Metal-Free Tanning Technology Enabled by Self-Catalysed *Triglycidylamine*: A Sustainable Alternative to Chromium-Based Process

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Contents

◆ Leather Industry : Efficient Utilization of Animal Biomass Resources

Leather manufacturing is a great creative undertaking of humanity's utilization of nature.

Breeding industry

"By-products"

Raw hides

Manufacturing

Waste to wealth

Leather

Leather products

01 Background

◆ **Tanning is the most important operation in the leather manufacturing process.**


Raw Hide


Beamhouse


Tanning


Wet Finishing


Coating


Finished Leather

√ Enhance shrinkage temperature

√ Improve physical and mechanical properties

√ Increase resistance to microbes and chemical reagents

◆ The essence of tanning is the cross-linking reaction between tanning agents and the active groups on collagen fibers, forming a stable cross-linked network structure.

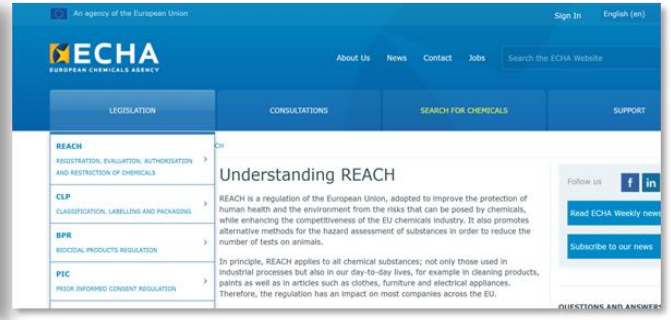
◆ Common tanning agents

- **Chrome tanning agent**
  - High Ts
  - Good performance
  - High tanning efficiency
- **Vegetable tannins**
  - Eco-friendliness
  - Dark brown color
  - Low yellowing resistance
- **Aldehyde tanning agents**
  - Light color
  - Formaldehyde
  - REACH-regulated

Chrome tanning faces challenges:

Effluent

Solid waste

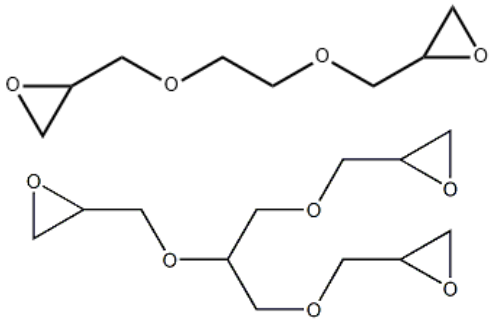


EU REACH: Cr (VI) ≤3mg/kg

◆ The development of chrome-free tanning agent has become a research hotspot.

01 Background

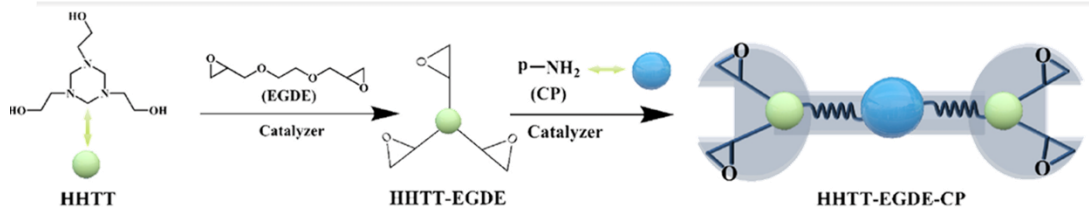
◆ Epoxy tanning agents received extensive attention because the epoxy functional groups can react with reactive groups on collagen side chains.



Ethylene glycol diglycidyl ether（EGDE）

Glycerol triglycidyl ether（GTE）

Functional modification

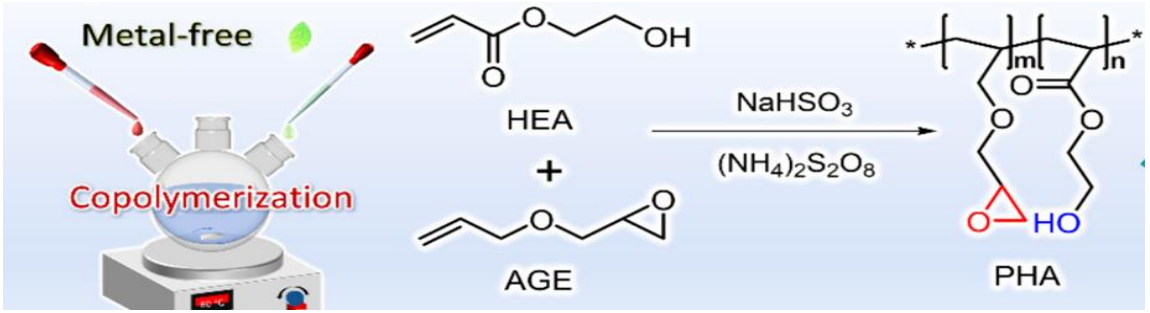


Xuechuan Wang. Journal of Cleaner Production 404 (2023) 136917*

Epoxy modified low molecular peptide

Xuechuan Wang.Science of the Total Environment 867 (2023) 161531*

Copolymerization



Taotao Qiang. Sustainable Materials and Technologies 45 (2025) e01574*

01 Background

◆ The current problems with epoxy tanning agents include the following:

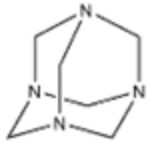
1. Poor Water Solubility

The poor water solubility of epoxy tanning agents affects their penetration into collagen fibers and prolongs the tanning time. This leads to lower tanning efficiency.

2. Higher Molecular Weight +Low Epoxy Content

Enhancing water solubility requires modification of the epoxy compound, which unfortunately increases its molecular weight and hinders penetration. Moreover, this modification consumes epoxy groups, reducing both group content and crosslinking capacity.

3. Toxic Catalyst: Methenamine



Toxic catalysts need to be added to accelerate the crosslinking rate, but it endanger human health. Not meeting environmental requirements.

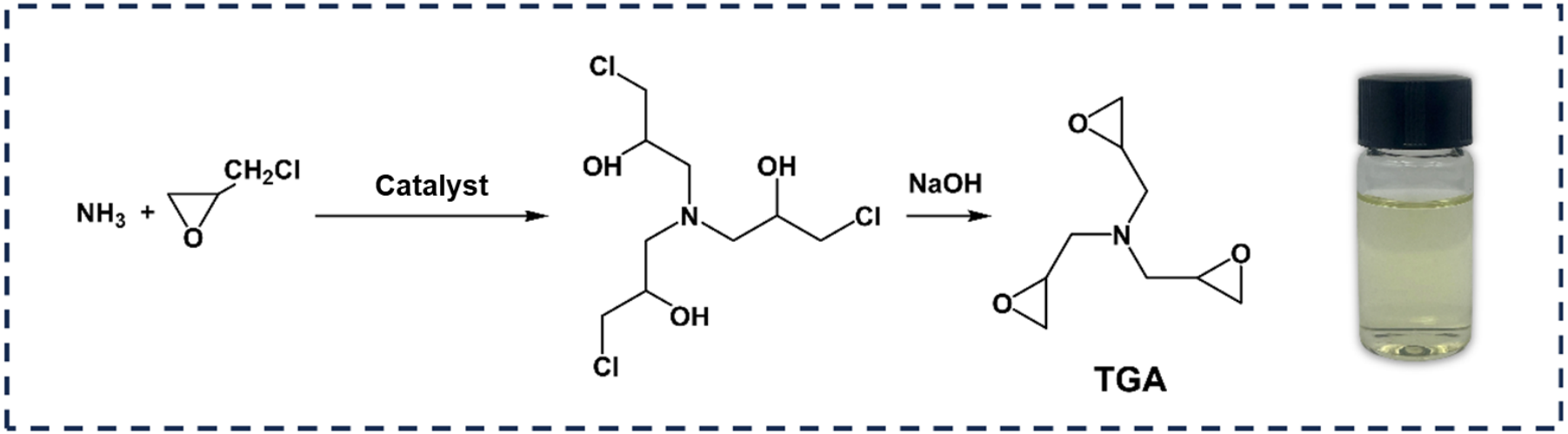
◆ Objectives of this work

◆ **In response to the current problems with epoxy tanning agents, we proposed the Triglycidylamine (TGA) tanning agent.**

- **solubility**
- **High reactivity**
- **Self-catalytic capability**

➢ Synthesis of Triglycidylamine (TGA)

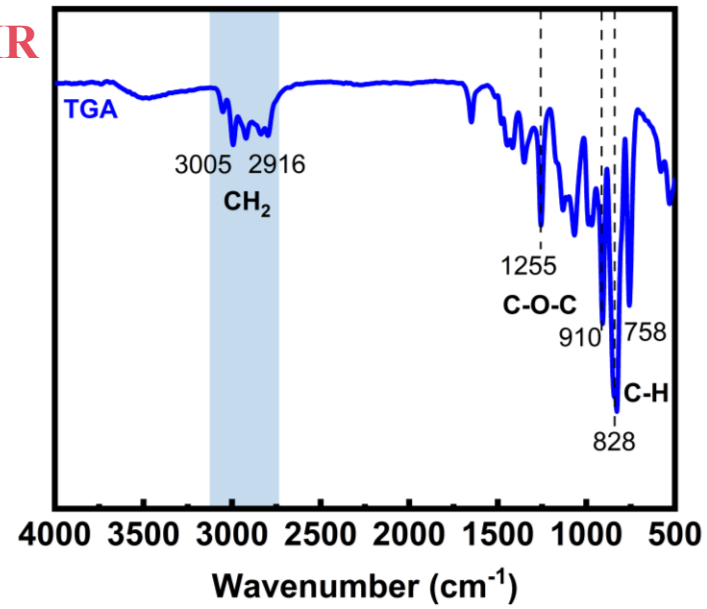
The TGA was synthesized from ammonia and epichlorohydrin.



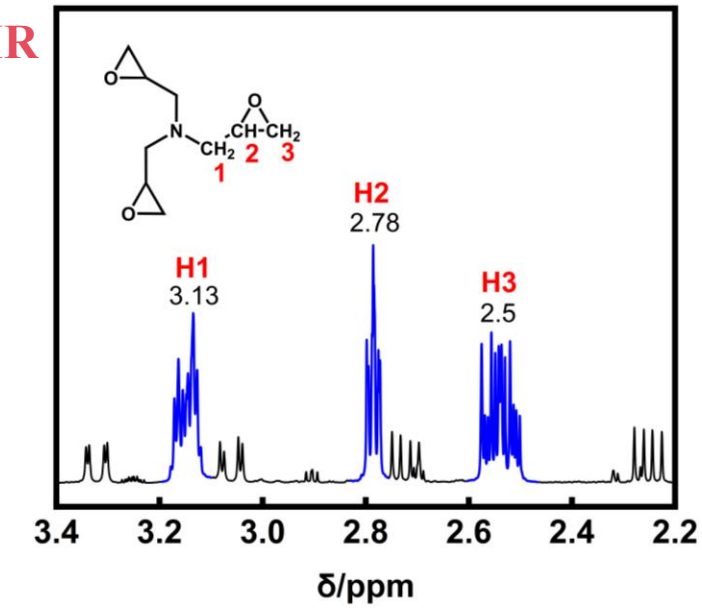
As determined by chemical analysis, the TGA exhibited an epoxy value of 1.54 (theoretical value: 1.62).

Structural Characterization of TGA

◆ FTIR



◆ ^{1}H NMR



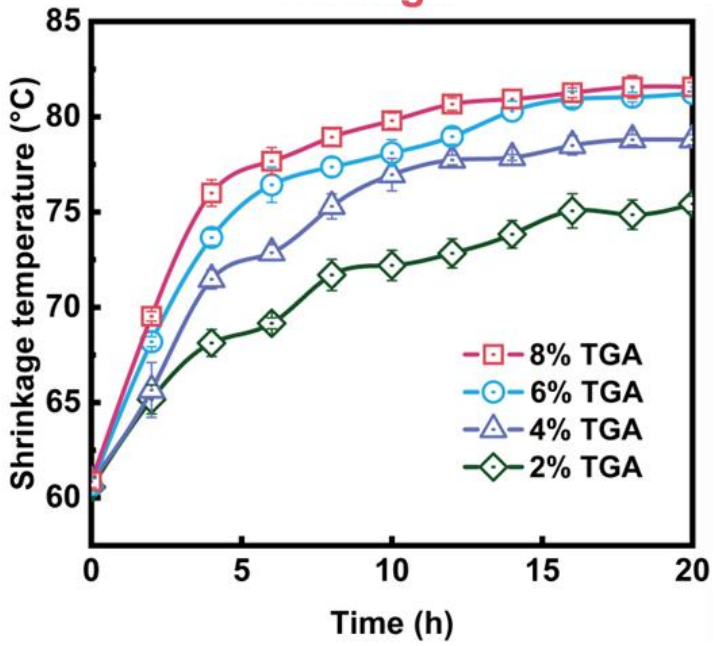
1. The absorption peaks at 1255 cm^{-1} and 910 cm^{-1} correspond to the stretching vibration of C–O–C in the epoxy group.

2. The chemical shifts at 3.13, 2.78, and 2.5 correspond to the proton absorption peaks of –NCH_2 (H_1), –epoxy CH (H_2), and –epoxy CH_2 (H_3) in TGA.

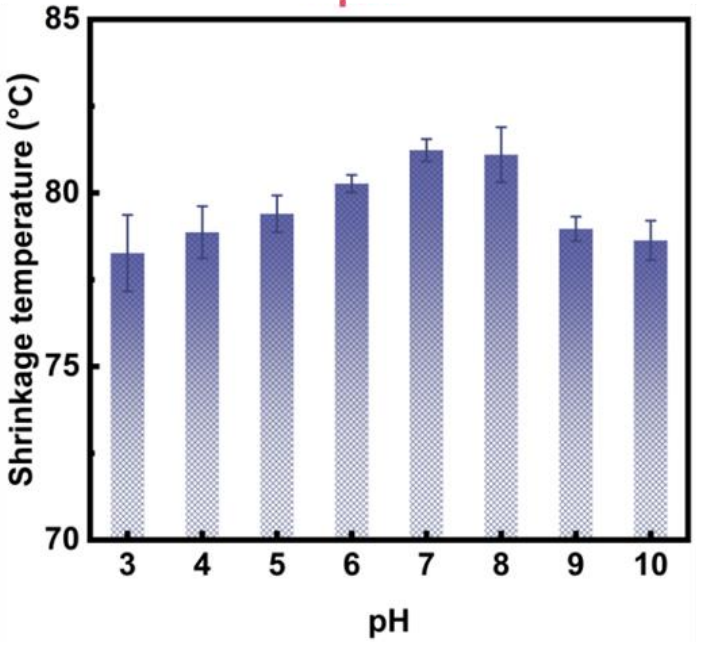
The structure of TGA was confirmed by FTIR and NMR.

Optimisation of TGA Tanning Process

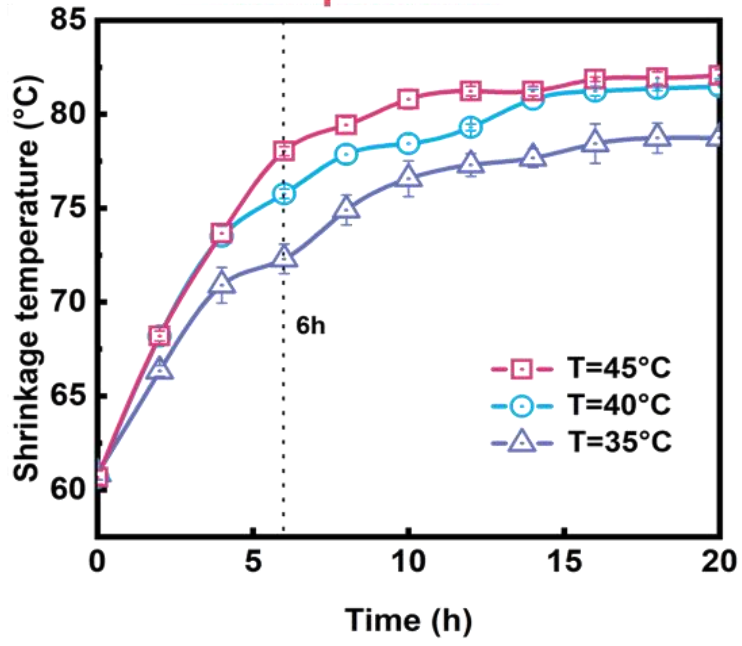
◆ Dosage



◆ pH



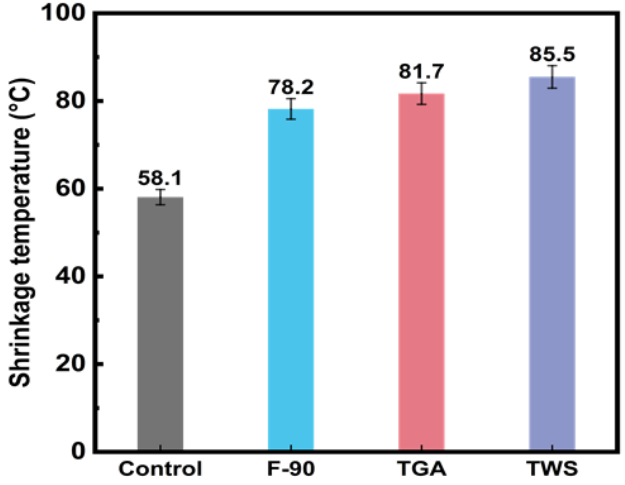
◆ Temperature



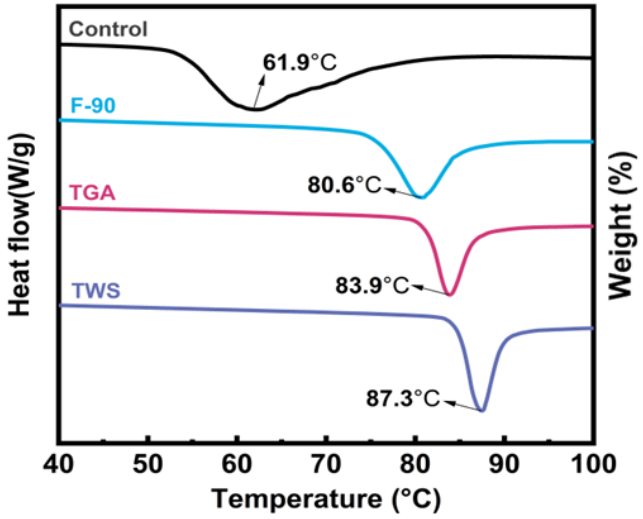
◆ **The optimal tanning conditions were determined. The initial pH value is 7-8, the tanning time is 18 hours, the tanning temperature is 40 ℃, and the TGA dosage is 6%.**

Thermal Stability of tanned leather

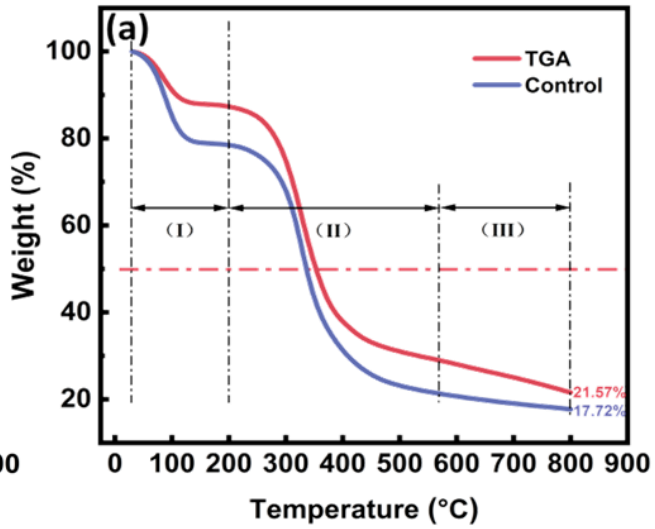
◆ Ts



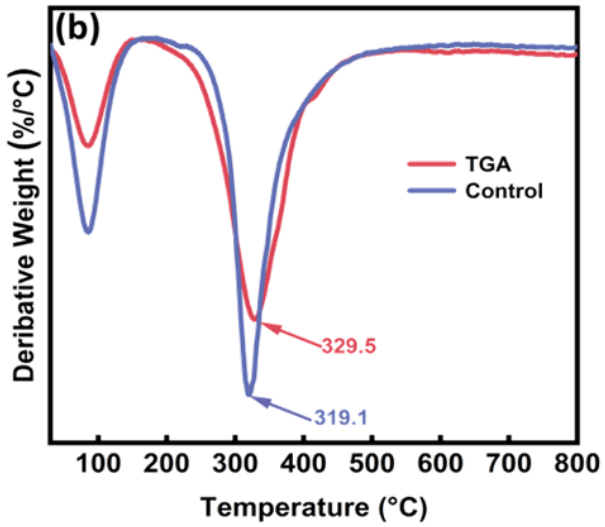
◆ DSC



◆ TG



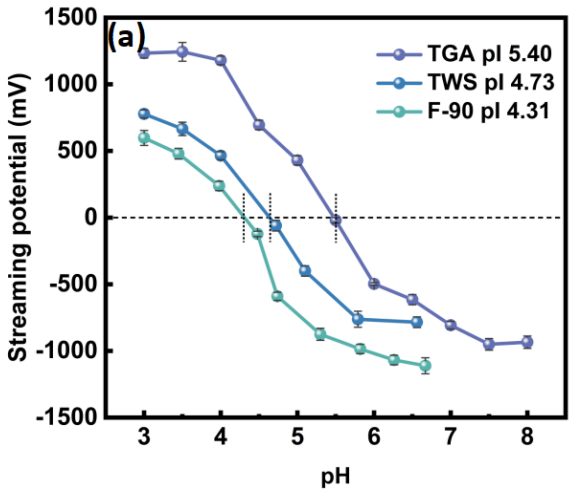
◆ DTG



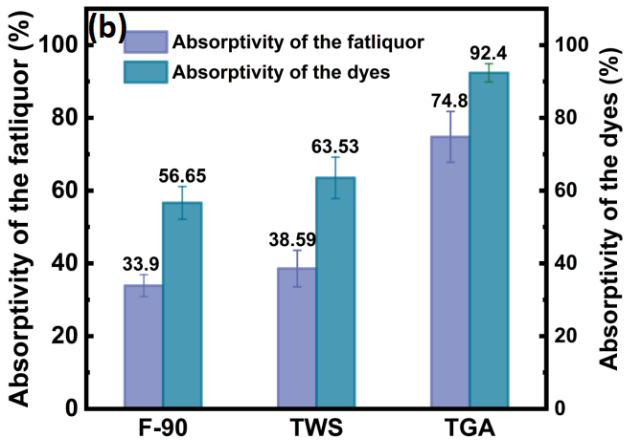
◆ **The shrinkage temperature of TGA tanned leather can reach 81.7 ℃, indicating good thermal stability. According to the DSC method, the denaturation temperature can reach 83.9 ℃.**

Evaluation of The Uptake of Dyes and Fatliquors

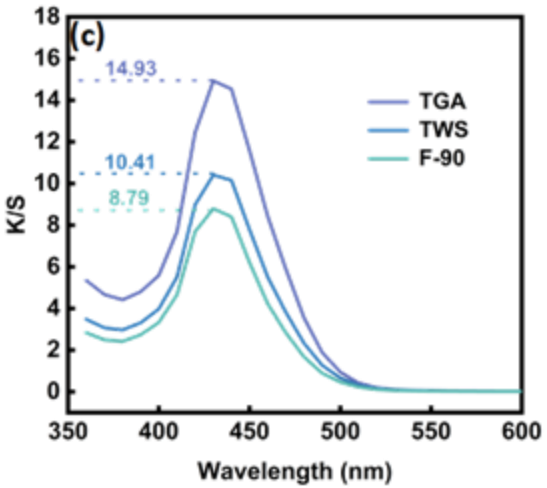
- Isoelectric Point



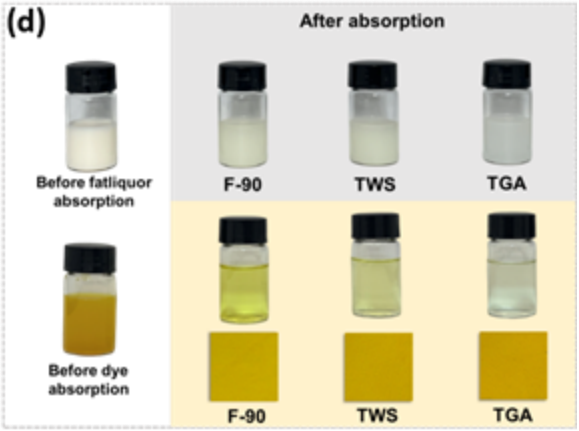
- Absorption Rate



- K/S

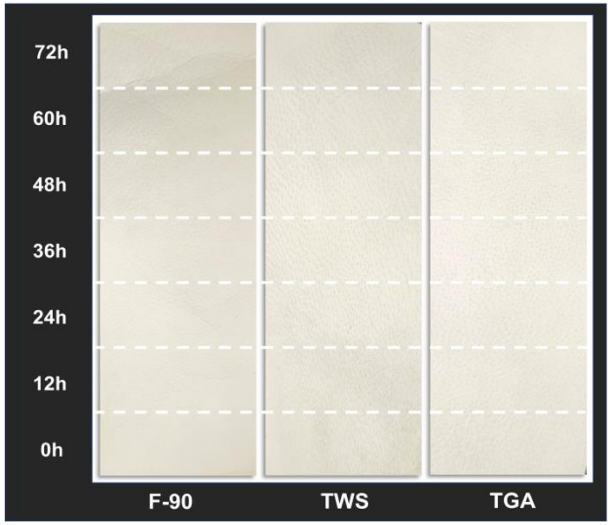


- Effluent Images



- The isoelectric point of TGA tanned leather is 5.40, significantly higher other organic tanning agents. Meanwhile, the TGA-tanned leather exhibited good uptake rates for both anionic dyes and fatliquors.

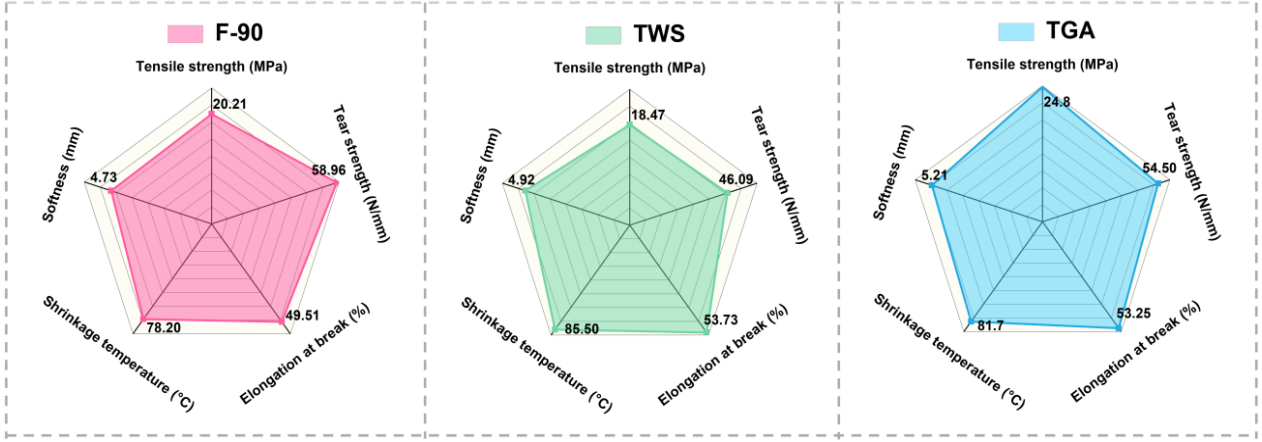
Yellowing Resistance



Sample	12h	24h	36h	48h	60h	72h
F-90	0.82±0.11	1.11±0.23	1.19±0.24	1.75±0.13	1.88±0.14	1.96±0.22
TWS	0.89±0.13	1.53±0.18	1.62±0.22	1.76±0.18	1.79±0.15	1.85±0.13
TGA	0.56±0.10	0.73±0.08	0.88±0.09	1.02±0.11	1.12±0.08	1.18±0.10

TGA-tanned leather has excellent yellowing resistance.

Mechanical Properties



Mechanical Properties	F-90	TWS	TGA	Standards
Tensile strength (MPa)	20.21±0.67	18.47±0.51	24.8±0.44	≥10
Tear strength (N/mm)	58.96±1.22	46.09±0.98	54.5+1.32	≥20
Elongation at break(%)	49.00±0.32	53.75±0.67	53.25±0.55	35~75
Ts (°C)	78.2±0.43	85.5±0.56	81.7±0.30	——
Softness (mm)	4.73±0.22	4.92±0.25	5.21±0.18	——

TGA-tanned leather exhibits good mechanical properties

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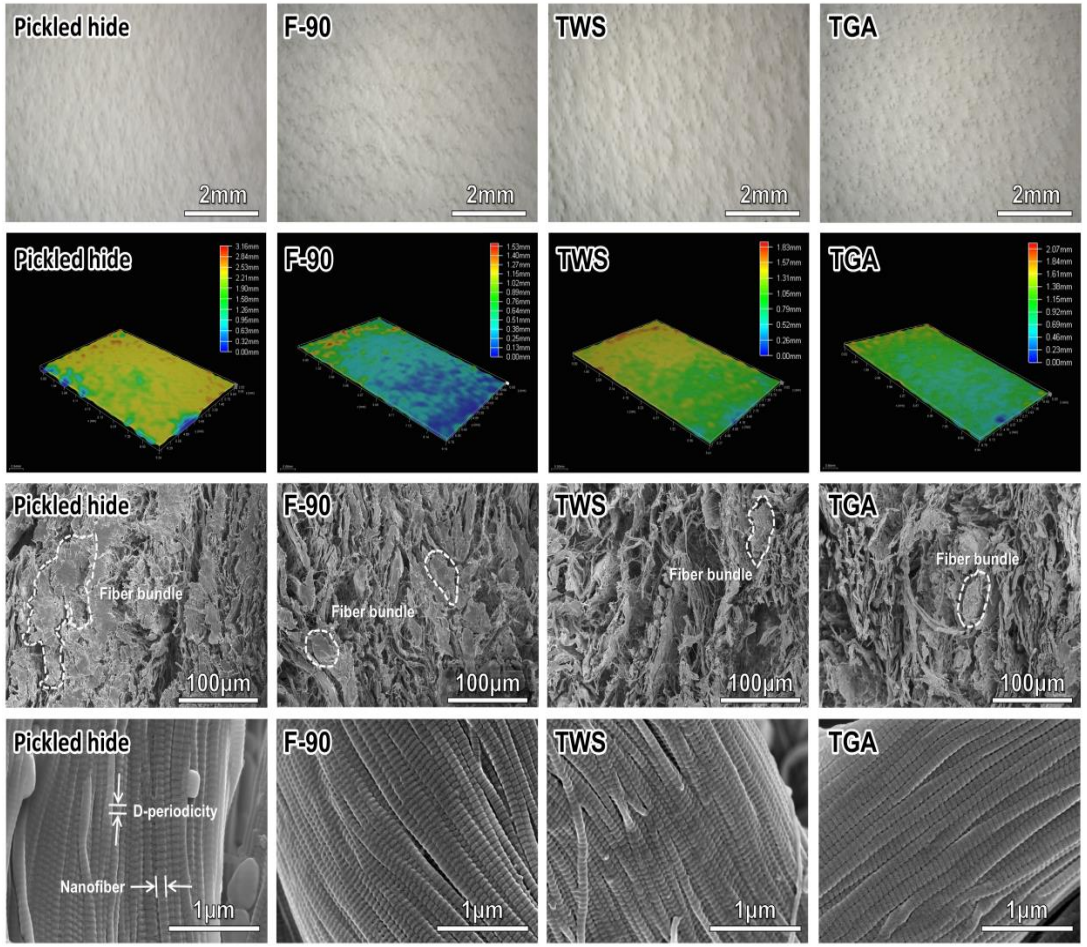
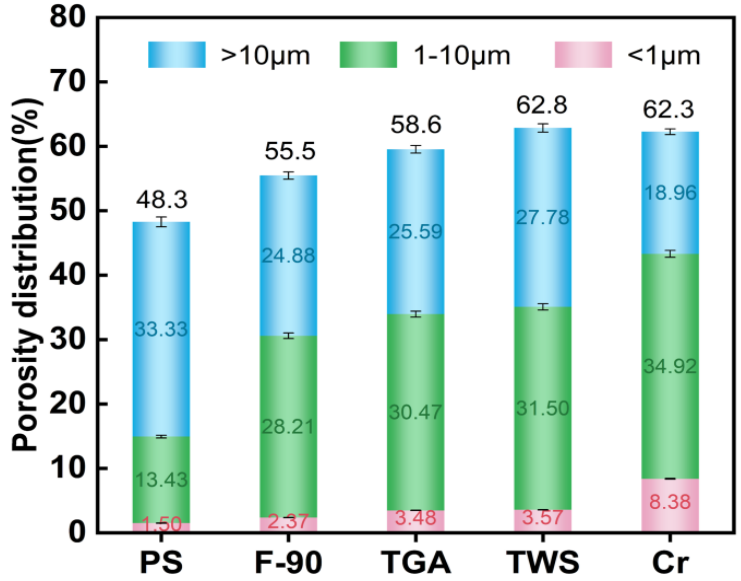
Morphological Observation

- SDM-2D
- SDM-3D
- SEM



Pore Structure and Pore Size Distribution



- After TGA tanning, the collagen fibers of leather are fully dispersed.
- The leather exhibited an increased proportion of small pores and medium pores ,with a decrease in large.

Degradability of tanning effluent

◆ Environmental evaluation index of tanning effluent

Sample	COD_{Cr}(mg/L)	BOD_5(mg/L)	BOD_5/ COD_{Cr}
F-90	2050±23	680±29	0.33
TWS	1630±31	430±35	0.26
TGA	1812±37	821±41	0.47

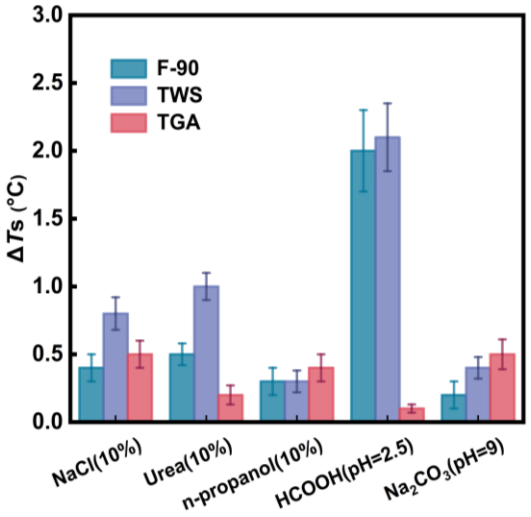
TGA tanning effluent was easily biodegraded.

Speculation of The Tanning Mechanism

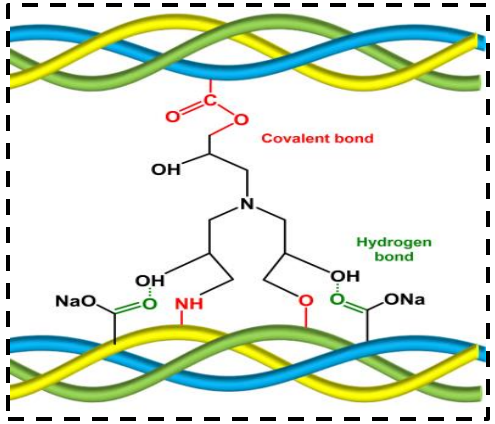
Analysis of amino acid content

Amino acid	Pickled skin	TGA-tanned leather	TGA reaction	
	ESTD conc/nmol	ESTD Conc/nmol	Conversion/mol/%	
Asp	0.449	0.399	11.14%	-COOH
Thr	0.217	0.198	8.76%	
Ser	0.368	0.333	9.51%	
Glu	0.791	0.709	10.37%	
Gly	3.125	2.758	11.74%	
Ala	0.994	0.875	11.97%	
Val	0.194	0.177	8.76%	
Met	0.057	0.018	68.42%	
Ile	0.108	0.105	2.78%	
Leu	0.244	0.236	3.28%	
Tyr	0.072	0.005	93.06%	-OH
Phe	0.198	0.118	40.40%	
Lys	0.283	0.042	85.16%	$-NH_2$
His	0.05	0.005	90.00%	
Arg	0.498	0.445	10.64%	
Pro	1.247	1.051	15.72%	

Chemical reagent stability



Schematic illustration



- Through amino acid analysis, TGA can react with the amino ($-NH_2$), hydroxyl (-OH), and carboxyl groups (-COOH) of collagen fibers.
- The TGA tanned leather has high resistance to both acidic and alkaline conditions, indicating the formation of covalent bonds.

02 Research Contents

◆ Tanning application of pilot scale—Longhua Material Technology Co., Ltd.

◆ The tanned crust leather received excellent evaluation from industry experts!

◆ Certified Third-Party Analysis

检 测 报 告

样品外观照片

无铬鞣白湿革

样品名称：无铬鞣白湿革

序号	检测项目		检测方法	技术要求	检测结果	单项判定	备注
1	收缩温度（℃）		QB/T 2713-2005	/	93.0	/	/
2	甲醛含量（mg/kg）		GB/T 19941.2-2019	/	未检出 检出限 20	/	/
3	重金属含量（mg/kg）	Cr	GB/T 22930.2-2021	/	42.3 (以绝干计) 检出限 1.0	/	/
		Al		/	102.1 (以绝干计) 检出限 1.0		
		Ti		/	58.4 (以绝干计) 检出限 1.0		
		Fe		/	89.0 (以绝干计) 检出限 1.0		
		Zr		/	4.4 (以绝干计) 检出限 1.0		

TGA provides a new approach for chromium free tanning.

Aldehyde-free & Metal-free

Ecological Leather

03 Summary

- **A new metal-free tanning agent, triglycidylamine (TGA), synthesized from ammonia and epichlorohydrin.**
- **TGA features a high epoxy value (1.54 mol/100g) and self-catalysed tanning capability.**
- **TGA-tanned leather exhibits good hydrothermal stability (Ts 81.7°C) and mechanical properties, and higher absorption rate for anionic dyes and fatliquors.**
- **The TGA tanning effluent showed good biodegradability (BOD_5/COD_{Cr}=0.47), reducing the burden of wastewater treatment.**

04 Acknowledgements

- Thanks toThe XXXVIII IULTCS CONGRESS
- Thanks to all members of our research group
- National Natural Science Foundation of China (Grant No. 22078165)

Thank you for your attention!