Preparation of Novel Leather Chemicals Based on Reactive Liquid Salt

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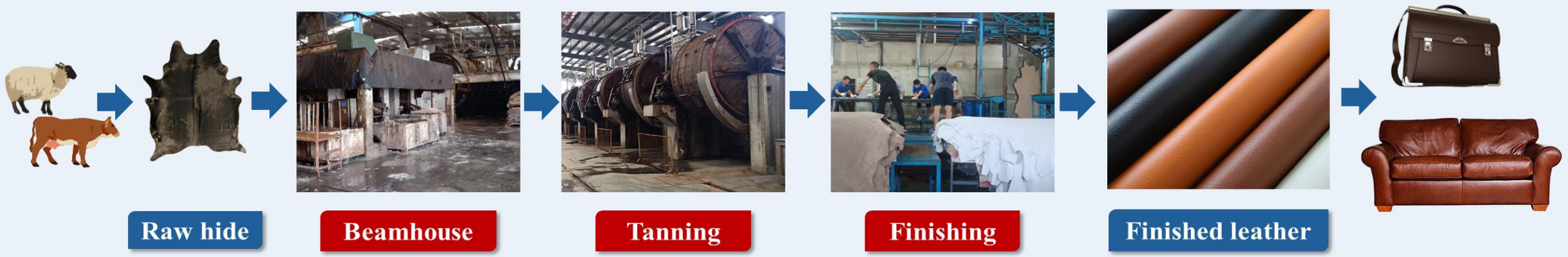
Contents

Background

The leather industry transforms raw hides into leather products through chemical treatments and mechanical processing.

Leather Industry



Different leather chemicals are required for various operations of the leather industry!

Background

With the improvement of living standards and the enhancement of sustainable development awareness, consumer demands for leather products have increased, driving innovation in leather chemicals.

Chrome-free Tanning Agent	*Multifunctional Fatliquors*	*Water-Based Coating Agent*
· *Triazine Derivatives*	· *Low Fogging Value*	· *Self-Cleaning Type*
· *Epoxy Compounds*	· *Light Resistance*	· *Antibacterial Type*
· *Nano Materials*	· *Waterproof Type*	· *Self-Repairing Type*

- Leather chemicals are advancing toward eco-friendly, safe, and multifunctional solutions!

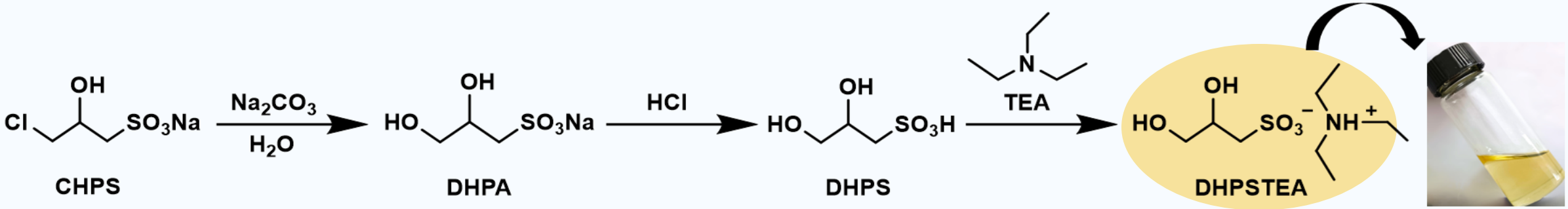
- ***One** Major Finding*
- ***Three** Innovative Products*

One Major Finding:

DHPSTEA—A New Reactive Liquid Salt

Preparation of New Reactive Liquid Salt ——DHPSTEA

2,3-Dihydroxypropanesulfonic acid triethylamine salt (DHPSTEA) was synthesized from Sodium 3-chloro-2-hydroxypropane sulfonate by hydrolysis, acidification, neutralization and purification.



• Physical properties

Appearance	pH	Solubility				
		Water	DMF	Methanol	Acetone	CCl_4
Transparent liquid	7	√	√	√	×	×

★ Advantages

- *Eco-friendly characteristics*
- *Excellent reactive stability*
- *Efficient operability*
- *Easy application*

Innovative Product One:

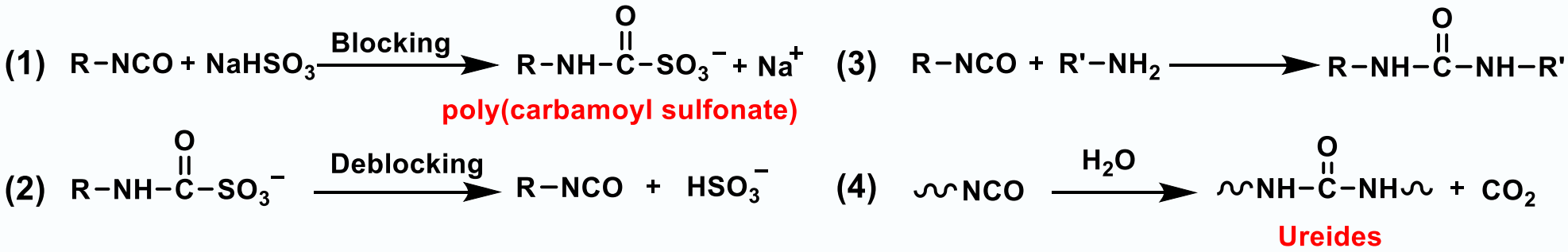
Preparation of Poly(Carbamoyl Sulfonate)

Tanning Agent Via DHPSTEA

Research Contents

Poly(carbamoyl sulfonate) emerges as a blocked polyurethane that can release NCO groups under certain conditions, reacting with compounds containing active hydrogen, such as -NH_2 or -OH.

Reaction Mechanism

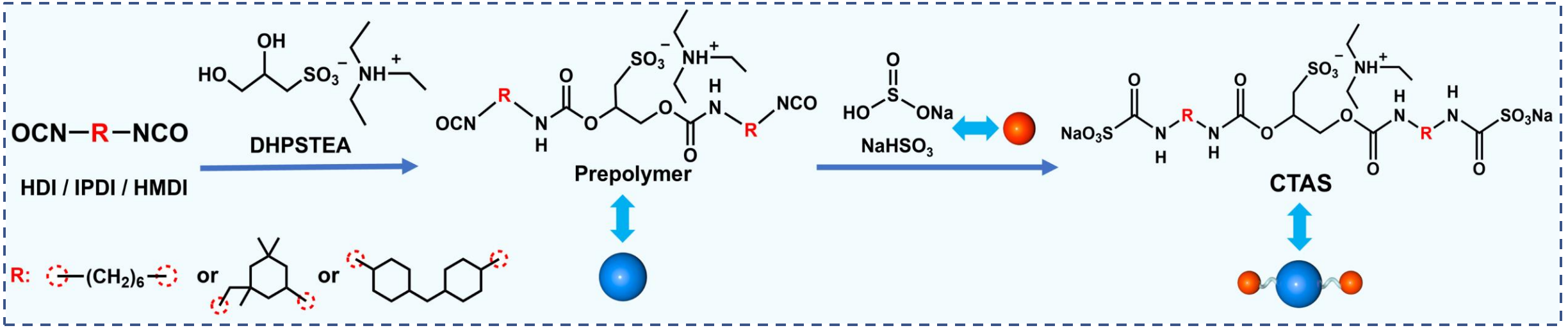


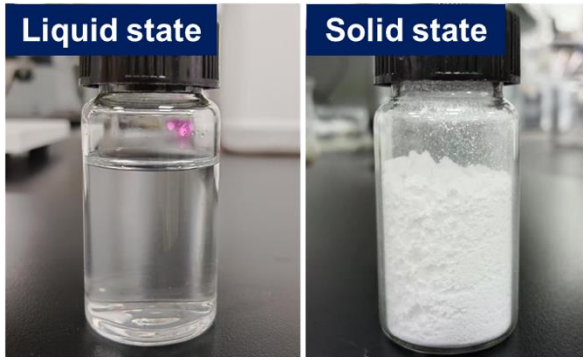
Existing Issues

- **Direct Blocking：** Homogeneous reaction requires cosolvent, increasing the product's VOC.
- **Prepolymer Blocking:** During DMPA chain extension, acidic $NaHSO_3$ solution reduces carboxyl hydrophilicity, yielding a low product blocking ratio (85~90%).

Propose using DHPSTEA to replace carboxylic acid chain extender!

Preparation of Poly(carbamoyl sulfonate) Tanning Agent via DHPSTEA.

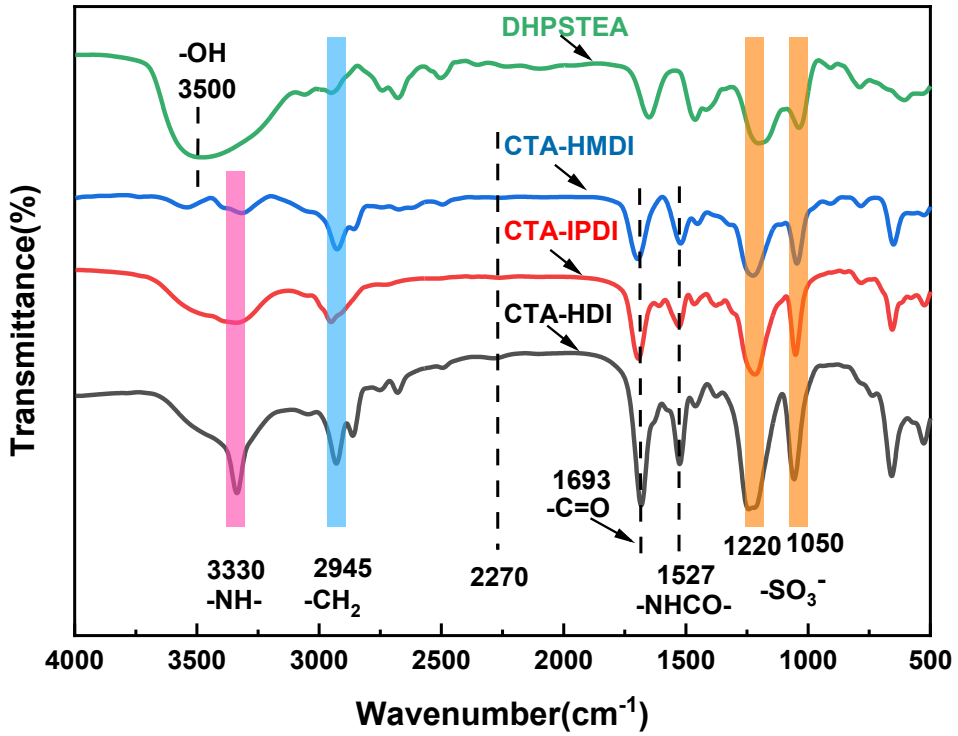




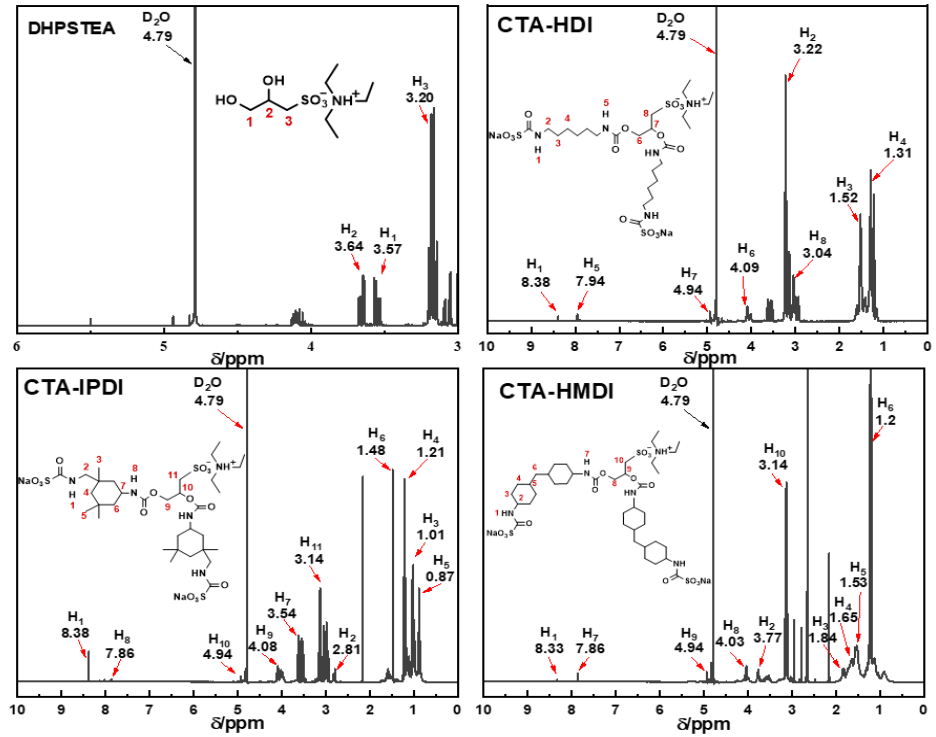
- *CTAS demonstrated over 99% blocking ratio !*
- *Synthesis process without cosolvent!*
- *Product with high water-solubility!*

Structural Characterization of DHPSTEA and CTAS

FTIR



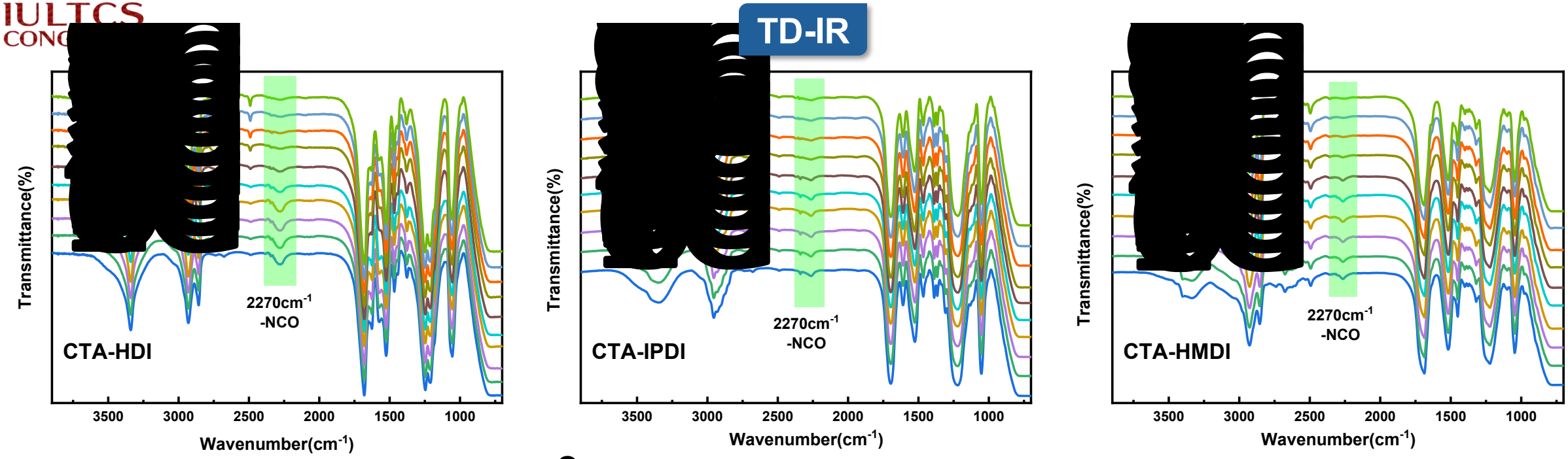
^{1}H-NMR



- **DHPSTEA and CTAS were successfully prepared.**

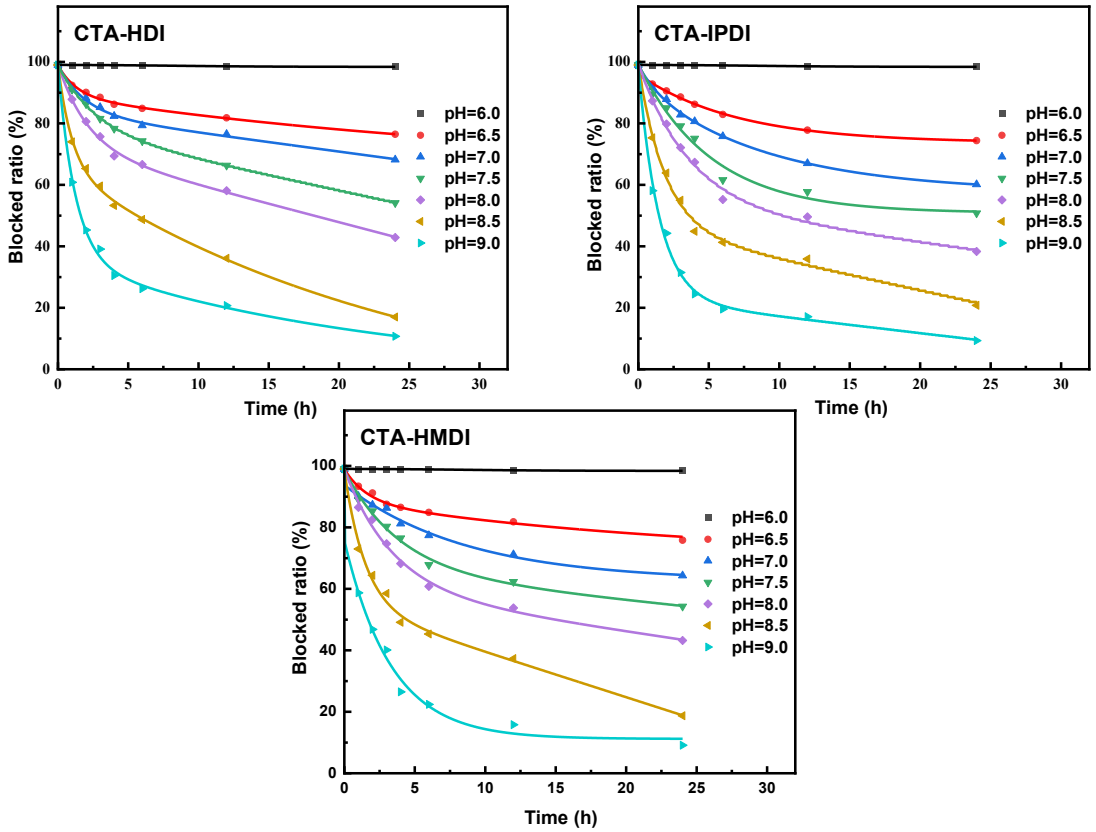
Determination of CTAS Deblocking Behavior—Temperature

TD-IR



- CTAS exhibit a deblocking temperature above 110°C and remain stable at room temperature.

Determination of CTAS Deblocking Behavior—pH



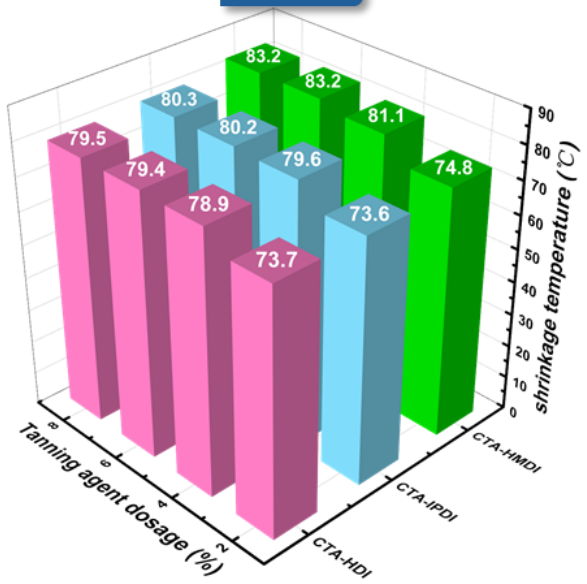
Process	chemicals	quantity/%	duration/min	Temperature/℃	pH
Depickling	Water	200		28	
	NaCl	10	10		
	$NaHCO_3$	2	10×3+60		6.5
Washing	Water	200	10	25	
Tanning	Water	100		25	
	CTAS	X	120		6.0
Basification	MgO	1	180	30	7
	MgO	1	180	35	7.5
	MgO	1	180	40	8
Washing	Water	200	10	25	

It is recommended to use MgO to gradually raise the pH of the tanning process.

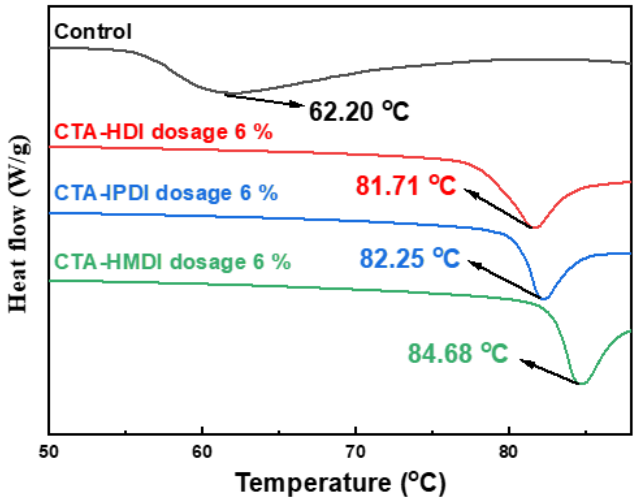
- CTAS exhibit pH-sensitive and readily deblock under alkaline conditions.

Tanning Properties of CTAS

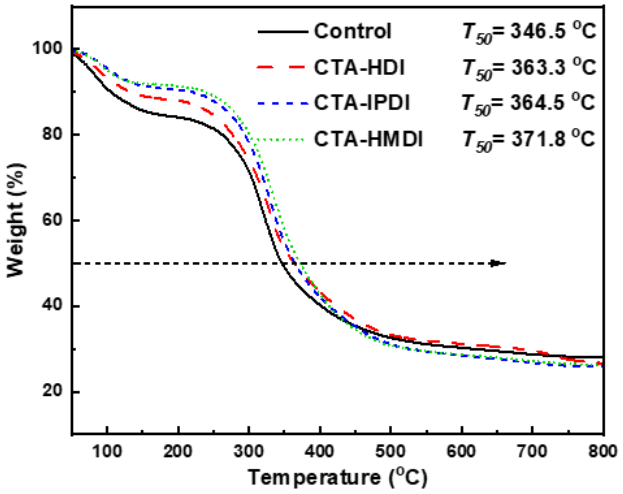
Ts



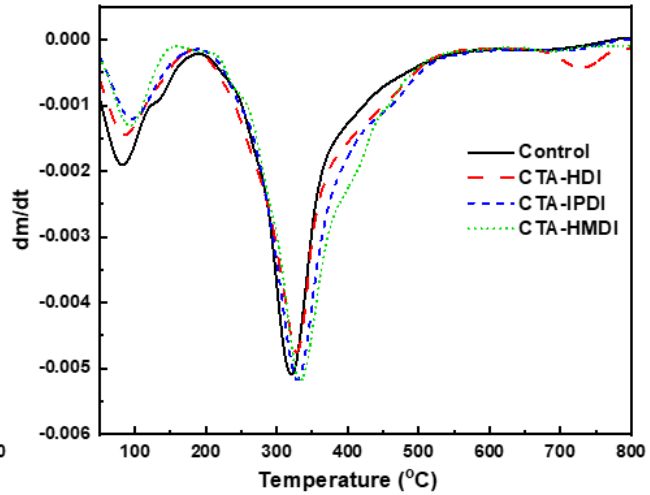
DSC



TG



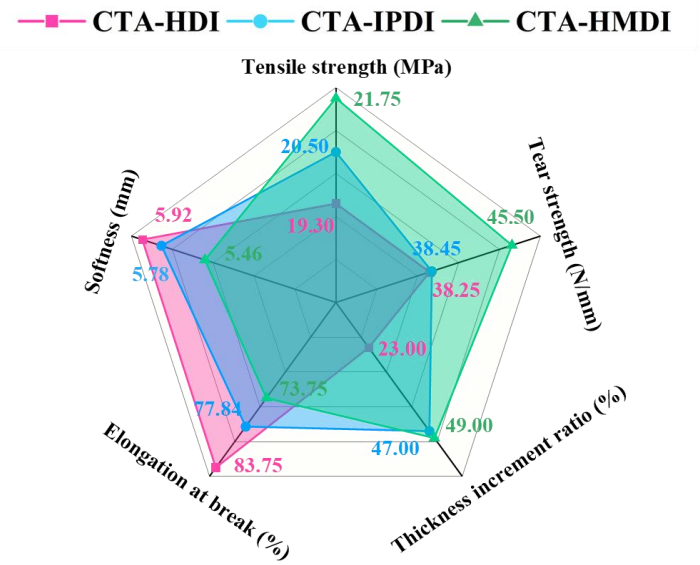
DTG



- **CTAS can significantly improve leather's thermal stability (Ts = 83.2℃ at 6% CTA-HMDI).**

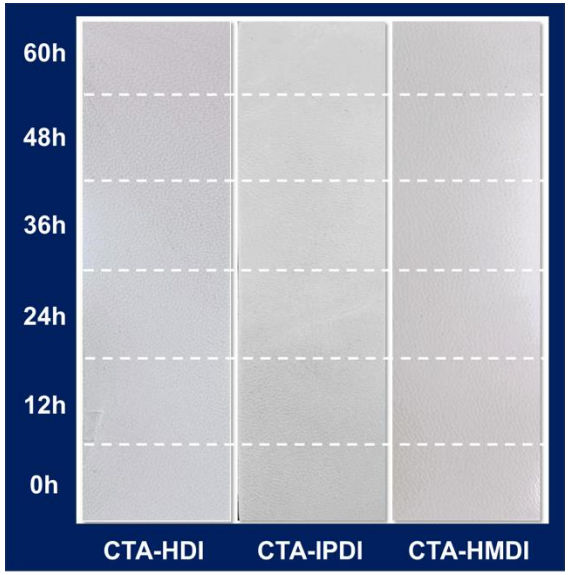
Research Contents

Mechanical Properties



Physical properties	CTA-HDI	CTA-IPDI	CTA-HMDI	Standards
Tensile strength (Mpa)	19.30	20.50	21.75	≥10
Tear strength (N/mm)	38.25	38.45	45.50	≥20
Elongation at break (%)	83.75	77.84	73.75	35~75
Thinkness increment ratio (%)	23.00	47.00	49.00	—
Softness (mm)	5.92	5.78	5.46	—

Yellowing Resistance

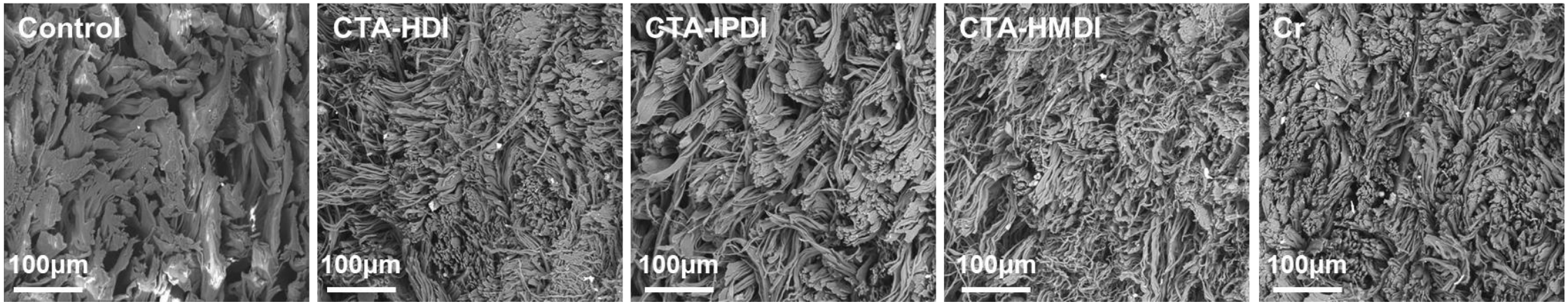


Time	CTA-HDI	CTA-IPDI	CTA-HMDI
12h	0.97±0.06	0.98±0.10	1.14±0.21
24h	1.14±0.11	1.69±0.07	1.12±0.24
36h	1.11±0.12	1.19±0.06	1.08±0.14
48h	1.03±0.13	1.19±0.08	1.07±0.23
60h	1.45±0.01	1.10±0.14	1.18±0.11

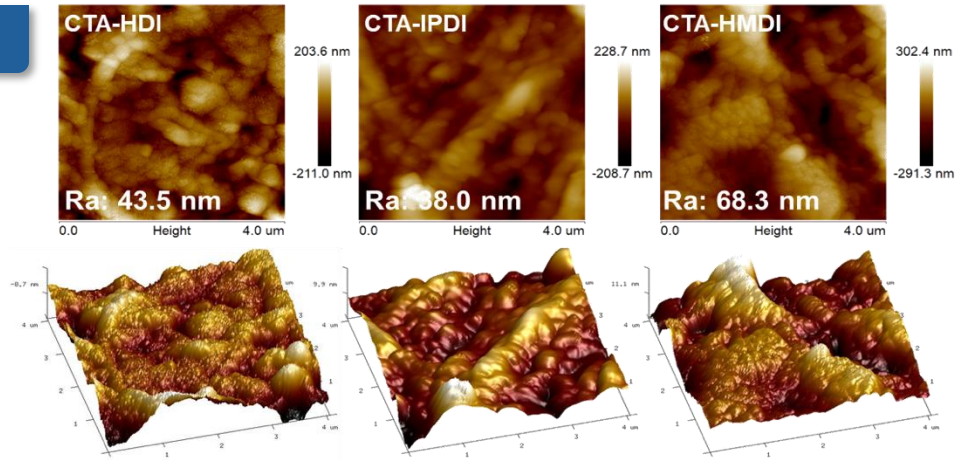
- CTAS tanned leather exhibits excellent mechanical properties and yellowing resistance.

Morphological Observation and Pore Structure Analysis

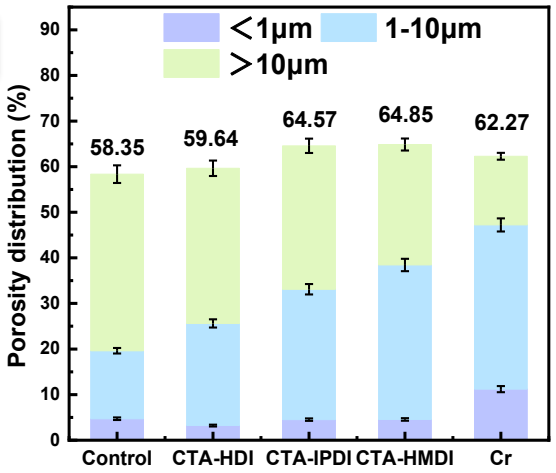
SEM

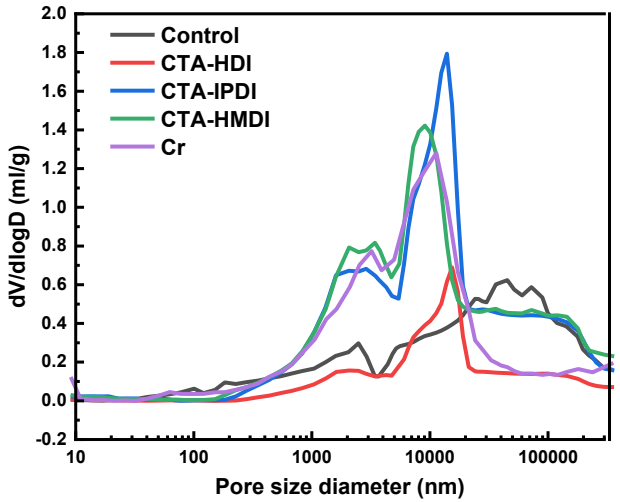


AFM



MIP

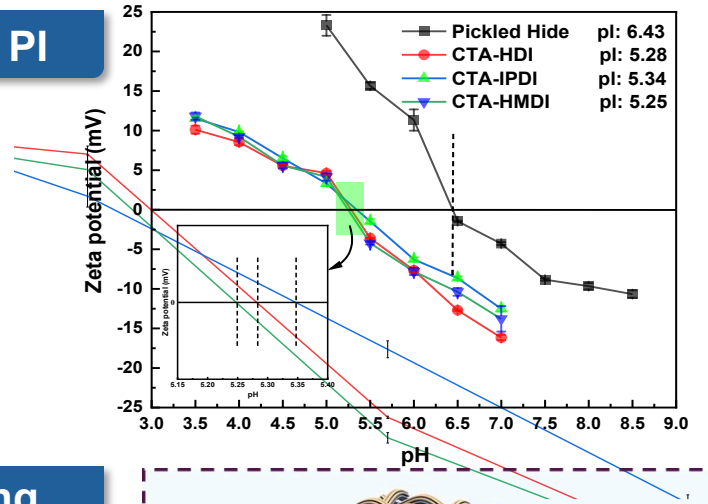




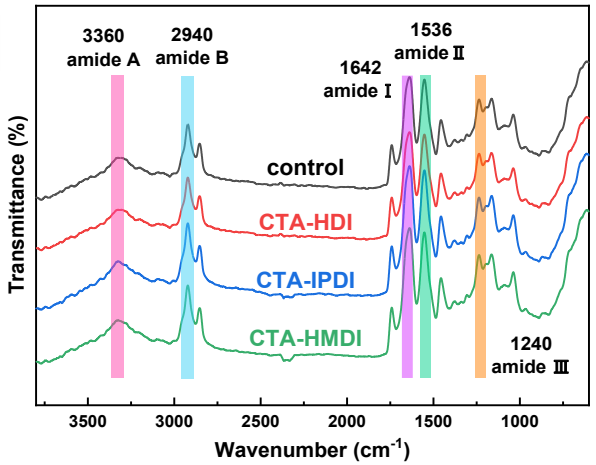
- CTAS tanned leather demonstrate well-dispersed collagen fibers and high porosity.

CTAS Tanning Mechanism

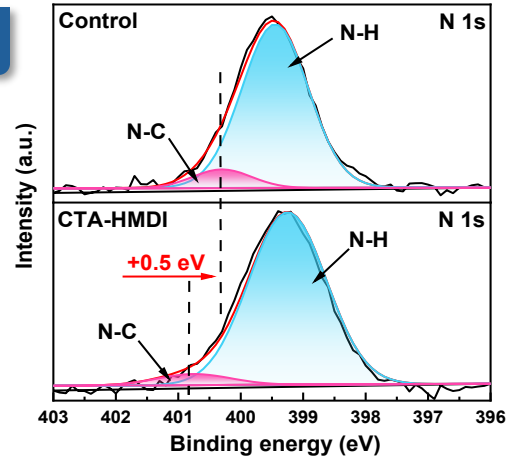
PI



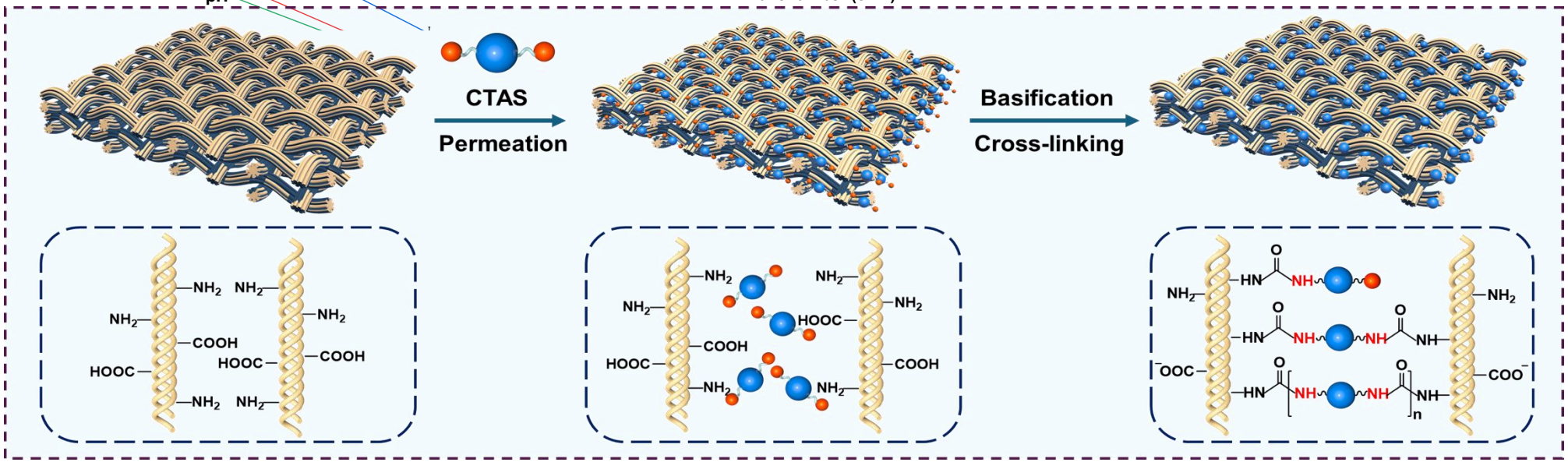
ATR



XPS

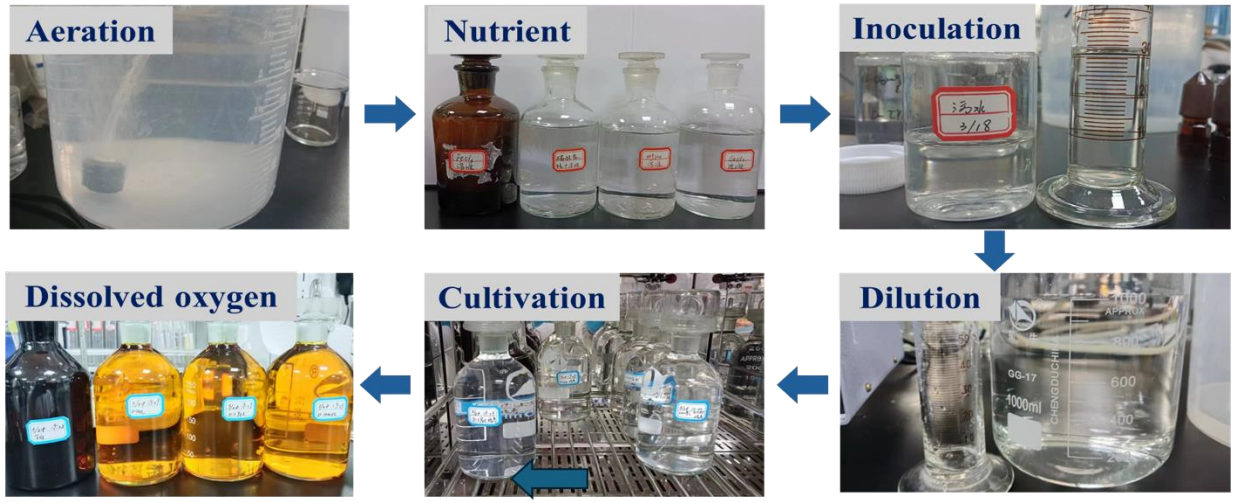


Tanning mechanism



CTAS Biodegradability

BOD_5: HJ 828-2017



COD: HJ 505-2009

Sample	COD (mg/L)	BOD_5 (mg/L)	BOD_5/COD	Biodegradability
CTA-HDI	114.67±12.86	55.27±5.03	0.49±0.06	Easy
CTA -IPDI	100.00±10.00	55.93±11.02	0.57±0.15	Easy
CTA -HMDI	105.00±5.00	53.93±13.05	0.51±0.09	Easy

- CTAS tanning agents exhibit good biodegradability.

Pilot-Scale Chrome-Free Tanning of Pickled Sheepskins

Pilot Trial

1. Longhua Material Technology Co., Ltd.
2. Juncheng Leather Co., Ltd.
3. Leaning New Material Technology Co., Ltd.

★ Cost Accounting

Cost content	Average cost	F-90 tanning		CTA-HMDI tanning	
		Amount [a]	Cost (CNY)	Amount [a]	Cost (CNY)
NaCl	0.6 CNY/kg	100 kg	60	100 kg	60
$NaHCO_3$	2.1 CNY/kg	20 kg	42	20 kg	42
F-90	18.0 CNY/kg	100 kg	1800	—	—
CTA-HMDI	23.0 CNY/kg	—	—	60 kg	1380
MgO	1.0 CNY/kg	—	—	30 kg	30
Water	0.005 CNY/kg	6600	33	5000	25
Composite cost			1935		1537

[a] The amount was calculated, accounting for the weight of 1000 kg limed sheepskins.

20.6% cost reduction

- **CTA-HMDI exhibits good economic viability.**

Collagen and Leather, 2025, 7, 9.

Innovative Product Two:

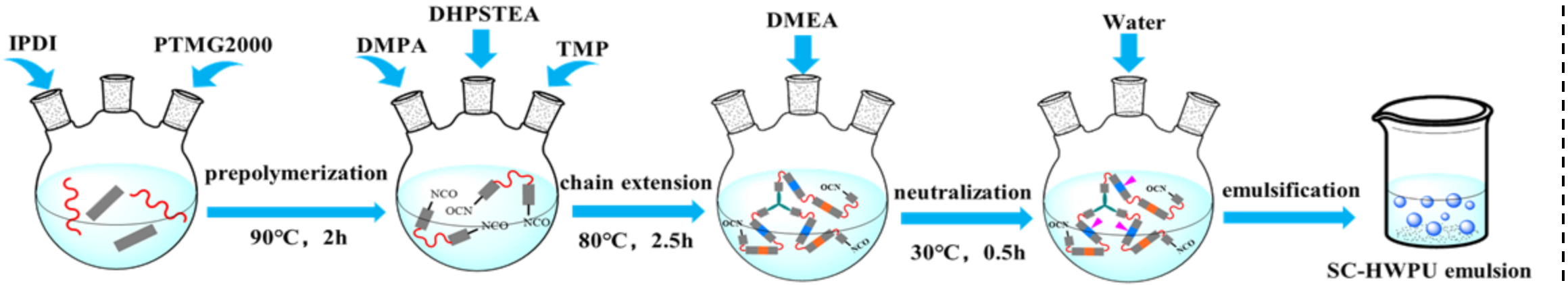
Preparation of High Solid Content Waterborne Polyurethane Emulsions Via DHPSTEA

Waterborne polyurethane (WPU) with water as the dispersion medium, has unique environmental advantages, and the film-forming is soft and elastic. Thus, WPU is widely used in leather finishing.

WPU

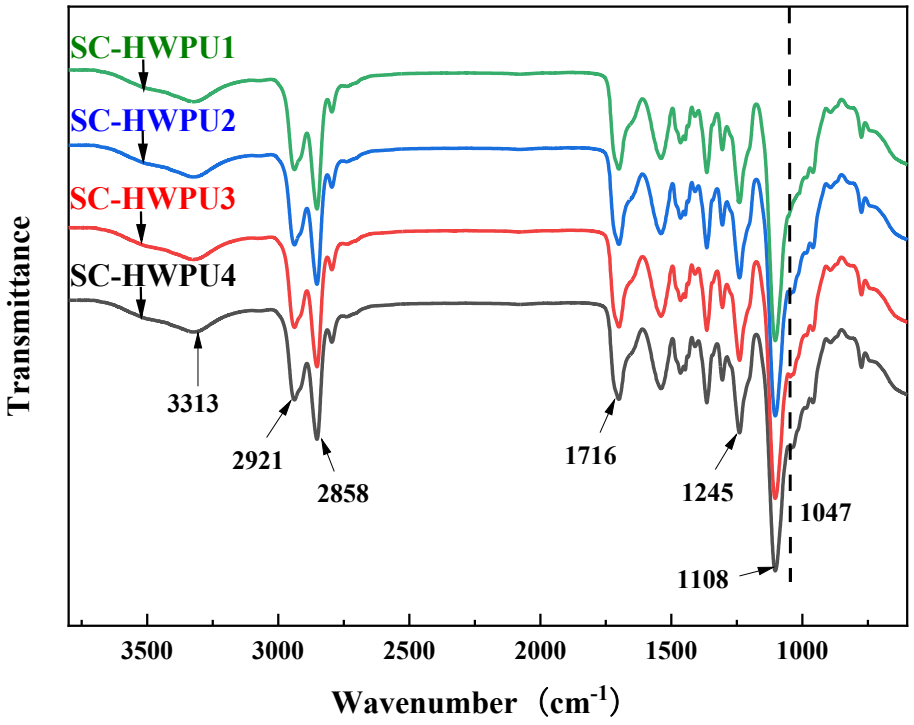
- Low Solid Content (25~40%) → × High Energy Consumption × Long Drying Time
- High Solid Content (50~60%) → √ Low Transportation Cost √ Easy Foam Coating

Propose using both DHPSTEA and DMPA as materials to prepare High-Solid Content WPU.

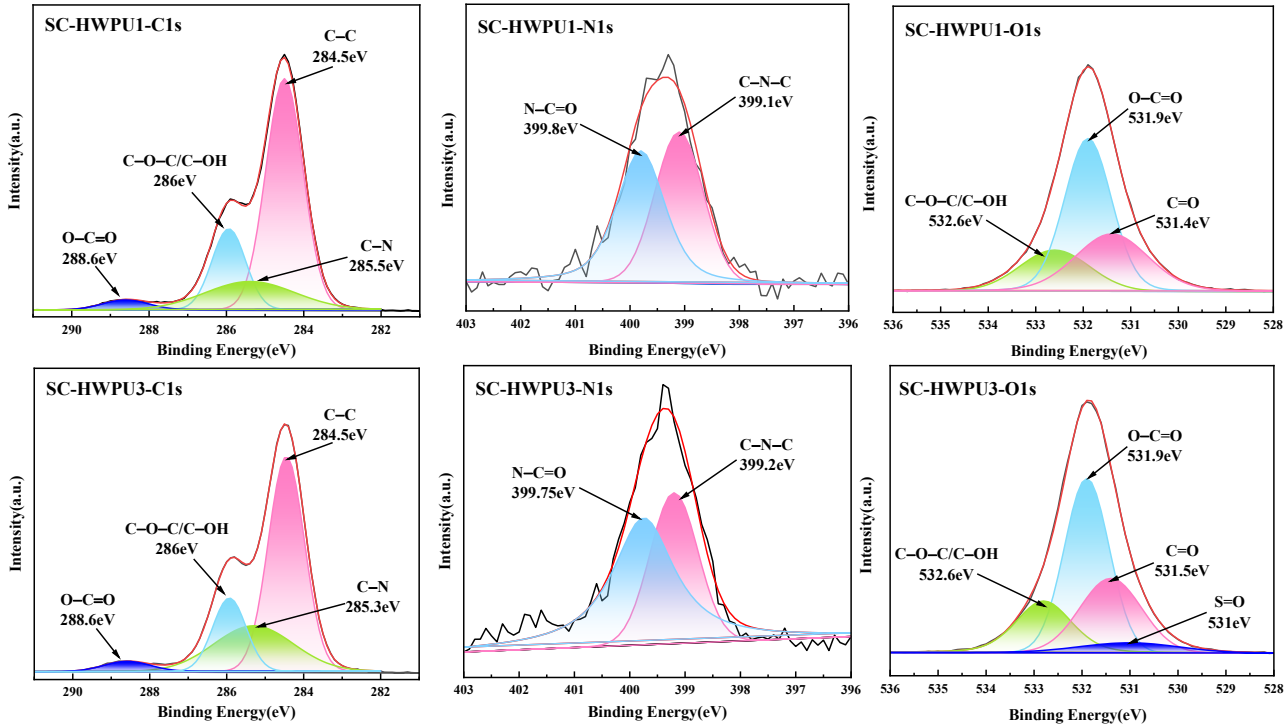


Structural Characterization of SC-HWPU

FTIR



XPS

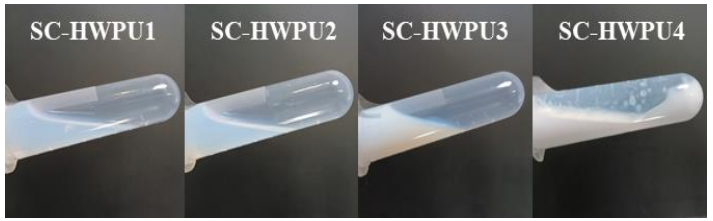


- **SC-HWPU emulsions were successfully prepared.**

The Properties of SC-HWPU Emulsion

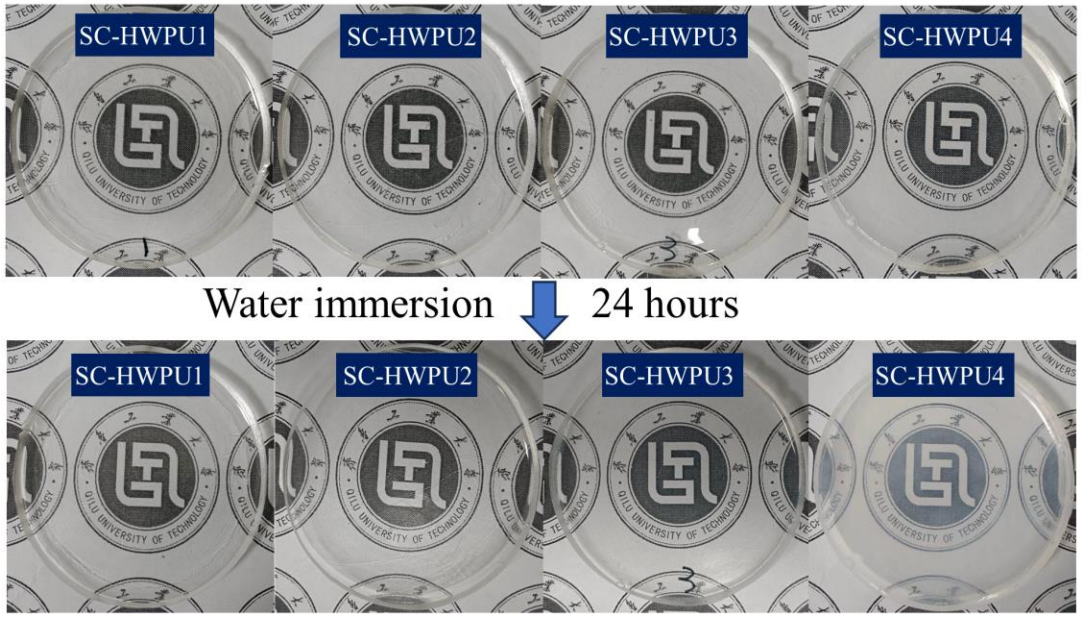
Emulsion properties

Sample	-COO^-/-SO_3^-	Average particle/nm	Solid content/%	PDI	Zeta /mV	Viscosity /mPa·s	Stability
SC-HWPU1	10:0	46.76	40.0	0.066	-46.9	619.6	Stable
SC-HWPU2	9:1	57.38	45.0	0.068	-47.9	1052	Stable
SC-HWPU3	8:2	141.20	51.6	0.073	-40.0	1291	Stable
SC-HWPU4	7:3	240.10	45.0	0.262	-42.2	2199	Instable



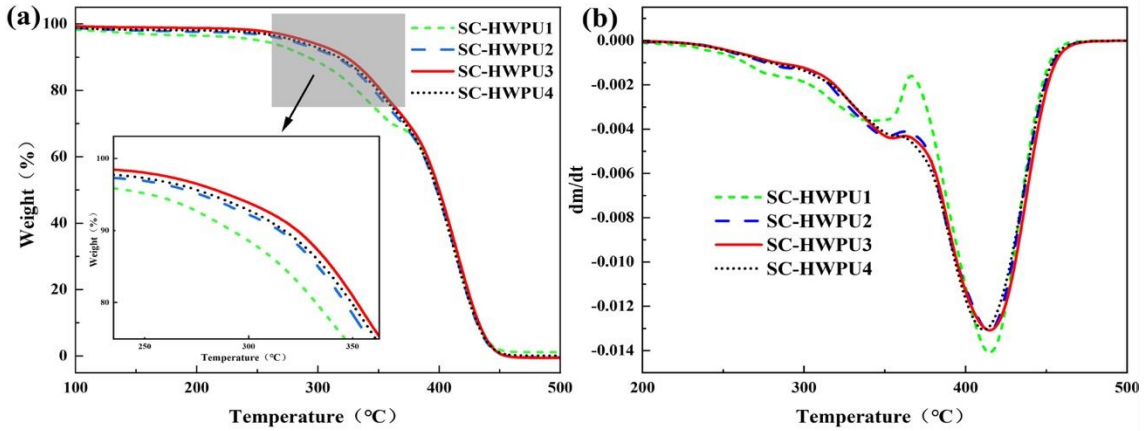
Water Resistance of Films

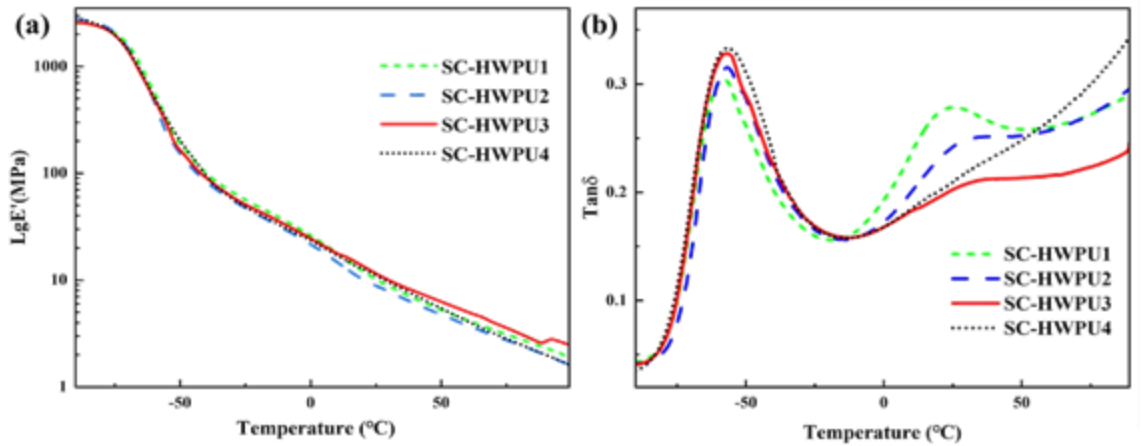
Appearance of films

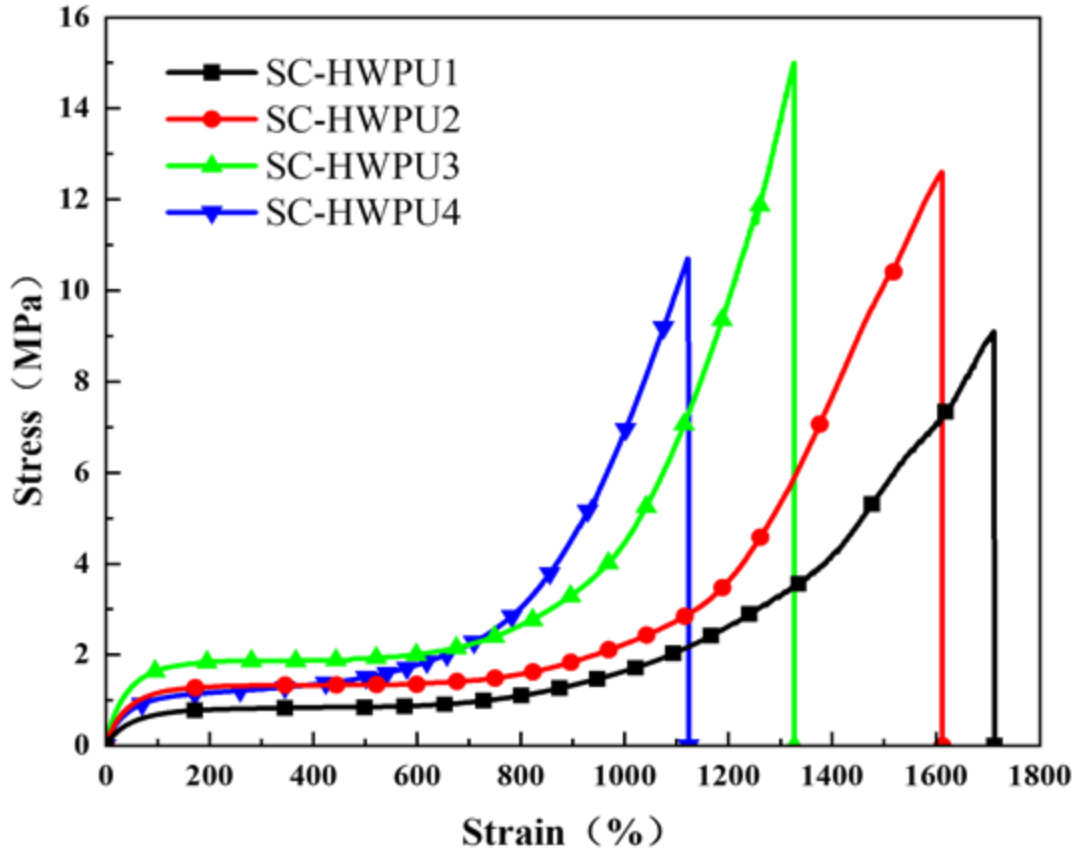


- The solid content, particle size, and viscosity of WPU increased with the liquid salt amount.
- After 24 hours of water immersion, the SC-HWPU1–3 films can still maintain good transparency.

The Properties of SC-HWPU films







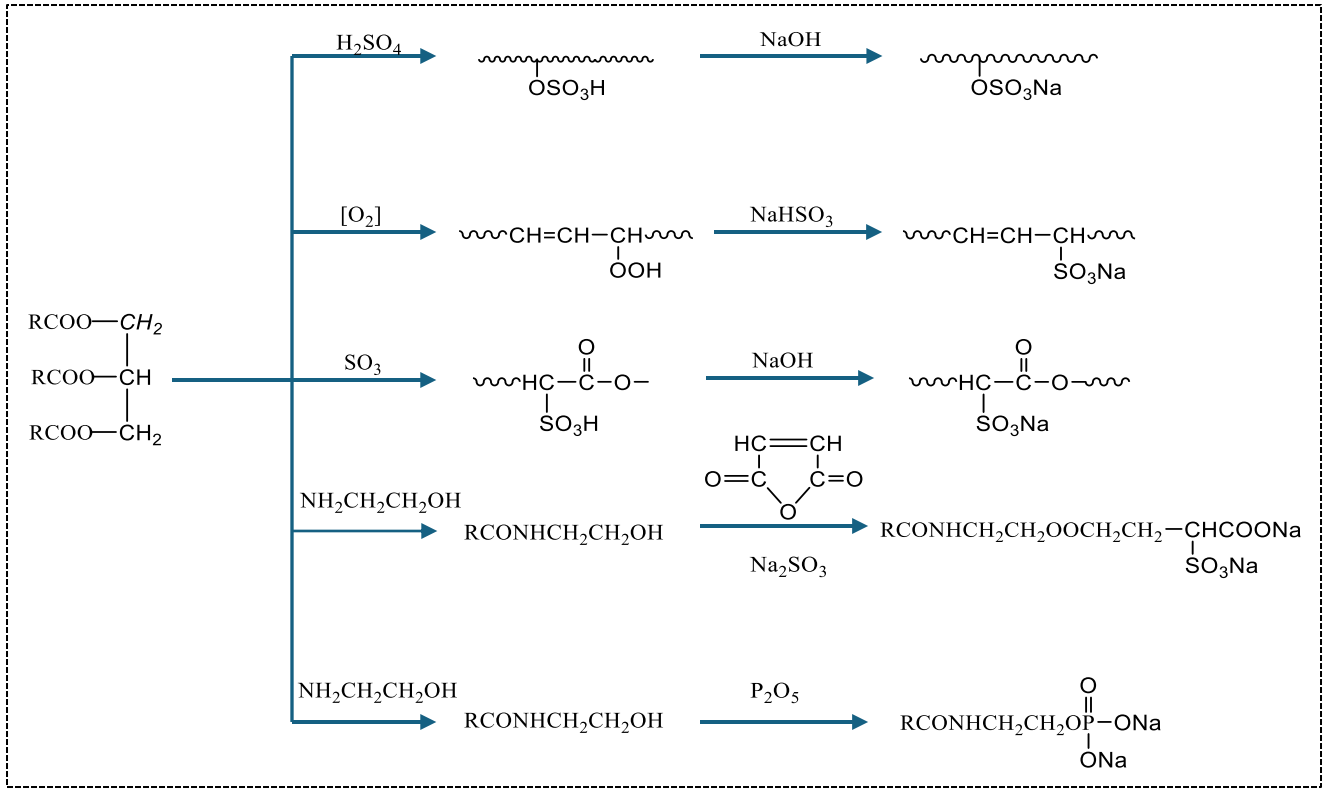
- **SC-HWPU films have good thermal stability and mechanical properties.**

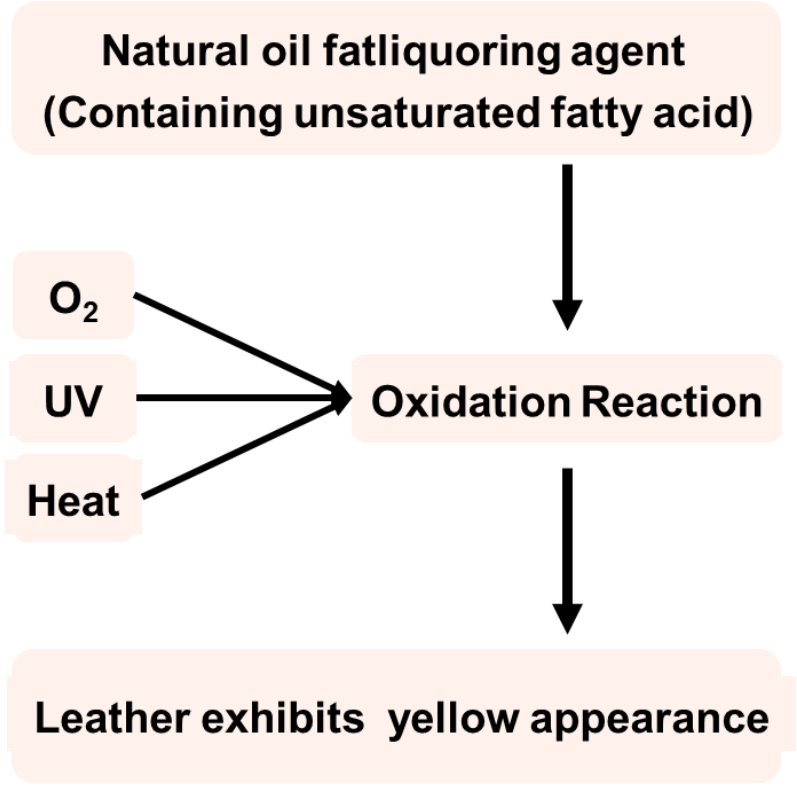
Journal of Applied Polymer Science, 2024, 141, 55926.

Innovative Product Three:

Preparation of Yellowing-Resistant Leather Fatliquors Via DHPSTEA

The Preparation Method of the Conventional Fatlqiuors

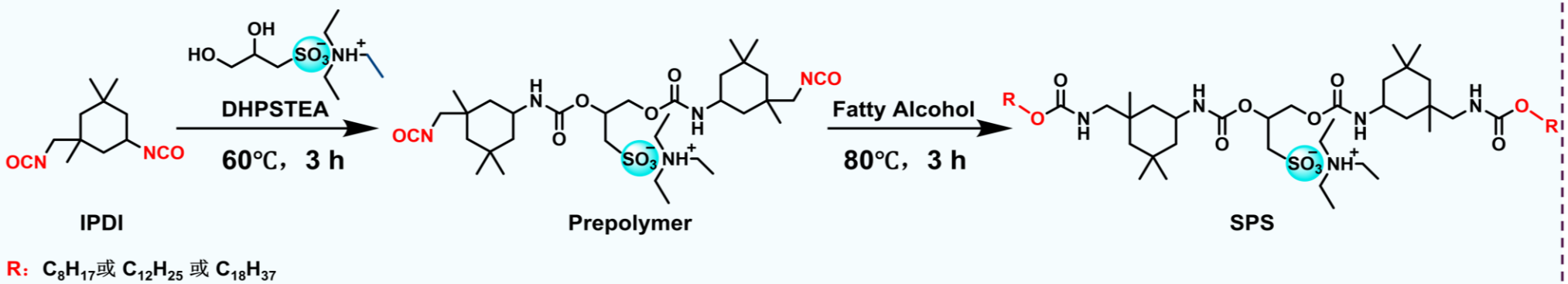


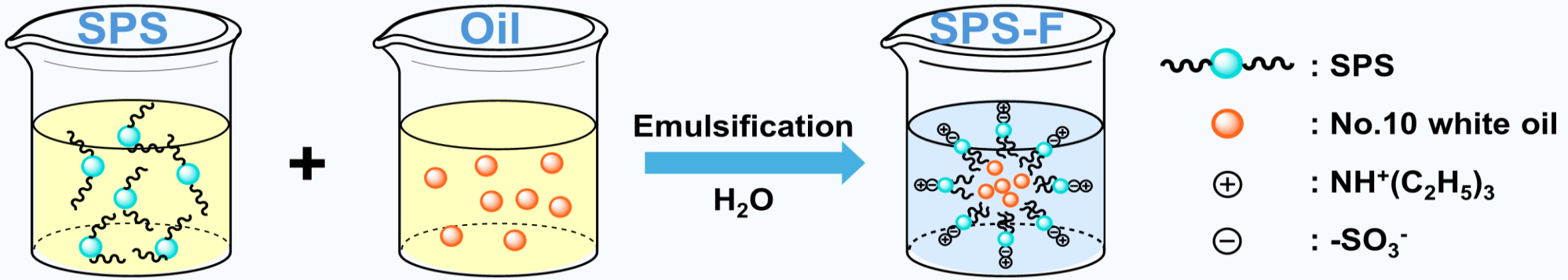


- Developing yellowing-resistant fatliquors is a **key objective** in the leather industry.

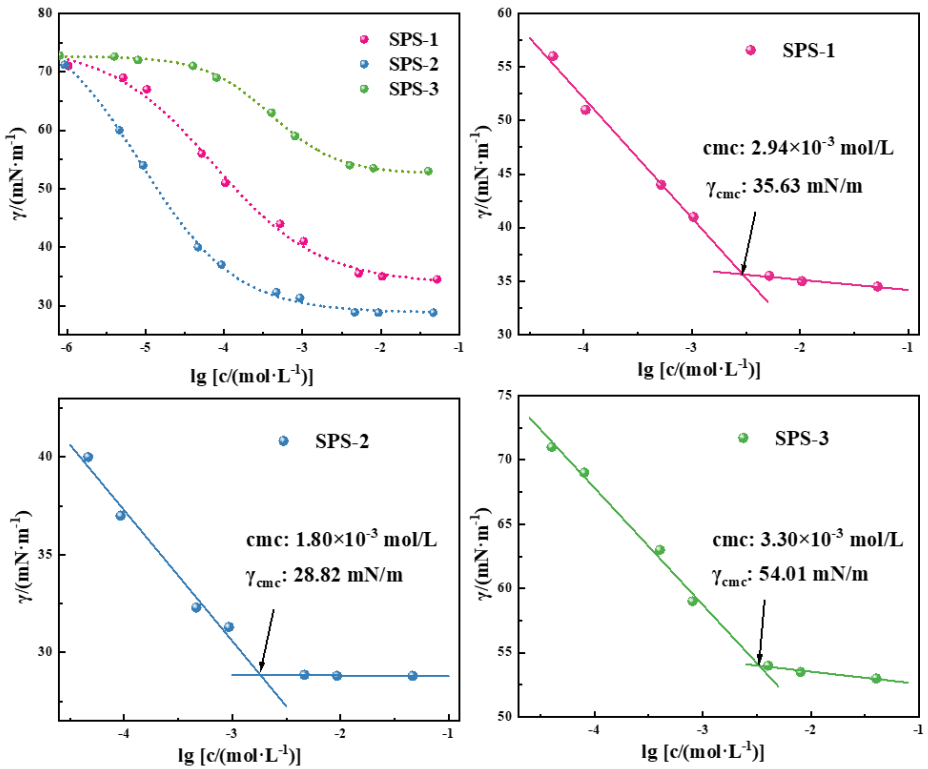
Preparation of Yellowing-Resistant Leather Fatliquors via DHPSTEA

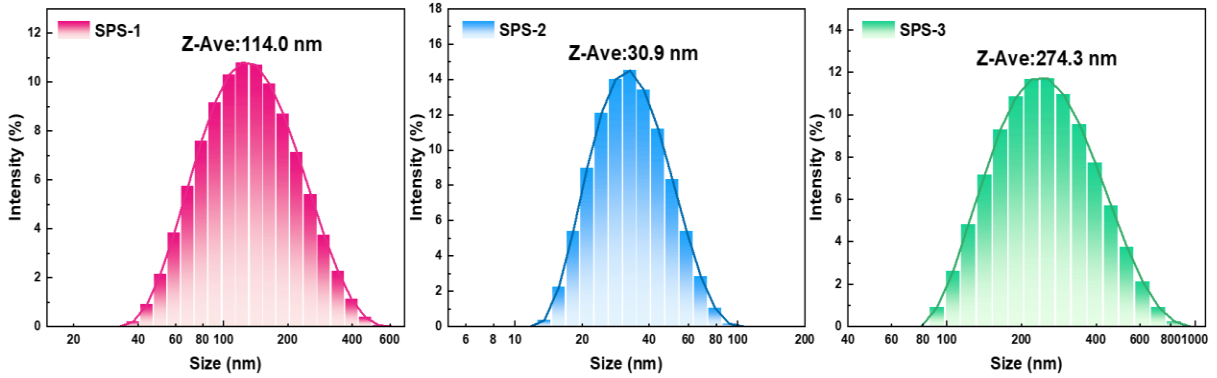
Sulfonate polyurethane surfactants (SPS) were first synthesized from DHPSTEA, then yellowing resistant leather fatliquors (SPS-F) were prepared by using SPS to emulsify mineral oil.





The Properties of surfactants and fatliquors



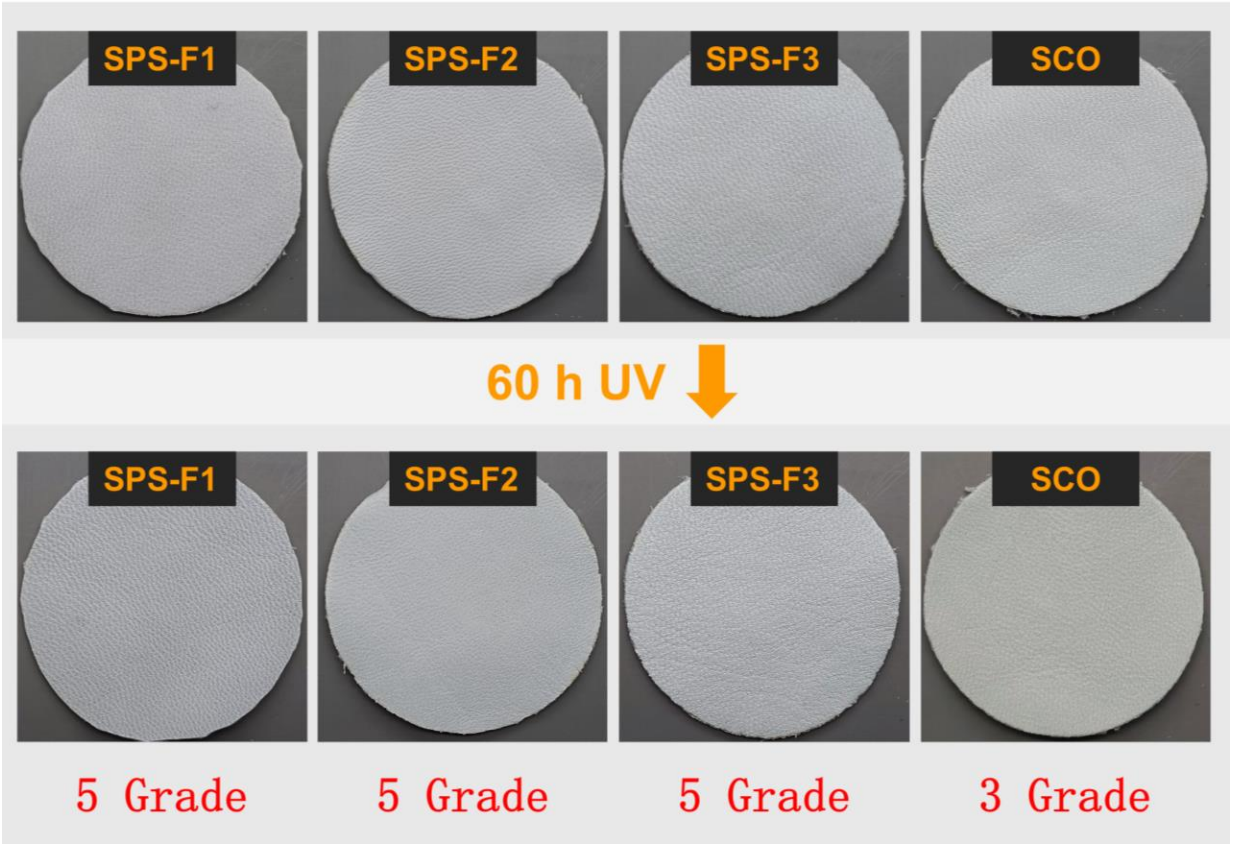


Sample	Emulsifier	Appearance	Solid Content/%	Stability
SPS-F1	SPS-1	White	60	Stable
SPS-F2	SPS-2	White	60	Stable
SPS-F3	SPS-3	White	60	Stable

- The surfactant synthesized with lauryl alcohol exhibits optimal surface activity and minimal particle size.
- The fatliquoring agent emulsified using SPS-2 also exhibits good stability.

Determination of Yellowing Resistance

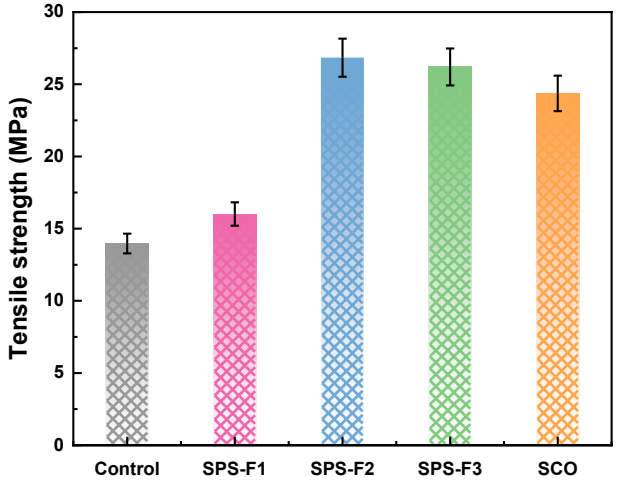
Sample	Parameter	0 h	12 h	24 h	36 h	48 h	60 h
SPS-F1	L	74.63±0.50	73.90±0.30	73.70±0.72	73.50±0.61	73.46±0.62	73.53±0.68
	a	-4.50±0.10	-4.90±0.10	-4.73±0.06	-4.80±0.11	-4.70±0.11	-4.83±0.21
	b	-0.07±0.02	-0.20±0.07	0.20±0.07	0.07±0.06	0.09±0.04	0.30±0.10
	ΔE	0	0.85±0.13	0.98±0.26	1.18±0.15	1.20±0.24	1.21±0.18
SPS-F2	L	79.83±0.42	79.09±0.63	79.07±0.75	78.97±0.15	78.95±0.39	78.96±0.74
	a	-3.23±0.15	-3.48±0.16	-3.49±0.17	-3.53±0.25	-3.60±0.35	-3.60±0.53
	b	1.10±0.05	0.30±0.06	0.33±0.06	0.50±0.10	0.49±0.12	0.60±0.05
	ΔE	0	0.91±0.24	0.95±0.15	1.13±0.26	1.16±0.16	1.22±0.23
SPS-F3	L	79.57±0.78	78.67±0.55	78.57±0.32	78.53±0.25	78.50±0.26	78.50±0.36
	a	-4.57±0.15	-4.73±0.31	-4.73±0.06	-4.93±0.15	-4.93±0.09	-4.97±0.12
	b	1.90±0.10	2.07±0.06	2.10±0.10	2.18±0.20	2.17±0.15	2.21±0.08
	ΔE	0	0.93±0.15	1.03±0.25	1.13±0.16	1.15±0.26	1.18±0.16
SCO	L	80.63±0.59	77.37±0.35	77.10±1.25	77.35±0.74	76.90±0.70	76.63±0.40
	a	-4.57±0.15	-6.90±0.10	-7.23±0.40	-7.30±0.26	-7.30±0.10	-7.30±0.20
	b	3.03±0.23	4.80±0.17	5.07±0.40	5.57±0.12	5.63±0.15	5.97±0.15
	ΔE	0	4.38±0.22	4.87±0.19	4.96±0.24	5.31±0.15	5.62±0.28



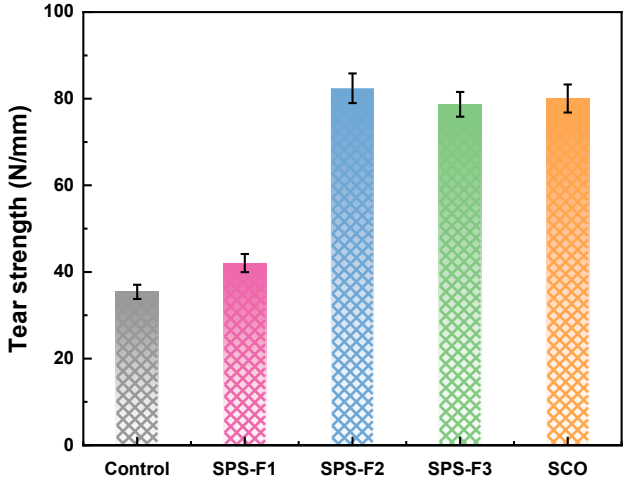
- **SPS-F fatliquored leather exhibit superior yellowing resistance.**

Mechanical Performances of leather

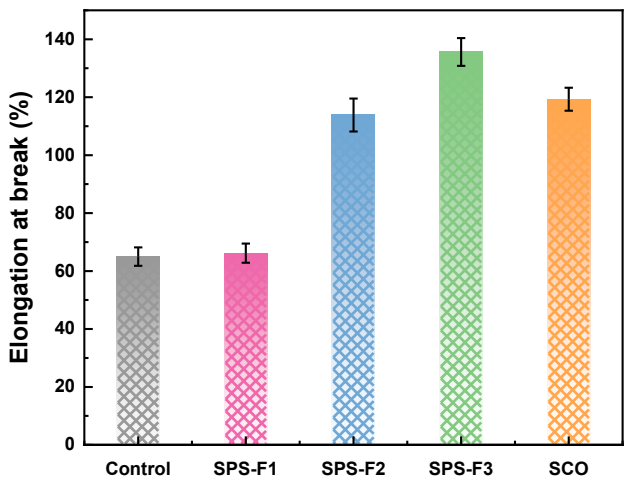
Tensile strength



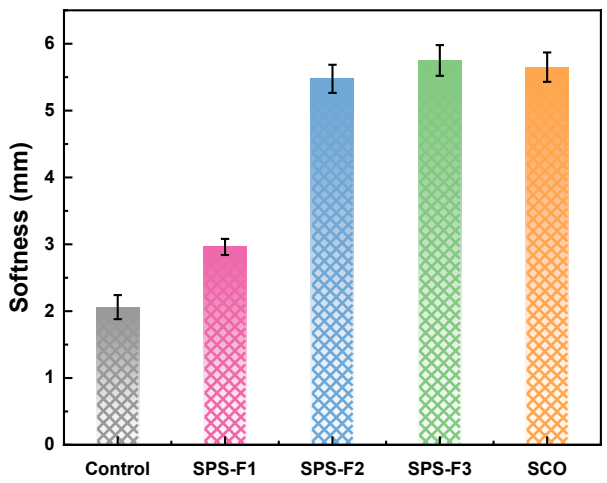
Tear strength



Elongation at break



Softness

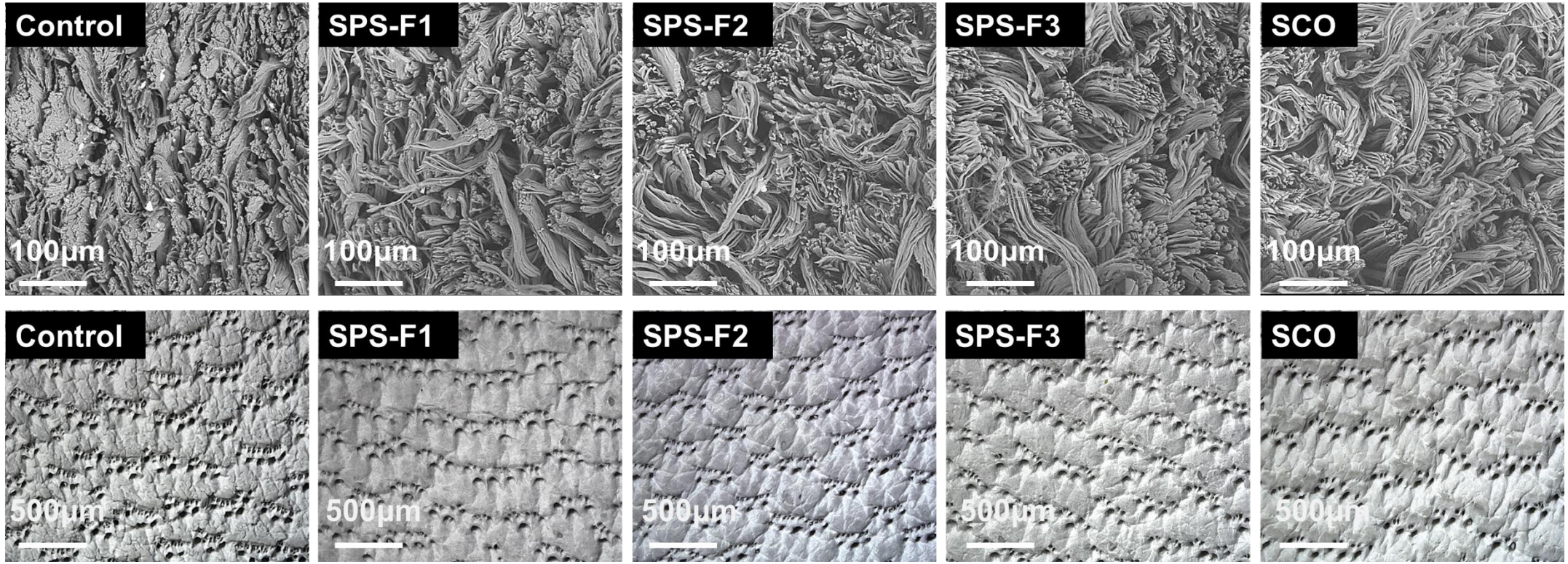


- **The crust leather fatliquored with SPS-F exhibits good mechanical properties, complying with China's garment leather standard (QB/T 1873-2023).**

Morphological Observation

SEM

SDM



- The SPS-F fatliquored leather exhibits highly dispersed collagen fibers, smooth and fine grain surface, and uniform pore size distribution.

Summary

- A new reactive liquid salt, DHPSTEA, was successfully synthesized, exhibiting favorable physicochemical properties as a reaction platform for developing innovative leather chemicals.

- Three new leather chemicals were developed based on DHPSTEA: Poly(Carbamoyl Sulfonate) Tanning Agent, High Solid Content Waterborne Polyurethane Emulsions and Yellowing-Resistant Leather Fatliquors. These three chemicals have good application performance and promising market prospects.

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