

Synthesis of Multi-Site Polyether Amine Triazine Derivative for Sustainable Leather Manufacturing

by

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Abstract

In this work, a multi-site polyether amine triazine derivative (ET) was prepared via a one-step process and its structure was confirmed using FT-IR and ¹H NMR analyses. Then, the ET was applied to the tanning process and the ET tanning approach optimized and evaluated. The result indicated that after tanning with 8% ET at pH 6 for 6 h, the shrinkage temperature of leather was 83.9°C and the thickness change rate was 97.5%. The XRD, DSC, TG, SEM and Zeta potential analyses demonstrated that ET could couple with the amino groups of the collagen side chains and breaking partial hydrogen bonds between fibers, brought significant improvement to the softness of leather without obvious damage to the high-level structure of collagen. Residual Cl⁻ concentration in the wastewater decreased 42.1% in the tanning process compared to the conventional chrome tanning method. The emissions of COD and TDS in the tanning process reduced by 40.5% and 27.2%, respectively. It is conceivable that the ET tanning approach provides an improved approach to promote leather industry to develop sustainably.

Introduction

As the most critical step in leather manufacturing, tanning is a process in which chemicals are used to introduce stable cross-linking between collagen and convert raw hide into leather. Chrome tanning is the most popular tanning method in the leather industry due to the prominent tanning performance of chrome. However, traditional chrome tanning technology and its subsequent wet finishing process could bring about consumption of the nonrenewable chrome salt and chrome-containing solid wastes and wastewaters¹ which could lead to consumption of resources and environmental pressure. In recent years, with the establishment of strategies of sustainable development, extensive studies have been conducted to develop substitute tanning agents of chrome. Aldehyde derivatives (such as modified glutaraldehyde,² oxazolidine,³ organic phosphorus⁴ have received special attention among researchers due to the significant potential in protein cross-linking. The aldehyde derivative tanning could endow wet-white with excellent hydrothermal stability and physical properties⁵ which has been regarded as an appropriate

alternative of conventional chrome tanning. Although an eco-friendly tanning technology can be achieved through aldehyde derivatives; there are some specific problems that can still be encountered. The principle of aldehyde derivative tanning is basically the aldehyde group or hydroxymethyl group coupling with the amino group of collagen side chain.⁶ But the cracking of hydroxymethyl groups and presence of aldehyde groups could lead to formaldehyde emission in the wet-white during storage.^{7, 8} Because of the biological toxicity of formaldehyde, it has been classified as a potential human carcinogen by the International Agency for Research on Cancer (IARC) and the products that contain aldehyde are facing stringent environmental regulations.⁹ To overcome the aforementioned limitations, a novel tanning agent is needed to be employed without chrome or aldehyde that has good tanning properties to meet the needs of the market.

Cyanuric chloride (TCT) is an important chemical intermediate which has many applications in the synthesis of reactive dyes.^{10, 11} The chlorine group in TCT has a strong reactivity with collagen under the action of a triazine ring. Specifically, the three chlorides can be substituted with the amino groups of the collagen side chain at 0-5°C, 35-40°C, 75-80°C, respectively.^{12, 13} When the TCT reacts with proteins, the optimal pH for the reaction of the second Cl⁻ on the TCT with collagen is 9.4 and the main reaction site is the amino group on the lysine residue,¹⁴ where significant improvement has been found in the thermal stability and physical and mechanical properties of the protein treated with TCT.^{15, 16} Besides, the rigid structural of the triazine ring in TCT could also bring stability of crosslinking.¹⁷ However, the poor water solubility of TCT makes it unachievable to directly apply in the aqueous phase of tanning. The commonly used methods is to couple TCT with sulfonated aromatic compounds to enhance the water solubility,¹⁵ but the introduction of aromatic compounds could increase the molecular size of tanning agent and prevent the penetration of tanning agent in skin. Besides, the commercial triazine tanning agent has insufficient tanning property due to the low active chlorine content.¹⁸

In this work, a novel chrome-free tanning agent based on polyether amine triazine derivatives (ET) was synthesized. The reaction between collagen and ET is shown in Figure 1. The structure of ET was characterized and the effect of ET alone when used as the

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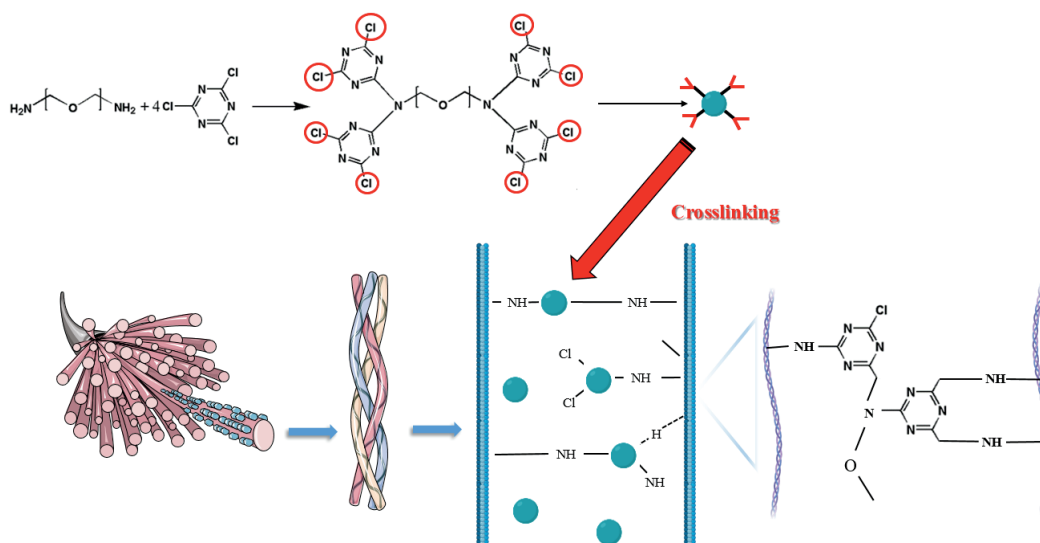


Figure 1. The crosslinking process and reaction of ET and collagen

main tanning agent was investigated and evaluated by comparing it with a commercial triazine derivative tanning agent (CTDT) and a chrome tanning agent. Based on the experimental results, a novel chrome-free and aldehyde-free approach for eco-friendly wet-white manufacturing was developed.

Experimental

Materials and Equipment

Raw cattle hides were used for leather processing. Polyether amine (ED) was purchased from Changke New Materials Technology Co., Ltd, Suzhou China. Cyanuric chloride was purchased from Aladdin Reagent Co., Ltd, Shanghai China. The chemicals employed in the subsequent operations were those normally used in leather industry.

Stainless Experimental Drum (GSD400-4, Wuxi Xinda Light Industry Machinery CO., Ltd, Wuxi, China); Fourier transform infrared spectrometer (Nicolet IS10, Nicolet CO., Ltd, Beijing, China); Nuclear magnetic resonance spectrometer (ARX400, Bruker CO., Ltd, Beijing China); Digital leather shrinkage temperature tester (MSW-YD4, Shaanxi University of Science & Technology, Shaanxi, China); Differential scanning calorimetry (DSC 200 PC, NETZSCH CO., Ltd, Beijing China); Thermal gravimetric analyzer (TG 209 F1, NETZSCH CO., Ltd, Beijing China); Potentiometric analyzer (SZP-10, BTG CO., Ltd, Beijing China); Scanning Electron Microscope (JSM-7500F/X-MAX50, JEOL CO., Ltd, Beijing China); Portable Colorimeter (CR-13, Konica Minolta CO., Ltd, Beijing China); Chloride ion selective electrode (9617BNWP, Thermofisher CO., Ltd, Beijing China); AES-ICP (QP 9100, Jena CO., Ltd, Beijing China); X-ray diffractometer (EMPYREAN, PANalytical B.V. CO., Ltd, Beijing China)

Preparation of polyether amine triazine derivatives (ET)

In a 300 ml 3-necked flask with stirring bar, 18.4g of cyanuric chloride and 100 mL of THF (dehydrated) and 0.25 mol of sodium carbonate (dehydrated) was charged. To this flask, 22.4g of ED (dehydrated) was added dropwise for a total of 0.5 h under the ice bath. After the addition of ED, the reaction took place at 25°C for 4 h under a stirrer of 300rpm. The viscous liquid ET was obtained by removing THF through rotary evaporation.

Fourier Transform Infrared Spectroscopy (FT-IR)

The functional groups present in the ET were characterized using FT-IR. The FT-IR was used to determine the pure sample at room temperature by using Nicolet iS10 infrared spectrometer. The sample was ground and pressed with spectrally pure KBr and scanned 32 times in the wavenumber range of 400 to 4000 cm^{-1} . The resolution was 2 cm^{-1} .

Nuclear Magnetic Resonance spectroscopy (^1H NMR)

After purification and drying, the product was analyzed by a 400MHz Bruker ARX400 nuclear magnetic resonance spectrometer. The solvent was deuterated chloroform (CDCl_3) and the internal standard was tetramethylsilane (TMS).

Leather tanning processing

The tanning process were carried out after conventional liming, unhairing (Sulfide), deliming (Ammonia sulfate) and softened (Trypsin), the ratio of leather chemicals for the tanning process was calculated according to the limed split pelt (2.5mm) weight and the cumulative input of tanning process is presented in Table I. A range of 4%-16% of ET was used for tanning and the tanning pH was adjusted to 3 to 9 and tanning temperature was controlled at 25°C, 35°C and 45°C.

Table I
ET tanning process

Processes	Chemical	Dosage/%	Temperature/°C	Time/min	Remarks
Wash	water	400	25	20	Repeat twice
Tanning	water	50			
	ET	X		30	Initial pH 6.0
Basification	Na ₂ CO ₃	1.5		180	Designated pH Y
	water	150	Z	150	overnight
Horse up					

X: The dosage of ET depending on the experiment: 4%, 8%, 16%; Y: The pH depending on the experiment: 3-9;
Z: The Temperature depending on the experiment: 25°C, 35°C, 45°C.

Table II
CTDT tanning process

Processes	Chemical	Dosage/%	Temperature/°C	Time/min	Remarks
Wash	water	400	25	20	Repeat twice
Tanning	water	50			
	CTDT	9		240	
	water	30	50	240	pH5
	Fungicide	0.1		60	overnight
Horse up					

The control process was carried out using a commercial triazine derivative tanning agent (CTDT) and the tanning process is presented in Table II.

The subsequent neutralization and fatliquoring processes were carried out according to the conventional process of cattle sofa leather.

Determination of the shrinkage temperature

The leather samples was measured by leather shrinkage temperature tester (MSW-YD4 Sunshine Electronic Research Institute of Shaanxi University of Science and Technology). Each experimental plot was obtained from an average of three samples.

Determination of the exhaustion rate of tanning agent

The waste liquor before and after tanning was collected and filtered, then digested with acid at 150°C for 2 hrs. The digestion solutions were appropriately diluted and the chemical oxygen demand (COD) determined by using the DR1010 COD detector. The exhaustion rate of tanning agent was calculated according to the following formula:

$$\text{Exhaustion rate (\%)} = 100\% \times \frac{a_2 - a_1}{a_1}$$

a1: COD in waste liquid before tanning (ppm)

a2: COD in waste liquid after tanning (ppm)

Determination of the percent thickness increase

Select four corners and five different parts in the middle of the leather were measured for thickness with thickness meter and the average determined by taking the arithmetic mean. The δ (percent thickness increase) was calculated according to the following formula:

$$\delta (\%) = 100\% \times \frac{d_2 - d_1}{d_1}$$

d1: thickness before tanning (mm)

d2: thickness after tanning (mm)

Thermal analysis

Thermogravimetric analysis (TG) measurements were carried out on the tanned leather. The untanned hide was used as a control sample. The dried samples were put into ceramic crucibles and heated at 10°C/min in a N₂ atmosphere. The range of temperature was from 40°C to 800°C. Thermal gravimetric analyzer was used for the determination.

Differential scanning calorimetry (DSC) measurements were carried out on the tanned leathers. The untanned hide was used as the control sample. The dried samples were put into aluminum crucibles and heated at 10°C/min in a N₂ atmosphere. The range of temperature was from 0°C to 200°C. Differential scanning calorimeter was used for the determination after vacuum drying and ground.

Zeta potential analyses

The leather was cut into small pieces, freeze-dried and crushed to powder, then dissolved in deionized water. The isoelectric point was determined by potentiometric analyzer.

Morphological analyses

The morphologies of crosslinked collagen fibers and grain patterns were observed using Desktop Scanning Electron Microscope. Samples of each tanning group were freeze-dried and then observed with an accelerating voltage of 5 kV.

Whiteness analysis

The Lab value of tanned leather was determined by CR-13 Portable Colorimeter (Konica Minolta CO., Ltd, Beijing China) and compared with the standard reference. The total color difference ΔE was calculated according to the following formula:

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2}$$

ΔL : Lab value of black/white

Δa : Lab value of red/green

Δb : Lab value of yellow/blue

X-ray diffraction (XRD) measurement

The sample was analyzed by EMPYREAN X-ray diffractometer (PANalytical B.V. CO., Ltd, Beijing China). The untanned hide was used as control sample. CuK as the ray source, the voltage of the tube was 40kV, the current of the tube was 30mA and the scanning speed was 1°/min, angle range 5°-55°.

Determination of physical and mechanical properties

The leather from different groups were kept under standard atmospheric conditions for 48 h prior to testing. The physical and mechanical properties i.e. the tensile strength, elongation at break, tear strength as well as the bursting strength of the resultant leather

were determined. These tests were performed according to the standards of IUP 2.²⁸

Environmental impact assessment

The chemical oxygen demand (COD) was analyzed by using the standard procedure (AWWA, 1998) for the spent tanning liquors. Total dissolved chlorides (TDC) was determined using a chloride ion selective electrode. The total dissolved solids (TDS) was calculated after one hour desiccation at 104°C. The content of chromium in spent liquor was determined using Inductively Coupled Plasma Emission Spectrometer (QP 9100, Jena CO., Ltd, Beijing China) after digestion.

Results and Discussions

Characterization of ET

FT-IR analyses

Figure 2 shows the FT-IR spectrum of TCT and ET. It can be seen from the figure that the TCT and ET showed obvious stretching vibration absorption of C-Cl bond at 532 cm⁻¹, while the characteristic absorption peak of triazine ring appears at 1303 cm⁻¹, 1353 cm⁻¹ and 1546 cm⁻¹. The C-N characteristic peak of ET at 1103 cm⁻¹ could not be observed in the structure of TCT which indicates that the polyether amine was introduced into the structure of the product.

¹H NMR analyses

Figure 3 shows the ¹H-NMR spectra of ET while using TMS as internal standard and deuterated chloroform as solvent. As can be seen from the figure, the chemical shift at 7.26 ppm belongs to the deuterated chloroform, the chemical shift at 1.81 ppm was caused by the residual solvent of tetrahydrofuran, the chemical shift at 3.70 ppm was caused by the ethyl hydrogen in the structure of polyether amine. It can be seen that the number of hydrogen atoms of the

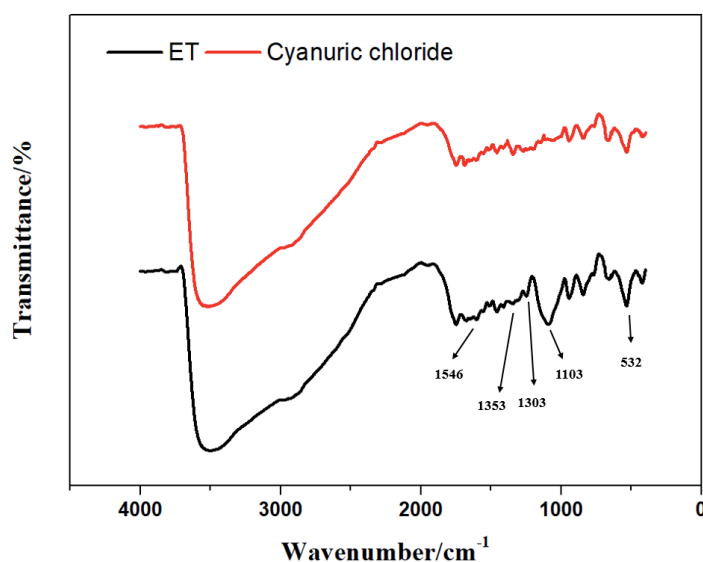


Figure 2. FT-IR spectrum of ET

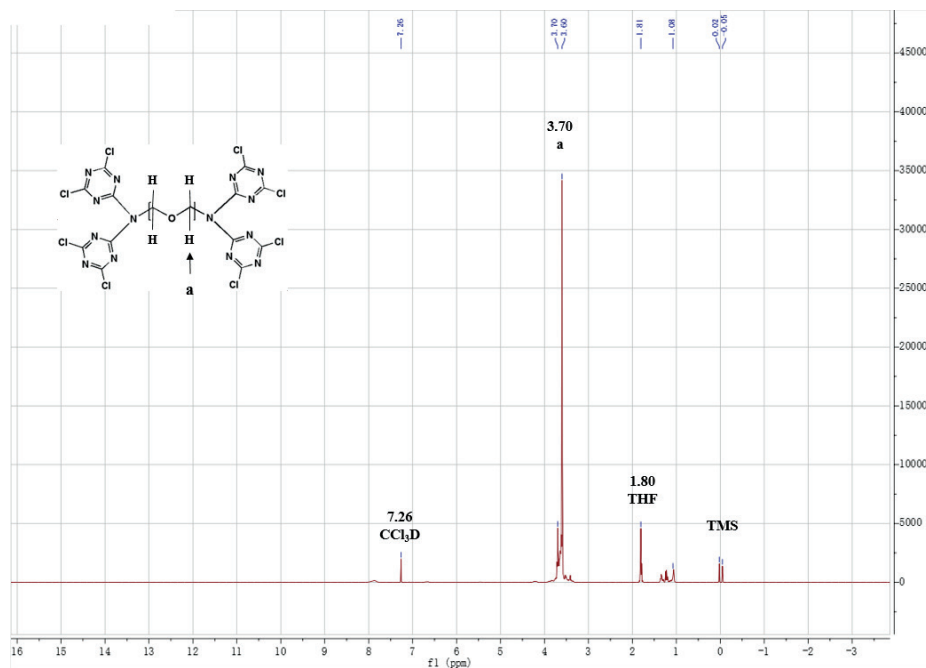


Figure 3. ^1H NMR spectrum of ET (CCl_3D , 400MHz)

product was consistent with the target product, which proves the existence of ET.

Optimization of the ET tanning conditions

Optimization of the ET tanning pH

The active chlorine in cyanuric chloride structure could be hydrolyzed at pH over 6, to prevent the excessive hydrolysis of tanning agent at the initial stage of tanning, the pH of tanning system was controlled at 6% and 8% of ET for tanning. With the reaction of skin collagen and ET, the formed HCl will lead to the decrease of bath pH. Therefore, sodium carbonate solution was used to adjust the pH and the percent thickness increase and shrinkage temperature of wet-white (after main tanning) was investigated. Figure 4 shows the percent thickness increase and shrinkage

temperature of wet-white after tanning at pH of 3 to 9. It can be seen from the figure that during the tanning process, the shrinkage temperature and percent thickness increase of wet-white slightly increased as the pH increased from 3.0 to 6.0 and rapidly decreased at a higher pH. The shrinkage temperature reached the maximum of 79.8°C and the percent thickness increase reached the maximum of 86% at the pH 6. This is due to the unique hydrolysis-binding equilibrium theory of TCT.¹² When the pH is lower than 6, the binding ability of active chlorine to collagen is insufficient, resulting in weak tanning property, low shrinkage temperature and percent thickness increase; When the pH is higher than 6, high pH will lead to the rapid hydrolysis of TCT,¹⁹ resulting in the loss of tanning property and the decrease of cross-linking rate. Therefore, it is an appropriate choice to tan at pH 6.

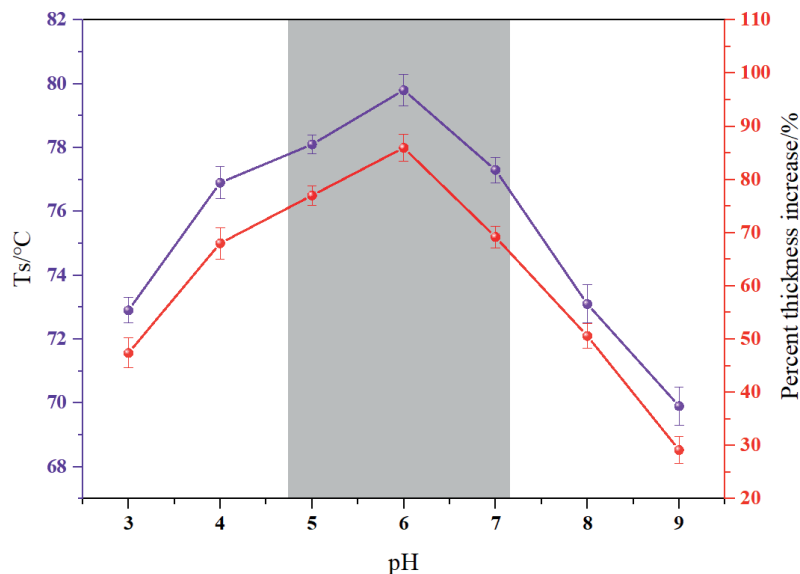


Figure 4. Shrinkage temperature and percent thickness increase of wet-white tanned with ET at different pH

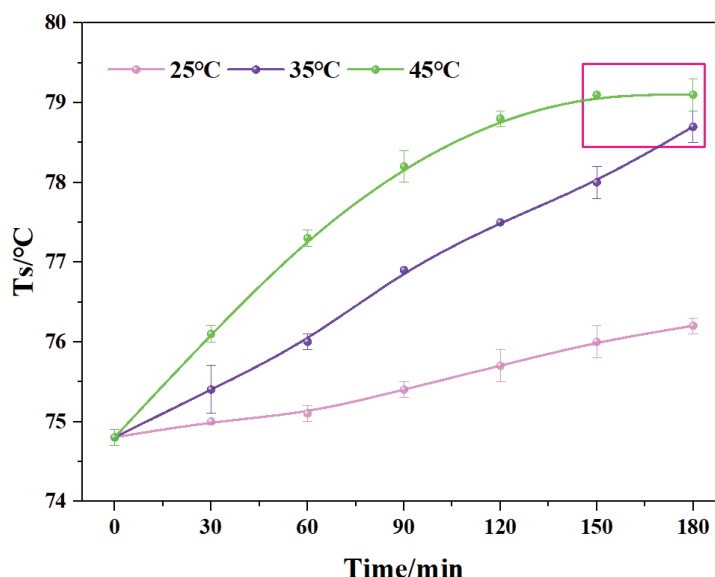


Figure 5. Shrinkage temperature of wet-white tanned with ET at different temperature

Optimization of the ET tanning temperature

Temperature is another important factor affecting the reaction between ET and collagen. For leather manufacturing, a lower temperature is usually used to promote the penetration of tanning agents in the initial tanning stage, and a higher temperature is used to promote the combination of tanning agents and collagen in the final tanning stage, which makes the tanning effect uniform. In order to investigate the effect of temperature at the final tanning stage using ET tanning, 8% ET was used at room temperature for 3h at the initial stage of tanning, and varying temperatures of 25°C, 35°C and 45°C were used at the final stage of tanning. The shrinkage temperature of wet-white was investigated at different times. The result in Figure 5 shows that the temperature increase at the final stage of tanning had a significant promoting effect on the shrinkage temperature of wet-white. Higher temperatures not only could accelerate the shrinkage temperature increase of wet-white, but also increases the final shrinkage temperature of wet-white to a certain extent. The shrinkage temperature of wet-white could reach 79°C after being treated at 45°C for 150 min. Considering that further heating may cause the destruction of the collagen structure and excessive hydrolysis of ET, it is suitable to treat at the temperature of 45°C for 150 min at the final stage of tanning.

Optimization of the ET dosage

The tanning agent of 4%, 8% and 12% was used for tanning according to the process mentioned in Table I. The subsequent neutralization and fatliquoring process was carried out according to the conventional process. As the Table III shows, with the increase of ET dosage, the shrinkage temperature and thickness of wet-white increased obviously. When the dosage of ET reached 8%, the shrinkage temperature of crust leather was 83.9°C, the percent thickness increase was 87.3% and no significant increase was achieved with the further increase of ET dosage. As for the exhaustion of tanning agent, when the ET dosage was higher than 8%, the exhaustion rate of ET decreases obviously, which indicates that the combination of ET and leather was reaching saturation. Further increasing the ET dosage contributes little to the leather properties. Besides, a large amount of ET remaining in the effluent liquor could increase the difficulty of post treatment. In order to ensure the effective utilization of materials and control cost, it is considered that 8% of ET dosage could be a more appropriate choice.

Thermal analysis

The thermodynamic analysis of leather is a reliable method to evaluate the thermal effect of chrome-free tanned leather. It can also

Table III
Tanning effect of different ET dosage

ET dosage/%	4	8	12
Ts of the wet-white /°C	73.9±0.1	78.9±0.1	79.3±0.2
Ts of the crust leather /°C	76.1±0.2	83.9±0.0	84.1±0.2
percent thickness increase /%	57.1±0.8	87.3±0.7	90.1±0.4
exhaustion rate %	81.6±0.7	79.6±0.5	59.3±0.9
Softness	7.6±0.0	8.8±0.0	8.9±0.1

reflect the effect of crosslinking on the advanced structure of leather. In this section, the thermal performance of wet-white tanned with ET was analyzed via TG and DSC, the untreated collagen was used as the control.

The thermal decomposition of leather is related to the cross-linking degree of collagen fibers. Covalent crosslinking in collagen could improve the thermal stability of skin, which is reflected in higher thermal decomposition temperature.²⁰ Figure 6 showed the TG curves of the ET and the corresponding characteristic parameters of them are given in Table IV. The first stage (I) is the vaporization of free water and bound water, the second stage (II) is the decomposition of collagen fibers, polymers and organic chemical materials used in tanning, and the third stage (III) is the decomposition of chemical bonds of polymers with collagen.²¹ According to the results, the crosslinking of ET can obviously slow down the thermal decomposition during the heating process, this is because the triazine ring structure in ET can form stable sites between the collagen chains and play a role in fixing the collagen chains.

The hide before and after tanning (after freeze drying) was crushed and analyzed by DSC. The thermal stability of different leather

powders before and after tanning can be judged by the position, width, strength and area of the peak in DSC spectrum. The differential scanning calorimeter (DSC) has been used to elucidate the degradation profile of wet-white tanned with ET in response to heat and the thermal stability of collagen before and after tanning can be judged by the position, width, strength and area of the peak in DSC spectrum. As showed in Figure 7, the peak of denaturation temperature of wet-white rises to 97.5°C while the peak of denaturation temperature of untanned collagen at 69.9°C and the position of the peak obviously drifts to the high temperature zone and gets wider. That is because the existence of triazine structure on the polypeptide macromolecular network could affect the three dimensional linkages and leads to the enhancement of heat resistance of collagen.

Zeta potential analysis

Collagen is a typical amphoteric polyelectrolyte. The blocking state of -COOH and -NH₂ in its structure can be described through zeta potential. Specifically, with the change of the pH value, different collagen structures become ions with many positive or negative charges. When the pH is lower than the isoelectric point of collagen, carboxyl groups are blocked, the amino groups are protonated and

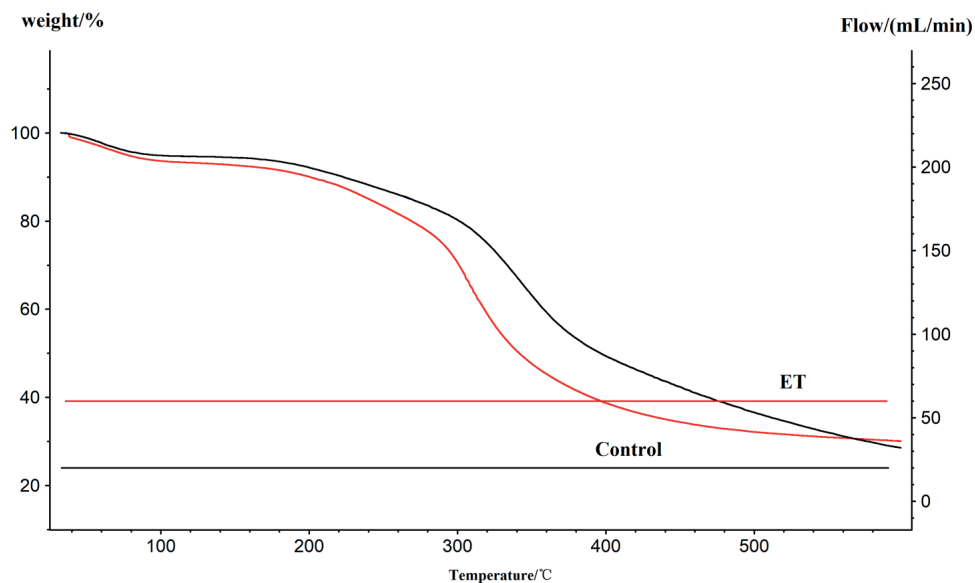


Figure 6. TG curve of wet-white tanned with ET

Table IV
Weight loss in different thermogravimetric stage

Simple	Thermal decomposition stages		
	I/wt%	II/wt%	III/wt%
ET tanning	8.03 (Room temperature-210.8°C)	50.11 (210.8°C-493.8°C)	9.88 (493.8°C-600.0°C)
Control	7.19 (Room temperature-209.2°C)	51.0 (209.2°C-397.3°C)	8.63 (397.3°C-600.0°C)

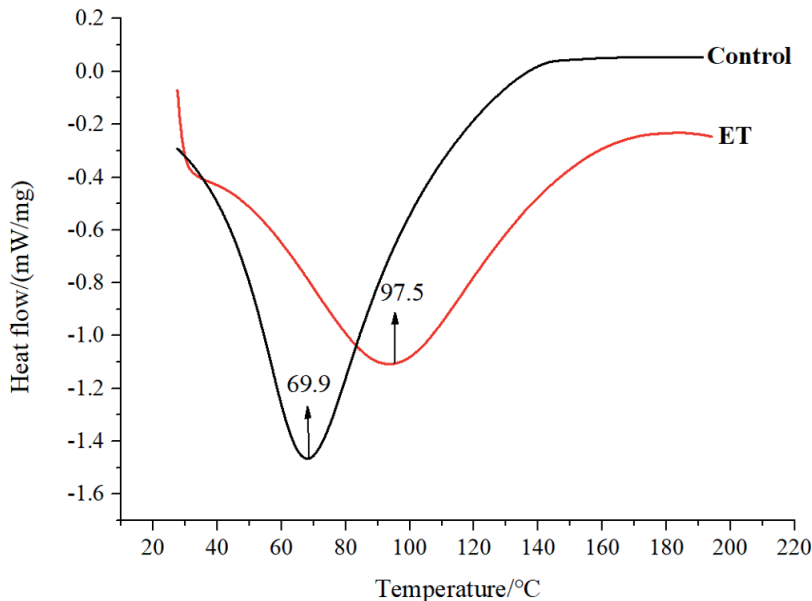


Figure 7. DSC curve of wet-white tanned with ET

the molecules carry a positive charge; when the pH is higher than the isoelectric point of collagen, the carboxyl groups are ionized and the molecules carry a negative charge. When the concentration of negatively charged carboxyl groups are equal to that of positively charged amino groups in solution, collagen will be in a state of equal charge.²²

In this study, the Zeta potential of wet-white tanned with ET was investigated and the untreated collagen was used as the control. Figure 8 shows the Zeta potential of wet-white tanned with ET at different pH values. After tanning with ET, the isoelectric point of collagen decreased from 4.71 to 2.85, that means ET could react with the amino groups of collagen, a large number of amino groups in the side chain of collagen were blocked, which is consistent with the results shown in Figure 4.

XRD analysis

In order to reveal the dispersion of ET in collagen, the white-wet tanned with ET was characterized by XRD, and the untreated collagen was used as the control group. In Figure 9, there were two obvious diffraction peaks at 8° (A) and 22° (B). The (A) peak reflects the distance between the molecular chains of the collagen fibers, and belongs to the α -helix region with more ordered structure.²³ The fact that peak shape of (A) got sharper indicated that the tanning process of ET broke part of the hydrogen bonds and van der Waals forces between collagen fibers and lead to the loosening of the fibers. The (B) peak was caused by numerous structural layers inside the collagen fibers, such as the b-fold. After tanning with ET, the (B) peak moved to the direction of low diffraction angle, which indicated that the introduction of ET breaks the original weak interaction between collagen, reduces the randomness of fibers, and macroscopically

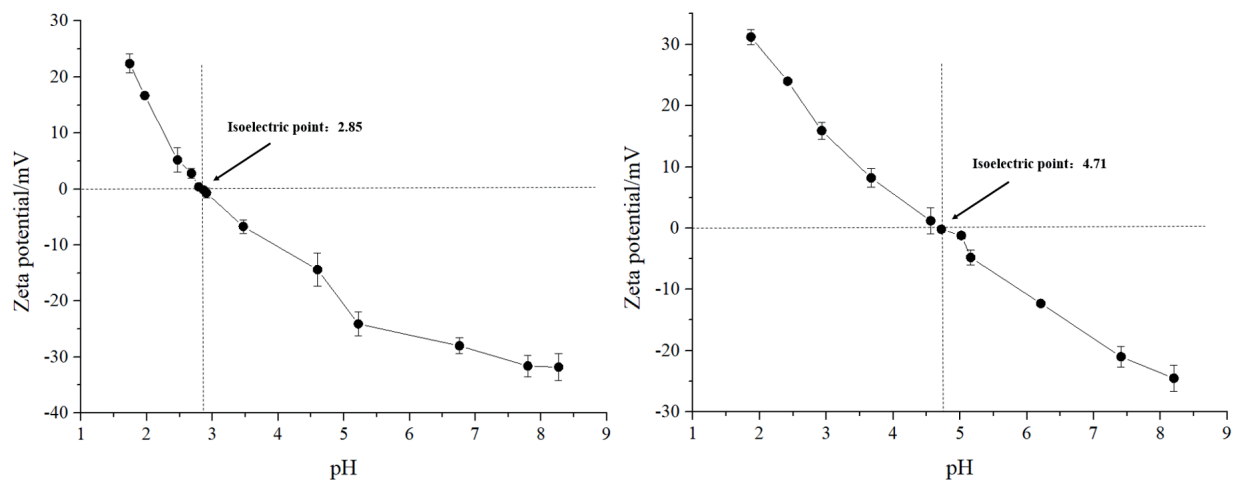


Figure 8. Zeta potential of wet-white tanned with ET

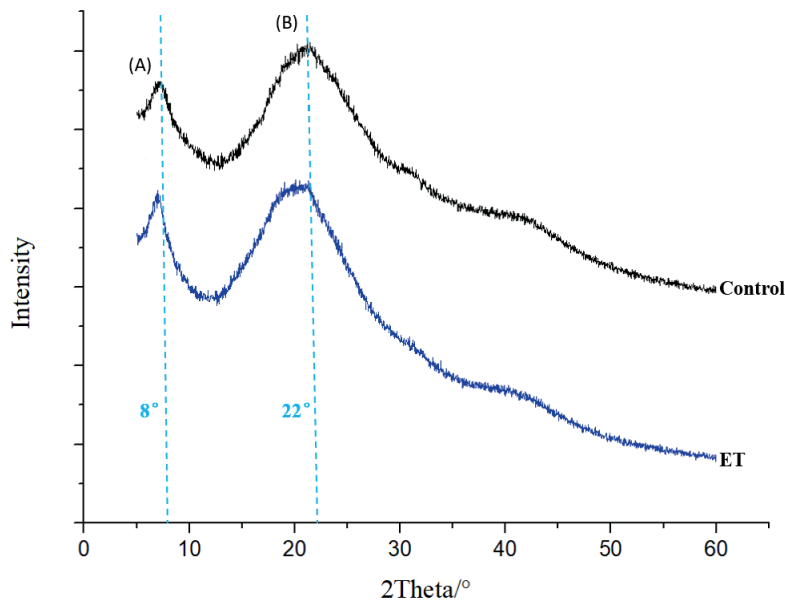


Figure 9. XRD curves for wet-white tanned with ET.

reflects the increase of softness. There was no obvious change of the diffraction peak at 43° , which indicated that ET tanning did not cause a change in the collagen crystalline region.

Physical performance of leather

In order to evaluate the physical performances of wet-white tanned with ET, wet-white was prepared with CTD T (9%) according to the process mentioned in Table II and wet-blue was prepared with conventional chrome tanning method (6.5%).²⁵ The subsequent neutralization and fatliquoring process was carried out according to the conventional process and the results were shown in Table V. As the results show, the physical performance of ET tanned leather were better than that of CTD T tanned leather, which was close to the physical performances of chrome tanning leather. This is because there were more active chlorine in ET structure than CTD T, which could be regarded as crosslinking sites when ET react with collagen.

In addition, ET tanning can significantly improve the softness of leather, which was due to the supporting effect of triazine structure between leather fibers, and the lubricating effect of polyether chain segments in the gap between collagen fibers,²⁶ which gives leather excellent softness.

Whiteness analysis

The Lab values of leather (without dyeing and retanning) were determined and compared with the standard reference to evaluate the whiteness of several leathers tanned with different methods. It can be seen from Table VI that the color difference between ET tanned wet-white and standard white is little, which is similar to that of CTD T tanned wet-white and obviously better than that of chrome tanned wet-blue. Besides, triazine derivatives can be coupled with subsequent dyes lead to a fixation effect, which present a wide application prospect.

Table V
Physical performances of leather tanned with different method

Tanning agent	ET	CTDT	Chrome
Shrinkage temperature ($^\circ\text{C}$)	83.9 ± 0.2	74.3 ± 0.3	109.2 ± 0.2
Tensile strength (MPa)	16.19 ± 0.00	14.1 ± 0.11	18.31 ± 0.07
Elongation (%)	65.1 ± 0.3	66.9 ± 0.1	65.2 ± 0.1
Tear strength (N/mm)	47.93 ± 0.24	38.9 ± 0.17	60.21 ± 0.30
Softness (mm)	8.8 ± 0.0	9.1 ± 0.0	7.8 ± 0.2
Fineness of grain	++++	+++	++++
Fullness	+++++	++++	+++++

Table VI
Whiteness of wet-white tanned by different methods

Tanning method	L	a	b	ΔE^*
Standard white	91.60	-0.47	5.10	---
Chrome tanning	42.71	-0.18	0.88	49.07
CTDT tanning	79.30	-0.26	3.80	12.37
ET tanning	79.82	-0.49	3.77	11.85

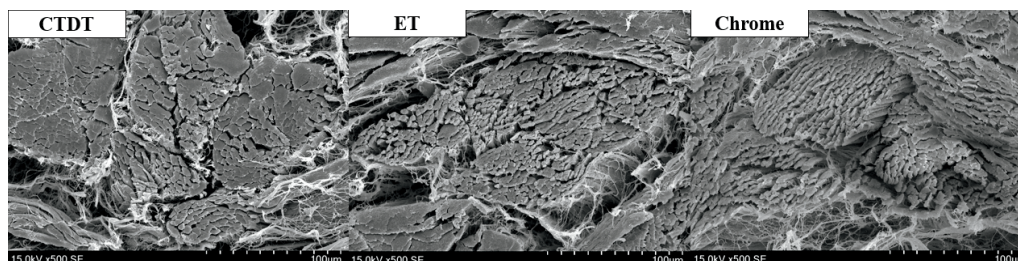


Figure 10. SEM observation of fiber patterns of the leather with different tanning method.

Morphology analysis

Figure 10 shows the SEM observation of leather tanned using three different methods. It can be seen from the result that the fibers of wet-white tanned with ET were more dispersed compared with the CTDI tanned leather, there was no obvious adhesion between fiber bundles, and the boundary of basic fibers was clear. Compared with the wet-blue tanned with chrome, the looseness of the fiber was similar, which indicates that the introduction of ET could break the adhesion between fibers, increase the sliding property of fibers and improve the softness of leather.

Environmental impact assessments

To evaluate the impact of the ET tanning process on the environment, biochemical analysis of leather processing waste liquor was carried out to assess its ecological risks to the environment.²⁷ The ET tanning effluent was evaluated to measure the environmental impact parameters of the ET tanning method and compare it with the CTDI and conventional chrome tanning methods. It is shown in Figure 11 that the residual Cl⁻ concentration in wastewater decreased 42.1% in tanning process compared to conventional chrome tanning method. That was because no pickling was needed in tanning process of ET and CTDI, the residual chloride ion in the waste liquid comes

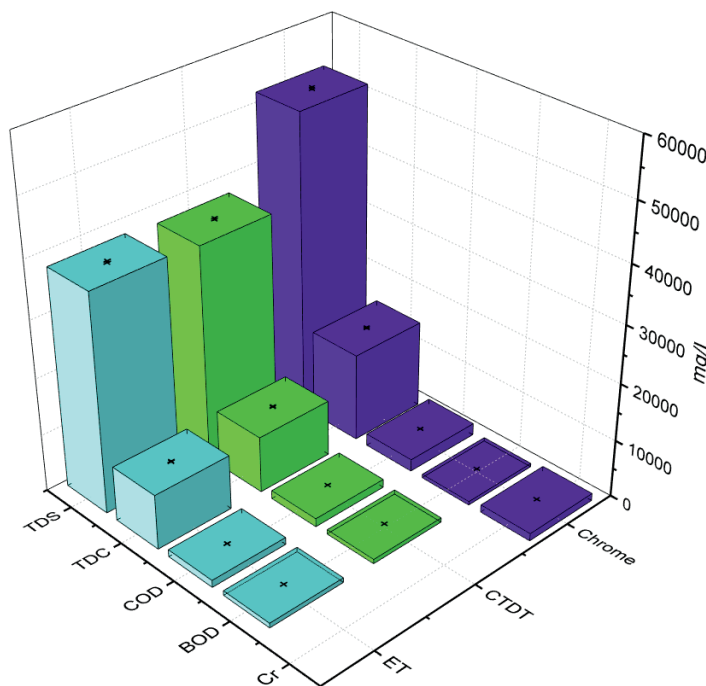


Figure 11. Environmental testing parameters of three tanning methods

from HCl formed by the reaction of tanning agent and collagen. The emissions of COD and TDS in waste liquor of ET were only 1242mg/L and 38118mg/L compared with 2088mg/L and 52300mg/L of chrome tanning waste liquor. The COD, TDS and TDC of ET tanning effluent were slightly lower than that of CTDT tanning effluent. ET tanning technology have a better biodegradability and no neutral salt was introduced in the process, which indicated that the lower environmental administration budget. ET as a novel tanning agent could provide guidance for develop sustainably and cleaner leather manufacturing.

Conclusion

Nowadays, a growing number of countries have implemented strict regulations to promote sustainable development. New criterion for clean leather manufacturing have been put forward for chrome-free tanning. In this work, polyether amine triazine derivative (ET) was prepared via a one-step process and a novel chrome-free tanning approach based on ET has been established and evaluated comprehensively. ET has been confirmed to combine with the amino groups of collagen mainly in the form of covalent bonds and produced crosslinking networks in the collagen structure, which greatly improved the thermal and physical properties of collagen. Due to the existence of polyether chain in ET structure, part of hydrogen bonds and van der Waals forces in collagen were broken, fibers loosened, and increased the softness of leather. After tanning with 8% of ET at pH 6 for 6 h, the wet-white present shrinkage temperature of 83.9°C (due to the introduction of covalent crosslinking) and percent thickness increase of 87.3% (due to the support effect of hydrophobic group of ET on fiber). The environmental impact assessments showed ET tanning shows better environmental protection than conventional chrome tanning as well as CTDT tanning.

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