

Nonionic Short Fluorocarbon Chain Surfactants for Improving Application Properties of Acrylic Resin in the Retanning of Wet-blue Leather

by

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Abstract

Acrylic resin (AR) is one of the most commonly used leather retanning agents owing to its excellent selective filling property and low cost. However, there are some defects affecting the quality of wet-blue leather in the practical application of AR, such as “excessive convergence”, “detanning”, and “fading”. Herein, the nonionic short fluorocarbon chain surfactants (F6-m) combined with AR for retanning wet-blue goat leather to further improve the application properties of AR. In a series of comparative experiments, the grain surface state and mechanical properties of leather retanned with 4 wt% AR and 2wt% F6-400 are preferred. Moreover, after dyeing, the dye adsorption rate and a^* (red-greenness) value of AR/F6-400 retanned leather are higher than that of leather retanned with AR alone. The above issues reveal that F6-400 can improve application properties of AR in the retanning of wet-blue leather to a certain extent, benefiting to further upgrade the quality of leather.

Introduction

Retanning is one of the most critical unit operations in leather manufacturing, which can significantly affect the properties of leather, such as homogeneity and fullness.¹ Currently, acrylic resin (AR) is still widely used in the retanning of leather owing to satisfactory selective filling property and low cost.² However, a large number of carboxyl ions on AR also yield some abominable defects in the practical application for chrome-tanned leather. For example, carboxyl ions of AR may over combine with chromium ions on the leather grain surface during the penetration, resulting in the “excessive convergence” of leather grain surface. Furthermore, chrome-free/less tanned leather has become an inevitable trend owing to the environmental pollution associated with the release of chrome.³ Predictably, during the retanning process of chrome-less tanning leather, carboxyl ions on AR could easily capture chromium ions originally combined with collagen fibers, bring about the leather “detanning”; and compete with dye molecules (anionic dyes commonly used in leather production) for binding sites on leather, engendering the leather “fading”.⁴ Eventually, these unamiable issues greatly affect the property and economic value of leather.

In leather manufacturing, surfactants, appearing in almost all processes, play an important role in wetting, dispersing, emulsifying, solubilizing, etc.^{5,6} The most fundamental reason is that surfactants can significantly reduce the surface tension of the solution⁷ containing leather chemicals, facilitating leather chemicals to spread on the leather surface or penetrate the leather interior, thereby enhancing the production efficiency and product quality. Different from ionic surfactants, nonionic surfactants are in possession of adorable resistance for salt and pH, which can still hold stable surface activities in the attendance of electrolytes.⁸ Especially, this feature of nonionic surfactants is extremely important in the face of complex electrolytes in leather processing. In addition, research^{9,10} has shown that in ionic/nonionic mixed systems, the nonionic species can shield the ionic groups on ionic species via the steric hindrance effect. Inspired by this, if AR and nonionic surfactants are used together in the retanning of wet-blue leather, nonionic surfactants can not only reduce the surface tension of the bath for promoting the spreading and penetration of AR, but also shield the part of carboxyl ions on AR for inhibiting the excessive combination with chromium ions. Hence, the above advantages are expected to ameliorate defects of AR in the retanning of wet-blue leather, and ultimately further improve the leather quality.

Compared with common hydrocarbon surfactants, fluorinated surfactants usually have a higher surface activity. Since their advent in the 1950s,¹¹ the traditional long fluorocarbon chain surfactants, represented by perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), have been widely applied in leather, textile and other fields.^{12,13} However, it has been found that PFOA and PFOS have awful disadvantages such as high persistence and bioaccumulation,^{14,15} and are subsequently classified as persistent organic pollutants,¹⁶ so they have been banned in many fields. In recent years, researchers have turned their attention to the development of short fluorocarbon chain (less than seven CF_n groups) surfactants, and these short fluorocarbon chain surfactants have been confirmed to be more environmentally friendly.^{17,18} At present, although there are many reports on short fluorocarbon chain surfactants, there are few reports on their application in leather retanning.

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In this paper, the nonionic short fluorocarbon chain surfactants (F6-m) reported in our previous work¹⁹ and AR were used together in the retanning of wet-blue goat leather.

At the same time, to better implement the current environmental protection concept of less chrome, the wet-blue goat leather was not processed with extra chrome-retanning. The effects of the type of F6-m as well as the dosage of AR and F6-m on the leather properties were systematically investigated. The grain surface and cross section morphologies of leather were carefully assessed. Furthermore, the dyeing effect of the retanned leather also was evaluated by the common color difference parameters. The results showed that when AR and F6-m were applied together in the retanning of wet-blue leather, those defects including the grain surface “excessive convergence”, “detanning”, and “fading” were eliminated to a certain extent, and the application properties of AR are obviously improved.

This work provides a promising method for further enhancement of leather quality, and broadens the application range of fluorinated surfactants in the leather industry.

Materials and Methods

Materials

Wet-blue goat leather was purchased from the Chengdu Qingyang District Century Leather Management Department (Chengdu, China). Wetting dispersant (SWA), sulfonated fatliquor (JM), sulfited fatliquor (JMK), lecithin fatliquor (FS-90), sulfited neatsfoot oil fatliquor (DF) and AR were obtained from Sichuan Dowell Science and Technology Inc. (Chengdu, China). Sodium formate, sodium bicarbonate and formic acid were supplied by Kelong Chemical Reagent Factory (Chengdu, China). Red anionic dye (ME) was purchased from Current Tech Fine Chemical Co., Ltd (Ningbo,

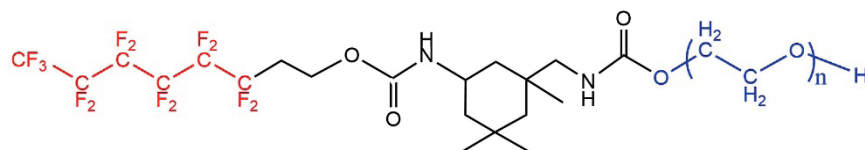


Figure 1. Chemical structure of F6-m.

Table I
Process Recipe for Leather Manufacture

Process/chemicals	Dosage(wt%)	Duration (min)	Temperature(°C)	Remarks
Rewetting				
Water	150		35	
SWA	0.2	60		Drain & Wash
Neutralization				
Water	150		35	
Sodium formate	1			
Sodium bicarbonate	1.5	60		pH 6.0 Drain & Wash
Retanning				
Water	150		35	
AR	X			X is 2, 4 or 6
F6-m	Y	90		Y is 1, 2 or 3
Formic acid	1	20 × 3 + 30		pH 4.0 Drain & Wash
Dyeing & Fatliquoring				
Water	150		40	
ME	1	45		Added only in the study of dye uptake
JM	6			
JMK	6			
FS-90	3			
DF	3	60		
Formic acid	0.6	20 × 3 + 30		pH 4.0 Drain & Wash
Horse up, hang-drying overnight				

China). F6-m (m is 400, 600, or 800, respectively, which represents the number average molecular weight of polyoxyethylene ether (PEO)) was synthesized according to the method in our previous work¹⁹, whose chemical structure is described in Figure 1. And the critical micelle concentrations (CMC) of F6-400, F6-600, and F6-800 are 0.120, 0.131, and 0.136 mmol, respectively; and their surface tensions at CMC (γ_{CMC}) are 25.8, 29.4, and 32.0, respectively.

Leather Processing

In order to ensure same leather fiber woven state, the wet-blue goat leather was cut into two pieces of the same size (30 cm × 30 cm) along the backbone. One of the wet-blue leather pieces was used as the control sample (C, no retanning) and the other was used as the experimental sample (E, retanning). All leather chemicals were offered according to the weight of wet-blue goat leather pieces. The process recipe of leather manufacture is listed in Table I.

Analysis of Leather Properties

Before performing tests, the resultant leather samples were kept at 65% relative humidity and 20°C for 24 h. The thickness of leather samples was measured by a GJ9B1 digital thickness tester (Gotech Testing Machines, China) according to the Chinese standard of QB/T 2709-2005. The softness of samples was tested on a GT-303 digital leather softness tester (Gotech Testing Machines, China) according to the standard method from QB/T 1872-2004. The mechanical properties, such as tensile strength (QB/T 2710-2005), elongation at break (QB/T 2710-2005) as well as tear strength (QB/T 2711-2005), were carried out using an AI-7000 SN tensile machine (Gotech Testing Machines, China) according to Chinese standards.

Morphology

The cross sections of resultant leather samples were observed using a JSM-7500F scanning electron microscopic (SEM) (JEOL, Japan). The grain surfaces of resultant leather samples were recorded on a M50 stereomicroscope (LEICA, Germany) equipped with a digital camera.

Dye adsorption rate

The dye (ME) solution was scanned in the range of 200-700 nm via a UV-1900 UV-visible spectrophotometer (Jinghua, China) to obtain the maximum absorption wavelength of ME. The dyeing bath samples at different time points were collected, and the absorbance of their diluents was determined at the maximum absorption wavelength. The adsorption rate (A) of dye was calculated using equation (1)²⁰:

$$A = \frac{(A_0 - A_t)}{A_0} \times 100\% \quad (1)$$

Where A_0 and A_t are the absorbance of dyeing baths at the beginning and other subsequent time points, respectively.

Color Difference Analysis

The color difference of dyed leather was tested on a MC-5 colorimeter (Konica Minolta, Japan). Total color difference (ΔE) was calculated from the CIE (L^* , a^* , b^*) 1976 formula²¹ (2):

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (2)$$

Where L^* , a^* , and b^* are black-white, red-green and yellow-blue color coordinates, respectively; ΔL^* , Δa^* , and Δb^* represent the change between L^* , a^* , and b^* values of leather samples, respectively.

Results and Discussion

Effects of Different Retanning Systems on Leather Properties

At the total dosage of 4 wt% (among them, the mass rate of AR/F6-m is 1:1), the organoleptic and mechanical properties of leather treated by different retanning systems are shown in Table II and Figure 2, respectively. It is seen clearly that the properties of leather retanned with AR or AR/F6-m are different. The thickening rates of leathers retanned with AR, AR/F6-400, AR/F6-600 or AR/F6-800 are 9.8%, 7.5%, 7.5% and 5.4%, respectively. Evidently, although the dosage of AR in the single AR system is twice as much as that of AR in the AR/

Table II
Organoleptic Properties of Control (C) and Experimental (E) Leathers Retanned with Different Retanning Systems at Total Dosage of 4 wt%.

Retanning agents	Groups	Thickness (mm)	Softness (mm)
AR	C	1.12	9.1
	E	1.23	8.8
AR/F6-400	C	1.34	8.5
	E	1.44	9.2
AR/F6-600	C	1.33	7.9
	E	1.43	8.6
AR/F6-800	C	1.3	8.1
	E	1.37	8.9

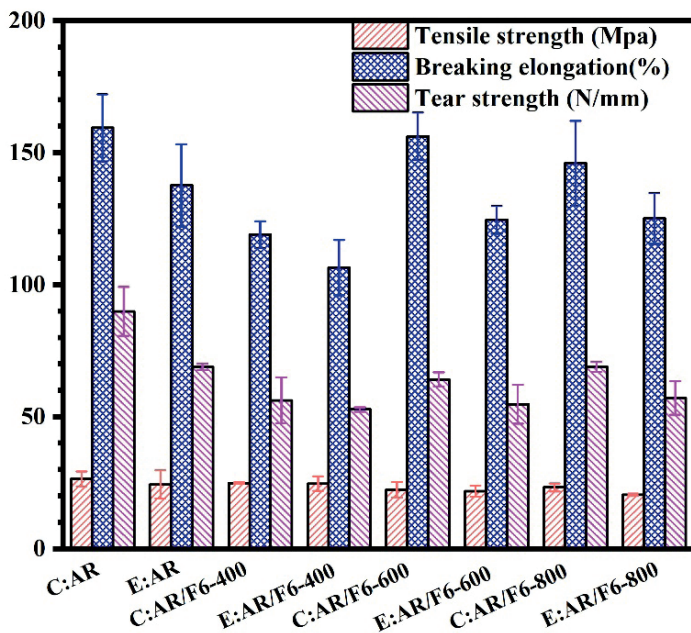


Figure 2. Mechanical properties of control (C) and experimental (E) leathers retanned with different retanning systems at total dosage of 4 wt%.

F6-m composite system, the thickening effect of single AR system does not reach twice of AR/F6-m composite system. It indicates that the combination of F6-m with AR shows a synergistic retanning effect on wet-blue goat leather.

The reasons for the synergistic retanning effect might be as follows: 1) the steric hindrance effect of nonionic F6-m shields the partially dissociated carboxyl groups on AR molecular side chains, avoiding the excessive binding of AR with chromium ions on the leather surface at the initial stage of retanning;²² 2) F6-m with high surface activity reduces the interface tension between AR and collagen fibers, promoting more AR molecules to enter the interior of leather;²³ 3) furthermore, when the bath pH is reduced at the later stage of retanning, the hydrogen bonding between carboxy groups on AR and ether groups on F6-m is strengthened,²⁴ which cooperates with the hydrophobic interaction offered by the fluorocarbon chain of F6-m to drive the formation of AR/F6-m composite aggregates,²⁵ and further results in nonionic F6-m also being fixed and filled inside the leather. These reasons make the thickening effect of the AR/F6-m composite system better than that of the single AR system.

Meanwhile, it is noteworthy that, compared with the further deteriorated softness of AR retanned leather (-3.3%), the softness of AR/F6-m retanned leather has a significant enhancement, with approximately 9.0%. It demonstrates that these fluorinated surfactants also facilitate the absorption of subsequent fatliquoring agents by leather to improve the mobility of collagen fibers.²⁶ In the fatliquoring process, fatliquoring agents may further be emulsified by the partial free F6-m with high surface activity (see the material statement above); and the electrostatic repulsion between AR and

anionic fatliquoring agents may be inhibited by nonionic F6-m due to the steric hindrance effect. Finally, these factors make it easier for the fatliquoring agent to enter the leather and further lubricate collagen fibers, thereby enhancing the softness of leather.^{27,28}

In terms of mechanical properties (as shown in Figure 2), the tensile and tear strengths of AR retanned leather exhibit a significant decline, about 7.9% and 23.4%, respectively, which shows the obvious “detanning” effect of AR. In contrast, intriguingly, the reducing rates of mechanical strength of AR/F6-400 retanned leather are lower, and the reducing rates of tensile and tear strengths are 0.6% and 6.1%, respectively, demonstrating that F6-400 can inhibit the “detanning” effect of AR for the chrome-less tanned leather. This is probably because that the carboxyl groups on AR capture the chromium ions originally combined with collagen fibers, resulting in the reduction of crosslinking density between collagen fibers (as shown in Figures 3a and 3b). Conversely, after combined use of AR and F6-400, since F6-400 and AR may self-assemble into composite aggregates to shield some carboxyl groups on AR, the capture ability of AR to chromium ions that have been combined with collagen fibers is weakened, which still maintains a better crosslinking effect between collagen fibers (as shown in Figures 3a and 3c). In forming composite aggregates process, the possible driving forces are as follows: 1) the hydrogen bonding between AR and F6-600, intensifying the molecular chain entanglement between AR and PEO of F6-400; 2) the hydrophobic interaction from fluorocarbon chains on F6-400, driving fluorocarbon chains to form the hydrophobic microdomain, and resulting in the surrounding AR and PEO molecular chains to shrink toward the hydrophobic microdomain.

Moreover, in AR/F6-m, with the increase of PEO chain length (m increases from 400 to 800), the inhibitory effect of F6-m on the “detanning” effect of AR is weakened, and the tensile and tear strengths of AR/F6-800 retanned leather reduce 12.2% and 17.2%, respectively. This is likely due to the fact that the longer PEO chain provides more hydrogen bonding sites that can interact with carboxyl groups of AR, which increases the possibility that chromium ions are encapsulated by AR/F6-m composite aggregates (as shown in Figures 3c and 3d), and eventually weakens the crosslinking effect of chromium ions on collagen fibers. In summary, the retanning performance of AR/F6-400 is superior to the other listed retanning system. Thus, AR/F6-400 would be allowed to be used in the following studies.

Effect of the Dosage of AR on Leather Properties

Based on the above research results of AR/F6-400 (2 wt%/2 wt%), the dosage of F6-400 was fixed at 2 wt%, and effects of the dosage of AR on leather properties were studied. The results are shown in Table III and Figure 4. With increasing dosage of AR from 2 wt% to 4 wt%, the thickening rates increase significantly from 7.5% to 22.3%, and the increasing rates of softness change little and remain at about 9.0%. The higher thickening rate indicates that more AR/F6-400

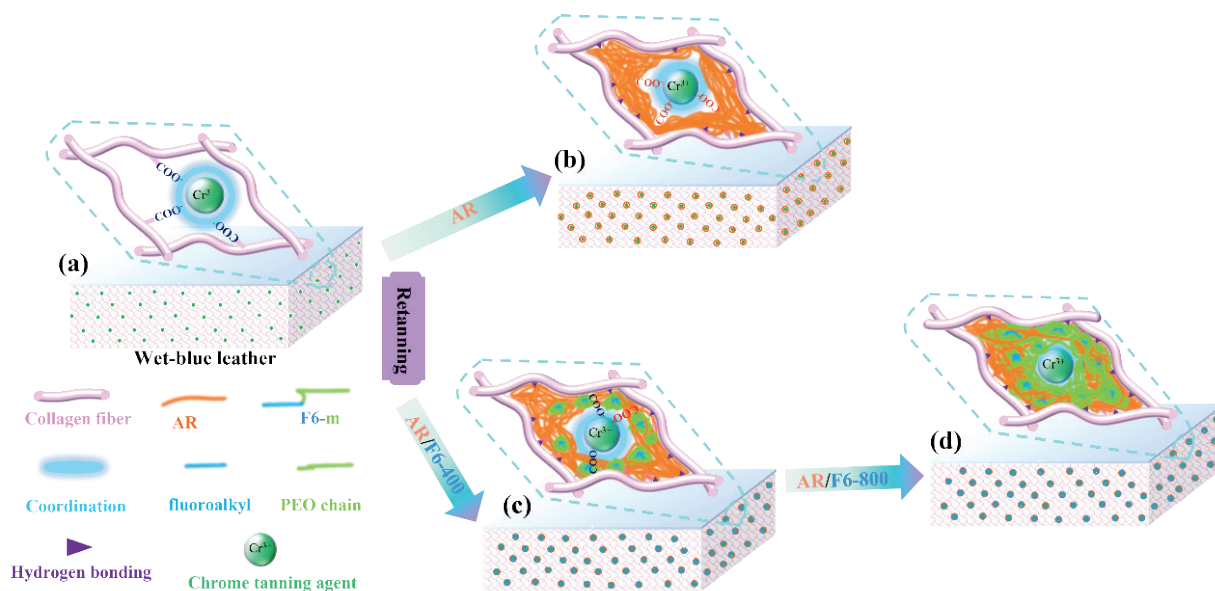


Figure 3. Schematic diagram of proposed retanning mechanism of wet-blue leather.

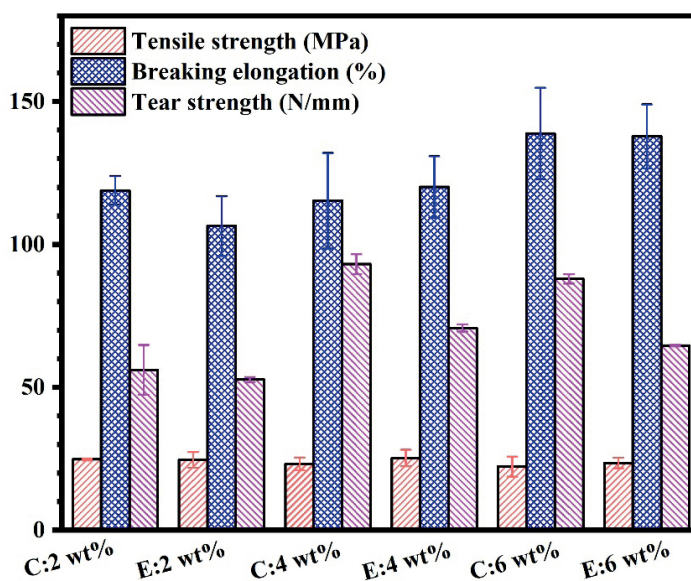


Figure 4. Mechanical properties of leathers retanned with different dosages of AR and 2 wt% F6-400.

TABLE III

Organoleptic Properties of Leathers Retanned with Different Dosages of AR and 2 wt% F6-400

Dosage (wt%)	Groups	Thickness (mm)	Softness (mm)
2	C	1.34	8.5
	E	1.44	9.2
4	C	1.12	8.2
	E	1.37	8.9
6	C	1.21	8.3
	E	1.41	8.6

Table IV
Organoleptic Properties of Leathers Retanned with Different Dosages of F6-400 and 4 wt% AR

Dosage (wt%)	Groups	Thickness (mm)	Softness (mm)
1	C	1.18	7.5
	E	1.36	8.4
2	C	1.12	8.2
	E	1.37	8.9
3	C	1.13	7.6
	E	1.17	8.2

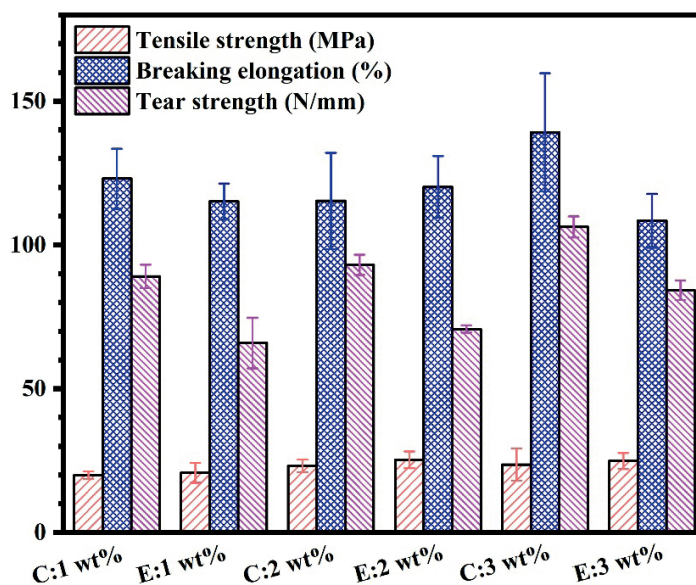


Figure 5. Mechanical properties of leathers retanned with different dosages of F6-400 and 4 wt% AR.

is filled in the gap between collagen fibers. And these AR/F6-400 would also provide more hydrogen bonding sites that can interact with carboxyl, amino, and hydroxyl groups on the collagen fibers, thus allowing AR/F6-600 to tightly cover the collagen fiber surfaces, and further increasing the maximum external force that the collagen fibers can withstand under axial stretching.²⁹ Ultimately, the tensile strength increases from -0.6% to 9.1%.

With the continuous increase of AR dosage to 6 wt%, the leather properties do not further improve significantly, and even deteriorate to some extent. This is likely because that when the dosage of AR is too high, the number of carboxyl anions provided by AR is higher, weakening relatively the role of F6-400. This would make AR to excessively combine with chromium ions on the superficial layer of leather, thereby preventing the penetration of retanning agent and subsequent fatliquoring agents into the leather, and affecting the improvement of leather properties. To sum up, when the dosage of F6-400 is 2 wt%, 4 wt% AR will optimize the comprehensive properties of the leather.

Effect of the Dosage of F6-400 on Leather Properties

The dosage of AR was fixed at 4 wt%, and effects of the dosage of F6-400 on leather properties were studied. The results are presented in the Table IV and Figure 5. When the dosage of F6-400 increases from 1 wt% to 2 wt%, the increasing rate of thickness raises from 15.3% to 22.3%, demonstrating that more AR/F6-400 is filled in leather. Meanwhile, the mechanical strength of leather is further improved, in which the increasing rate of tensile strength increases from 3.9% to 9.1%. There are two possible reasons that 1) when more AR/F6-400 is filled in leather, the hydrogen bonding between AR/F6-600 and collagen fibers is strengthened; 2) with growing dosage of F6-400 in AR/F6-400 composite system, the capture ability of AR to chromium ions that have been combined with collagen fibers is weakened because the possibility of carboxyl ions on AR being shielded by F6-400 increases. The above two reasons maintain the cross-linking strength between collagen fibers, but also hinder the mobility of collagen fibers, which declines the improved softness from 12.0% to 8.5%.

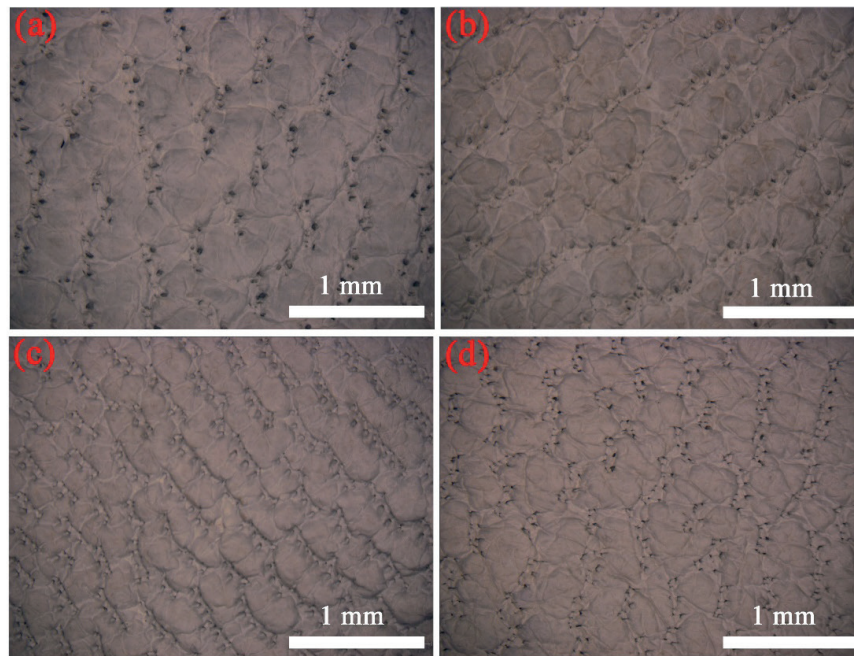


Figure 6. Images of leather grain surfaces under different retanning conditions: no retanning (a); 4 wt% AR (b); 2 wt% AR, 2 wt% F6-400 (c); 4 wt% AR, 2 wt% F6-400 (d).

In addition, when the dosage of F6-400 continuously increases to 3 wt%, the increasing rates of thickness and softness do not continue to increase, and even present a downward trend. It may be ascribed to the fact that with increasing dosage of F6-400, the hydrogen bonding between F6-400 and AR as well as AR/F6-400 and collagen fibers is also boosted, which makes AR/F6-400 easier to aggregate and adhere to the leather surface and further hinders the subsequent fatliquoring effect. Additionally, at this time, the increasing rate of tensile strength decreases from 9.1% to 5.3%. Ultimately, considering

the economic cost and leather properties, the optimal result is the combination of 4 wt% AR and 2 wt% F6-400 in the retanning of wet-blue leather.

Morphology Analysis of Grain Surfaces

Morphology features of leather grain surfaces were obtained by a stereomicroscope and shown in Figure 6. It is easy to find that compared with the leather without retanning, the pores of leather retanned with AR obviously shrink, which demonstrates that AR

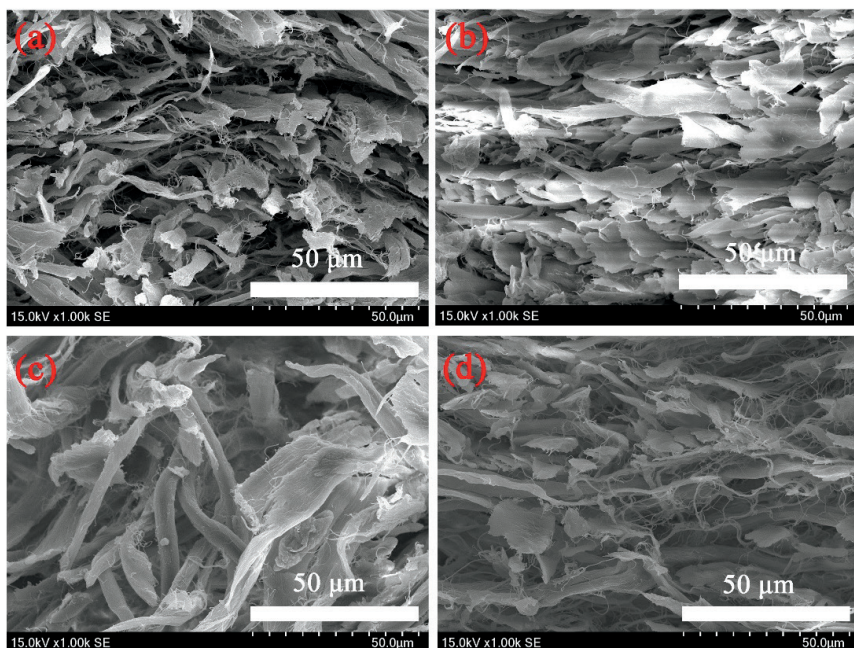


Figure 7. Images of the leather cross section under different retanning conditions: no retanning (a); 4 wt% AR (b); 2 wt% AR, 2 wt% F6-400 (c); 4 wt% AR, 2 wt% F6-400 (d).

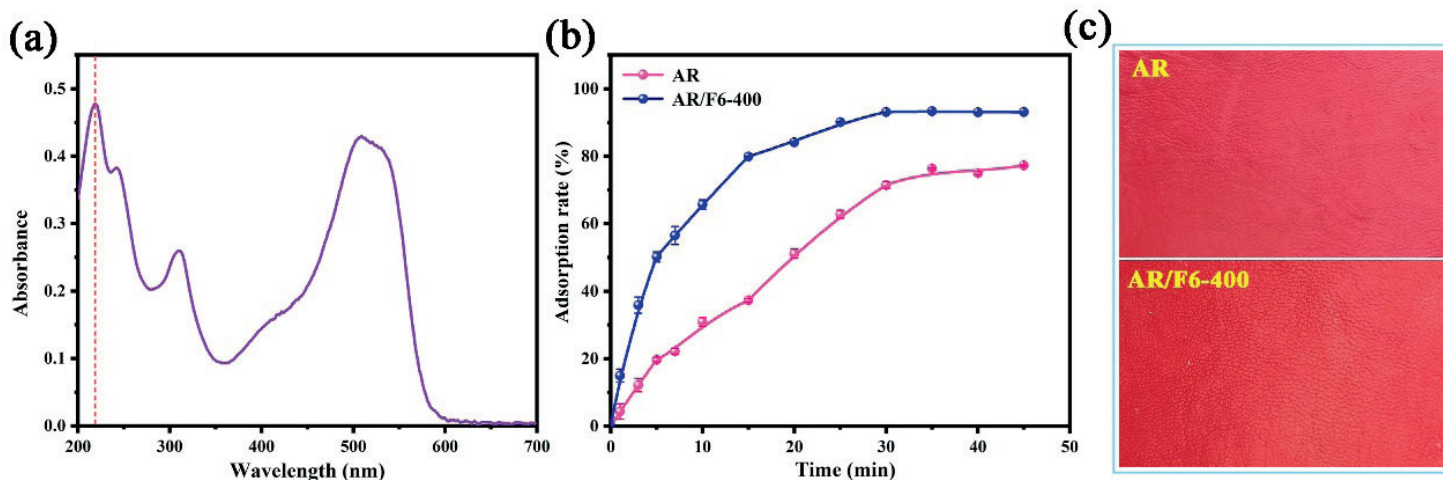


Figure 8. Full wavelength spectrum of ME (a); adsorption rate of dye on leather retanned by 4 wt% AR or 4 wt% AR/F6-400 (b); and the resultant leather after dyeing (c).

Table V

Chroma Color Difference Values of Dyed Leather

	L*	A*	B*	ΔE^*
4 wt% AR	50.3±0.3	48.7±0.4	32.8±0.6	4.6
4 wt% AR/F6-400	46.4±0.7	50.2±0.4	34.7±0.7	

shows an apparent “convergence” to leather grain surface. While the pores of AR/F6-400 retanned leathers shrink slightly, and they are still clear. This additionally proves that F6-400 promotes the penetration of AR in leather, thereby weakening the combination of AR and chromium ions on the leather grain surface and avoiding “excessive convergence” of leather grain surface.

Morphology Analysis of Cross Section

The fiber weave structure of leather cross section was observed by SEM, and the results are shown in Figure 7. It can be clearly seen that the fibers of leather without retanning are thicker and the fiber gap is uneven; and the gap between fibers of AR retanned leather is narrower. By contrast, the space between fibers of AR/F6-400 retanned leathers is wider, and their arrangement is looser, which indicates that F6-400 promotes the penetration and absorption of subsequent fatliquoring agents in leather and is consistent with the former softness result.

Dyeing

It can be obtained from Figure 8a that the maximum absorption wavelength of dye (ME) is 219 nm. The dye adsorption rate calculated by measuring the absorbance of the dyeing bath at 219

nm is shown in Figure 8b. Under the same operation time and total dosage with 4 wt%, the dye adsorption rate of AR/F6-400 (1:1) retanned leather is higher than that of AR retanned leather, with dye adsorption rates reaching 93.1% and 77.3% at the end of dyeing, respectively. Simultaneously, as expected, Figure 8c indicates that compared with AR, AR/F6-400 retanned leather shows a higher adsorption capability to dye. The main reason is that the steric effect of nonionic F6-400 weakens the electrostatic repulsion between AR and anionic ME, and some incompletely fixed F6-400 also further promotes the dispersion and penetration of ME in leather.

The color of dyeing leathers is evaluated by the CIE Lab 1976 standard colorimetric system. As shown in Table V, L* (black-whiteness) and a* (red-greenness) values of AR/F6-400 retanned leather are lower and higher than those of the AR retanned leather, respectively, which indicates that the AR/F6-600 retanned leather is brighter and redder. And ΔE^* (total color difference) value is 4.6 and higher than the industrial color difference approving limit of 1.0,³⁰ revealing that there is obvious color difference between two samples. These results show that the dyeing effect of AR/F6-400 retanned leather is better as compared to the AR one, and F6-400 improves the “fading” defect of AR in the retanning of wet-blue leather.

Conclusions

In this work, the nonionic short fluorocarbon chain surfactants (F6-m) and AR were used in combination to retan wet-blue goat leather. The results showed that the combination of 4 wt% AR and 2wt% F6-400 is the optimal retannage ratio. After retanning, the grain surface state and mechanical properties of AR/F6-400 retanned leather were better than that AR retanned leather, illustrating that F6-400 could greatly improve the application properties of AR, and correspondingly avoid the occurrence of defects like the grain surface “excessive convergence” and “detanning”, in the retanning of wet-blue leather. Furthermore, the dyeing effect of AR/F6-400 retanned leather was better than that of AR retanning leather, which indicates that F6-400 can ameliorate the “fading” effect of AR. Most importantly, it provides a promising ideal for further improving application properties of AR in the retanning of wet-blue leather, which is conducive to further enhance leather quality and broaden the application range of fluorocarbon surfactants in leather industry.

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