

Preparation and application of polyether amine triazine derivatives as a chrome-free tanning agent for cleaner production

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ABSTRACT: In this work, a polyether amine triazine derivatives (ET) was prepared via one-step process and its structure was confirmed using FT-IR, ¹H NMR analyses. Then, the ET was applied to the tanning process and a novel chrome-free tanning approach has been optimized and evaluated. The result indicated that after tanning with 8% of ET at pH6 for 6h, the shrinkage temperature of leather was 83.9°C and the thickness change rate was 97.5%. The ET tanned leather was endowed with a close mechanical and organoleptic performance as conventional chrome tanned leather. The XRD, DSC, TG, SEM and Zeta potential analyses demonstrated that ET could couple with the amino group of collagen side chain and breaking partial hydrogen bond between fibers, brought significantly improvement to the softness of leather, but has no impact on the high-level structure of collagen. Another promising features of this tanning approach is that the residual Cl⁻ concentration in wastewater decreased 42.1% in tanning process compared to conventional chrome tanning method. The emissions of COD and TDS in tanning process reduced by 40.5% and 27.2%, respectively. It is conceivable that the ET tanning approach satisfactorily solves the longstanding problems of conventional chrome tanning and provides an improved approach to promote leather industry to develop sustainably.

Key words : Polyether amine; Chrome-free tanning; Environmental friendly; Cyanuric chloride; Triazine derivatives

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40 1. INTRODUCTION

41 As the most critical step in leather manufacturing, tanning is a process in which chemicals are used
42 to introduce stable cross-linking between collagen and convert raw hide into leather. Chrome tanning
43 method is the most popular tanning method in the leather industry due to the prominent tanning
44 performance of chrome. However, because of the low uptake of chrome in tanning process, about
45 170,000 tons of Cr wastes/year is released into environment worldwide^[1] which could lead to
46 consume of resources and environmental pressure. In recent years, with the establishment
47 of strategies of sustainable development, extensive studies have been conducted to develop substitute
48 tanning agents of chrome. Aldehyde derivatives (such as modified glutaraldehyde^[2], oxazolidine^[3],
49 organic phosphorus^[4] have received special attention among researchers due to the significant
50 potential in protein cross-linking. The aldehyde derivatives tanning could endow wet-white with
51 excellent hydrothermal stability and physical properties^[5], which has been regarded as an
52 appropriate alternative of conventional chrome tanning. Although an eco-friendly tanning technology
53 seems can be achieved through aldehyde derivatives, there are some specific problems can still be
54 encountered. The principle of aldehyde derivatives tanning is basically the aldehyde group or
55 hydroxymethyl group coupling with the amino group of collagen side chain^[6]. But the cracking of
56 hydroxymethyl group and present of aldehyde group could lead to the formaldehyde emission of
57 wet-white during storage^[7,8]. Because of the biological toxicity of formaldehyde, it has been classified
58 as a potential human carcinogen by the International Agency for Research on Cancer (IARC) and the
59 products contain formaldehyde were facing stringent environmental regulations^[9]. To overcome the
60 aforementioned limitations, a novel tanning agent is needed to be employed without chrome or
61 aldehyde and have good tanning property to meet the needs of the market.

62 Cyanuric chloride (TCT) is an important chemical intermediate which have many applications in
63 synthesis of reactive dyes^[10,11]. The chlorine group in TCT have strong reactivity with collagen under

64 the action of triazine ring. Specifically, the three chlorides can be substituted with the amino groups of
65 collagen side chain at 0-5°C, 35-40°C, 75-80°C, respectively^[12, 13]. When the TCT react with protein, the
66 optimal pH for the reaction of the second Cl⁻ on the TCT with the collagen is 9.4 and the main
67 reaction site is the amino group on the lysine residue^[14], significant improvement has been found in
68 the thermal stability and physical and mechanical properties of the protein treated with TCT^{[15,}
69 ^{16]}. Besides, the rigid structural such as triazine ring of TCT could also bring stability of
70 crosslinking^[17]. However, the poor water solubility of TCT makes it unachievable to direct apply in
71 aqueous phase tanning, The commonly used methods is to couple TCT with sulfonated aromatic
72 compounds to enhance the water solubility^[15], but the introduction of aromatic compounds could
73 increase the molecular size of tanning agent and prevent the penetration of tanning agent in skin.
74 Besides, the active chlorine content of commercial triazine derivatives tanning agents is limited
75 considering that the third chlorine in the structure of cyanuric chloride could be difficult to be
76 involved in the crosslinking reaction, which leads to low crosslinking rate and the shrinkage
77 temperature^[18].

78 In this work, a novel chrome-free tanning agent based on polyether amine triazine derivatives
79 (ET) was synthesized. The introduction of the polyether amine as backbone endowed the product with
80 good water solubility without excessive increase in molecular size and there are multi-site of active
81 chlorine in product structure. The structure of ET was characterized and the effect of ET alone use in
82 the main tanning was investigated and evaluated by comparing with the commercial triazine
83 derivatives tanning agent (CTDT) and the chrome tanning agent. Based on the experimental results, a
84 novel chrome-free aldehyde-free approach for eco-friendly wet-white manufacturing was developed.

85

86 **2. EXPERIMENTAL**

87 **2.1 Materials and Equipment**

88 The raw material of cowhide was used for leather processing. Polyetheramine (ED) was purchased
89 from Suzhou Changke New Materials Technology Co., Ltd. Cyanuric chloride was purchased from
90 Aladdin Reagent Co., Ltd. The chemicals employed in the subsequent operations were those normally
91 used in leather industry.

92 Stainless Experimental Drum (GSD400-4, Wuxi Xinda Light Industry Machinery CO., Ltd). The digital
93 leather shrinkage temperature tester (MSW-YD4) was produced by Shaanxi University of Science &
94 Technology, China.

95

96 **2.2 Preparation of polyether amine triazine derivatives (ET)**

97 0.1 mol of cyanuric chloride and 100mL of THF (dehydrated) and 0.25 mol of sodium carbonate
98 (dehydrated) was charged in a 300 ml 3-necked flask equipped with stirring bar. 0.0245 mol of ED
99 (dehydrated) was add dropwise within 0.5 h under the ice bath. After the dropping of ED, the
100 reaction took placed at 25°C for 4 h under the high speed stirrer. The viscous liquid ET was obtained
101 by removing THF through rotary evaporation.

102

103 **2.3 Fourier Transform Infrared Spectroscopy (FT-IR)**

104 The functional groups present in the ET were characterized using the FT-IR. The FT-IR was used to
105 determine the pure sample at room temperature by using Nicolet iS10 infrared spectrometer. The
106 sample was grinded and pressed by spectral pure KBr, and scanned 32 times in the wavenumber
107 range of 400 to 4000 cm⁻¹. The resolution was 2 cm⁻¹.

108

109 **2.4 Nuclear Magnetic Resonance spectroscopy (¹H NMR)**

110 After purification and drying, the product was analyzed by 400MHz Bruker ARX400 nuclear
111 magnetic resonance spectrometer. The solvent was deuterated chloroform CDCl₃ and the internal
112 standard was tetramethylsilane TMS.

113

114 **2.5 Leather tanning processing**

115 The tanning process were carried out using depilated and softened cattle hide, the ratio of leather
116 chemicals of tanning process was calculated according to the limed split pelt weight and the
117 cumulative input of tanning process was presented in **Table. 1**.

118

119 **Table. 1 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
120	Horse up				

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

123

124 The control process was carried out using commercial triazine derivatives tanning agent (CTDT)
 125 and the cumulative input of tanning process was presented in **Table. 2**

126

127 **Table. 2**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					

128

129 The subsequent neutralization and fatliquoring process was carried out according to the
 130 conventional process.

131

132 2.6 Determination of the shrinkage temperature

133 The similar parts were selected for sampling and the leather samples was measured by leather
 134 shrinkage temperature tester (MSW-YD4 Sunshine Electronic Research Institute of Shaanxi University
 135 of Science and Technology). Each experimental plot was obtained from an average of three samples.

136

137 2.7 Determination of the exhaustion rate of tanning agent

138 The waste liquor before and after tanning was collected and filtered, then digested with acid at 150°C
 139 for 2hrs. The digestion solutions were appropriately diluted the chemical oxygen demand (COD) were
 140 analyzed by using the DR1010 COD detector. The a_1 (ppm) stand for COD in waste liquid before

141 tanning while the a_2 (ppm) stand for COD in waste liquid after tanning. The exhaustion rate of
142 tanning agent is calculated according to the following formula:

143

$$144 \text{exhaustion rate(\%)}=(a_1-a_2)/a_1 \times 100\%$$

145

146 **2.8 Determination of the thickening rate**

147 Select four corners and five different parts in the middle of the leather, measure the thickness
148 with thickness meter, get the average thickness by taking the arithmetic mean. The d_2 (mm) stand
149 for the thickness after tanning while the d_1 (mm) stand for the thickness before tanning. The δ
150 (thickening rate) can be calculated according to the following formula:

151

$$152 \delta (\%)=(d_2-d_1)/d_1 \times 100\%$$

153

154 **2.9 Thermal analyses**

155 Thermogravimetric analyses (TG) measurements were carried out on the tanned leathers, the
156 untanned hide was used as control sample. The dried samples were put into ceramic crucibles and
157 heated with $10^\circ\text{C}/\text{min}$ heating rate in a N_2 atmosphere. The range of temperature was from 40 to 800°C
158 A NETZSCH TG 209 F1 thermal gravimetric analyzer (Germany) was used for the determination.

159 Differential scanning calorimetry (DSC) measurements were carried out on the tanned leathers, the
160 untanned hide was used as control sample. The dried samples were put into aluminum crucibles and
161 heated with $10^\circ\text{C}/\text{min}$ heating rate in a N_2 atmosphere. The range of temperature was from 0 to 200°C
162 A DSC 200 PC differential scanning calorimeter (Germany) was used for the determination.

163

164 **2.10 Zeta potential analyses**

165 The leather was cut into small pieces, freeze-dried and crushed to powder, then dissolved in
166 deionized water. The isoelectric point was determined by SZP-10 potentiometric analyzer.

167

168 **2.11 Morphological analyses**

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

172

173 **2.12 Whiteness analysis**

174 The Lab value of tanned leather was determined by color reader CR-13 Portable Colorimeter and
175 compared with the standard reference. The total color difference ΔE was calculated according to the
176 following formula

$$177 \Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2}$$

178

179 **2.13 X-ray diffraction (XRD) measurement**

180 The sample was analyzed by EMPYREAN X-ray diffractometer, the untanned hide was used as
181 control sample. CuK α as the ray source, the voltage of the tube was 40 kV, the current of the tube was
182 30 mA and the scanning speed was 1°/min, angle range 5-55°.

183

184 **2.14 Determination of physical and mechanical properties**

185 The leather from different groups were kept under standard atmospheric conditions for 48 h prior
186 to testing. The physical and mechanical properties i.e. the tensile strength, elongation at break, tear
187 strength as well as the bursting strength of the resultant leather were determined. These tests were
188 performed according to the standards of IUP 6, 2000; IUP 8, 2000; IUP 9, 1996.

189

190 **2.15 Environmental impact assessment**

191 The chemical oxygen demand (COD) were analyzed by using the standard procedure (AWWA, 1998)
192 for the spent tanning liquors. Total dissolved chlorides (TDC) was determined using Thermo Orion
193 9617BNWP chloride ion selective electrode. The total dissolved solids (TDS) was calculated after one
194 hour desiccation at 104°C. The content of chromium in spent liquor was determined using Inductively
195 Coupled Plasma Emission Spectrometer (AES-ICP) after digested.

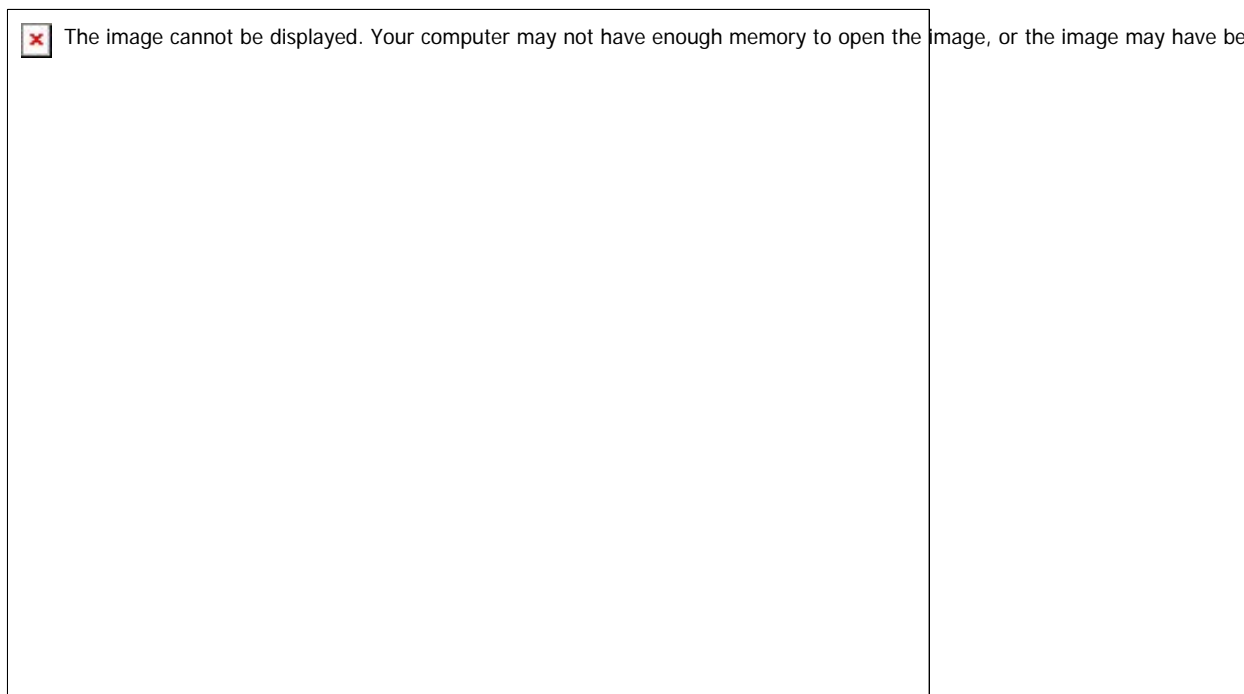
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197 **3. RESULTS AND DISCUSSIONS**

198 **3.1 Characterization of ET**

199 **FT-IR analyses:**Fig. 1 shows the FT-IR spectrum ofTCT and ET.It can be seen from the figure that
200 the TCT and ET showed obvious stretching vibration absorption of C-Cl bond at 532 cm^{-1} , while the
201 characteristic absorption peak of triazine ring appears at 1303 cm^{-1} , 1350 cm^{-1} and 1546 cm^{-1} . The C-N
202 characteristic peak of ET at 1103 cm^{-1} could not be observed in structure of TCT which indicates that
203 the polyether amine was introduced into the structure of the product.

204



205

206

Fig. 1 FT-IR spectrum of ET

207

208 **^1H NMR analyses:** Fig.2 shows the ^1H -NMR spectra of ET while using TMS as internal standard and
209 deuterated chloroform as solvent.As can be seen from the figure, the chemical shift at 7.26 ppm
210 belongs to the deuterated chloroform, the chemical shift at 1.81 ppm was caused by the residual
211 solvent of tetrahydrofuran, thechemical shift at 3.70 ppm was caused by the ethyl hydrogen in the
212 structure of polyether amine. It can be seen that the characteristic hydrogen in the structure of
213 tanning agent can be assigned, which proves the existence of ET.

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3.2 Optimization of the ET tanning conditions

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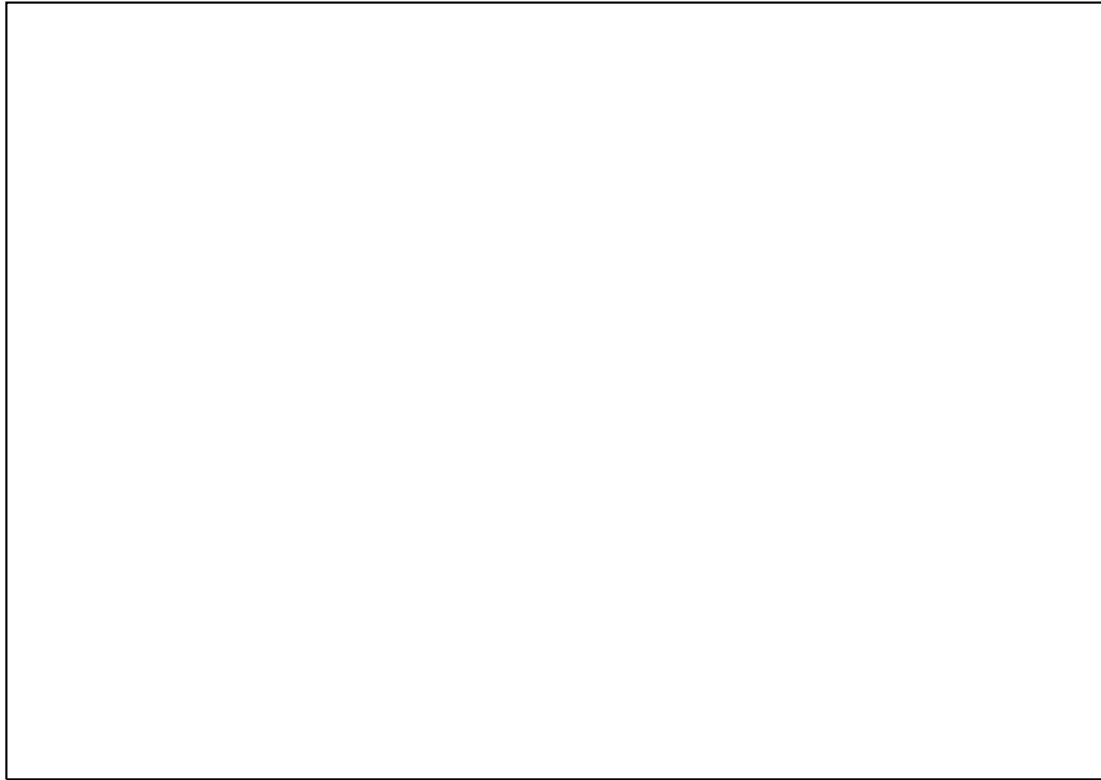
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Fig. 2 ^1H NMR spectrum of ET (CCl_3D , 400MHz)

Optimization of the ET tanning pH: In order to prevent the excessive hydrolysis of tanning agent at the initial stage of tanning, the pH of tanning system was controlled at 6 at the initial stage of tanning, 8% of ET was used for tanning and the sodium carbonate solution was used to adjust the pH at varying pH, the thickening rate and shrinkage temperature of wet-white was investigated. **Fig. 3** shows the thickening rate and shrinkage temperature of wet-white after tanning at different pH. It can be seen from the figure that during the tanning process, the shrinkage temperature and thickening rate of wet-white slightly increased as the pH increased from 3.0 to 6.0 and rapidly decreased at higher pH. The shrinkage temperature reached the maximum of $79.8\text{ }^\circ\text{C}$ and the thickening rate reached the maximum of 86% at the pH 6. This is due to the unique hydrolysis-binding equilibrium theory of TCT^[12]. When pH is lower than 6, the binding ability of active chlorine to collagen is insufficient, resulting in weak tanning property, low shrinkage temperature and thickening rate; 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 tanning at pH 6.



233

234 **Fig. 3** Shrinkage temperature and thickening rate of wet-white tanned with ET at different pH

235

236 **Optimization of the ET tanning temperature:** Temperature is another important factor affecting
237 the reaction between ET and collagen. For the leather manufacturing, a lower temperature is usually
238 used to promote the penetration of tanning agent in the initial tanning stage, and a higher
239 temperature is used to promote the combination of tanning agent and collagen in the final tanning
240 stage, which makes the tanning effect uniform. In order to investigate the effect of temperature at
241 the final tanning stage on ET tanning properties, 8% of ET was used at room temperature for 3h at
242 the initial stage of tanning, and varying temperatures of 25°C, 35°C and 45°C were used at the final
243 stage of tanning, the shrinkage temperature of wet-white was investigated at different times. The
244 result in **Fig. 4** shows that the temperature rise at the final stage of tanning had a significant
245 promoting effect on the shrinkage temperature of wet-white. High temperature not only could
246 accelerate the shrinkage temperature rise of wet-white, but also increase the final shrinkage
247 temperature of wet-white to a certain extent. The shrinkage temperature of wet-white could reach
248 79 °C after being treated at 45 °C for 150 min. Considering that further heating may cause the destruction
249 of collagen structure and excessive hydrolysis of ET, it is suitable to treat at the temperature of
250 45 °C for 150 min at the final stage of tanning.



251

252 **Fig. 4** Shrinkage temperature of wet-white tanned with ET at different temperature

253

254 **Optimization of the ET dosage:** The tanning agent of 4%, 8% and 12% was used for tanning
 255 according to the process mentioned in **Table.1**. The subsequent neutralization and fatliquoring
 256 process was carried out according to the conventional process. As the **Table. 3** shown, with the
 257 increase of ET dosage, the shrinkage temperature and thickness of wet-white increased obviously.
 258 When the dosage of ET reached 8%, the shrinkage temperature of crust leather was 83.9°C the
 259 thickening rate was 87.3% and no significant increase was achieved with the further increase of ET
 260 dosage. As for the exhaustion of tanning agent, when the ET dosage was higher than 8%, the
 261 exhaustion rate of ET decreases obviously, which indicates that the combination of ET and
 262 leather was reaching saturation. Further increasing the ET dosage contribute a little to the leather
 263 properties. Besides, a large amount of ET remained in the effluent liquor could increase the difficulty
 264 of post treatment. In order to ensure the effective utilization of materials and control the cost, it is
 265 considered that 8% of ET dosage could be a more appropriate choice.

266

267 **Table.3** Tanning effect of different ET dosage

ET dosage/%	4	8	12
Ts of the wet-white /°C	73.9	78.9	79.3

Ts of the crust leather /°C	76.1	83.9	84.1
thickening rate /%	57.1	87.3	90.1
exhaustion rate %	81.6	79.6	59.3
Softness	76	88	89

268

269 3.3 Thermal analysis

270 The thermodynamic analysis of leather is a reliable method to evaluate the thermal effect of
 271 chrome-free tanned leather. It can also reflect the effect of crosslinking on the advanced structure of
 272 leather. In this section, the thermal performance of wet-white tanned with ET was analyzed via TG
 273 and DSC, the untreated collagen was used as the control.

274 The pyrolysis property of leather is related to the cross-linking degree of collagen fibers. The cross-
 275 linking degree of collagen fibers is negatively related to the collagen mass of thermal
 276 decomposition^[20]. **Fig. 5** showed the TG curves of the ET, and the corresponding characteristic
 277 parameters of them are given in **Table. 4**. The first stage (I) is the vaporization of free water and
 278 bound water, the second stage (II) is the decomposition of collagen fibers, polymers and organic
 279 chemical materials used in tanning, and the third stage (III) is the decomposition of chemical bonds
 280 of polymers with collagen^[21]. According to the results, the crosslinking of ET can obviously slow down
 281 the thermal decomposition during the heating process, this is because the triazine ring structure in et
 282 can form stable sites between the collagen chains and play a role in fixing the collagen chains, but
 283 these are amorphous structures, which have limited effect on improving the thermal stability.

284 The thermal stability of different leather powder before and after tanning can be judged by the
 285 position, width, strength and area of the peak in DSC spectrum. The differential scanning calorimeter
 286 (DSC) has been used to elucidate the degradation profile of wet-white tanned with ET in response to
 287 heat and the thermal stability of collagen before and after tanning can be judged by the position,
 288 width, strength and area of the peak in DSC spectrum. As showed in **Fig. 6**, the decomposition peak of
 289 wet-white rises to 97.5°C while the decomposition peak of untanned collagen at 69.9°C, and the
 290 position of the peak obviously drifts to the high temperature zone and get wider, That is due to the
 291 stabilizing effect of the triazine structure on collagen advanced structure.

292



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294 **Fig. 5** TG curve of wet-white tanned with ET

295

296 **Table. 4** 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)

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301 **Fig. 6** DSC curve of wet-white tanned with ET

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303 **3.4 Zeta potential analysis**

304 Collagen is a typical amphoteric polyelectrolyte. The blocking state of $-\text{COOH}$ and $-\text{NH}_2$ in its
305 structure can be described through zeta potential to a certain extent. Specifically, when the carboxyl
306 group is blocked, the amino group is protonated and the molecule carry positively charged; in the
307 alkaline range, the carboxyl group is ionized, the peptide chain is hydrolyzed and broken, and the
308 molecule carry negatively charged. When the concentration of negatively charged carboxyl group is
309 equal to that of positively charged amino group in solution, collagen will be in the state of equal
310 charge^[22].

311 In this study, the Zeta potential of wet-white tanned with ET was investigated and the untreated
312 collagen was used as the control.**Fig. 7** shows the Zeta potential of wet-white tanned with ET at
313 different pH. After tanning with ET, the isoelectric point of collagen decreased from 4.71 to 2.85, that
314 means ET could react with the amino groups of collagen, a large number of amino groups in the side
315 chain of collagen were blocked, which indicated that the enhancement of acid resistance of wet-
316 white, which is consistent with the results in **Fig. 3**

317

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320 **Fig. 7** Zeta potential of wet-white tanned with ET

321

322 **3.5 XRD analysis**

323 In order to reveal the dispersion of ET in collagen, the white-wet tanned with ET was characterized
324 by XRD, and the untreated collagen was used as control group. In **Fig. 8**, there were two obvious
325 diffraction peak at 8° (A) and 22° (B). The (A) peak reflects the distance between the molecular chains
326 of the collagen fibers, and belongs to the α -helix region with more ordered structure ^[23]. The peak
327 shape of (A) got sharper, which indicated that the tanning process of ET broke part of hydrogen bond
328 and van der Waals force between collagen fibers to a certain extent, loose the fiber. The (B) peak
329 primarily due to the diffuse scattering caused by numerous structural layers inside the collagen fibers,
330 such as the β -fold with irregular zigzag structure ^[24]. After tanning with ET, the B peak moved to the
331 direction of low diffraction angle, which indicated that crosslinking had an effect on the secondary
332 structure of collagen and reduce the randomness of collagen braiding. There was no obvious change
333 of the diffraction peak at 43° , which indicated that ET tanning did not cause the change of collagen
334 crystalline region.

335



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337 **Fig. 8**XRD curves for wet-white tanned with ET.

338

339 **3.6 Physical performances of leather**

340 In order to evaluate the physical performances of wet-white tanned with ET, wet-white was
341 prepared with CTDT (9%) according to the process mentioned in **Table. 2** and wet-blue was
342 prepared with conventional chrome tanning method (6.5%). The subsequent neutralization and
343 fatliquoring process was carried out according to the conventional process and the results were
344 showed in **Table. 5**. As the results shown, the physical performances of ET tanned leather were better
345 than that of CTDT tanned leather, which was close to the physical performances of chrome tanning
346 leather. This is because there were more active chlorine in ET structure than CTDT, which could be
347 regarded as crosslinking sites when ET react with collagen. In addition, ET tanning can significantly
348 improve the softness of leather, which was due to the supporting effect of triazine structure between
349 leather fibers, and the lubricating effect of polyether chain segments in the gap between collagen
350 fibers ^[25], which gives leather excellent softness.

351

352 **Table.5**Physical performances of leather tanned with different method

Tanning agent	ET	CTDT	Chrome
Shrinkage temperature (°C)	83.9	74.3	109.2
Tensile strength (MPa)	16.19	14.1	18.31

Elongation (%)	65.1	66.9	65.2
Tear strength (N/mm)	47.93	38.9	60.21
Softness (mm)	8.8	9.1	7.8
Fineness of grain	++++	+++	++++
Fullness	+++++	++++	+++++

353

354 3.7 Whiteness analysis

355 The Lab values of leather were determined and compared with the standard reference to evaluate
 356 the whiteness of several leather tanned with different method. It can be seen from **Table.6** that the
 357 color difference between ET tanned wet-white and standard white is little, which is similar to that of
 358 CTDT tanned wet-white and obviously better than that of chrome tanned wet-blue. Besides, triazine
 359 derivatives can be coupled with subsequent dyes lead to a fixation effect, which present a wide
 360 application prospect.

361

362 **Table.6 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

363

364 3.8 Morphology analysis

365 **Fig.9** showed the SEM observation of leather tanned with three different method. It can be seen
 366 from the result that the fibers of wet-white tanned with ET were more dispersed compared with the
 367 conventional chrome tanned leather, there was no obvious adhesion between fiber bundles, and the
 368 boundary of basic fibers was clear. Compared with the wet white tanned with CTDT, The looseness of
 369 the fiber was similar, which indicates that the hydrophilicity of polyether chain in the ET structure
 370 was conducive to the entry of subsequent materials.

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373 **Fig. 9** SEM observation of fiber patterns of the leather with different tanning method.

374

375 **3.9 Environmental impact assessments**

376 To evaluate the impact of the ET tanning process on the environment, biochemical analysis of
 377 leather processing waste liquor was carried out to assess its ecological risks to the environment ^[26].

378 The ET tanning effluent was detected to evaluate the environmental impact parameters of the ET
 379 tanning method, and compared with CTDT tanning method and conventional chrome tanning
 380 method. It is shown in **Table. 7** that the residual Cl⁻ concentration in wastewater decreased 42.1% in
 381 tanning process compared to conventional chrome tanning method. The emissions of COD and TDS in
 382 tanning process reduced by 40.5% and 27.2%, respectively. The COD, TDS and TDC of ET tanning
 383 effluent were slightly lower than that of CTDT tanning effluent. Better biodegradability and no neutral
 384 salt had been introduced in the process of ET tanning indicated that the low environmental
 385 administration budget of ET tanning could benefit the development sustainably and provide inclined
 386 futuristic prospects for cleaner leather manufacturing.

387

388 **Table.7 Comparison of three tanning methods**

Items	Conventional chrome tanning	ET tanning	CTDT tanning
Neutral salt (%)	6	0	0
Chromium (%)	6	0	0
COD _{Cr} (mg/L)	2088.27±16.90	1242±21.20	1443.21±15.7
TDC (mg/L)	15360.13±96.40	8893.60±49.50	9844.40±69.90
TDS (mg/L)	52330.20±211.30	38118±171.12	37554.70±144.80
Undegradable pollutants	Neutral salt and chromium	—	—

389

390 **4. CONCLUSION**

391 Nowadays, a growing number of countries have implemented strict regulations for promote of
392 sustainable development. Adequacy in achievement of chrome-free tanning is put forward as a new
393 criterion for clean leather manufacturing. In this work, polyether amine triazine derivatives (ET) was
394 prepared via one-step process and a novel chrome-free tanning approach based on ET have
395 been established and evaluated comprehensively. ET has been confirmed to combine with the amino
396 group of collagen mainly in the form of covalent bond and produced crosslinking network in the
397 collagen structure, which greatly improved the thermal and physical properties of collagen. Due to
398 the existence of polyether chain in ET structure, part of hydrogen bond and van der Waals force in
399 collagen was broken, loosen fibers, and increased the softness of leather. In addition, the rigidity
400 structure of triazine ring in ET could make a significant contribution to the hygrothermal stability of
401 collagen, after tanning with 8% of ET at pH6 for 6h, the wet-white present shrinkage temperature of
402 83.9°C and thickening rate of 87.3%, the environmental impact assessments showed ET tanning shows
403 better environmental protection than conventional chrome tanning as well as CTDT tanning.

404

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407

408 **CRediT authorship contribution statement**

409 **Xinju Jia:** Conceptualization, Methodology, Formal analysis, Writing original draft.

410 **Ran Tan:** Validation, Data curation.

411 **Biyu Peng:** Funding acquisition, Supervision

412 **Declaration of competing interest**

413 The authors declare no conflict of interest.

414

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