i.e., pH>7.0) promoted the hydrolysis reaction of chlorine

Table III

The average molecular weight and molecular-weight distribution of COS and DTCS.

Sample	M_n	M_w	M_z	M_w/M_n
COS	765	1077	1948	1.4
DTCS	789	1465	3836	1.9

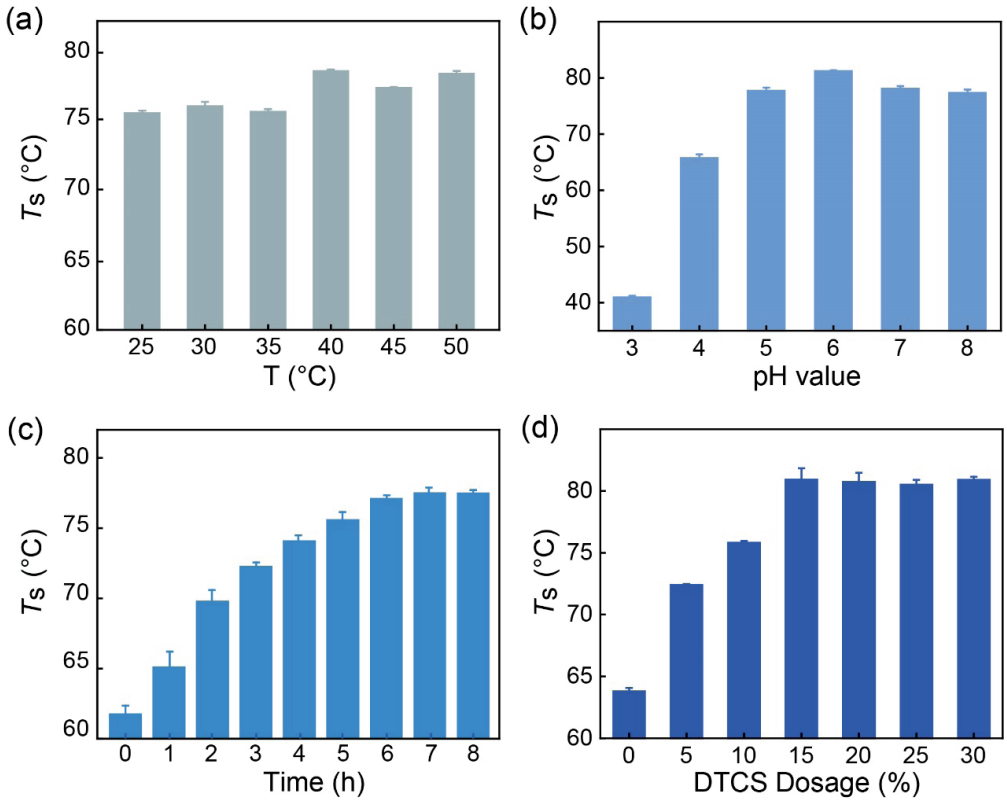

Figure 4. (a) T_s of leather tanned at different temperature, **(b)** T_s of leather tanned at different pH, **(c)** T_s of leather tanned at different time, **(d)** T_s of leather tanned with different dosage of DTCS tanning agent.

groups in DTCS and inhibited the effective covalent interaction between DTCS and collagen fibers.[42] Therefore, the pH in tanning process is optimized as ~6.0.

3.3.3 Tanning time

We further investigated the relationship of tanning time to the T_s of tanned leather (Figure 4c). The T_s elevated gradually with the extension of tanning time, while the T_s of tanned leather was nearly constant (~77.5 °C) after 7 h of tanning time. This indicated that sufficient crosslinking between DTCS tanning agent and collagen fibers occurred. Hence, the optimum tanning time is 7 h.

3.3.4 Dosage of DTCS tanning agent

The T_s of tanned leather was also evaluated by using various dosages of DTCS tanning agent (Figure 4d). The T_s of 5% DTCS-tanned leather reached 72.4 °C, suggesting that the substantial crosslinking between DTCS and collagen fibers was formed to significantly improve the hydrothermal stability of DTCS-tanned leather. Notably, tanning with 15% DTCS provided DTSC-tanned leather with significant increase in the T_s (~80.9 °C). Further increasing the DTCS dosage (>15%) showed no obvious effect on the T_s of tanned leather, due to the saturated absorption of DTCS. The use of 15% DTCS in tanning process can improve the hydrothermal stability of tanned leather with reasonable utilization rate of the tanning agent.

Overall, the optimum tanning process is obtained and summarized in Table IV by optimizing the tanning conditions. Specifically, 15% DTCS tanning agent is used in the tanning system and the tanning process is conducted at pH ~6.0 and 40 °C for 7 h, raising the T_s of DTCS-tanned leather to ~82.0 °C.

Table IV

The optimum tanning process of DTCS.

Process	Chemical	Dosage/%	Temperature/°C	Time/ h	Remarks
Wash	Water	400	25		
Tanning	Water	100			
	DTCS	15	40	7	pH ~6.0
Wash	Water	400	25		Overnight
Horse up					

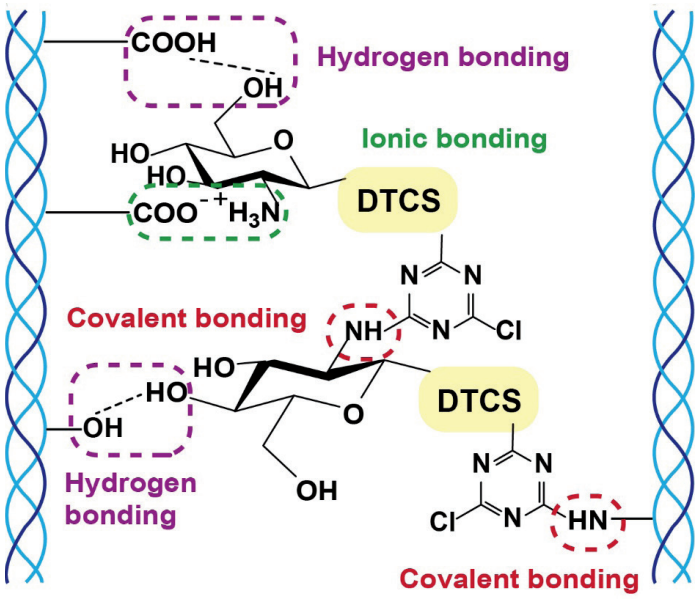

Figure 5. The possible interactions of DTCS in the tanned leather matrix.

3.4 The proposed tanning mechanism of DTCS

We proposed the possible interactions between DTCS and collagen fibers in the tanning system (Figure 5). The active chlorine groups on DTCS can not only react with amino groups of collagen fibers by covalent bonding, but also form intermolecular crosslinking with amino groups of DTCS molecules. Substantial number of hydroxyl groups of DTCS molecules can also interact with hydroxyl, carboxyl and amino groups of collagen fibers by hydrogen bonding.[43] In addition, the carboxyl groups ($-COO^-$) on collagen may bond with $-NH_3^+$ of DTCS by ionic interaction.[44] Collectively, the robust crosslinking effects within collagen fibers are formed, which consequently contribute to the enhanced hydrothermal stability of the tanned leather.

3.5 Leather morphology analysis

The dispersion of collagen fibril and fibrous network structure of leather can reflect the crosslinking/tanning effect of tanning agent.[45] The microstructure of bated pelt, DTCS-tanned leather, Cr(III)-tanned leather and F-90-tanned leather were analyzed (Figure 6). The dispersion degree of collagen fibers of DTCS-tanned leather was higher than that of bated pelt, and was comparable to those of Cr(III)-tanned leather and F-90-tanned leather. This was due to the increased degree of the crosslinking within the collagen fibers (i.e., tanning effect), which makes the collagen fibers of tanned leathers arrange regularly and disperse distinctly.[45,46] The results demonstrated that the DTCS has good tanning property and can form effective crosslinking between collagen fibers.

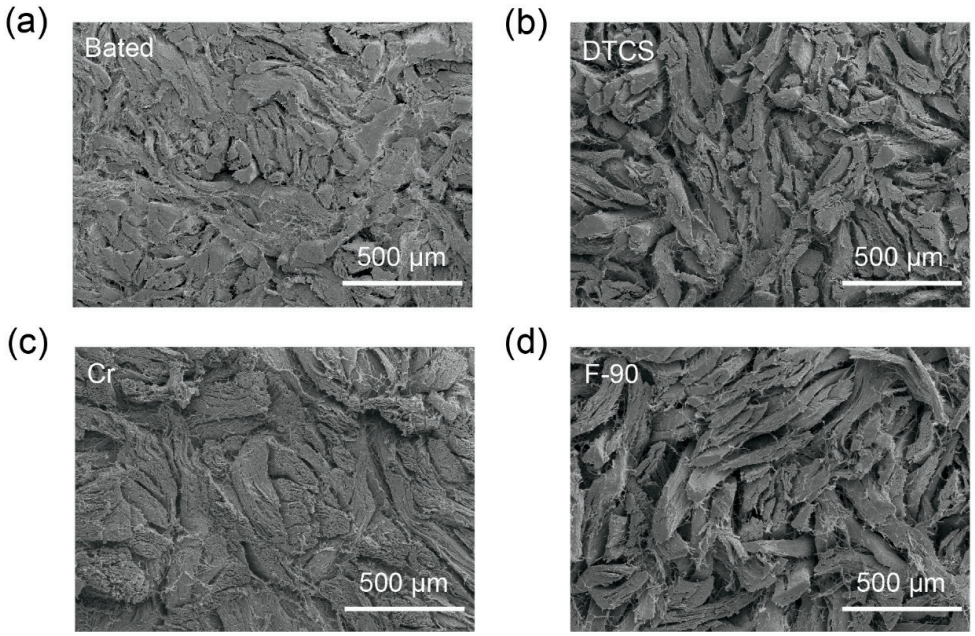

Figure 6. SEM observation of cross section microtopography of **(a)** bated pelt, **(b)** DTCS-tanned leather, **(c)** Cr(III)-tanned leather and **(d)** F-90-tanned leather.

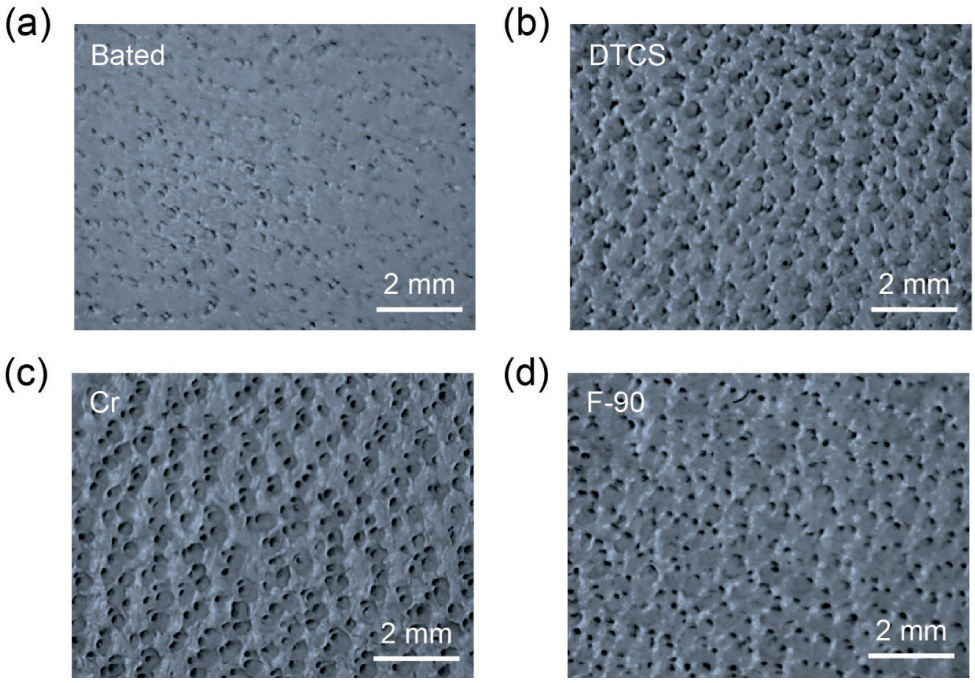

Figure 7. Stereomicroscope images of grain surface of leather tanned by different processing strategies: **(a)** bated pelt, **(b)** DTCS-tanned leather, **(c)** chrome-tanned leather and **(d)** F-90-tanned leather.

The morphology features of grain surface of leathers are the important evaluation parameters of leather performance. The grain surface morphologies of bated pelt and tanned leather were observed by a stereomicroscope (Figure 7). The bated pelt exhibited irregular grain with disordered and indistinct pores. In contrast, the grain surface of all tanned leathers presented clearer pores without apparent surface deposition of tanning agents. This could ascribe to the well penetration of tanning agent and the efficient crosslinking network forming between collagen fibers.[46] In addition, the grain of DTCS-tanned leather was smoother with relatively small aperture than that of Cr(III)-tanned leather and F-90-tanned leather, suggesting the DTCS exhibited better filling ability.[47]

3.6 Thickening rate analysis

The thickening rate of leather tanned with DTCS, F-90 and Cr(III) was determined, respectively (Figure 8a). The thickening rate of DTCS-tanned leather (~64.4%) was significantly higher than that of F-90-tanned leather (~30.2%) and Cr(III)-tanned leather (~27.6%) owing to the large molecular weight of DTCS, suggesting the DTCS exhibited better filling ability.

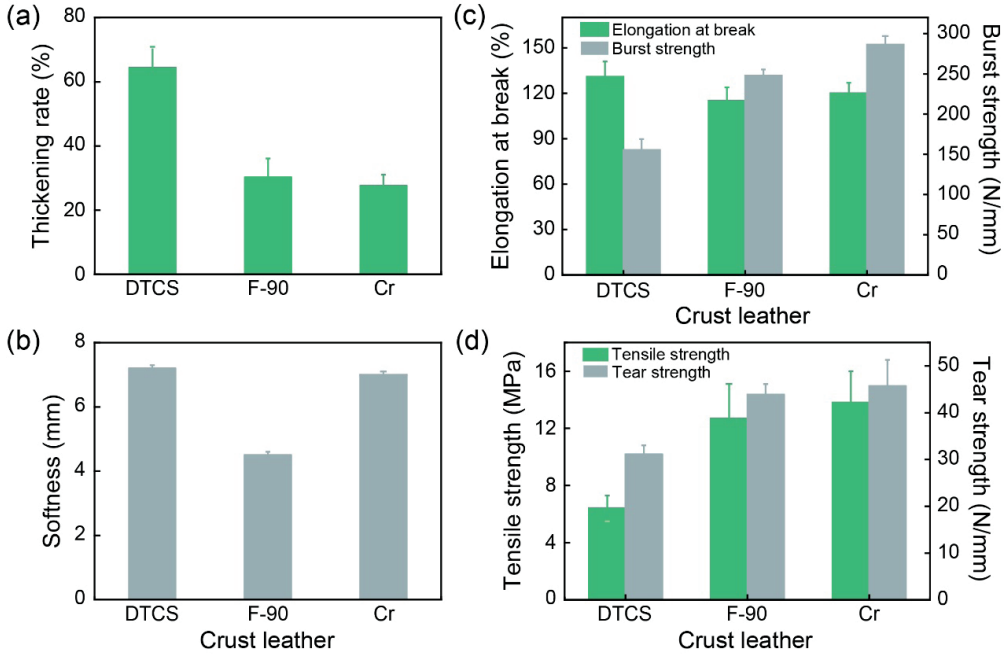

Figure 8. (a) Thickening rate of different tanned leather. **(b-d)** Physical and organoleptic properties of different crust leathers.

3.7 Physical and organoleptic properties analysis

The physical and organoleptic properties of crust leather can be determined to characterize the intrinsic quality and machinability of leather. We evaluated the physical properties (i.e., softness, tensile strength, elongation at break, tear strength and burst strength) of crust leathers tanned with DTCS, F-90 and Cr(III), respectively (Figure 8b-d). The softness of DTCS-tanned leather (7.2 mm) was similar to that of Cr(III)-tanned leather (7.0 mm) and much higher than F-90-tanned leather (4.5 mm) (Figure 8b). This might due to the flexible molecular chains of DTCS.[10] The elongation at break of DTCS-tanned leather (131%) was higher than Cr(III)-tanned leather (120%) and F-90-tanned leather (115%) (Figure 8c), indicating that DTCS-tanned leather had great extensibility. Even though the tensile strength, tear strength and burst strength of DTCS-tanned leather were not as good as crust leathers tanned with Cr(III) or F-90 (Figure 8c, d), DTCS endowed the leather with good sensory and acceptable physical properties, suggesting that DTCS had promising application in leather manufacturing.

4. Conclusions

A biomass-based tanning agent (i.e., DTCS) was prepared by conjugating COS with CC. The characteristic structure and physical properties of DTCS were characterized by several techniques including FT-IR, ^{13}C NMR, UV-vis, XRD, and XPS. The optimum synthesis protocol was obtained when the mass ratio of sodium carbonate to CC was 0.3 and the mass ratio of CC to COS was 0.5. The DTCS tanning agent was used in delimed and bated cattle hides without pickling process, aiming at eco-leather manufacturing. The tanning system using DTCS conferred the tanned leather with satisfactory T_s (~82.0 °C), improved thickness (by 64.4%), light color and good sensory. We confirmed the interaction between collagen fibers and DTCS tanning agent, which resulted in the dispersed structure of collagen fibers and the improvement of grain smoothness and porosity of tanned leather. This biomass-based tanning agent DTCS shows great potential in chrome-free tanning technology and provides a promising approach for cleaner leather manufacture.

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