Preparation and application of cyanuric chloride cationic chrome-free tanning agent

Xuyang Wang [1,2], Xihuai Qiang [1, 2], Chao Xie [3], Xuebin Ding [3]

[1] College of Bioresources Chemical and Materials Engineering, Shaanxi University of Science and Technology, Xi'an, 710021, China, 943064502@qq.com

[2] National Demonstration Center for Experimental Light Chemistry Engineering Education (Shaanxi University of Science & Technology), Xi'an, 710021, Shaanxi, China, qiangxihuai@163.com

[3] Decision New Material Technology Co., Ltd, Deyang, 618019, Sichuan, China, 1729906236@qq.com

Abstract

Traditional chrome-free tanning agents, especially organic chrome-free tanning agents, tend to enhance the electronegativity of the fibers of crust leather during the tanning, which is negative for the absorption and binding of anionic materials in the subsequent processes. In this research, two kinds of cyanuric chloride-based cationic chrome-free tanning agents (TADM and TYDM) were synthesized, and their preparations were characterized by Fourier transform infrared spectrometer (FT-IR) and nuclear magnetic resonance spectroscopy (^{1}H-NMR). The thermal properties and morphology of the tanned leather were analyzed by using thermogravimetric analysis and scanning electron microscope (SEM). The results indicated that the multi-point active chlorine groups in syntans had an excellent cross-linking effect on collagen fibers, which increased the shrinkage temperatures of leathers tanned by TADM and TYDM to 74.3°C, and 75.4°C, respectively. The tanned leathers exhibited flat and fine grain, clear pore texture, and highly dispersed collagen fibers. The tensile strength, tear strength, and load elongation of the TADM tanned leather were 22.38MPa, 65.86N/mm, and 21.88%, respectively, and those of the TYDM tanned leather were 35.85MPa, 72.87N/mm, and 27.46%, respectively. Based on dyeing experiments, both TADM and TYDM tanning agents can improve the absorption of anionic dyes and subsequent chemical materials. In addition, the TADM and TYDM tanning agents had excellent environmental benefits by significantly reducing the levels of total solids (TS), dissolved solids (DS), suspended solids (SS), and chloride compared with traditional chrome tanning technology.

Keywords: chrome-free tanning; no-pickling; cleaner production; syntans

1. Introduction

The entire world can produce 17.1 billion pieces of all kinds of rawhides every year, totaling about 13.1 million tons (Ran, 2021). If these rawhides are not used fully but dumped as waste, it will cause serious harm to the environment. At present, rawhide waste is mainly used in tanning, agriculture, medical materials, and other fields (Sundar et al., 2011; Buttafocl et al., 2006; Vidal et al., 2020; Borrajo et al., 2019). Tanning plays an important role in leather processing, and the key chemicals (tanning agents) used in its operation are the key factors that cause the qualitative change in rawhides (Chen et al., 2009).

Researchers have conducted many studies on chrome-free tanning agents and tanning methods, and have achieved remarkable results. Granofin F-90 tanning agent is prepared by replacing chlorine atoms on the triazine ring with sodium p-aminobenzenesulfonate using cyanide chloride (TCT) as crude material. F-90 tanning agent is suitable for softened leather tanning, which can reduce the tanning time and effectively avoid the harm of inorganic salts in the pickling section to the environment. The grain side of tanned leather is white and fine, the yellowing resistance is excellent, and the Ts can reach 74 ℃ (Lu., 2017; Sun et al., 2012). Zeolite tanning agent converts zeolite into a functionalized polymer structure to make it tanning by special means. The white wet leather tanned by it can be used as a crude material with excellent performance for leather making (Bacardit et al., 2014; Bacardit et al., 2016). TWT/TWS tanning agents are amphoteric organic macromolecules containing aldehyde groups, carboxyl groups, and tertiary amines, of which the smaller molecular weight is TWS tanning agents (Li et al., 2013; Luo et al., 2014).

This paper proposes a technical idea of the preparation of cyanide chloride cationic derivatives using cyanide (TCT) and tertiary amine compounds as crude materials, based on the reference of Starr's Granofin F-90 tanning agent, combined with the development of the industry and existing reports. The leather tanned by this tanning agent can make the wet dyeing material more easily absorbed and combined without changing the electrical properties of the collagen fibers of the raw skin, and can provide guidance for the cleaning production of chrome-free tanning and subsequent dyeing and finishing processes from both theoretical and practical aspects.

2 Material and method

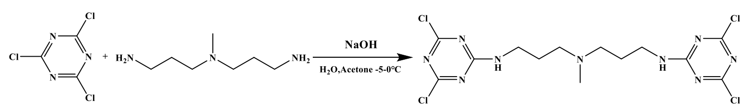
2.1 material

N-MethyldiethanolaMine, N, N-Bis (3-aminopropyl) methylamine, and cyanide chloride (AR), which were bought from Search banner reagents ltd. Other chemical materials (AR) used in the synthesis experiment were purchased from Sinopharm Chemical Reagents Co., Ltd. The materials for leather tanning are all commercial grade. Deliming softened sheepskin was made in the lab.

2.2 The synthesis of TADM/TYDM

First, added the mixture of cyanuric chloride, cold-treated acetone, and water (-5~ 0 ℃, $V_{acetone}$: V_{water} = 3:1) to the three-necked flask, and stirred the mixed system for 30 min with keeping the temperature at -5~0℃ to make it evenly distributed. Next, slowly dropped N-methyldiethanolamine or N, N-bis (3-aminopropyl) methylamine into the mixed system within 60-90 min with the stirring speed of the mixing constant and the pH of the system was less than 7. When the dropping is done, kept the reaction for 6~10 hours, and used sodium hydroxide solution (30%) to maintain the pH of the system between 5 and 6 meanwhile. Last, the mixed system was filtered under reduced pressure.

The synthesis reaction formula of TADM/TYDM is shown in Fig. 1.



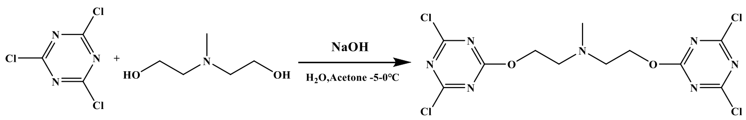


Fig. 1. The synthesis reaction formula of TADM/TYDM

2.3 The application of TADM/TYDM

2.3.1 tanning process

The tanning process was carried on in a quadruple stainless steel drum (GSD400-4, Wuxi Xinda Light Industry Machinery Co., Ltd.). In order to get the best tanning conditions, the tanning process was optimized by the single-factor experiment. The tanning process formula is listed in Table 1 (the dosage of tanning experimental materials is based on the weight of liming skin).

Table 1 TADM/TYDM tanning process.

Process	Material	Quantity/%	Temperature/°C	Time/h	Remark
Washing	Water	200	25		
	Degreasing agent	0.2		0.5	Drain
Tanning	Water	180/80	25		
	TADM/TYDM	15/15		2.0/1.5	
	Dispersed tannins	0.5			
	Penetrant	0.5			
Basifying	$NaHCO_3/Na_2CO_3$	1.5	35	2.0/1.5	pH=6.0
Diluting	Water	20	50	4.0/4.0	

Note: The solids content of TADM and TYDM tanning agents is 25% and 40% respectively.

2.3.2 Dyeing and oiling process

Took the crust tanned by a TADM/TYDM tanning agent under the optimal process (obtained by dividing the sheep-softened skin along the dorsal line and tanning) and let it age for 2~3 days, the moisture content of the crust was maintained at 40~50%, and then dyed and oiled it after weighing (the mass of the material in each step in the dyeing process is calculated as a percentage of this mass), and last compared TADM/TYDM dyed leather and F-90 dyed leather. The dyeing process formula was shown in Table 2.

Table 2 Dyeing and oiling process of TADM/TYDM tanning leather

Process	Material	Quantity/%	Temperature/°C	Time/min	Remark
Washing	Water	200	25	30	pH=6.5, Drain
Dyeing and oiling	Water	150			
	Direct red 23	2			

	SE Synthetic fatliquor	10	50	60	
Fixing	Formic acid（1:10）	1.0	40	60	pH=3.5~4.0, Drain

2.4 Detection and analysis

2.4.1 Infrared analysis

The infrared spectrum of the purified and dried TADM/TYDM powder was tested by the potassium bromide tableting method.

2.4.2 Nuclear magnetic analysis

Take 3 mg of the synthesized TADM/TYDM powder, dissolved it in an NMR tube with d-DMSO (deuterated dimethylsulfoxide) reagent, and performed nuclear magnetic hydrogen spectroscopy at 600MHz (AVANCE NEO 600MHz, Bruker, Germany).

2.4.3 Shrinkage temperature analysis

According to the standard method GB/T 2713-2005, measure the shrinkage temperature of the leather by using a collagen thermal deformation analyzer (TMA-YD4, Institute of Sunshine Electronics, Shaanxi University of Science and Technology, China).

2.4.4 Microscopic morphology analysis

The microscopic morphology of leather includes grain surface which can reflect the surface convergence property to a certain degree and longitudinal section surface that can show the dispersion degree of collagen fibers before and after tanning. Sampled ($2*2mm^2$) from the leather sample, and measured its microscopic morphology by field emission electron fiber microscopy (Vega 3 SBH, Tescan Co., Czech) at a field voltage of 15kV after being freeze-dried and surface sprayed with gold.

2.4.5 Mechanical property analysis

The physical and mechanical properties of leather mainly refer to tensile strength and tearing strength. After dyeing and oiling the tanned leather, measured the tensile strength and bilateral tear strength of the sample leather according to standard methods. Sampled and measured from the dyed and oiled leather using standard sampling area.

2.4.6 XRD analysis

XRD measurements were carried out in an X-ray diffractometer (XRD, D8 Advance, Bruker Co., Germany).

2.4.7 TG-DSC analysis

Thermogravimetric analysis (dry thermal stability analysis) was performed in a synchronous thermal analyzer (STA, 449F3-1053-M, Netzsch, Germany).

2.4.8 Exhaustion rate of dye

The exhaustion rate is an essential important indicator reflecting the absorption property of dyes by materials. The rate is calculated according to the dyeing standard curve and the change of absorbance of the dyeing waste liquid.

2.4.9 Biological properties (COD_{Cr}/BOD_5)

The values of COD_{Cr}/BOD_5 can be used to characterize the biodegradability of water samples, thereby indicating the easy degradability of organic. Compared the biological properties of waste produced by TADM/TYDM tanning and F-90 tanning. And compared and analyzed the absorption properties of each tanning agent and the absorption performance of tanning to fatliquor. Biochemical oxygen demand and chemical oxygen demand were determined by standard method HJ505-2009 and potassium dichromate method HJ 828-2017.

3 Results and Discussion

3.1 Chemical structure of TADM/TYDM

3.1.1 Characterization of TADM/TYDM by FT-IR

Fig. 2 shows the infrared spectrum of TADM/TYDM. In the infrared spectrogram of TADM (Fig. 2a), the N-H stretching vibration absorption peak is at 3240cm^{-1}; $-CH_2$-stretching vibration absorption peak is at 2972cm^{-1} and 2788cm^{-1}; 1610cm^{-1} is the stretching vibration absorption peak of C=N in the triazine ring skeleton; 1406cm^{-1} is the stretching vibration absorption peak of $-CH_3$; 1232,1048cm^{-1} is the characteristic absorption peak of the triazine ring skeleton, and 788 cm^{-1} is the stretching vibration of C-Cl (compared with the peak of the triazine ring skeleton on cyanide at 1517,1269cm^{-1}, C-Cl at the peak at 844 cm^{-1}, and the absorption peak is redshifted), combined with the above analysis, it can be proved that the objective product TADM was successfully prepared.

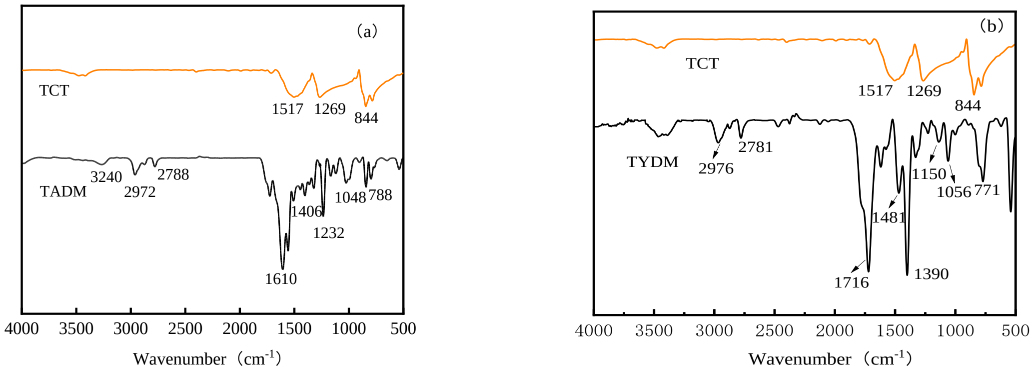


Fig. 2. FT-IR spectrum of TADM (a) and TYDM(b)

In the TYDM infrared spectrum (Fig. 2b), 2781cm^{-1} is the methylene stretching vibration; 2976cm^{-1} and 1390cm^{-1} are the stretching vibrations of $-CH_3$; 1716cm^{-1} is the stretching vibration of C = N in the homogeneous triazine ring; 1150cm^{-1} is the stretching vibration of the ether bond; 1481,1056 cm^{-1} is the characteristic absorption peak of the triazine ring skeleton, and 771 cm^{-1} is the C-Cl stretching vibration (compared with the triazine ring skeleton in cyanide, which peaks at 1517cm^{-1},1269cm^{-1}, and C-Cl peaks at 844 cm^{-1}, The absorption peak is redshifted). Combined with the above analysis, it was proved that the objective product TYDM was successfully prepared.

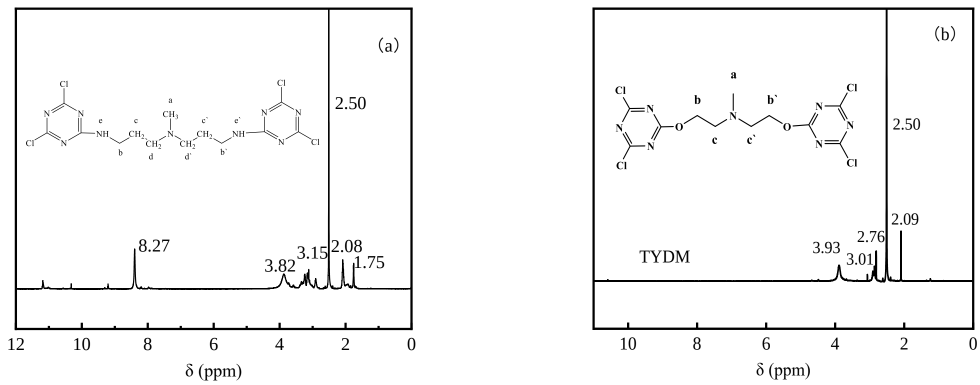


Fig. 3. ^{1}H-NMR spectrum of TADM(a) and TYDM(b)

3.1.2 Characterization of TADM/TYDM by ^{1}H-NMR

Fig. 3 shows the hydrogen NMR spectrum of TADM/TYDM. Fig. 3a shows the ^{1}H-NMR (600 MHz, δ, ppm) spectrum of TADM. From the spectrum, it can be seen that the characteristic peak of the solvent is δ = 2.50 ppm (DMSO-D6); the characteristic peak of TADM is δ = 8.27 ppm [TCT-NH-CH_2-, (e, e `)], δ= 3.82 ppm [-NH-CH_2-CH_2-, (b, b ')], δ = 3.15 ppm [-CH_2-CH_2-N-, (d, d')], δ = 1.75 ppm [-CH_2-CH_2-CH_2-, (c, c ')], δ = 2.08 ppm [- (CH2) 2-N-CH_3, a]. Combined with the above analysis, the objective product TADM was successfully prepared.

Fig. 3b shows the 1H-NMR (600 MHz, δ, ppm) spectrum of TYDM. From the spectrum, it can be seen that the characteristic of the solvent is δ = 2.50 ppm (DMSO-D6); the characteristic peak of TYDM is δ = 3.93 ppm [O-CH_2-CH_2-, (b, b `), δ = 2.76 ppm [-CH_2-CH_2-N-, (c, c ')], δ = 2.09 ppm [- $(CH_2)_2$-N-CH_3, a]. Combined with the above analysis, it can be seen that the objective product TYDM was successfully prepared.

3.2 Hydrothermal stability

Compare and analyze (Fig 4) the shrinkage temperature (Ts) of each crust and can be seen: TWS tanning crust has the highest Ts, which is 89°C, indicating that the TWS tanning fiber has a high degree of cross-linking and has a better tanning effect on the hide. The Ts of TYDM, TADM, and F-90 tanning crust are 75.4°C、74.3°C、74°C, respectively. It can be found that the shrinkage temperatures (Ts) of these three tanning leathers are the same.

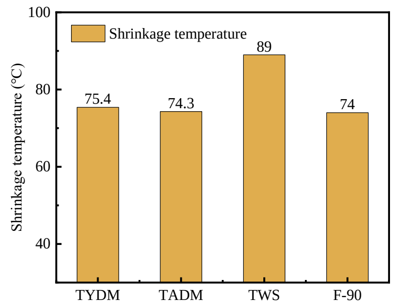


Fig.4 Hydrothermal stability of tanned leather

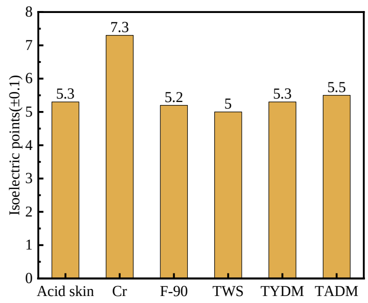


Fig.5 Isoelectric point of each tanned fiber

3.3 Isoelectric point of crust leather

As can be seen from Fig. 5, the order of the isoelectric points of the pickled skin and each tanning leather fiber is chrome tanned leather > TADM tanned leather > TYDM tanned leather > pickled skin > F-90 tanned leather > TWS tanned leather. The isoelectric points of F-90, TWS, TYDM/TADM tanned crust leather fibers are lower than traditional chrome tanning leather, which indicates that each tanning agent has an inferior ability to absorb subsequent anionic materials compared with chrome tanned leather. The isoelectric point of F-90 and TWS tanning leather fibers is low because of the strong anionic characteristics the tanning agent itself has, although amphoteric tanning agents can partially supplement the cation city of fibers in the tanning process, they are relatively rare, so the external performance is a slight reduction in the isoelectric point. TADM/TYDM tanning leather fiber has a higher isoelectric point compared with pickled skin, that is the anion city tanning agent molecular owns, can supplement the atonicity of the fiber well in the tanning process.

3.4 Thermal stability

From Fig. 6 (A) thermogravimetric curve, it can be seen that the thermal decomposition trend of leather samples (untanned raw leather and tanned green leather) is consistent. The first stage is losing weight slightly. The second stage is losing weight rapidly. The third stage is losing weight steadily, When the outside temperature is 450~600℃, the refractory substances in the skin are further carbonized in the thermal environment, and the weight loss of leather is relatively gentle (Liu, 2019; Lyu et al., 2018).

As can be seen from Fig. 6 (B), when the external temperature is 100℃, the order of skin weight conversion is TADM > TYDM > raw skin. When the external temperature was 450℃, the order of skin weight conversion is raw skin > TADM > TYDM. Considering the relationship between peak tanning temperature (T_p) and weight loss rate (-DTG) and conversion rate (α) (Table 3), when each tanning temperature reaches peak temperature (T_p), the relationship between the weight loss rate of tanning is: raw skin > TADM > TYDM, the weight loss rate is positively correlated to the weight conversion rate of the leather. The weight loss rate of TYDM/TADM tanning leather is lower than that of raw skin. The weight loss rate of TYDM tanning is the lowest, indicating that when the external temperatures are the same, the thermal decomposition of TYDM tanning leather per unit of time is slower than that of other tanning leather.

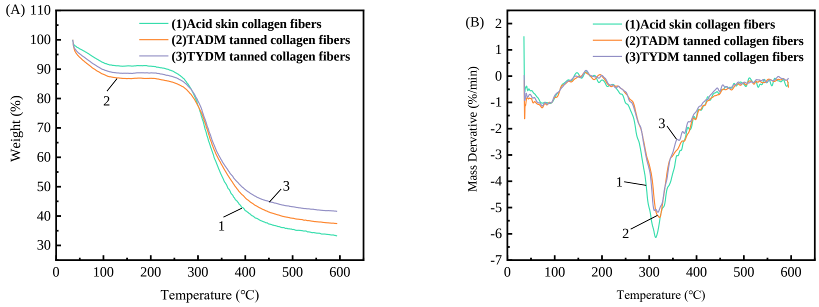


Fig.6 (A)TG and (B)DTG Acid skin collagen fibers, TADM, and TYDM tanned leather fibers

Table 3 Weight loss in different thermogravimetric stages tanned after tanning agents.

Project	Acid skin	TADM	TYDM
Peak temperature (T_p)/℃	312.3	321.3	320.5
percent conversion(α)/%	30.1	32.2	30.4
-DTG/(%/min)	6.08	5.27	5.13

3.5 SEM analysis

Fig. 7 and Fig.8 are the SEM comparative analysis images of TYDM/TADM tanning agent tanned leather and untanned skin. As can be seen from Fig. 7, the untanned sheep skin's three-dimensional collagen fiber bundles lose water and transform into a two-dimensional stacking structure after being dried, which shows a smooth particle surface, while dispersed particle surface pores and poor three-dimensional effect from a macro perspective. The grain surface convergence of TYDM/TADM tanned leather is obviously enhanced compared with untanned skin, and the grain surface pores have a three-dimensional sense, which contributes crust's thickening and feeling improvement. The particle surface convergence of tanned leather: TADM > TYDM.

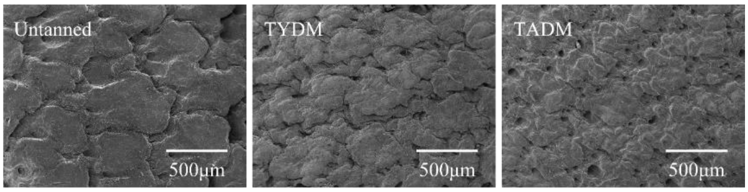


Fig.7 SEM image of crust leather grain

From Fig. 8, it can be seen that after the untanned leather block is dried, the longitudinal section fiber bundles are compact and the surface is smooth; The longitudinal section fiber bundles of TYDM/TADM tanned leather are relatively dispersed and the surface is rough, indicating that the cross-linking effect of tanning agent and collagen fibers builds a stable link between the collagen fiber bundles, the force between the intradermal fiber bundles is enhanced, which shows the loosely arranged fiber bundles from a macro perspective. The dispersion degree of the longitudinal section of TYDM/TADM tanning leather fiber is basically consistent with the damp and heat stability of each tanning leather fiber, that is, the higher the dispersion of tanning fiber to a certain extent, the higher the shrinkage temperature of crust and the order of size is TYDM > TADM.

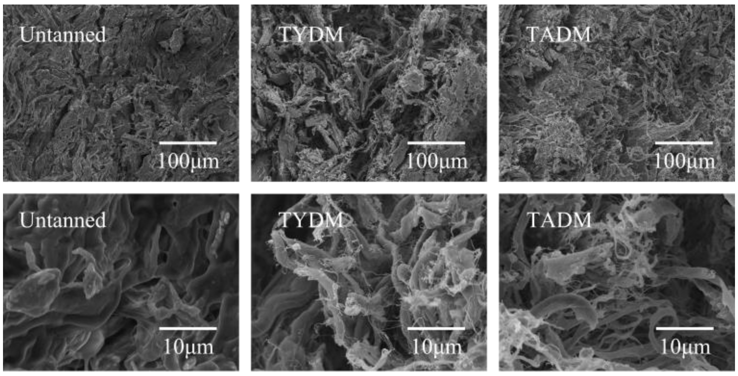
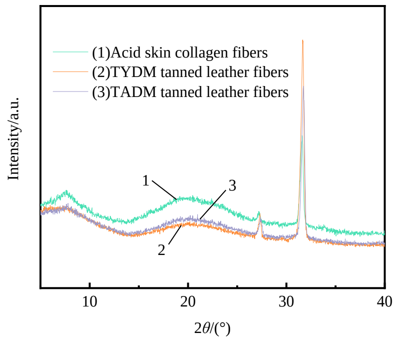


Fig.8 Section SEM images of crust leather



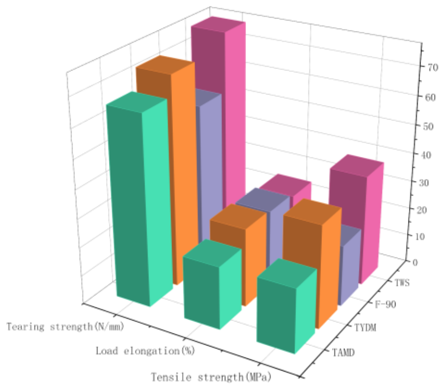


Fig.9 XRD patterns of three fibers

Fig.10 Physical and mechanical properties tests of leather

3.6 XRD analysis

Fig. 9 shows the XRD diffraction patterns of each tanned leather. It can be seen from the spectra that when 2θ is in the range of 5° ~ 40°, the diffraction peak spectra of TYDM/TADM tanned leather and untanned leather are the same in macroscopic view, indicating that the diffraction peaks in this range are highly correlated with the structure of collagen fibrin. The diffraction peaks are weak and wide in the range of 5° ~ 10°. It is speculated that this is the diffraction peak of the collagen fiber chain spacing, and the structure belongs to the α-helical region with an ordered structure on the collagen fiber. The diffraction peak is wide in the range of 15 °~ 25°, and it's formed due to the diffuse reflection of the collagen fibers with a complex structure that belongs to the amorphous region of the disordered collagen fiber structure. The diffraction peak intensity is high and the peak shape is narrow in the range of 25° ~ 40°, and it's speculated to be the three-stranded helix height diffraction peak of collagen fibers here (Yu et al., 2020). As mentioned above, TYDM/TADM tanning agent has a slight impact on the crystallinity of collagen fibers in raw skin, and the effect between this series of tanning agents and collagen fiber only shows the elongation of chain cross-linking and the amorphous interaction.

3.7 Mechanical strength

Fig. 10 shows the physical and mechanical properties of each tanned leather. The results show that: tensile strength: TWS > TYDM > TADM > F-90; specified load elongation: TYDM > F-90 > TWS > TADM; bilateral tear strength: TWS > TYDM > TADM > F-90.

3.8 Exhaustion rate analysis

Table 4 exhibits a comparison of the dyeing properties of different tanning agents. It can be seen from it that the order of absorption rates of each dye is: TADM > TYDM > F-90 > TWS. The exhaustion rate and residual liquid state of crust tanned by different tanning agents show that it is a complex process to tan leather with a tanning agent, and a cationic tanning agent can improve the absorption and bonding of anionic dyes and subsequent chemical materials to a certain extent compared with traditional tanning agent.

Table 4 Comparison of dyeing properties of tanned leather with different tanning agents.

Project	Dye-uptake/%	Residual liquid senses	Dry and wet rubbing fastness/grade	
			Dry rubbing	Wet rubbing
TYDM	95.77	Cloudy, dark, and bright red	3-4	1-2
TADM	96.29	Transparent and dark color	4	2
TWS	94.69	Cloudy and dark red	3	1
F-90	95.47	Cloudy, dark, and bright red	3-4	1-2

3.9 Biological toxicity

Table 5 shows the biodegradability of substances according to different B/C values (Wang et al., 2011). According to the test results, the B/C values of TYDM and TADM are 0.551 and 0.483, respectively, and the B/C values of tanning agents are all greater than 0.45, indicating that these tanning agents are easy to biodegrade, and the tanning agent itself is also an environmentally friendly material, which provides a direction for the development of ecological tanning agents.

Table 5 The relationship between the value of BOD_5/COD and the biodegradability of the organic tanning agent.

BOD_5/COD	>0.45	0.3~0.45	0.25~0.30	<0.25
Biodegradability	easier	easy	difficult	more difficult

4 Conclusion

FT-IR and ^{1}H-NMR prove that the object products are prepared successfully. TADM and TYDM tanning technology can directly tan without pickling, which can effectively reduce the pollution of salt in the waste produced during leather manufacture.

The active chlorine at both ends of TYDM and TADM molecules can combine with the amino groups in the collagen fibers to form a cross-linked network structure with strength, improving mechanical properties and shrinkage temperatures of leather.

Both tanning agents can avoid the problem of the decrease of the catholicity of tanning leather collagen fiber, the absorption and binding properties of dye in subsequent wet processing section are better than those of F-90. Both tanning agents have a little effect on the crystallinity of fibers. At the same time, these two tanning agents have great biodegradability.

Acknowledgments

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