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Clean Production for Chrome Free Leather by Using a Novel Triazine Compound

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Abstract: Based on a novel triazine compound, the properties of tanned leather and commercial feasibility in pilot scale have been investigated. Then this novel approach tanning was compared with conventional chrome tanning: in the condition of less-salt pickling and chrome free, the physicochemical properties including thermal stability and mechanical strength were analyzed. Meanwhile, the surface roughness and fiber dispersion were evaluated as well. The results show that the thermal stability and mechanical strength of the triazine compound tanned leather are similar to conventional chrome tanned leather, the fiber bundle is well-dispersed and much evener than that of chrome treating. The optimized tanning approach has obvious reduction in environmental impact and leads an excellent biodegradability of tanning liquor. In industrial application, the cost of materials and water treatment are reduced effectively. The production of chrome free leather can encourage the sustainable development of leather industry and protects ecological environment in some extent.

Keywords: Triazine compound; clean production; chrome free leather; less-salt pickling

1 Introduction

Environmental protection totally is a global revolution [1]. And cleaner chemistry or manufacture technology in the industrial sustainable development is the improved of novel chemical products and different processes that can diminish or eliminate the addition and generation of hazardous materials [2-5]. In the import and export trade, considerable stringent environmental legislations on the discharge of pollutants and the pressure from the importing countries to source finished leathers have prompted researchers to seek cleaner alternative products and relevant processing technologies [6]. The life cycle assessment (LCA) of leather making studies shows that tanning process is the main contributor to environmental impact categories in leather manufacturing [7]. But in fact, nearly 80～90% of the resultant leathers is still tanned by chrome. Conventional chrome tanning is known to contribute more than 98% of the pollution loads from leather processing and results in serious environmental impact, particularly the sulfates, chlorides and chromium [8,9]. The formation of Cr (VI) easily causes severe allergic contact dermatitis in human skin and respiratory tract, even at very low concentration [10]. In 2014, a narrower regulation of the Cr (VI) concentration for leather products was revised by the European Commission in Annex XVII of regulations of REACH (Registration, Evaluation, Authorization and Restriction of Chemicals). It provides that the leather products would be forbidden if they contained Cr (VI) in concentrations equal to or higher than 3 mg/kg, because there would be a direct damage to the leather production and circulation.

According to the current situation of leather industry, it is still unable to completely get rid of labor

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intensive, semi-automation and energy consumption. Among them, cleaner production is the primary task to achieve the goal of the development of advanced manufacturing industry. Generally, disposal, recycle and reuse are the main methods to implement cleaner processing. Besides, it's effective and suitable to eliminate hidden dangers from the source. For example, recycling technology can reduce partial use of chrome from chrome tanning effluent. But the Cr (III) can be easily converted into Cr (VI) during recycling process, it could lead the decline in leather performance and cause unpredictable harm to the operators. From the perspective of environmental protection, the recycling method reduces the environmental impact of the process to some extent, and BOD (biochemical oxygen demand), COD (chemical oxygen demand), SS (suspended solids) as well as pollutants may be diminished. It also guarantees resource saving [11-13]. A great deal of literature has documented the treatment of chrome wastewater and solid management [14], including chemical precipitation, coagulation, solvent extraction process, ion exchange, nano filtration, ultrasonic method and absorption method [15-21]. Prevention is not only achieved by omission but also by replacement and improvement [22]. For cleaner production of leather tanning, chrome free tanning agent is considered as an optimal eco-friendly option for replacing chrome. In recent decades, urea, melamine, phenol, formaldehyde [23,24], vegetable tannins [25], polymers [26,27], other metal ion [28] are used as conventional alternative chemical product [29,30], but it always causes other kinds of pollutions to organism and damage to human health. In order to improve above-mentioned shortages, lots of novel greener methods have been studied by using oxazolidine [31], nanocomposite [32], tetra-hydroxymethyl phosphonium chloride [33], unnatural amino acids [34,35], etc. Nevertheless, most of the substitutable methods reduce versatility to make different resulting products, such as limited availability, poor recoverability, reusability and biodegradability.

We seek to a novel chrome free tanning agent which can significantly minimize the environmental impact of tanning liquor based on a novel tanning approach with less-salt pickling. In this work, the tanning condition with strong adaptability is similar to traditional chrome tanning. A lot of primary tanning performances including thermal stability, mechanical properties, sensory properties, grain surface roughness and fiber dispersion in comparison to chrome tanned leather were studied. And the environmental impact assessment of tanning liquor and economic analysis of this tanning method has been compared with chrome tanning process, too. This chrome free tanning agent could be considered as a promising alternative to conventional chrome tanning due to its eco-friendly environmental assessment and appropriate tanning properties of leather. Our aim is to obtain a wet-white leather with low pollution and low energy consumption. This research has widely prospect in application and means a lot in theory or practical engineering in leather industry.

2 Experiments

2.1 Materials

The raw skin material of pickled pelt processed from wet-salted sheep skin was used for tanning process. The triazine compound was prepared in lab. And the other chemicals used in subsequent operations were commercial grade, calculated on limed weight which was normally used in leather industry.

2.2 Methods

2.2.1 Preparation of Triazine Compound

The reaction was done according to a literature reported with some modifications in the procedure [36]. Cyanuric chloride (4.66 g, 2.52 mmole) was dissolved in acetone (50ml). The ice-water mixture (125 ml) was then added to this solution to generate a white precipitate. Sulfanilic acid (4.32 g, 2.5 mmole) was neutralized with sodium hydroxide solution and adjusted the pH to 6.5, then added in a drop-wise fashion to the cyanuric chloride solution. The pH was adjusted to 5.5 by adding 1M Na_2CO_3 solution. The reaction was carried at -5 to 0℃ under inert atmosphere for 1 hour. The system was heated to 45℃ and added p-hydroxybenzaldehyde (3.08 g, 2.52 mmole) dissolved in acetone (20ml) in a drop-wise fashion, then the pH was adjusted to 6 by adding 1M NaOH solution for 4 hours. And continued to heat up to 85℃, while added p-hydroxybenzaldehyde (3.08 g, 2.52 mmole) dissolved in acetone (20 ml) in a drop-wise fashion, then adjusted pH to 7 by adding 1M NaOH solution with reaction lasting for 5 hours. The mixture was cooled, filtered, washed with acetone and vacuum dried to a solid powder, then the desired product was obtained. The proposed structure of the triazine compound was shown in Fig. 1.

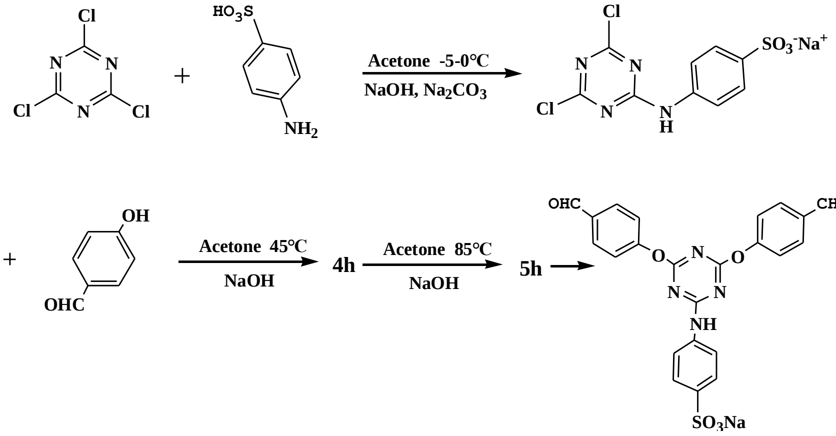


Figure 1: Synthesis of the triazine compound

2.2.2 Chrome free tanning process with triazine compound

The two groups of trails were implemented using wet-salted sheep skins which were conducted soaking → paint unhairing → weighting → liming → fleshing → weighting → deliming → bating as usual. The skins with thickness of 2.0 mm were divided into two parts symmetrically. Then the experimental group was treated with the novel triazine compound, while the control group was carried out with chrome tanning process. About 6%~8% sodium chloride (based on the limed skins) were added to prevent the skin from swelling due to the higher acidity resulting from the chrome tanning process, while the triazine compound had a good permeability at pH 4.5-5 which could decrease the dosage of sodium chloride, sulphuric acid and formic acid. The experimental group could give a wet-white leather and the control group obtained a wet-blue leather. Finally, the two groups' leathers were removed from the drum without any treatment. The physicochemical characterization such as Ts (shrinkage temperature), Td (denaturation temperature) and mechanical strength of the tanned leather was judged and compared. Each of the tanning liquor from both trials had been collected for the EIA (environmental impact assessment analysis). The tanning process of the two groups is shown in Tab. 1.

Table 1: Chrome free tanning process and traditional chrome tanning process

Material	Experimental group (%)	Control group (%)	
H_2O	100	100	-
NaCl	4	8	Rotate-15'
HCOOH (1:10)	0.4	0.9	Rotate-30'
H_2SO_4 (1:10)	0.5	1.2	Rotate-90'
Chromosal B [a]	0	4	Rotate-240' pH=2.5
Triazine compound	4	0	Rotate-240' pH=4.5-5
$NaHCO_3$	2	2	Rotate-120'

2.3 Testing and Analysis

2.3.1 FTIR Analysis

The synthesized product was washed with acetone for several times, owing to its reactants were soluble in acetone and then the purified product was homogeneously mixed with the dried potassium bromide (about 1: 20 mass ratio) to make a thin sheet, then it was immediately measured on Fourier transform infrared spectrometer (FTIR Bruker VECTOR-22).

2.3.2 ^{1}HNMR Analysis

To further determine whether the product was what we expect, so the purified product was dissolved in DMSO (deuterated dimethylsulfoxide) for the detection of Nuclear magnetic resonance spectroscopy (NMR Bruker ADVANCE Ⅲ).

2.3.3 Shrinkage Temperature

The shrinkage temperature of tanned leather from the two groups was measured using a Micro shrinkage tester. The standard strip of the tanned leather was placed on a specific water-grooved microscope slide with heating equipment. The rate of heating was maintained at 2 ºC/min, so the shrinkage temperature was determined by the strip shrinks to one-third of its original length.

2.3.4 Denaturation Temperature

The denaturation temperature of the tanned leather is often used to measure the thermal stability of the collagen, which in turn reflects the degree of tanning. It can be studied using Differential scanning calorimetric (DSC TA DSC-Q2000). Selected specimens from the two groups were naturally dried at first. The thermogram was showed by heating to 20-200ºC at the rate of 10 ºC/min. According to the position, height, width and symmetry of the thermogram peaks showed the thermal denaturation of the tanned leather a defined temperature range. The denaturation temperature of the tanned leather is always positively proportional to the thermal stability of collagen.

2.3.5 Mechanical Strength

Mechanical strength is an important indicator of tanning performance including tensile strength and % elongation which could be carried out in accordance with international standards [37,38]. The experimental specimens for the mechanical tests were taken parallel to backbone of the tanned leather following the standard procedure for sampling. The mechanical strength of experimental group was assessed in comparison with chrome tanned leather after conditioning the experimental specimens at 25ºC with 65% ± 2% RH over a period of 48 hours. The mean values of mechanical properties corresponding to each trial are given in Tab. 2.

2.3.6 Sensory Property

The quality and grade of the tanned leather depend largely on sensory properties, such as fullness, flatness, surface smoothness, grain tightness and general appearance. By hand and visual examinations, then we had invited three experienced leather engineers to score from 1-10, where 10 is the best, for each sensory property of the two groups.

2.3.7 Grain Surface Micro-Morphology

Different tanning agents will produce different tanning effects, the most obvious performances are the changes of grain surface roughness and fiber dispersion. The selected specimens from the tanned leather were cut from the standard sampling position without any pre-treatment. The grain surface and cross section of the specimens, subjected to even sputter coating of gold ions, were tested by the Scanning electron microscopic (SEM TESCAN vega 3 SBH) which could show the conditions of grain surface and fiber dispersion. The micrograph was also analyzed by using AFM (AFM Seiko SPA 400) to study the grain surface roughness.

2.3.8 Environmental Impact Assessment

Analysis and comparison of EIA (environmental impact assessment) is a reliable way to investigate the degree of cleaner production in tanning approach. The tanning liquor from the two groups were directly collected and analyzed. There are several important indexes for this evaluation of tanning liquor including BOD, COD, TS (total solids content), DS (dissolved solid) and SS. The values shown here are the average values of three sets of parallel experiments along with their standard deviation.

3 Results and Disscusion

3.1 Structure Analysis of Triazine Compound by FTIR

The structure of triazine compound was confirmed by FTIR (fourier transform infrared spectroscopy) (Fig. 2). The FTIR spectra shows the typical skeleton vibration of triazine ring at 1382 cm^{-1}, 1508 cm^{-1}, 1556 cm^{-1}, 1633 cm^{-1}. The typical vibration of -NH- has absorption peaks at 1596 cm^{-1} [δ(N-H)], 1218 cm^{-1} [ν(C-H)], 3442 cm^{-1} [ν(N-H)] and the two strong absorption peaks of sulfonate at 1218 cm^{-1}, 1037cm^{-1} indicate that the amino group of sulfanilic acid was sufficiently reacted with cyanuric chloride. We can see four characteristic peaks of benzene ring at 1928 cm^{-1}, 1816 cm^{-1}, 1747 cm^{-1} and lateral vibration at 831 cm^{-1}. In addition to the above mentioned, characteristic absorption peaks of Ar-O-R found in 1037 cm^{-1}[ν(C-O-C)], 1218 cm^{-1}[νas(C-O-C)] and the typical vibration of -CHO displayed at 1747 cm^{-1} [ν(C=O)], 2817 cm^{-1} [ν(C-H)], 2742 cm^{-1} [ν(C-H)] totally carried by p-hydroxybenzaldehyde. We can consider that the expected triazine compound was successfully synthesized.

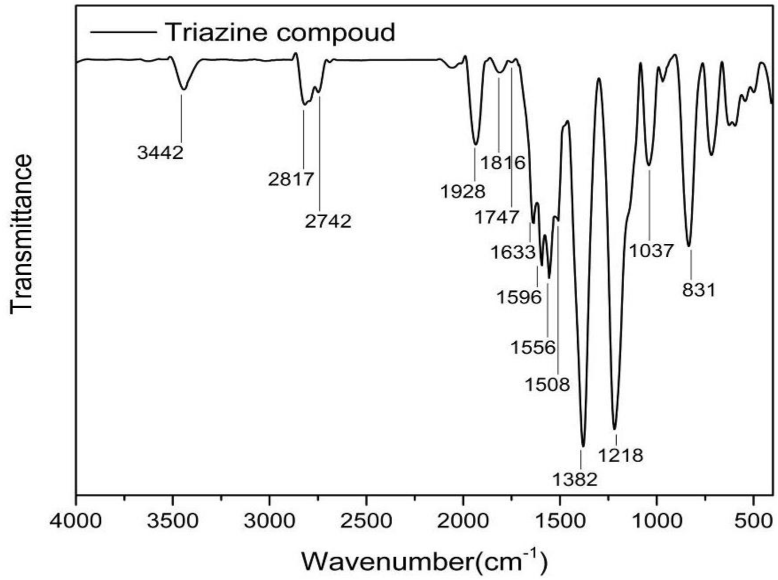


Figure 2: FTIR spectra of triazine compound

3.2 Structure Analysis of Triazine Compound by ^{1}HNMR

The hydrogen spectrum of triazine compound is shown in Fig. 3 owing to further confirm the structure of the product, and Fig. 3(A) shows the blank nuclear magnetic spectrum of DMSO. By comparison of the two graphs, the five groups (a, b, c, d, e) of hydrogen are observed as the target product, and the proportion of integral is a: b: c: d: e = 4:4:1:4:2. The peaks at δ = 7.33 (4H), δ = 7.55 (4H), δ = 10.03 (2H) are carried by p-hydroxybenzaldehyde, and the peaks at δ = 7.85(1H) , δ = 8.04(4H) illustrate the introduction of sulfanilic acid. Wherefore the nuclear magnetic analysis supported the results of infrared.

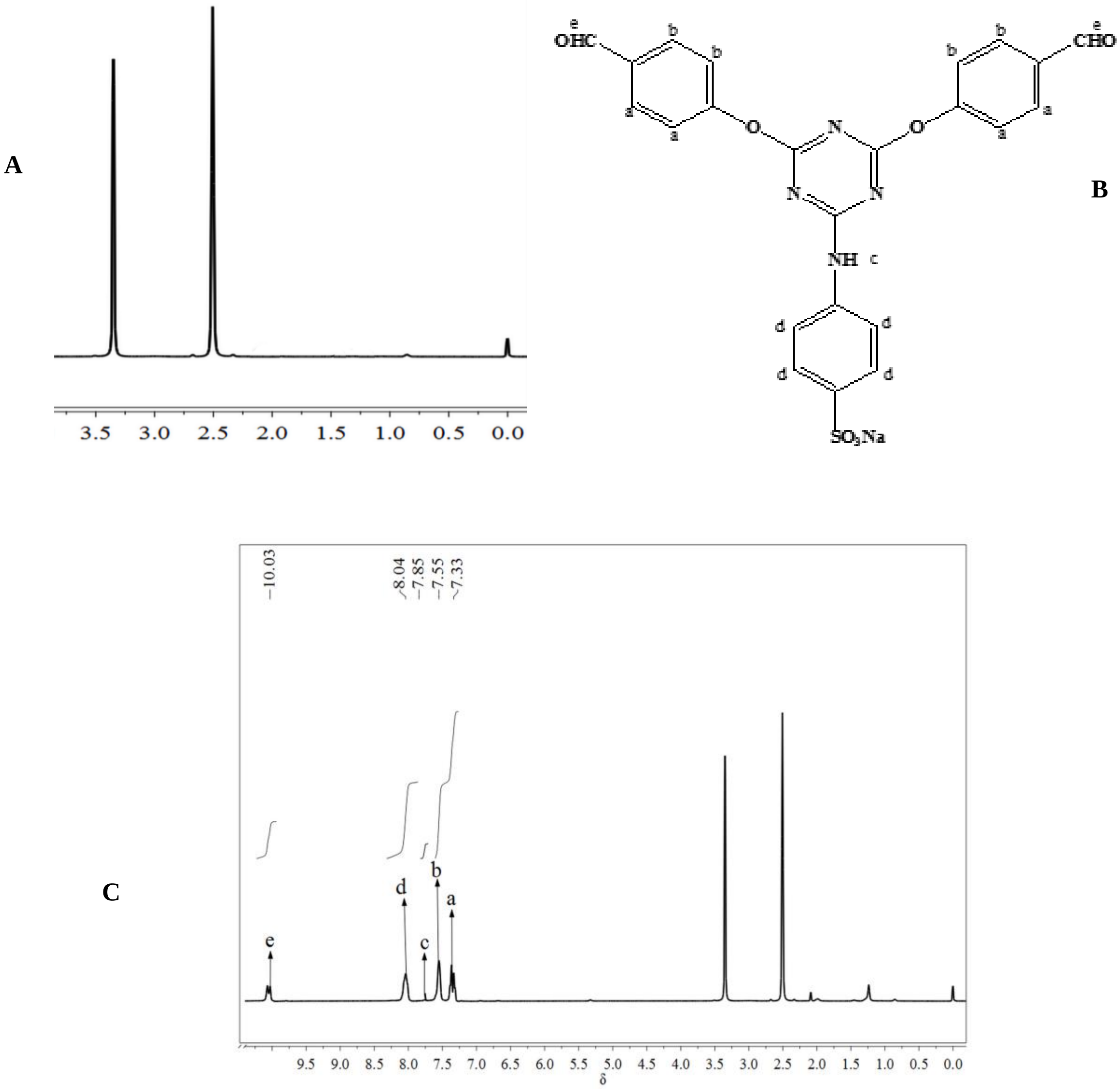
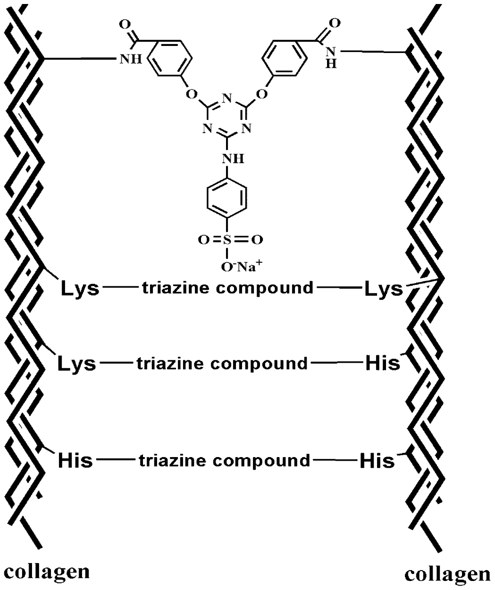


Figure 3: Nuclear magnetic resonance hydrogen spectrum: A) The blank nuclear magnetic spectrum of DMSO, B) Hydrogen species on triazine compound structure, C) 1HNMR of triazine compound

3.3 Tanning Mechanism of Triazine Compound

It can be seen in scheme 1 that this novel triazine compound multipoint crosslinked with amino groups on the collagen side chain like lysine or histidine, it can produce tanning effect and improve the hydrothermal stability and mechanical strength of the tanned leather. The main binding mode is the amino group of collagens and the two hydroxyl groups in the side chain of triazine compound, and these two functional groups undergo the condensation reaction to form the Schiff base. On the one hand, Schiff base can give the tanned leather a certain antibacterial property. On the other hand, as an excellent ligand of the metal ions, it can combine with other materials such as aluminum salt, zirconium salt and metal complex dyes, then improves the absorption rate and enhance the retanning effect or dyeing effect in retanning process. Meanwhile, sulfonate ions on the triazine compound can contribute to tanning effect and increase the solubility of triazine compound in water.



Scheme 1: Schematic representation of proposed structure of side chain crosslinking bridge of collagen with triazine compound

3.4 Thermal stability of tanned leather

The Td is tightly bound to the onset temperature of the peak in thermogram, as a measurement of the thermal stability of tanned leather. The Td values of tanned leather subjected to triazine compound and traditional chrome are shown in Fig. 4. There is an increase intent in Td which can indicate an increase in the stability of the tanned leather. Fortunately, tanned by triazine compound, the position, width, height and symmetry of the thermogram peaks resemble chrome tanned leather. In the same dosage of tanning agent, the Ts of triazine compound and chrome tanned leather reach 79°C ± 4°C and 82°C ± 3°C (Tab. 1). The triazine compound tanned leather and chrome tanned leather have brought out an approximate tanning effect with improved thermal stability of the tanned leather. Obviously, in terms of the effect degree and cross-linking ability, the triazine compound could completely replace chrome for making leather due to the close tanning effect between experimental group and control group. Furthermore, the novel method for tanning leather by triazine compound could provide a flat wet-white leather, which is easy to dye varieties of colors.

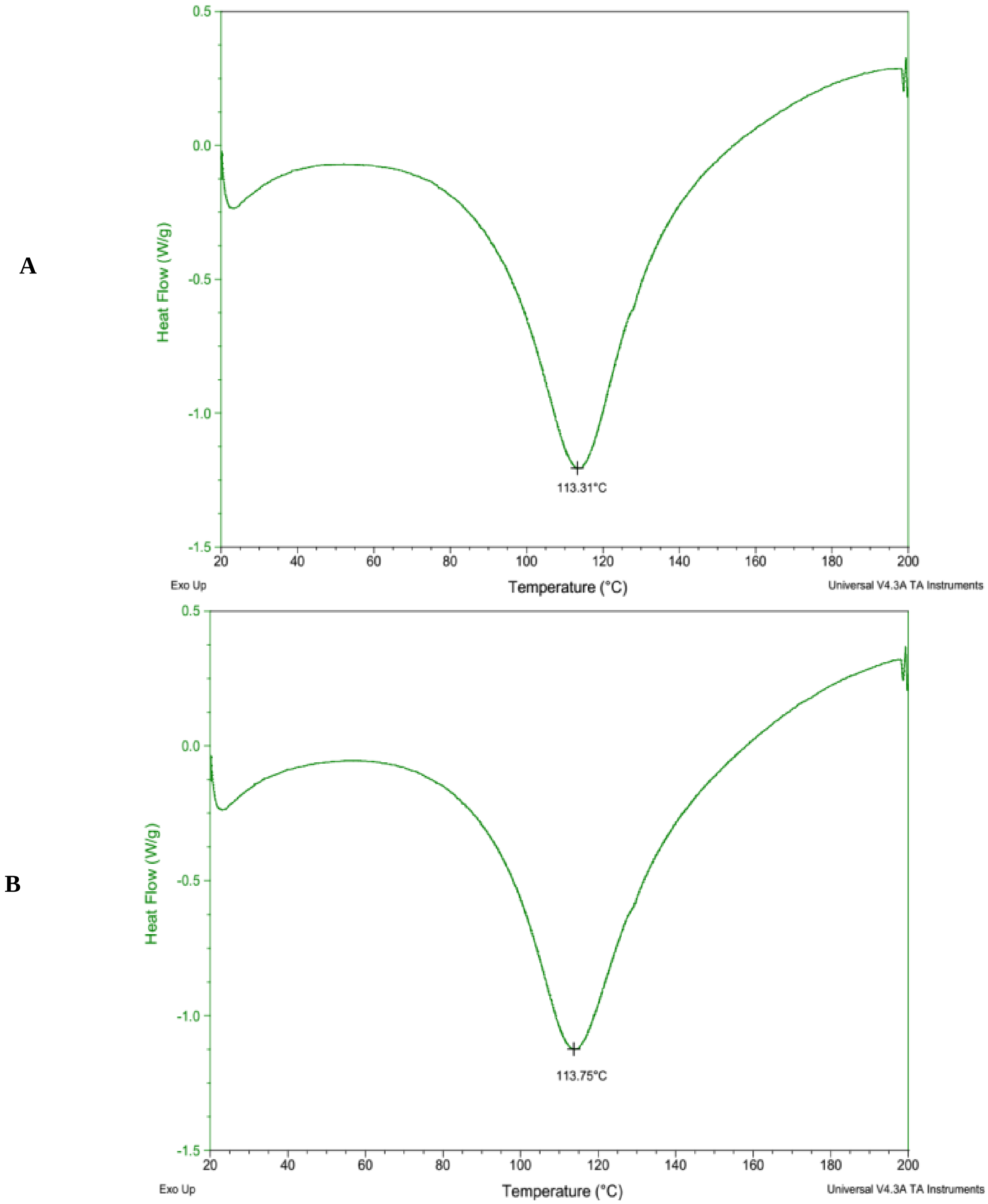


Figure 4: DSC analysis of triazine compound and chrome tanned leather: A) Triazine compound tanned leather, B) Chrome tanned leather

Table 2: Denaturation temperature (Td), shrinkage temperature (Ts), tensile strength (TS) and percentage of elongation (%E) of triazine compound and chrome tanned leather

Tanning agent	*T*d (°C)	*T*s (°C)	TS (MPa)	%E
Triazine compound	113 ± 3	79 ± 4	39	89 ± 3
Chrome	114 ± 3	82 ± 3	43	80 ± 3

3.5 Mechanical Properties of Tanned Leather

In comparison in experimental group and control group (Tab. 1), the mean values were calculated from at least 5 tests for each term. It shows that the mechanical properties of triazine compound tanned leather is close to the chrome tanned leather, while the former exhibits lower TS (tensile strength) and higher %E (%elongation). We can conclude that the triazine compound tanned leather has great mechanical strength like chrome tanned leather, it is suitable for making shoe upper leather, sofa leather and garment leather. It has better %E for the reason that the fibers bundles are well-dispersed in the case of triazine compound based on its space conformation, while chrome tanned leather is shown compact fiber bundles.

3.6 Sensory Property of Tanned Leather

From Fig. 5, it is observed that the triazine compound tanned leather exhibits same sensory properties viz: good fullness, tightness, flatness, grain smoothness and general appearance compared with chrome tanned leather. From the result, it is evident that the triazine compound tanned leather has better flatness and smoothness. However, the tightness of the tanned leather is strengthened due to chrome treating, and fullness is unaltered. It illustrates that the triazine compound could bring out better dispersion of the collagen fibers, further to impart softness to the tanned leather. And in the meantime, it also enhances the handle feeling of the final leather and improves the penetration of the subsequent materials.

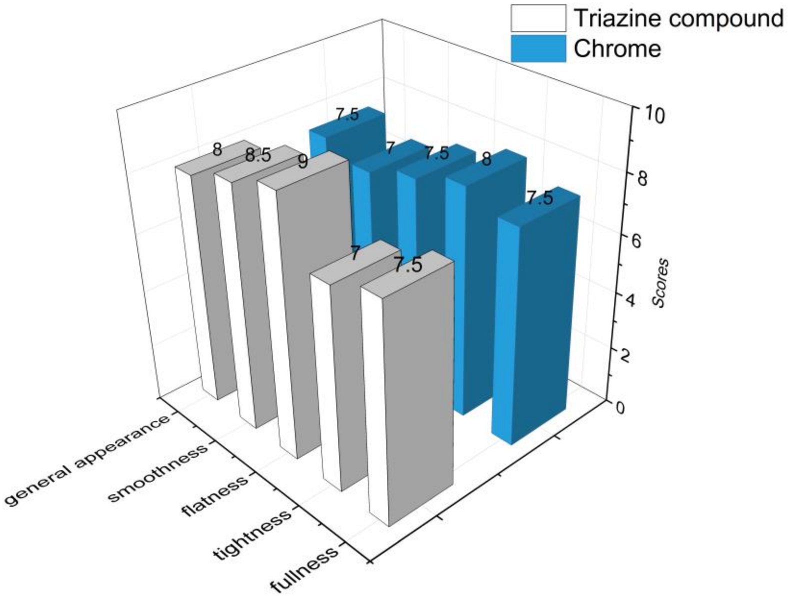


Figure 5: Rating of sensory property of triazine compound and chrome tanned leather

3.7 SEM Analysis of Grain Surface and Cross Section

Scanning electron photomicrographs of tanned leather specimens from the two groups showing the grain surface roughness at a magnification of 1000×/300× are given in Figs. 6(A) and 6(B), and the condition of cross section at a magnification of 3000× is clearly given in Fig. 6(C). From Fig. 6(A), we can find that the grain surface of triazine compound tanned leather seems to be much smoother and no wrinkles, while the grain surface of chrome tanned leather is rough and uneven significantly. There are plenty of ridges and grooves due to the rapid reaction of chromium with the collagen of grain surface. In order to avoid the interference of the pores and foreign materials, increasing the magnification to 1000×, it shows the triazine compound provide uniform surface and better quality of tanned leather than chrome tanned one. It confirms that this novel triazine compound could carry out a well-distributed tanning effect on the grain surface of leather and maintain a low roughness. The distinct cross sections of two specimens in a magnification of 3000× are depicted in Fig. 6(C). The experimental specimen shows favorable dispersibility in fiber bundles throughout the cross section and indicates uniform structure of fibers compared with chrome tanned one. The fiber bundles seemed to be well-dispersed, since the chrome tanned leather shows the fibronectin and poor dispersibility of fiber bundles.

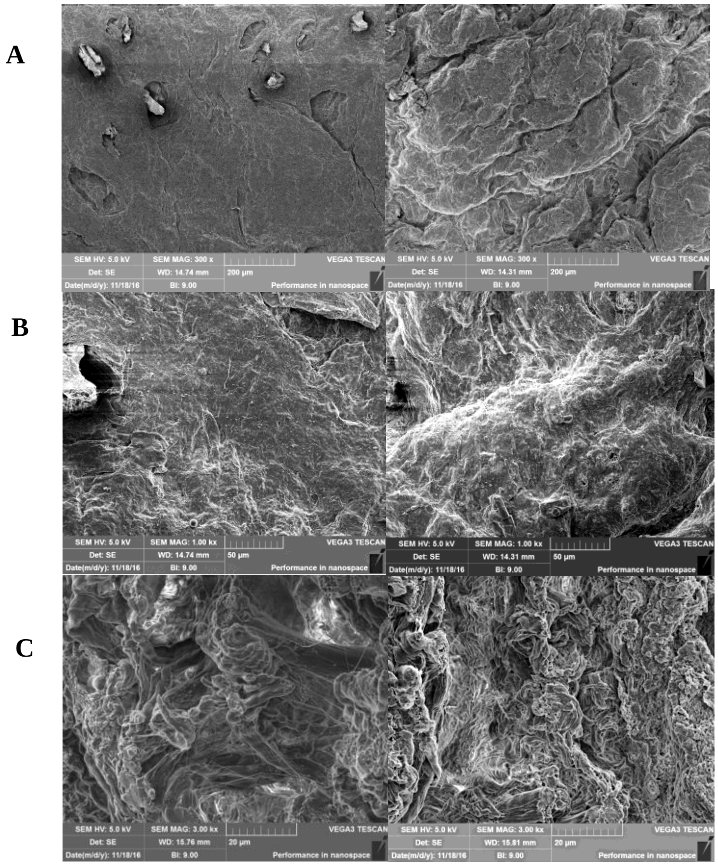
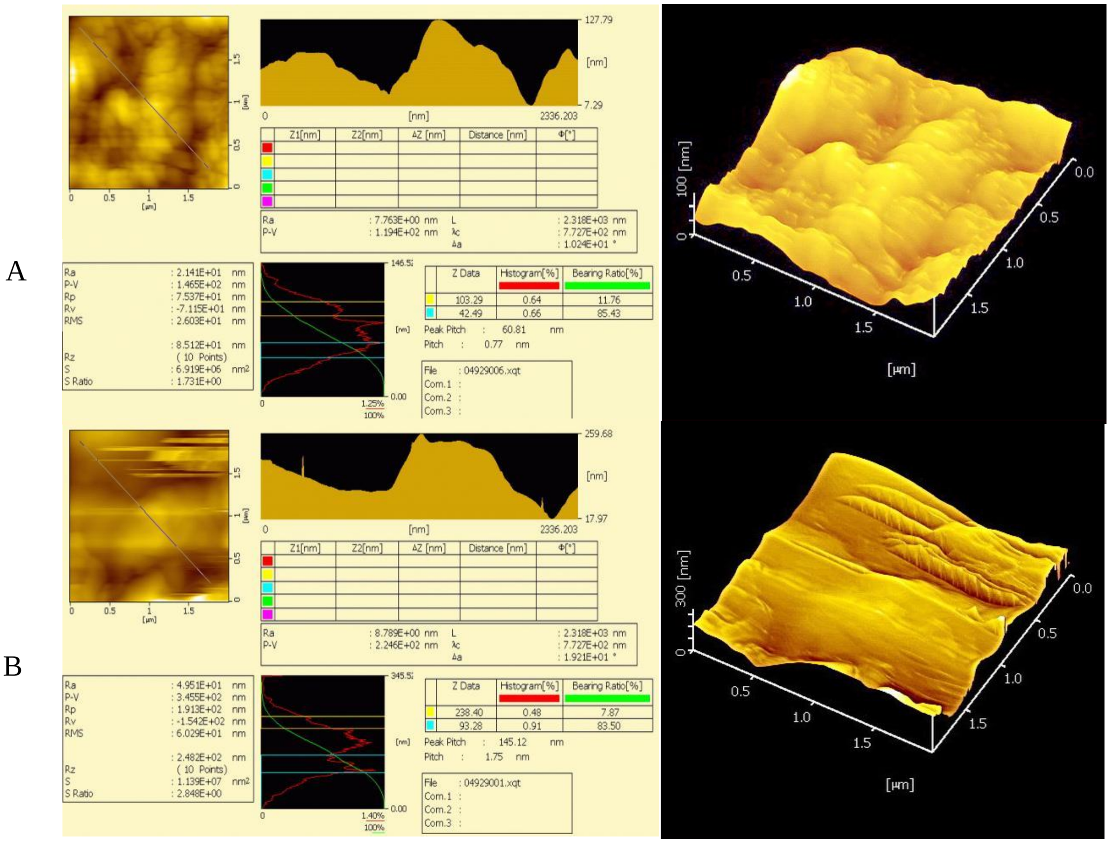


Figure 6: SEM images of grain surface and cross section of triazine compound tanned leather (left part) and chrome tanned leather (right part): A) SEM images of grain surface at a magnification of 300×, B) SEM images of grain surface at a magnification of 1000×, C) SEM images of cross section at a magnification of 3000×. The grain surface of triazine compound tanned leather is smoother and the fiber bundles are well-dispersed in comparison with chrome tanned leather

3.8 AFM Analysis of Grain Surface Roughness

The results of AFM can be used to make a more intuitive analysis of grain fineness from the micro level. The roughness of grain surface is displayed in scanning range (2 um × 2 um) (Fig. 7). The plane and three-dimensional profiles show the grain surface roughness of triazine compound tanned leather and chrome tanned leather. Based on the change of brightness, the lighter and darker areas of the pictures correspond to higher and lower topographies. The triazine compound tanned leather gives a fine texture with lower peaks than chrome tanned leather. The values of P-V reflect the diameter of the fiber bundles from the side. It demonstrates that the fiber bundles of chrome tanned leather are thicker and not well-dispersed. The values of Rms and Ra both reflect the grain surface roughness, which are thought to be the reason for the specific tanning performance of the triazine compound tanned leather with great smoothness and flatness.



A

	Z1[nm]	Z2[nm]	ΔZ [nm]	Distance [nm]	Φ[°]
🟥					
🟨					
🟦					
🟩					
🟪					

Ra : 7.763E+00 nm
P-V : 1.194E+02 nm
L : 2.318E+03 nm
λc : 7.727E+02 nm
Δa : 1.024E+01 °

Ra : 2.141E+01 nm
P-V : 1.465E+02 nm
Rp : 7.537E+01 nm
Rv : -7.115E+01 nm
RMS : 2.603E+01 nm
Rz : 8.512E+01 nm (10 Points)
S : 6.919E+06 nm2
S Ratio : 1.731E+00

	Z Data	Histogram[%] 🟥	Bearing Ratio[%] 🟩
🟨	103.29	0.64	11.76
🟦	42.49	0.66	85.43

Peak Pitch : 60.81 nm
Pitch : 0.77 nm

File : 04929006.xqt
Com.1 :
Com.2 :
Com.3 :

B

	Z1[nm]	Z2[nm]	ΔZ [nm]	Distance [nm]	Φ[°]
🟥					
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🟦					
🟩					
🟪					

Ra : 8.789E+00 nm
P-V : 2.246E+02 nm
L : 2.318E+03 nm
λc : 7.727E+02 nm
Δa : 1.921E+01 °

Ra : 4.951E+01 nm
P-V : 3.455E+02 nm
Rp : 1.913E+02 nm
Rv : -1.542E+02 nm
RMS : 6.029E+01 nm
Rz : 2.482E+02 nm (10 Points)
S : 1.139E+07 nm2
S Ratio : 2.848E+00

	Z Data	Histogram[%] 🟥	Bearing Ratio[%] 🟩
🟨	238.40	0.48	7.87
🟦	93.28	0.91	83.50

Peak Pitch : 145.12 nm
Pitch : 1.75 nm

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Com.2 :
Com.3 :

Figure 7: AFM analysis of tanned leather: A) Triazine compound tanned leather, B) chrome tanned leathers. Vertical scale bar lighter areas correspond to higher topography and darker areas correspond to lower topography of tanned leather grain surface of the images

3.9 Environmental Impact Assessment

EIA of the collected tanning liquor can be regarded as assessments of the impact have on the environmental and economic aspects as well. From Table 3, COD, BOD, TS, DS and SS values in experimental group are obviously lower than in chrome tanning, because of the application of triazine compound. It concludes this novel approach eliminates chrome and reduces sodium chloride, while approximately decrease the TS value by 40%, the DS and SS load value are considerably lower than that of the chrome tanning process owning to the good absorption of triazine compound. In comparison to chrome tanning, the BOD/COD value is greater for experimental group than for chrome tanning process. It demonstrates that the effluent of the novel approach by using triazine compound is easier biodegradable than that of chrome tanning process. This novel approach not only eliminates some hazardous substances, but also avoids the subsequent damage to environment and organism. The obvious reduction in COD, BOD, TS, DS and SS helps in alleviating pollution of the tanning liquor. This novel approach is beneficial to the clean production process and reduces the cost of sewage treatment in leather production.

Table 3: Biochemical oxygen demand (BOD), chemical oxygen demand (COD), total solid contents (TS), dissolved solid (DS) and suspended solid (SS) analyses of triazine compound tanned leather and chrome tanned leather

Tanning agent	COD (ppm)	BOD (ppm)	TS (ppm)	DS (ppm)	SS (ppm)
Triazine compound	1200-3000	250-600	20,000-40,000	12,000-20,500	400-1000
Chrome	1000-2500	500-1000	35,000-60,000	25,000-52,500	1000-2500

3.10 Commercial Feasibility

The assessment of every new approach of production requires commercial feasibility and cost efficacy. The chrome free tanning process by using triazine compound, considered as sustainable developments, must contribute to reduction in environmental impact and be economically viable. This novel approach and traditional process were respectively carried out using 30 pieces of wet-salted sheep skins for the middle trial, and each of the 10 pieces in a drum for 3 groups parallel tests. Then the total composite cost for processing 10 pieces of sheep skins through field trials chrome and chrome free tanning process schemes are given in Tab. 5 and the detailed chemical cost for 1 kg sheep skins is given in Tab. 4. It shows that for triazine compound treated leather, only 4% of sodium chloride, 0.4% formic acid and 0.5% sulfuric acid were offered against 8% of sodium chloride, 1.2% formic acid and 0.9% sulfuric acid in comparison of chrome treating. Apparently, the usage of triazine compound provides tanning process with less-salt pickling to cuts down the chemical cost and exhibits possibly decrease in chemical cost is about ¥0.041 for processing 1 kg of sheep skins. It drives chrome free tanning process to reduce the discharge of liquor wastes and have great reduction of pollutant treatment cost.

From the pilot-scale test (Tab. 5), in absence of chromium, the water cost is reduced by about 33% as well as the sludge treating cost is dropped by about 83%, compared to chrome tanning. Due to the reduction in the dosage of chemicals, the dosage of sodium chloride is reduced, chloride, TS, DS and SS loads lead further profitable in effluent treating cost compared to chrome tanning process. In total, the chrome free tanning process provides about 10% reduction in composite cost compared to the chrome tanning process. It concludes that the chrome free tanning process by using triazine compound is more economical and cleaner than chrome tanning process. The suggested tanning method does not demand any extra investment or additional equipment. The chrome free tanning process by triazine compound is an effective method of cleaner production without affecting the sensory properties and physicochemical properties of tanned leather. Hence, this would lead to a financial benefit and reduction of environmental impact. The chrome free tanning process is a greener option to develop eco-friendly leather in tannery.

Table 4: Chemical cost of chrome and chrome free tanning process: 1 kg of sheep skins

Chemicals	Cost per kg (CNY/¥)	Chrome tanning		Chrome free tanning	
		Dosage (kg)	Cost (¥)	Dosage (kg)	Cost (¥)
Sodium chloride	0.30	0.080	0.012	0.004	0.012
Formic acid	3.50	0.012	0.042	0.004	0.014
Sulfuric acid	1.50	0.009	0.013	0.005	0.008
Triazine compound	16	0	0	0.040	0.640
Chrome	8.10	0.080	0.648	0	0
Sodium bicarbonate	2.25	0.020	0.045	0.020	0.045
Total			0.760		0.719

Table 5: Comparison of composite cost for chrome tanning and chrome free tanning: 10 pieces of sheep skins

Item	Chrome tanning (¥)	Chrome free tanning (¥)
Water cost	0.09	0.06
Chemical cost	11.40	10.79
Effluent treating cost	1.08	0.52
TS treating cost	0.09	0.04
Sludge treating cost	0.06	0.01
Composite cost	12.72	11.42

4 Conclusion

With the progress of our world, resource shortage and environmental pollution have caused irreparable damage to human living and nature. There is a great challenge to achieve cleaner production for the leather industry which is regarded as a highly polluting industry. However, the discharge of liquor and solid waste with plenty of pollutants has led too much burden on the ecological environment. In this investigation, the novel approach to tanning process based on the triazine compound synthesized by cyanuric chloride, sulfanilic acid and p-hydroxybenzaldehyde in aqueous systems, and the structure of the product was confirmed by FTIR and ^{1}HNMR. The novel tanning agent is adopted for employing a chrome free tanning with less-salt pickling. The physicochemical properties of the tanned leather were explored by analyzing shrinkage temperature, denaturation temperature, mechanical strength and sensory properties, which are similar to conventional chrome tanned leather. The grain surface roughness and fiber dispersibility were observed by SEM and AFM, it depicts that the fiber bundles of triazine compound tanned leather can be well-dispersed with fine grain surface compared to chrome tanned leather. The most important improvement of the chrome free tanning process by triazine compound is that excellent environmental benefits achieved. Consideration of the reduction of environmental impact, the crucial parameters including BOD, COD, TS, SS and DS are significantly decreased in some extent. In addition, the composite cost of chrome free tanning process is lower than chrome tanning process, with the rate of cost reduction close to 10%. Good commercial viability is a great advantage of the novel approach for making chrome free leather. Furthermore, the triazine compound tanned leather could be more convenient for dry-finishing, such as shaving, splitting and buffing. The favorable ability of fiber dispersion could improve the permeability of subsequent materials. It ensures the safety of workers and reduces the risks of tanneries, meanwhile leading to a great progress in realizing cleaner production. This novel approach of chrome free tanning by triazine compound can be regarded as an eco-friendly tanning technology for developing leather industry in the future.

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