Research Article

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Polyurethane-based retanning agents with antimicrobial properties

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Abstract: Polyurethane-based retanning agents with antimicrobial properties were synthesized by the chemical incorporation of ciprofloxacin (CPFX) units into polyurethane chains. The chemical structures were characterized by Fourier transform infrared (FTIR) and gel permeation chromatography (GPC). Then, the retanning agents were applied in the leather retanning process. Owing to the conjugation of CPFX into polyurethane chains, the molecular weight increases, further leading to the decrease in hydroxyl value and increase in particle size. The shrinkage temperature was improved after retanning. Owing to the filling of retanning agents in the gap of collagen fibers, the average thickness of leather increased by 65.8%. The mechanical properties of leather were visibly improved because of the large number of –COOH coordinate with Cr^{3+} and more hydrogen crosslinking with carboxyl group, amino group, and hydroxyl group of leather collagen. Furthermore, leather retanned by these polyurethane-based retanning agents presented good antimicrobial properties. The antibacterial activity could be conserved above 89% even after rinsing for ten times.

Keywords: polyurethanes, antimicrobial, ciprofloxacin, leather, retanning

1 Introduction

Leather is a collagen fibrous material produced by tanning the collagen fiber network of animal hides and skins, and its productions can be seen almost everywhere in our life (1–3). As a natural material, leather can serve as a carbon and nitrogen source for microbial growth. Moreover, the collagen fibrous network of leather can provide suitable temperature, moisture, and oxygen for the growth and rapid colonization of bacteria. As a result, the formation of a biofilm will severely reduce the service life of the leather products (4–6). Hence, it is of great importance to inhibit bacteria growth on leather.

Antimicrobial properties of leather can be achieved through retanning process. As one of the significant steps in leather manufacturing process, retanning process can overcome some drawbacks of chrome tannage, improve leather shrinkage temperature, assist dyeing performance, and more importantly, endow some functional properties to the final leather, such as antimicrobial, antifouling, waterproof, fire-retardancy, and so on (7–9). For example, a chromotropic acid grafted amphoteric polyurethane was synthesized and then applied in the retanning process of the aldehyde tanned leather (10). The reaction between chromotropic acid and formaldehyde occurred between two naphthalene rings, effectively reducing the free formaldehyde content in leather.

Among the retanning agents, hyperbranched polyurethane has attracted increasing attention because of its novel structures and unique properties. A great number of active groups in hyperbranched polyurethane can coordinate with groups of collagen fiber macromolecules (such as hydroxyl, amino, and carboxyl), and form stable interaction (11–13). For instance, Ren and coworkers synthesized a hydroxyl-terminated hyperbranched retanning agent. All the leather samples retanned by it exhibited better tearing strength, tensile strength, cracking strength, dry rub fastness, and surface properties (12). Another research found that hyperbranched polymer retanning agent can effectively improve the shrinkage temperature of hide and chrome uptake (13). In particular, the structure of hyperbranched polyurethane can be easily designed by changing the types of raw materials during the manufacturing process to meet the desired performances (14,15). For example, a phosphorous polyol and expandable graphite were incorporated into polyurethane. The obtained hyperbranched polyurethane not only possesses high physical performances, but also significantly reduces the release of contaminative smoke CO and NOx in fires (16). Therefore,

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the antimicrobial moieties can be covalently conjugated into the chains of hyperbranched polyurethane. However, to the best of our knowledge, no research has been done on preparing hyperbranched polyurethane with antimicrobial properties for leather retanning.

Ciprofloxacin (CPFX), a low-molecular-weight antimicrobial agent, is one of the new generation of fluorinated quinolones structurally related to nalidixic acid (17,18). Its primary mechanism is inhibition of bacterial DNA gyrase. It is a broad-spectrum antibacterial drug to which most Gram-negative bacteria are highly susceptible *in vitro* and many Gram-positive bacteria are susceptible or moderately susceptible. Blending CPFX with retanning agents might cause its migration during the following leather manufacturing process (19,20). So, it is better to chemically incorporate CPFX into chains of retanning agents. In this study, we aim to endow leather antimicrobial properties in retanning process. Polyurethane-based retanning agents were prepared by chemically incorporating CPFX units into polyurethane chains. Then, they were applied in the leather retanning process. The shrinkage temperature, average thickness, and mechanical properties of final leather were measured. Besides, the antimicrobial properties of leather after retanning were investigated in detail. It was found that these retanning agents endowed leather with good bacteriostatic effect on Gram-positive and Gram-negative bacteria.

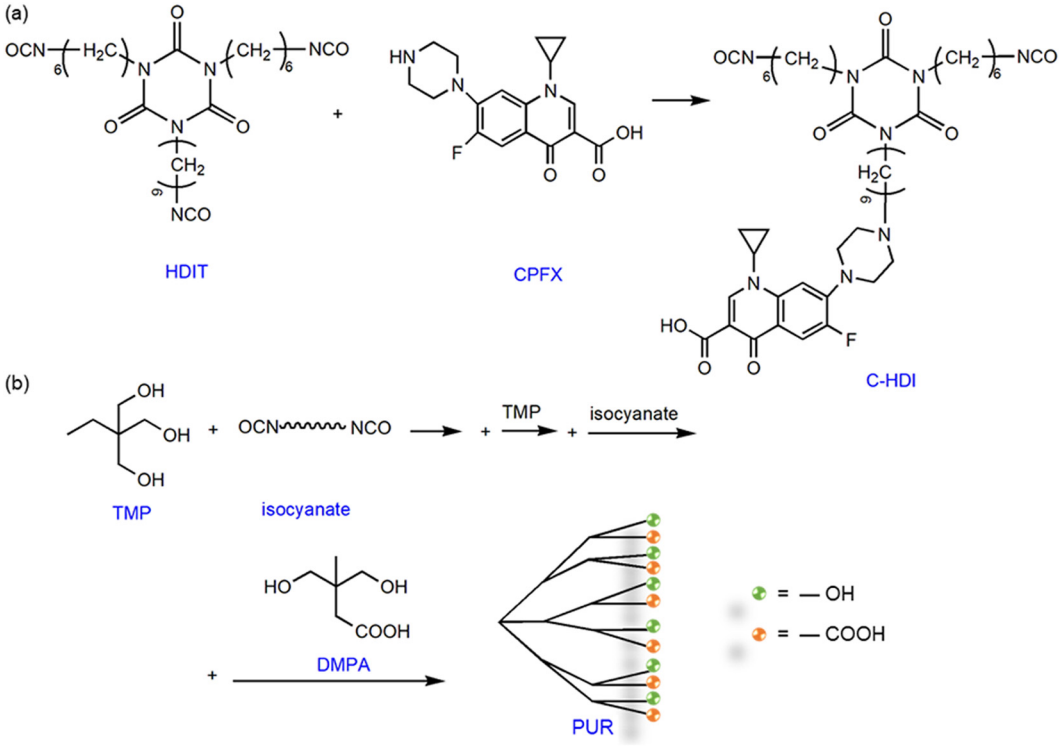
2 Materials and methods

2.1 Materials

1,1,1-Tris(hydroxymethyl)propane (TMP), hexamethylene diisocyanate (HDI), *2, 2*-bis(hydroxymethyl)propionic acid (DMPA), CPFX, and *N,N*-dimethylformamide (DMF) were purchased from Shanghai Macklin Biochemical Co., Ltd (Shanghai, China). Formic acid (HCOOH), sodium formate (NaCOOH), and sodium bicarbonate ($NaHCO_3$) were acquired from Aladdin Industrial Corporation (Shanghai, China). Hexamethylene-1,6-diisocyanate trimer (HDIT) was supplied by Bayer Co. Ltd (Germany). Other chemicals were used as received.

2.2 Preparation of polyurethane-based retanning agents (PUR) and PUR-CPFXs

First, HDIT (0.011 mol), CPFX (0.01 mol), and appropriate DMF were added into a three-necked separable reaction flask equipped with a nitrogen inlet. The reaction was stirred at room temperature until the molar ratio of –NCO reached the theoretical value (0.02 mol) (21). The mixture was filtered, and then washed by DMF several times.



Scheme 1: Preparation of (a) C-HDI and (b) PUR.

Finally, it was dried at 30°C in the oven. The prepared isocyanate with two-NCO groups was named C-HDI (Scheme 1a). TMP (0.001 mol) and isocyanate (0.003 mol) were added to the mixture to form the branched structures. HDI was applied as isocyanate in the preparation process. In the meantime, appropriate DMF was poured in case of crosslink reaction. Next more TMP (0.003 mol) was charged into the reactor and kept stirring. After that, isocyanate (0.006 mol) was added for continued reaction. Subsequently, DMPA (0.006 mol) was added to react with the residual –NCO groups. Then, the DMF was removed at room temperature by rotary vacuum evaporation under reduced pressure. The obtained polymer was dissolved in ethanol and centrifuged at high speed. The supernatant after centrifugation was evaporated at room temperature by rotary vacuum evaporation under the reduced pressure, and the polyurethane-based retanning agents (PUR) were obtained (Scheme 1b). To acquire PUR with antimicrobial properties, C-HDI was utilized as isocyanate to replace part of HDI. Polyurethane-based retanning agents with antimicrobial properties were abbreviated as PUR-CPFX-*x*, and *x* represents the weight concentrations of C-HDI used in Scheme 1b as isocyanate.

2.3 Retanning technology

The wet blue is cattlehide tanned by Cr^{3+} of tanning agents and was retanned according to the technology reported in our previous work, as listed in Table 1 (22). PUR and PUR-CPFX were applied to treat the wet blue with the same technology. All chemicals were used based on the weight of evenly shaved wet blue.

Table 1: Retanning process

Process	Chemicals	Weight (%)	Time
Weighing			
Bleaching	Water (35°C)	200	15 min
	HCOOH	0.2	
Discharging the solution			
Neutralizing	Water (30°C)	150	
	HCOONa	1	40 min, pH 4–4.5
	$NaHCO_3$	0.4–0.5	60 min, pH 5–5.5
Discharging the solution			
Retanning	Water (35°C)	100	60 min
	PUR/PUR–CPFX	8	
		Horse up	

2.4 Measurements

2.4.1 Fourier transform infrared (FTIR)

FTIR (Thermo Fisher Nicolet Is5, USA) Spectroscopy measurements were performed, and the spectra of each sample were acquired at a resolution of 2 cm^{-1} in a wavelength range of 400–4,000 cm^{-1} with 32 scans.

2.4.2 Gel permeation chromatography (GPC)

Gel permeation chromatography was conducted on an Agilent Technologies 1260 Infinity chromatograph (United States) to determine the relative molecular weight and polydispersity of the polymers. All the tests were performed at 35°C and tetrahydrofuran (chromatographic grade) was used as an organic solvent.

2.4.3 Hydroxyl value

Hydroxyl value was measured using the acetic anhydride/pyridine refluxing method (23).

2.4.4 Particle sizes

Particle sizes were obtained by laser particle size analyzer (Mastersizer 3000E). Each sample was tested three times, and its average value was taken.

2.4.5 Shrinkage temperature

The shrinkage temperature (T_s) of leather samples was measured by MSW–YD4 shrinkage meter (Yangguang Research Institute of Shanxi University of Science and Technology) according to the Chinese Industrial Standard (QB/T 2713-2005). Different parts of leathers were tested, and the average T_s was calculated.

2.4.6 Thickness

A leather thickness gauge (Dongyan, DY-701) was applied to test the leather thickness. Different parts of the leather were tested, and the average thickness value was calculated.

2.4.7 Mechanical properties

Mechanical properties were determined using a universal testing machine (model tensiTECH, Woodstock, USA).

Before measurement, samples were dried in an oven for 24 h at 60°C. Each sample was cut into dumbbell-shaped specimens of 50 mm length and 10 m neck width and measured with a 50 mm·min^{-1} cross-head speed at 25°C. Measurements were taken five times for each sample.

2.4.8 Antimicrobial properties

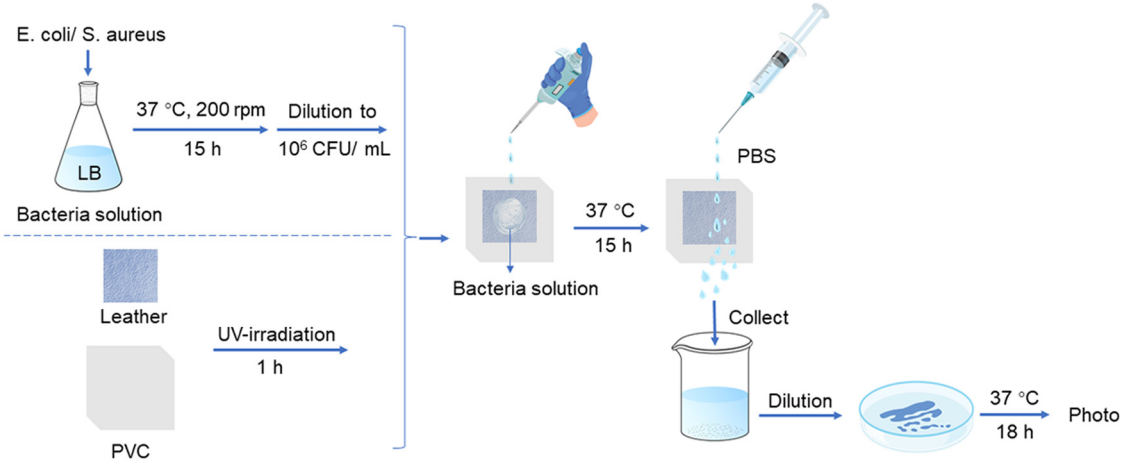
Gram-negative bacterium *E. coli* (ATCC 29213) and Gram-positive bacterium *S. aureus* (ATCC 25922) were used as the indicator microorganisms to evaluate the antimicrobial properties of leather. The measurement process for the antimicrobial properties of leather retanned by PUR and PUR-CPFXs is shown in Scheme 2. First, *E. coli* and *S. aureus* were inoculated into three 12 mL bacterial culture tubes with 3 mL fluid Luria-Bertani (LB) medium, respectively. These bacteria were shaking cultured at 37°C for 15 h. Meanwhile, leather samples retanned by PUR and PUR-CPFXs were cut into specimens of 20 mm × 20 mm and sterilized by UV-irradiation for 1 h. Afterward, the concentration of both *E. coli* and *S. aureus* bacteria solution was diluted to 10^6 CFU·mL^{-1}. Flesh side was selected as the representative to measure the antimicrobial properties in this study. Next 50 µL of bacteria solution was dropped on the flesh layer of each leather sample, respectively, and was covered by sterile PVC film. Then, they were put into boxes with constant humidity (relative humidity ≥90%) and incubated for 24 h at 37°C. After that, the flesh layer of each sample was washed with 5 mL of sterile phosphate buffered saline (PBS) solution. After washing, each PBS solution was collected and diluted 10^3, 10^4, 10^5 times, respectively. Finally, 100 µL of diluted solution was dropped on the solid LB medium and put into a constant temperature incubator at 37°C for 18 h.

3 Results and discussion

3.1 Preparation and characterization

The presence of CPFX moieties in the polymer could be verified by FTIR analysis (Figure 1). PUR-CPFX-9 was chosen as a representative example. In the spectra of PUR and PUR-CPFX-9, absorption peaks at 3,324 cm^{-1} (N–H) and 1,659 cm^{-1} (C═O) were found, which were attributed to the urethane bond in polyurethane chains. Besides, peaks at 2,931 and 2,860 cm^{-1} corresponded to the stretching vibration of C–H in $-CH_3$ and $-CH_2-$ (24–26), respectively. These peaks proved the polyurethane structure of PUR and PUR-CPFX-9. As for the spectrum of CPFX, the strong absorption peak at 1,623 cm^{-1} can be assigned to the –COOH (27) and C–F (28), respectively. These two peaks were found in the spectrum of PUR-CPFX-9, but not appeared in that of PUR. As a result, the CPFX was successfully introduced to PUR-CPFX-9.

GPC measurement was applied to obtain the molecular weight of PUR and PUR-CPFXs (Table 2). With the content of CPFX increased, both the M_w and M_n of PUR-CPFXs gradually increased. Because of the covalent conjugation of CPFX into polyurethane chains, the molecular weight inevitably grew larger. However, the polydispersity was not distinctly influenced after incorporating antimicrobial moieties. The hydroxyl value decreased when the molecular weights of the PUR increased. With the



Scheme 2: Measurement process for the antimicrobial properties of leather retanned by PUR and PUR-CPFXs.

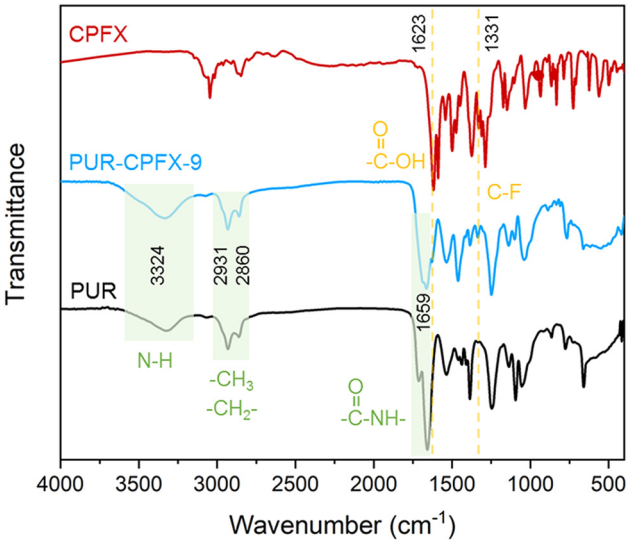


Figure 1: FTIR spectra of CPFX, PUR-CPFX-9, and PUR.

Table 2: GPC data, hydroxyl value as well as particle size of PUR and PUR-CPFXs

Sample	M_n (g·mol^{-1})	M_w (g·mol^{-1})	M_w/M_n	[OH]m (mg KOH·g^{-1})	d (nm)
PUR	1,856	2,153	1.16	153.61	33.6
PUR–CPFX–3	1,963	2,316	1.18	132.54	38.4
PUR–CPFX–6	2,046	2,476	1.21	131.04	41.1
PUR–CPFX–9	2,098	2,497	1.19	126.59	43.9
PUR–CPFX–12	2,173	2,521	1.16	128.49	44.8

increase in molecular weights, the number of terminal hydroxyl groups increased simultaneously, but the increasing extent of the former was more significant than the latter. Therefore, the hydroxyl value decreased. Besides, with the increasing content of DPA, the particle size accordingly increased. In summary, owing to the conjugation of CPFX into polyurethane chains, the molecular weight increases, further leading to the decrease in hydroxyl value and increase in particle size.

3.2 Application in retanning process

As a significant parameter to appraise the hydrothermal stability of leather (29,30), the T_s of leather before and after retanning was acquired (Figure 2a). After retanned

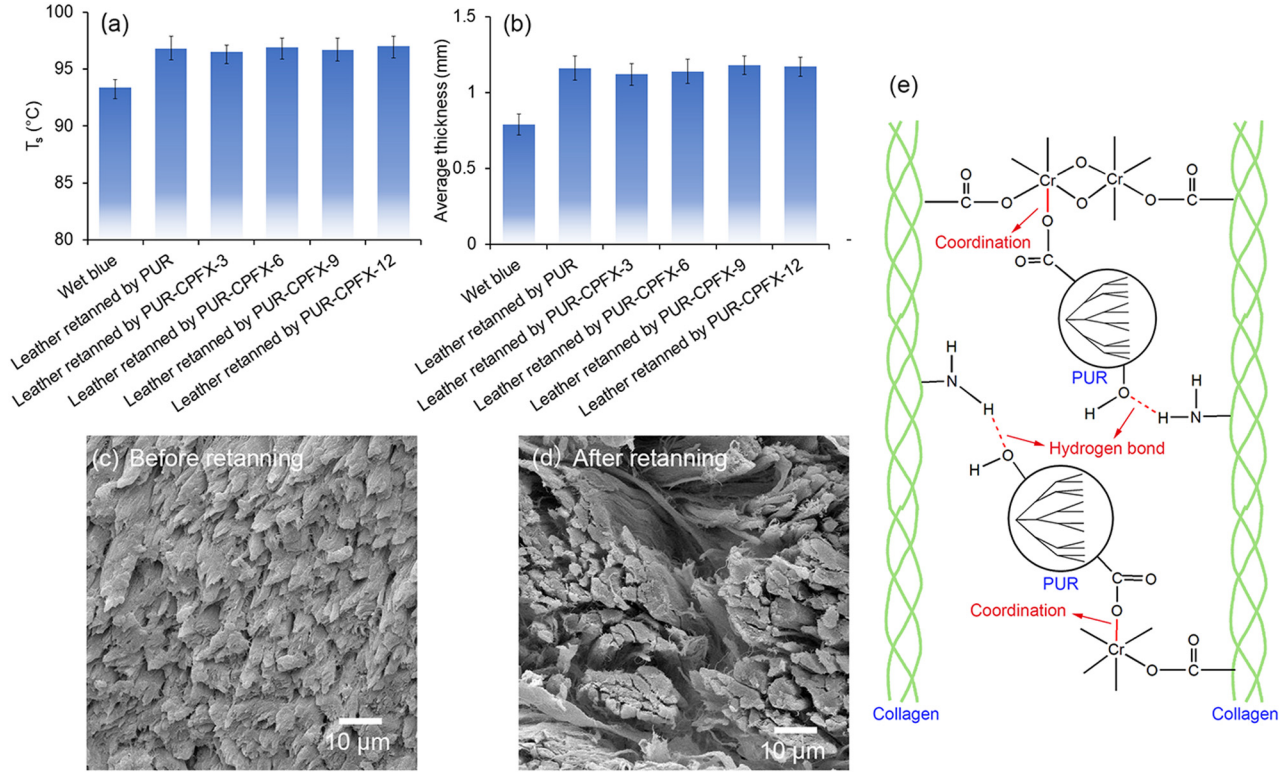


Figure 2: (a) T_s, (b) average thickness of Wet blue and leather retanned by PUR and PUR-CPFXs. SEM images of leather (c) before and (d) after retanning. (e) Schematic diagram of retanning by PUR.

by PUR and PUR-CPFXs, the T_s is obviously increased. The average thickness of leather was also measured (Figure 2b). Before the test, the wet blue and retanned leather were dried at room temperature. The thickness of leather after retanning by polyurethane was dramatically increased. Furthermore, the SEM images of leather before and after retanning are presented in Figure 2c and d, respectively. Before retanning, the leather fibers were dense, and only small gaps could be found between collagen fiber bundles. However, evident gaps were investigated, and the fibers were separated from each other after being retanned. On the one hand, quantities of –OH in the polyurethane chains can form hydrogen bonds with the $-NH_2$ in the side chains of collagen fibers. On the other hand, a large quantity of –COOH in PUR can coordinate with Cr^{3+} of tanning agents (8). As a result, the higher crosslinking effectively improved the T_s of leather (Figure 2e) (31). Owing to the filling of retanning agents in the gap of collagen fibers, the average thickness of leather increased by 65.8%. The mechanical properties of leather before and after retanning by PUR and PUR-CPFXs were also measured (Figure 3). The mechanical properties of leather were visibly improved after retanning. This was on account of the large number of –COOH and –OH in the PUR forming coordination with Cr^{3+} and more hydrogen crosslinking with carboxyl group, amino group and hydroxyl group of leather collagen (11,32). The elongation at break is visibly improved due to the outstanding lubricating and filling of polyurethane between collagen fibers (22).

3.3 Antimicrobial properties of retanned leather

The antimicrobial properties of retanned leather were evaluated using Gram-negative bacterium *E. coli* and Gram-positive bacterium *S. aureus* according to the previous reports (33–36) (Figure 4). Both *E. coli* and *S. aureus* grew well in the flesh layer of leather retanned by PUR. However, no bacterial colony was found in the medium with the PBS solution after washing flesh layer of leather retanned by PUR-CPFXs. After incorporated into polyurethane chains, the antibacterial properties of CPFX were reserved but not destroyed. The CPFX units in retanning agents effectively inhibited bacterial DNA gyrase. This result showed that the PUR-CPFX retanning agents endowed leather with good bacteriostatic effect on Gram-positive and Gram-negative bacteria (37,38). Nowadays, antimicrobial resistance has been a growing problem in microorganisms. It is of great importance to fabricate antimicrobial polymers by incorporating micromolecular antibacterial agents into polymer chains.

Compared with low-molecular-weight antimicrobial agents, antimicrobial polyurethane-based retanning agents are seldom leached out from the leather because of their interaction with collagen fibers, which promises their long-lasting function. In this study, *E. coli* and *S. aureus* were selected as indicators to quantitatively investigate the long-lasting antibacterial property of leather retanned by PUR-CPFXs. PUR-CPFX-9 was chosen as a representative example. As could be seen in Figure 4c, leather retanned

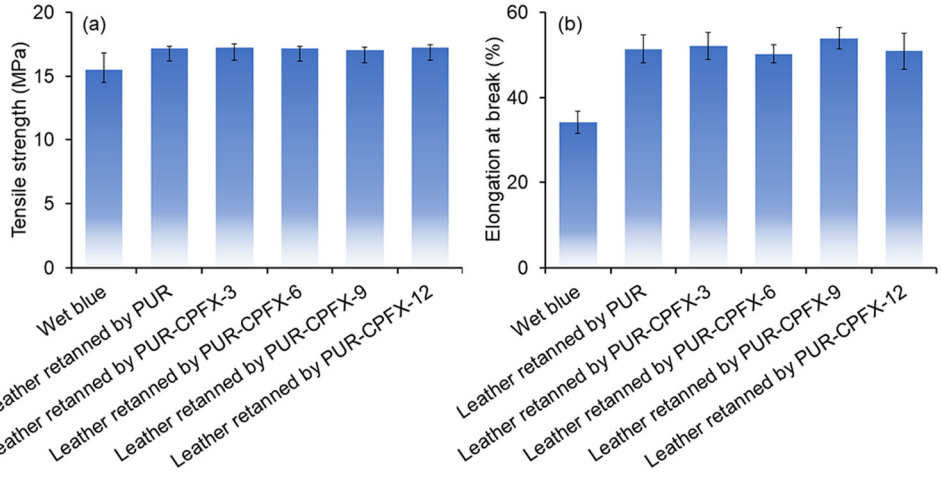


Figure 3: (a) Tensile strength and (b) elongation at break of Wet blue and leather retanned by PUR and PUR-CPFXs.

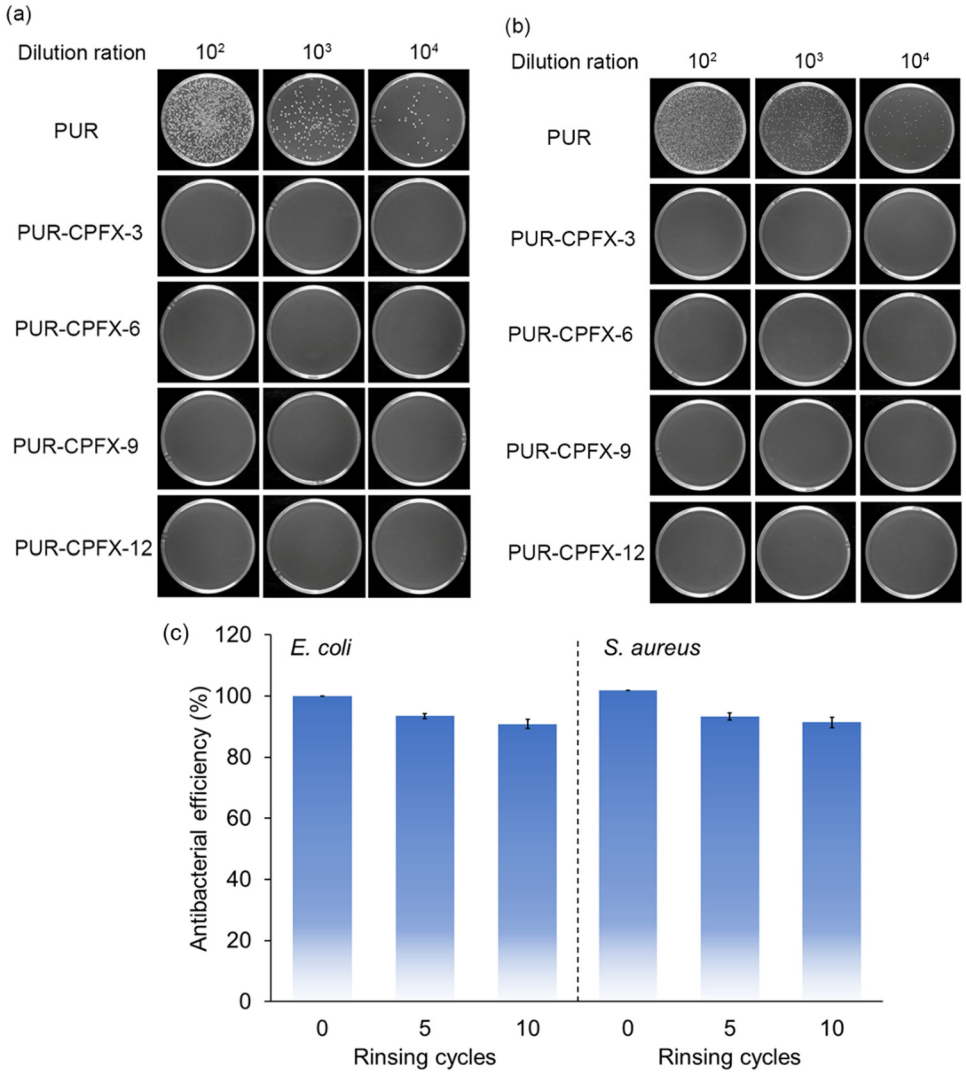


Figure 4: Antibacterial activity against (a) *E. coli* and (b) *S. aureus* of leather retanned by PUR and PUR-CPFXs. (c) Antibacterial efficiency against *E. coli* and *S. aureus* vs rinsing cycle.

by PUR-CPFX-9 displayed excellent antimicrobial properties against both strains, demonstrating a desirable antibacterial efficiency. It was found that the antibacterial activity could be conserved even after rinsing ten times, and the antibacterial efficiency against both strains remained above 89%. Only a slight decline was found, which could be due to the loss of retanning agents among collagen fibers. PUR-CPFX can endow leather products stable antimicrobial properties.

4 Conclusion

In this study, we designed and synthesized polyurethane-based retanning agents (PUR-CPFXs) with antimicrobial properties via chemically conjugating CPFX into polyurethane branched chains. Then, the PUR-CPFX was utilized as retanning agents in the leather manufacturing process. After the conjugation of CPFX into polyurethane chains, the molecular weight increases, further leading to the decrease in hydroxyl value and increase in particle size. As for wet blue, after being retanned, the shrinkage temperature is obviously increased. After retanning, the leather fibers were separated from each other, owing to the filling of retanning agents in the gap of fibers. Hence, the average thickness of leather increased by 65.8%. The mechanical properties of leather were visibly improved after retanning, on account of the large number of –COOH in the PUR coordinating with Cr^{3+} and more hydrogen cross-linking with carboxyl group, amino group, and hydroxyl group of leather collagen. Particularly, leather retanned

by PUR-CPFX exhibited good antimicrobial properties against Gram-positive or Gram-negative bacteria. The antibacterial activity could be conserved above 89% even after rinsing for ten times. These results suggested the potential application of PUR-CPFX as an antimicrobial retanning agent for leather manufacturing.

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