Sustainable Leather Processing: pH-Driven in Situ Self-Assembly of Biomass-Based Tanning Agents from Tea Polyphenols

Conference: 13th AICLST, Kolkata, 6–8 March 2026

Paper reference: TI-35/O

Printed pages: 141–145

Source: *Leather 2050: Challenges & Opportunities*, ILTA (2026)

Sustainable Leather Processing: pH-Driven in Situ Self-Assembly

of Biomass-Based Tanning Agents from Tea Polyphenols

Wenlong Chen a,b,c, Xu Zhang a,b,c, Chunxiao Zhang a,b,c, and Biyu Peng a,b,c*

a College of Biomass Science and Engineering, Sichuan University, Chengdu 610065, China

b Key Laboratory of Leather Chemistry and Engineering of Ministry of Education, Sichuan University, Chengdu 610065, China

c National Engineering Laboratory for Clean Technology of Leather Manufacture, Sichuan University, Chengdu 610065, China

Ref. No. TI-35/O

Abstract

To mitigate chromium pollution in leather manufacturing, we developed a novel biomass-based chrome-free tanning agent (polyphenol–cyanuric chloride derivative, PCC) by grafting cyanuric chloride (CC) onto tea polyphenol (TP). Exploiting the pH-responsive phenolic hydroxyl groups of TP, PCC exhibits a phase-adaptive tanning mechanism: it permeates collagen as nanoscale particles (100–200 nm) under mildly acidic conditions (pH 4.5–6.0), then undergoes HCl-triggered supramolecular selfassembly into micron-scale networks (<“2000 nm) via ð–ð stacking under strong acidity (pH < 3.0). This biphasic behavior enables salt-free processing while promoting complete collagen cross-linking, evidenced

Fig. 1 Graphic for paper

Corresponding author email: 2023323080002@stu.scu.edu.cn

by an increased shrinkage temperature (Ts) of 80.7 ± 1.2 °C, comparable to commercially available glutaraldehyde tanning agents. PCC-tanned leather shows improved fullness and photostability; yellowing is suppressed after UV aging (< 1.5), outperforming aldehyde-tanned leather (> 4.0). Supporting measurements indicate markedly reduced effluent burdens (COD 850 mg/L; TDS 420 mg/L) versus conventional chrome and aldehyde systems. Overall, this work demonstrates a practical route to convert agricultural polyphenols into high-performance, ecofriendly tanning materials through pH-driven in situ self-assembly.

Δb* Δb*

Keywords: tea polyphenols; cyanuric chloride; supramolecular self-assembly; salt-free tanning; chrome-free leather; sustainability

1. Introduction

Chromium-based tanning has long underpinned leather manufacturing because it provides rapid penetration and strong collagen stabilization; however, the associated chromium-containing wastes and potential Cr(III)/Cr(VI) risks motivate the development of chrome-free alternatives.1-3 Conventional vegetable and aldehyde tanning approaches can reduce chromium emissions, but often require high salt loads for pickling and penetration control, and they may suffer from limitations in reactivity, yellowing, or downstream environmental burdens.1, 4-9

Polyphenols are attractive biomass-derived building blocks for sustainable tanning because they can interact with collagen through hydrogen bonding and other noncovalent interactions. Tea polyphenol (TP), an abundant agricultural byproduct, offers multiple phenolic hydroxyl groups (Ar– OH) that can be chemically modified to introduce controlled reactivity.10 Here, we design a TP-based tanning agent by grafting cyanuric chloride (CC) to form a polyphenol– cyanuric chloride derivative (PCC).11 Importantly, PCC is engineered to be pH-responsive: it remains dispersed as nanoparticles under mild acidity for efficient penetration, then self-assembles under strong acidity to form larger supramolecular networks that enhance filling and cross-linking. This “phase-adaptive” behavior aims to eliminate salt (NaCl) requirements while maintaining or improving leather performance.11

2. Materials and Methods

2.1 Materials and PCC synthesis. TP and CC

were used as received. PCC was synthesized

Table 1. PCC tanning process (based on twice the weight of bated sheepskin pelt)

Stage	Chemicals (dosage, %)	Temperature (°C)	Time
Penetration	Water (70); PCC (10)	25	120 min; pH ~6.2
Assembly / tanning	Hot water (45 °C) (50)	45	120 min
Maturation	Hot water (45 °C) (50)	45	240 min; then overnight
Washing	Water (400)	25	10 min; horse up 24 h

under low temperature (0–4 °C) to suppress unwanted hydrolysis. An alkaline agent was introduced to neutralize released HCl and control substitution. Under optimized conditions, the molar ratio n(Ar–OH):n(CC):n(Na2CO3) was 1.00:0.90:0.54. After reaction, the crude product was freeze-dried. Purified PCC (PCCp) was obtained by dissolving the crude product in acetone, filtering to collect the precipitate, and washing alternately with acetone/water to remove soluble salts and residual TP/CC.

2.2 Characterization. Chemical structure changes

from TP to PCCp were examined using FT-IR and UV–vis spectroscopy. Elemental and bonding-state information was evaluated by Xray photoelectron spectroscopy (XPS). The pHdependent aggregation/self-assembly behavior was assessed by tracking particle size evolution across relevant pH and temperature windows.

2.3 Tanning procedure and testing. Sheepskin

pelts were tanned with PCC using a temperature-programmed protocol to couple penetration (nanoparticle state) and in situ assembly (network state). A simplified PCC tanning process is summarized in Table 1. A conventional vegetable tanning process was used as a reference. Ts was measured according to ISO 3376:2020. Yellowing resistance was evaluated under UV exposure (ISO 105-B02). Morphology was observed by scanning electron microscopy, and mechanical properties were assessed following relevant ISO standards.

3. Results and Discussion

3.1 Optimizing TP modification and reactivity

control. Substitution of CC onto TP introduces reactive dichlorotriazine motifs while partially consuming Ar–OH groups. Process optimization focused on neutralization strategy, temperature control, and reagent stoichiometry. Sodium

Fig. 2 Particle size of PCCp at different pH values (A); pH variation of PCCp tanning liquor at

different temperatures (B); PCC ‘growth in situ’ process (C)

3.2 pH-driven phase-adaptive behavior

(“growth in situ”).

As is shown in Fig. 2, PCC displays distinct

size regimes governed by pH. Under mildly acidic conditions (pH 4.5–6.0), PCC remains dispersed as nanoparticles (100–200 nm), enabling rapid diffusion through collagen fiber networks. Under stronger acidity (pH < 3.0), hydrolysis of the remaining chlorotriazine (active chlorine) groups liberates chloride and releases HCl; together with proton binding by

carbonate (Na2CO3) was selected as a costeffective acid scavenger. Under the optimized molar ratio n(Ar–OH):n(CC):n(Na2CO3) =1.00:0.90:0.54 and low-temperature operation (0–4 °C), PCC achieved a controlled substitution degree that balanced penetration behavior and subsequent self-assembly/crosslinking performance.

collagen, the system autonomously acidifies (to ~pH 3.0 within ~6 h at 45 °C), driving irreversible aggregation and supramolecular self-assembly via hydrogen bonding and š–š interactions (with ~80% of particles reaching ~2000 nm under strong acidity, e.g., pH ~2.0). Temperature further accelerates aggregation kinetics, which motivates a two-step tanning schedule: a low-temperature infiltration period followed by a warmer period to promote assembly and consolidation.

3.3 Leather performance.

By coupling nanoparticle penetration with in situ

assembly, PCC enables effective collagen stabilization and filling. During the penetration stage (25 °C, 2 h), PCC infiltrates efficiently; subsequent heating (45 °C, 6 h) promotes network formation and reinforcement. As a result, Ts increases to 80.7 ± 1.2 °C. PCCtanned leather also exhibits improved fullness and mechanical robustness that satisfies garment-leather requirements. Photostability is enhanced: after UV aging, the yellowing index is low (< 1.5), substantially better than aldehyde-tanned leather (> 4.0).

Δb

Δb

Table 2. Key performance and environmental metrics of PCC versus conventional systems

Metric PCC (this work) Chromium tanning Aldehyde tanning

Salt usage None 5–8% NaCl 5–8% NaCl

Penetration state 100–200 nm at pH 4.5–6.0 — —

Assembly state ~2000 nm at pH < 3.0 — —

Shrinkage temperature, Ts 80.7 ± 1.2 °C — Comparable level*

Yellowing after UV aging Δb* < 1.5 — Δb* > 4.0

COD (mg/L) 850 3000–6500 4500–7500

TDS (mg/L) 420 >2000 1500–3000

Dominant toxins Biodegradable organics Cr(Ⅲ)/Cr(Ⅵ) risk Formaldehyde/VOCs

* Ts comparison is to commercially available glutaraldehyde tanning agents as reported in the article abstract.

4. Conclusion

PCC, synthesized by grafting cyanuric chloride onto tea polyphenols, delivers a phase-adaptive tanning strategy that couples nanoparticle penetration under mild acidity with HCl-triggered supramolecular self-assembly under strong acidity. This mechanism enables salt-free tanning while achieving strong collagen stabilization (Ts = 80.7 ± 1.2 °C), improved fullness, and superior yellowing resistance. Together with markedly reduced COD/TDS burdens, PCC provides a practical, scalable route to convert agricultural polyphenols into high-performance and eco-friendly tanning materials.

3.4 Environmental performance and sustainability.

A key advantage of PCC is the elimination of

neutral salt (NaCl) in tanning, reducing total dissolved solids and minimizing salt-related wastewater burdens. Supporting measurements show that PCC tanning effluent has COD of 850 mg/L and TDS of 420 mg/L, much lower than reported ranges for chromium (COD 3000– 6500 mg/L; TDS >2000 mg/L) and aldehyde systems (COD 4500–7500 mg/L; TDS 1500– 3000 mg/L). The biomass-derived design and salt-free processing align with circular-economy principles and offer a scalable route to ecofriendly leather production.

References

1. Yu, Y.; Wang, H.; Zeng, Y.; Zhou, J.; Zhang, Y.;

Shi, B.; Wang, Y. Biomass-derived polycarboxylate–aluminum–zirconium complex tanning system: A sustainable and practical approach for chrome-free eco-leather manufacturing. J. Clean. Prod. 2024, 452, 142261.

2. Sundar, V. J.; Raghava Rao, J.; Muralidharan, C. Cleaner chrome tanning — emerging options. J. Clean. Prod. 2002, 10, 69-74.

3. Yu, Y.; Lin, Y.; Zeng, Y.; Wang, Y.; Zhang, W.; Zhou, J.; Shi, B. Life Cycle Assessment for Chrome Tanning, Chrome-Free Metal Tanning, and Metal-Free Tanning Systems. ACS Sustain. Chem. Eng. 2021, 9, 6720-6731.

4. Gao, D.; Cheng, Y.; Wang, P.; Li, F.; Wu, Y.; Lyu, B.; Ma, J.; Qin, J. An eco-friendly approach for leather manufacture based on P(POSSMAA)-aluminum tanning agent combination tannage. J. Clean. Prod. 2020, 257, 120546.

5. Fatema-Tuj-Zohra; Shakil, M. S. R.; Aktar, M. S.; Rahman, S.; Ahmed, S. A novel vegetable tannin for eco-leather production: separation, characterization and application of facile valorized indigenous Acacia nilotica bark extract. Bioresource Technology Reports 2023, 23, 101591.

6. Crudu, M.; Deselnicu, V.; Deselnicu, D. C.; Albu, L. Valorization of titanium metal wastes as tanning agent used in leather industry. Waste Manage. 2014, 34, 1806-1814.

7. Zhu, H.; Liu, H.; Tang, K.; Liu, J.; Zheng, X.; Pei, Y.; Zhong, J. Optimization of dialdehyde

soluble soybean polysaccharide: preparation by response surface methodology for cleaner leather tanning. RSC Adv. 2022, 12, 7506-7515.

8. Ding, W.; Remón, J.; Jiang, Z. Biomass-derived aldehyde tanning agents with in situ dyeing properties: a 'Two Birds with One Stone' strategy for engineering chrome-free and dye-free colored leather. Green Chem. 2022, 24, 3750-3758.

9. Sun, Q.; Zeng, Y.; Wang, Y.; Yu, Y.; Shi, B. A deeper exploration of the relation between sulfonation degree and retanning performance of aromatic syntans. Journal of Leather Science and Engineering 2021, 3, 31.

10. Wu, X.; Qiang, X.; Liu, D.; Yu, L.; Wang, X. An

eco-friendly tanning process to wet-white leather based on amino acids. J. Clean. Prod. 2020, 270, 122399.

11. Sethiya, A.; Jangid, D. K.; Pradhan, J.; Agarwal,

S. Role of cyanuric chloride in organic synthesis: A concise overview. J. Heterocycl. Chem. 2023, 60, 1495-1516.