

Interaction between Amphoteric Polymer and Silicic Acid Tanned Leather: Ingenious Regulation of pH based on Isoelectric Point

by

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Abstract

Silicic acid-based tanning system is an effective and promising chrome-free tanning technology, and it is urgent to develop compatible post-tanning processes. Fatliquoring is one of the key procedures to determine the quality of resulted leather and fatliquoring agents mainly play the role of an effective softer/plasticizer in leather production. However, there is a mismatch between most commercial fatliquoring agents (mainly compatible with chrome tanned leather) and silicic acid tanned leather (named SATL). Herein, an amphoteric polymer emulsion (APE) was prepared by free radical polymerization using methacryloxyethyl trimethyl ammonium chloride (DMC), 2-acrylamido-2-methylpropanesulfonate (AMPS), lauryl methacrylate (LMA), dimethylaminoethyl methacrylate (DMAEMA) as monomers. And in order to improve the lubricating property, APE was further compounded with castor oil to obtain an amphoteric fatliquoring agent (named COAPE). Comprehensive characterization showed that the amphoteric ($pI=8.22$) and amphiphilic APE could reduce the surface tension of water to 38.6 mN/m. The fatliquoring process was controlled by ingenious regulation of pH based on isoelectric points (pIs) of APE and SATL. In the initial stage, the pH of the bath was adjusted to be lower than the pIs of APE and SATL, amphoteric polymer molecules could easily penetrate into SATL leather as they are all positively charged. While during the fixing stage, the pH of the bath was adjusted between the pIs of APE and SATL, so the electrostatic interaction between amphoteric polymer molecules and SATL leather, as well as the aggregation of amphoteric polymers can promote their combination synergistically. As a fatliquoring agent, the application of COAPE demonstrated that its absorption rate (90.5%) was much higher than anionic commercial fatliquoring agent (63.2%), thus imparting SATL leather better softness (6.5 mm), elongation at break (95.5%) and tensile strength (11.6 N/mm²). These findings therefore provided scientific basis and technical support for the application of amphoteric materials to silicic acid-modified collagen matrix and would promote the practical application of silicic acid-based chrome-free tanning technology.

1. Introduction

Currently, chrome tanning still occupies the dominant position in leather industry as it can endow leather with excellent thermal stability and organoleptic properties.¹ However, chrome tanning process is facing severe restrictions due to the pressure of environmental protection and resource conservation.² Therefore, in recent years, people have devoted themselves to the research of chrome-free tanning systems, and some of them have achieved satisfactory results in practical application, including a multi-metal complex tanning system,³ Tanfor TTM tanning system,⁴ TWT/TWS tanning system,⁵ F-90 tanning system⁶ and so on. Our team also developed a silicic acid-based chrome-free tanning system, which can obviously improve shrinking temperature and the porous structure of leather.⁷ The analysis of tanning mechanism revealed that the intermolecular co-condensation of Si-OH groups of silicic acid as well as hydrogen bonds between silicon hydroxyl groups and collagen amino groups played major roles in the tanning process.⁸ Moreover, this silicic acid-based tanning process can be further improved by adding pretreatment additives or combination tanning methods.^{7,9} However, the comprehensive properties of silicic acid tanned leather (SATL), such as lack of sufficient softness and flexibility, need to be improved through subsequent post-tanning processes. Therefore, it is an impending requirement for its practical application to develop matchable post-tanning processes.

Among post-tanning processes, fatliquoring is one of the key operations since it gives leather softness, fullness and elasticity.¹⁰ During the fatliquoring process, the fatliquoring agent can penetrate into collagen fibers, and play a role in lubrication and plasticization by reducing friction in woven fiber network, preventing the collagen fibers from adhesion to each other during drying, thus providing pleasant softness and flexibility for leather.¹¹ However, at present, the fatliquoring agents used in leather production are mainly those with anionic charges that are compatible with chrome tanned leather. Unfortunately, similar to most organic tanning processes, in the silicic acid tanning process, amino groups of collagen fibers are mainly consumed which makes tanned leather have a lower isoelectric point, thus leading to poor absorption of anionic

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Manuscript received March 193, 2023, accepted for publication May 7, 2023.

fatliquoring agent.^{8,12,13} Hence, it is necessary to develop novel fatliquoring agents matching well with SATL leather.

Fortunately, the amphoteric polymeric fatliquoring agent contains both anionic and cationic groups with pH-responsive function, exhibiting positive or negative charges at different pH.^{14,15} By changing the pH of bath liquid, the charge state of amphoteric fatliquoring agent can be adjusted to adapt to the surface charge state of chrome-free tanned leather, allowing them to carry the same or opposite charge, thus effectively overcoming the problem of absorption caused by weak electrostatic interaction, which has been confirmed by recent reports.^{16,17} Hao et al. synthesized an imidazole ionic liquid-based amphoteric polymer as fatliquoring agent for F-90 tanned leather, which has higher absorption rate than a commercial anionic fatliquoring agent.¹⁸ Sun et al. obtained an amphoteric peptide-based fatliquoring agent, which has good compatibility with F-90 organic chrome-free tanning system.¹⁹ Liu et al. designed a amphoteric polymer P(AA-AM-C12DM) with retanning and fatliquoring dual functions, which endows the organic chrome-free TWS tanned leather with excellent softness, thickening rate and mechanical properties, and has greater absorption rate (96%) than that of an anionic commercial fatliquoring agent (75.8%).²⁰ However, a systematic analysis of the penetration and combination of amphoteric fatliquoring agents in leather from the perspective of their surface charge states, and especially the application of amphoteric polymers to silicic acid tanned leather or silica-modified collagen materials has not been reported yet.

On the other hand, leather made from animal skin or hide is rich natural biomass polymer matrix, which is mainly composed of collagen.²¹ Collagen is a typical amphoteric polyelectrolyte since it contains basic amino acid residues (lysine, arginine and histidine) and acidic amino acid residues (glutamic acid and aspartic acid), which also confer amphoteric character to leather.²² During the process of leather manufacture, the variation of pH of bath liquid can directly affect the surface charge state of leather.¹⁶ Additionally, the electrostatic interaction between the chemicals (including fatliquoring agents) and leather is the decisive factors of their mass transfer and combination in leather.²³ Therefore, based on their pIs, the surface charge states of amphoteric fatliquoring agent and leather can be changed by ingeniously regulating the pH value of bath liquid, so as to accurately control the penetration, distribution and fixation of amphoteric fatliquoring agents in the leather matrix. What's more, the combination mechanism between amphoteric fatliquoring agents and leather can be easily explored from the perspective of their surface charge states.

Herein, in this work a novel amphoteric polymer emulsion (APE) was synthesized by free radical polymerization with methacryloxyethyl trimethyl ammonium chloride (DMC), 2-acrylamido-2-methylpropanesulfonate (AMPS), lauryl methacrylate (LMA) and dimethylaminoethyl methacrylate (DMAEMA) as monomers,

and it was compounded with castor oil to prepare amphoteric fatliquoring agent (COAPE). Both of them were applied to the fatliquoring process of SATL leather for comparison. Meanwhile, a commercial anionic polymer fatliquoring agent was adopted as a contrast. From the point of view of surface charge states, the interaction mechanism between the amphoteric polymer and SATL leather as well as the function of amphoteric characteristics were systematically studied. The research results can provide technical support for the application of amphoteric polymers in silicic acid tanned leather, which is of great significance for the improvement of silicic acid-based tanning system. It can also provide reference for the development of other chrome-free technologies.

2. Experimental

2.1 Materials

Silicic acid tanned goatskins were prepared in our laboratory according to our previous work.⁷ DMC (75%) was purchased from Macklin Biochemical Co., Ltd. (Shanghai, China). AMPS (98%), LMA (96%) and DMAEMA (99%) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Sodium dodecyl sulfonate (SDS, AR), Aliphatic alcohol polyoxyethylene ether (AEO-9, AR), potassium persulfate (KPS, AR), and sodium hydroxide (NaOH, AR) were purchased from Chengdu Kelong Chemical Reagent Co., Ltd. (Sichuan, China). Commercial fatliquoring agent (copolymer of modified natural/synthetic oil and acrylic acid, anionic) and other chemicals used for leather manufacturing were of industrial grade. All reagents were used directly without any further purification.

2.2 Synthesis of amphoteric polymer emulsion (APE) and amphoteric fatliquoring agent (COAPE)

APE was synthesized by free-radical emulsion polymerization. Firstly, the required amount of water-soluble monomers AMPS (anionic), DMC (cationic), DMAEMA (cationic) and deionized water were uniformly mixed in a beaker, and the pH value was adjusted to 5.0 with 10wt% sodium hydroxide to prepare a water-soluble monomer mixture. Then, emulsifier AEO-9 and SDS were added into a four-neck round-bottom flask equipped with a reflux condenser, a mechanical stirrer, a thermometer and additional funnels together with appropriate water, and stirred at 75°C for 30 min in nitrogen atmosphere. After that, the water-soluble monomer mixture, LMA (oil-soluble monomer) and the pre-prepared initiator solution were respectively dropped into the flask simultaneously within 2 h. The reaction continued at 80°C for 2 h, and then the reaction was kept at 85°C for another 2 h in order to complete the conversion. Finally, the milky white emulsion APE with a solids content of about 33% was obtained by naturally cooling to ambient temperature and filtering through a 200-mesh nylon net. In addition, the APE sample was precipitated and washed with anhydrous ethanol to remove residual monomers, and then the precipitate was dried in a vacuum oven at 40 °C for 24 h to obtain pure amphoteric polymer poly(AMPS-DMC-DMAEMA-LMA). The synthetic route of APE is shown in Figure 1a.

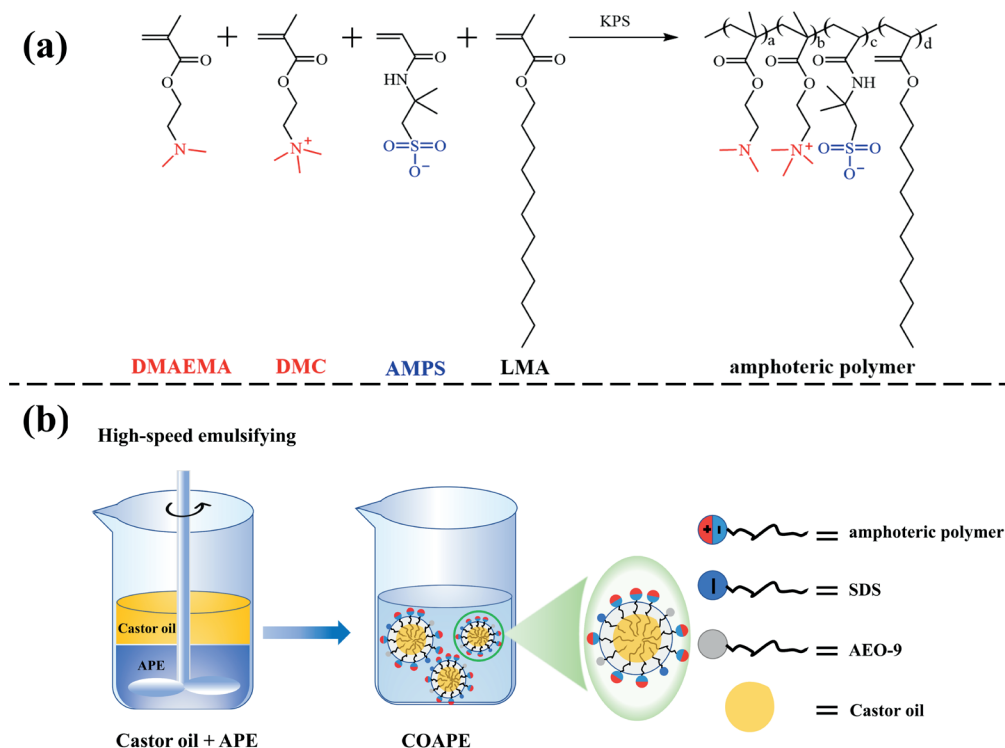


Figure 1. Synthetic route of (a) APE and (b) COAPE

Furthermore, castor oil was emulsified by APE at about 1:1 mass ratio to prepare COAPE. In brief, 30.0 g of APE, 9.9 g of castor oil and 9.6 g of deionized water were mixed at 3500 rpm for 20 min by a high-speed dispersion homogenizer (XHF-DY, SCIENTZ, China). The solid content of COAPE was maintained at 40 % (Figure1b).

2.3 Characterization and properties of APE and the amphoteric polymer

2.3.1 Fourier transform infrared (FTIR) spectrometry

FTIR spectra was collected at ambient temperature using a Nicolet iS10 FTIR spectrometer (Thermo Scientific, USA). The samples were prepared by KBr tablet method, which was measured in the range of 400 - 4000 cm^{-1} .

2.3.2 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy spectra were conducted using the Escalab-220i XPS (Kratos, Japan) with a monochromated Al K α ($h\nu = 1100$ eV) X-ray source of 250 W at 15 kV. Particularly, the high-resolution XPS spectra of the N1s and O1s was measured respectively at energy 20 eV.

2.3.3 Determination of surface tension

The surface tension of APE and the corresponding amphoteric polymer aqueous solution were respectively measured by Wilhelmy plate method on an automatic surface tensiometer (BZY-1, Shanghai Hengping Instrument and Meter Co., ltd., China).²⁴ Thus, various concentrations of APE were prepared for measurement, and each test was conducted in triplicate at ambient temperature.

2.3.4 Average particle size, particle size distribution and zeta potential

Average particle size, particle size distribution and zeta potential of APE were determined using a dynamic light scattering particle size analyzer (Zetasizer nano zsp, Malvern, England). The pH of APE with a mass fraction of 0.2% was adjusted to 3.0 - 10.0 by 0.1 mol/L HCl or NaOH solution before test.

2.4 Application of APE and COAPE in leather fatliquoring process

2.4.1 The pI of SATL leather

The pI of SATL leather was represented approximately by the pI of silicic acid treated gelatin solution, which was prepared according to the literature.⁸ Then the zeta potential of silicic acid treated gelatin solution (0.2 wt.%) under different pH conditions were recorded, and its pI was calculated.

2.4.2 Fatliquoring process

The detailed fatliquoring process is shown in Table I. In order to better promote the penetration and absorption of APE in SATL leather and further explore the binding mechanism between amphoteric copolymer and SATL leather, we preset different initial pH values of fatliquoring and fixing pH values at the end of fatliquoring to control the surface charge states of amphoteric copolymer and SATL leather during fatliquoring. The corresponding preset initial pH value and fixing pH value are shown in Table II. In schemes 1, 2 and 3, sufficient penetration of fatliquoring agent was expected at the initial stage (setting the initial pH value below the pI of APE and

Table I
Fatliquoring process

Process	Chemicals	Dosage ^a (%)	Temperature(°C)	Time(min)	Remarks
Washing	Water	200×2	25	15×2	Drain
Adjusting pH value	Water	100	25		
	Sodium bicarbonate or formic acid	0.5×n		30	Achieving the initial pH, drain
Fatliquoring	Water	150	50		
	Fatliquoring agent	5		90	
Fixing	Sodium bicarbonate or formic acid	0.5×n		30	Achieving the fixing pH, drain
Washing	Water	200×2	25	10×2	Drain
Hang drying					

^aThe dosage of chemicals was calculated based on the weight of SATL leather.

SATL to 4.0) aiming at obtaining optimal fixing pH value that can achieve the best combination effect. Then, on this basis, in schemes 4, 5 and 6, the optimal fixing pH was kept constant to explore the optimal initial pH that can achieve the best penetration effect. Finally, in schemes 7, 8 and 9, under the above-obtained optimal initial pH and fixing pH conditions, SATL leather was fatliquored with APE, COAPE, and a commercial fatliquoring agent, so as to investigate whether the amphoteric fatliquoring agent COAPE matched with the silicic acid-based tanning system. Notably, the silicic acid tanned goatskin leather was cut symmetrically into small samples (20 cm × 20 cm) along the back ridge line to keep the starting states roughly identical.

2.4.3 Absorption of fatliquoring agent

The total organic carbon concentration (TOC) of bath liquid samples at the beginning and the end of fatliquoring were measured

using a TOC analyzer (Vario TOC, Elementar, Germany). Then the absorptivity of fatliquoring agent was calculated by the following formula (1):

$$\text{Absorptivity (\%)} = \frac{(T_0 - T_1)}{T_0} \times 100\% \quad (1)$$

where T_0 is the TOC of bath liquid sample at the beginning fatliquoring, and the T_1 is the TOC of bath liquid sample at the end fatliquoring.

2.4.4 Shrinkage temperature (T_s)

Shrinkage temperatures of leather samples treated with different schemes were tested on a digital shrinkage thermometer (MSW-YD4, Sunshine Electronic Research Institute of Shaanxi University of Science and Technology, China). Each sample was tested three times and the average value of these tests was calculated.

Table II
Fatliquoring agent and pH value of bath liquid used in different fatliquoring schemes

Schemes	Fatliquoring agent	Initial pH	Fixing pH
Scheme 1	APE	4.0	6.0
Scheme 2	APE	4.0	7.5
Scheme 3	APE	4.0	8.0
Scheme 4	APE	4.0	7.5
Scheme 5	APE	5.0	7.5
Scheme 6	APE	6.0	7.5
Scheme 7	APE	4.0	7.5
Scheme 8	COAPE	4.0	7.5
Scheme 9	Commercial polymer fatliquoring agent	4.0	7.5

2.4.5 Thickening rate

The thicknesses of leather before and after fatliquoring were measured with a thickness gauge. The thickness of untreated leather was marked as d_0 (mm), while the thickness of fatliquored leather was recorded as d_1 (mm). Subsequently, the thickening rate (Tr) was calculated according to the following formula (2):

$$Tr (\%) = \frac{(d_1 - d_0)}{d_0} \times 100\% \quad (2)$$

2.4.6 Physical and mechanical properties

The tensile strength and elongation at break were measured by a tensile tester (AI-7000S, Gotech Testing Machines Inc., China) according to ISO 3376-2020. According to the principle of symmetrical position sampling, two horizontal and two vertical samples were taken from the corresponding positions of leathers treated with different schemes, then these samples were conditioned according to ISO 2419-2012 before test.

The softness of leather samples before and after fatliquoring was measured by a leather softness tester (GT-303, Gotech Testing Machines Inc., China) referring to the standard of ISO 17235-2015. Each sample was tested at least three times at different parts of leather, the average value of these tests was calculated.

2.4.7 Scanning electron microscope (SEM)

The cross-sections of leather samples treated with different fatliquoring agents were observed using field emission scanning electron microscopy (SEM, JSM-7500F, JEOL, Japan) at 3.0 kV with different magnifications. The specimens with uniform size were coated with gold before testing. Finally, the pore size distribution and the average pore diameter were calculated by software Nano-Measurer according to these SEM images.

2.4.8 Light fastness

A discoloration meter (GX-503-A, Gaoxin Testing Machines Inc., China) was applied to measure the light fastness of leather samples under simulated sunlight. Specifically, the leather samples with the size of 120 mm×40 mm were placed on the tray of discoloration meter and aged by at 50°C for 12h with a 300 W bulb constituted the simulated sunlight source. The grain of leather faced the bulb and was 250 mm apart. Then the color of the leathers was measured according to the Commission Internationale de l'Éclairage (CIE) 1976 $L^*a^*b^*$ color spaces.²⁵ The L^* (lightness-darkness), a^* (redness-greenness), b^* (yellowness-blueness) values were measured by Chromaticity analyzer (CM3700A, Konica Minolta Inc., Japan), and the color difference between unaged and aged leather was calculated by the following formula (3):

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (3)$$

3. Results and Discussion

3.1 Characterization and properties of APE and the amphoteric polymer

3.1.1 FT-IR spectrum analysis

The FT-IR spectrum of the corresponding amphoteric polymer is presented in Figure 2a. The wideband nearby 3446 cm^{-1} is attributed to the stretching vibration peak of -NH in the amide group (-CONH-).²⁶ Two typical peaks at 2926 cm^{-1} and 2855 cm^{-1} are ascribed to the symmetric and asymmetric stretching vibrations of C-H from the -CH₃ and -CH₂ groups in dodecyl.²⁷ The absorption peak at 1731 cm^{-1} belongs to the stretching vibration of C=O in the ester group (-COOR), while the peak at 1657 cm^{-1} is related to the stretching vibration of C=O in the amide group (-CONH-).^{28,29} The characteristic peaks appeared at 1183 cm^{-1} and 1039 cm^{-1} are

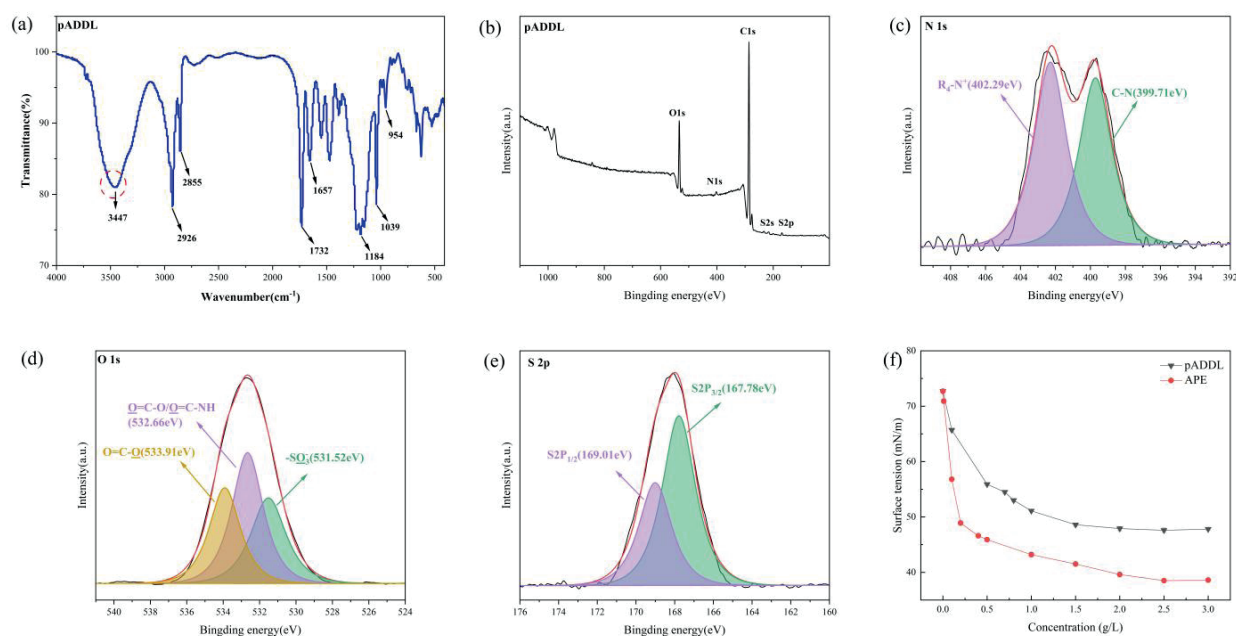


Figure 2. (a) FT-IR spectrum, (b) full XPS spectrum of the amphoteric polymer; High-resolution XPS spectra of the amphoteric polymer: (c) N1s, (d) O1s, (e) S2p; (f) Surface tension versus concentration of the amphoteric polymer and APE, respectively.

due to the stretching vibration and asymmetric deformation of S=O in the sulfonic acid group (R-SO₃⁻).³⁰ The absorption peak at 957 cm⁻¹ corresponds to the stretching vibration of the quaternary ammonium group (N⁺).³¹ In addition, the absorption peak near 1640 cm⁻¹ corresponding to C=C is absent. Therefore, these results preliminarily confirmed the success of copolymerization.

3.1.2 XPS analysis

The structure of the corresponding amphoteric polymer was further confirmed by XPS analysis. As expected, Figure 2b shows that it was composed of C, N, O, and S elements. Particularly, the existence of S2s peak and S2p peak indicated the incorporation of AMPS. In addition, the high-resolution deconvolution peaks of N1s, O1s and S2p (Figure 2c-e) shows that the N1s peak can be deconvoluted into two corresponding sub-peaks of C-N at 399.71 eV (coming from DMAEMA) and quaternary N at 402.29 eV (coming from DMC).³² Moreover, individual contributions of O1s peak were located at 531.52 eV, 532.66 eV and 533.91eV, which corresponds to -SO₃⁻, O=C-O and O=C-O, respectively.^{33,34} The S2p was divided into two peaks namely S2p_{1/2} and S2p_{3/2} with the binding energies of 169.01 eV and 167.78 eV.^{33,35} Taking together, all these above well further illustrated the successful copolymerization of AMPS, DMAEMA, DMC and LMA.

3.1.3 Surface tension

Surface activity is the ability of amphiphilic molecules to reduce the surface tension (or interfacial tension) at low concentration, which is the cornerstone of their formation of kinetically stabilized emulsions. Surface tension measurement is a usual way to evaluate the surface activity of amphiphilic materials.³⁶ Curves of surface tension versus concentration for APE and the amphoteric polymer aqueous solution are shown in Figure 2f. It can be clearly seen that the surface tension of amphoteric polymer aqueous solution decreases with the increase of its concentration, and reaches the minimum value of 47.6 mN/m at the concentration of 2.5 g/L. The significant reduction in surface tension indicates that amphoteric polymer has amphiphilic structure, which also proves the successful copolymerization of hydrophilic and hydrophobic monomers to some extent. Similarly, with the increase of APE concentration, the surface tension of water solution decreases, which also confirms the surface activity of APE. Compared with the aqueous solution of amphoteric polymer, the surface tension of APE dropped more dramatically with increasing concentration, reaching a lower value of 38.6 mN/m, which is mainly due to the existence of small amount of emulsifiers (SDS and AEO-9) in APE.²⁸ Thus, APE has good surface activity. On the one hand, it has the potential of emulsifying castor oil to ensure the stability of COAPE; On the other hand, it would make fatliquoring liquid easier to wet and penetrate into leather.

3.1.4 Zeta potential and pI, particle size and its distribution

The pI is defined as the pH value of amphoteric materials when they are electrically neutral, which can be determined by the zeta

potential change at different pH values.^{14,34} The zeta potential of APE as a function of pH is presented in Figure 3a. It can be clearly observed that with the increase of pH value, the potential of APE gradually changes from positive to negative, which may be mainly related to the neutralization of the positive charge carried by DMC, the exposure of the negative charge carried by AMPS, and the deprotonation of the tertiary amine group in DMAEMA.³⁷ This obviously revealed the amphoteric characteristics of APE, and the pI is 8.22, which indicated the successful copolymerization of cationic and anionic monomers. In addition, the pI of SATL leather can also be figured out from Figure 3a, was 4.62. Fortunately, the difference of the pI values of APE and SATL is beneficial for us to master the situation that APE and SATL are charged with same/opposite sign under different pH environments, and further adjust the ability of penetration and combination of APE in SATL leather.

In addition, particle size is one of the crucial parameters of fatliquoring agent, which is directly related to the penetration into leather.³⁸ The average particle size and poly dispersion index (PDI) of APE at different pH values are summarized in Figure 3b, and the corresponding particle size distribution is shown in Figures 3c-j. From Figure 3b, there is little fluctuation in average size values of APE at different pH, with a range of 150 - 185 nm. On the one hand, the small particle size of APE can ensure better permeability and avoid surface deposition,¹¹ on the other hand, it also means that the surface area of emulsion per unit volume increases, which is helpful for chemical reactions and increases the combination of APE and leather fibers.³⁹ However, the PDI increased initially and then decreased as the pH increased, exhibiting a dramatically high value near the pI of APE. Especially, when the pH is 7.15, 8.11 or 8.52, the existence of particles even larger than 1000 nm can be conspicuously observed, as shown in Figures 3f-h, which directly indicates that some particles in APE have obviously agglomerated near the pI of APE, forming larger particles. This is mainly because the closer to pI, the lower the absolute value of zeta potential, and the smaller the electrostatic repulsion between particles in APE, so that particles will agglomerate together.⁴⁰

The above results comprehensively proved the success of copolymerization, and the emulsion APE with amphoteric and amphiphilic characteristics was obtained. The pI values of APE and SATL leather were also measured, which were 4.62 and 8.22 respectively. Based on this, we then will try different pH regulation schemes to explore the interaction mechanism between amphoteric polymer and SATL leather from the perspective of their surface charge states.

3.2 Insight into interaction between amphoteric polymer and silicic acid tanned leather

3.2.1 Effect of fixing pH value at the end of fatliquoring

In Schemes 1, 2 and 3, the absorption rate of APE in SATL leather at different fixing pH values at the end of fatliquoring and physical properties of fatliquored SATL leather are compared and represented

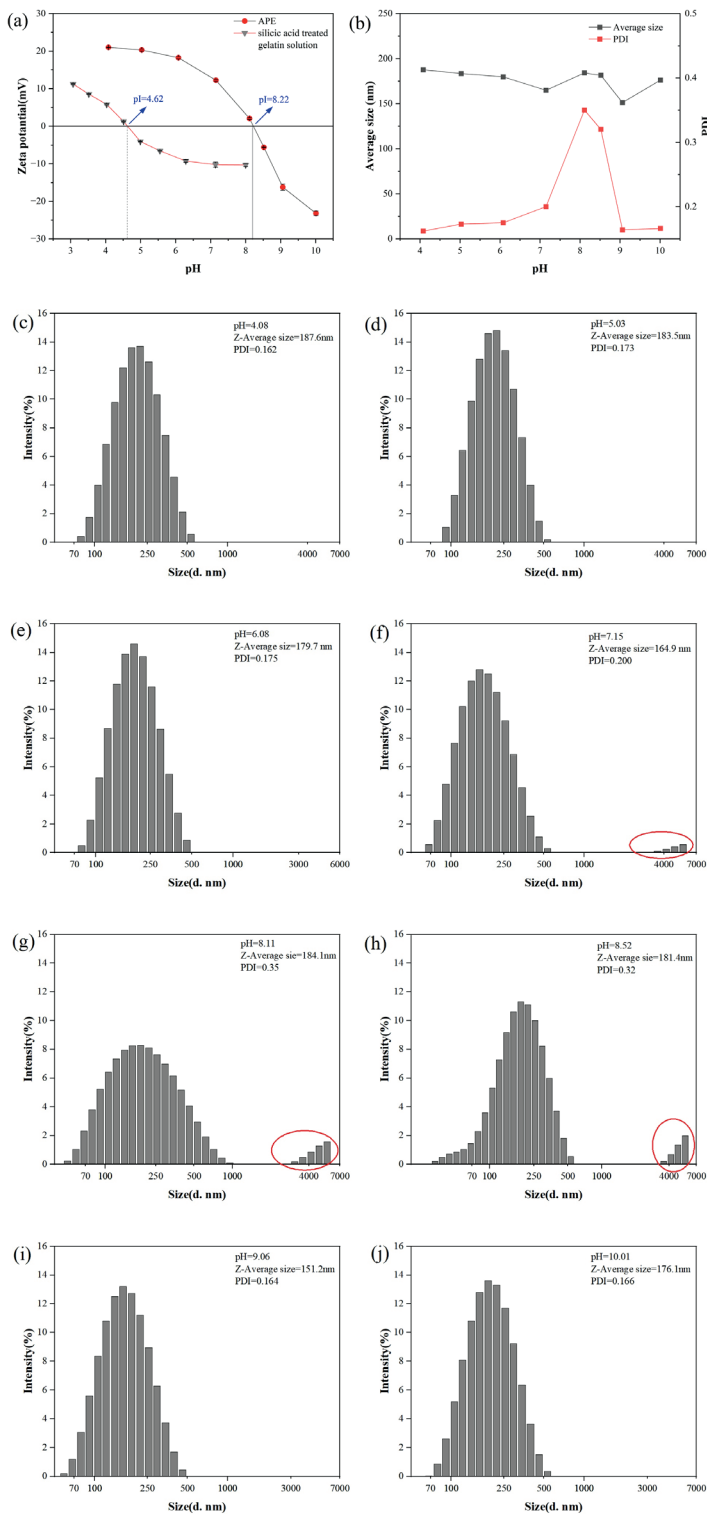


Figure 3. (a) Zeta potentials of APE and silicic acid treated gelatin solution at different pH values; (b) average size and poly dispersion index of APE at different pH values; Particle size distribution of APE at (c) pH=4.08, (d) pH=5.03, (e) pH=6.08, (f) pH=7.15, (g) pH=8.11, (h) pH=8.52, (i) pH=9.06, (j) pH=10.01.

in Figure 4. Figure 4a shows that APE was well absorbed at different fixing pH values, which may be mainly due to the fact that: (1) at the beginning of fatliquoring under the initial pH of 4.0 (below the pIs of SATL leather and APE), the leather and APE are both positively charged, thus making APE easier to penetrate into the leather, while at the end of fatliquoring under the fixing pH of 6.0, 7.5 or 8.0 (below the pI of APE, but above the pI of SATL leather), the leather exhibits negative charged surface while APE is still positive charged, thus promoting their interaction with each other through electrostatic attraction. That is, the strategy of penetration at first and then combination was achieved; (2) the plentiful functional groups in APE, such as tertiary amine, N^+ and $-SO_3^-$, can ensure good interaction of APE and collagen fibers. Furthermore, it can also be found that the absorption rate of APE increased with the increase of fixing pH from 6.0 to 8.0. This is mainly related to the amphoteric characteristics of APE. As the pH value approaches the pI of APE, in addition to the electrostatic interaction between leather and APE, proper aggregation of internal particle caused by the instability of APE is also conducive to the absorption of APE.

Meanwhile, the aggregation of particles in APE leads to their easier deposition in the collagen fiber gaps of leather, especially in the loose parts, which is beneficial to better filling effect. Therefore, the thickening rate increases with the increase of the fixing pH value, leading to the highest thickening rate at the fixing pH of 8.0 (Figure 4b). In addition, the softness of leather treated with APE was much better than that of untreated leather (the softness value is 4.6 mm), however, what deserves attention is that the softness reaches the maximum when the fixing pH is 7.5 (Figure 4b). This is mainly because the aggregation and deposition of APE near its pI are double-edged. Typically, the polar groups in APE interacted with collagen fibers of SATL leather through ionic bonds and hydrogen bonds during fatliquoring, while the hydrophobic long alkyl chains in APE arranged and coated on the surface of collagen fiber to form a lubricating layer, thus reducing the sliding friction, enhancing the relative movement between collagen fibers, and showing the softer hand feeling macroscopically. Moreover, the tertiary amine of APE may form hydrogen bonds with Si-OH groups in SATL leather,⁸ thus probably inhibiting further intramolecular condensation of Si-OH groups during storage and thereby improving softness of SATL leather. It can be considered that these are the main reasons why the softness of SATL is improved after APE treatment. On the other hand, the excessive filling effect of APE at the fixing pH of 8.0 limited the relative sliding between and inside collagen fibers, resulting in the softness of fatliquored leather being lower than of leather obtained at the fixing pH of 7.5. As for the leather fatliquored at the fixing pH of 6.0, its softness is relatively low, mainly due to the low absorption rate of APE, which leads to insufficient lubrication.

Figure 4c shows the tensile strength and elongation at break of leather after APE treatment. Compared with the tensile strength of leather

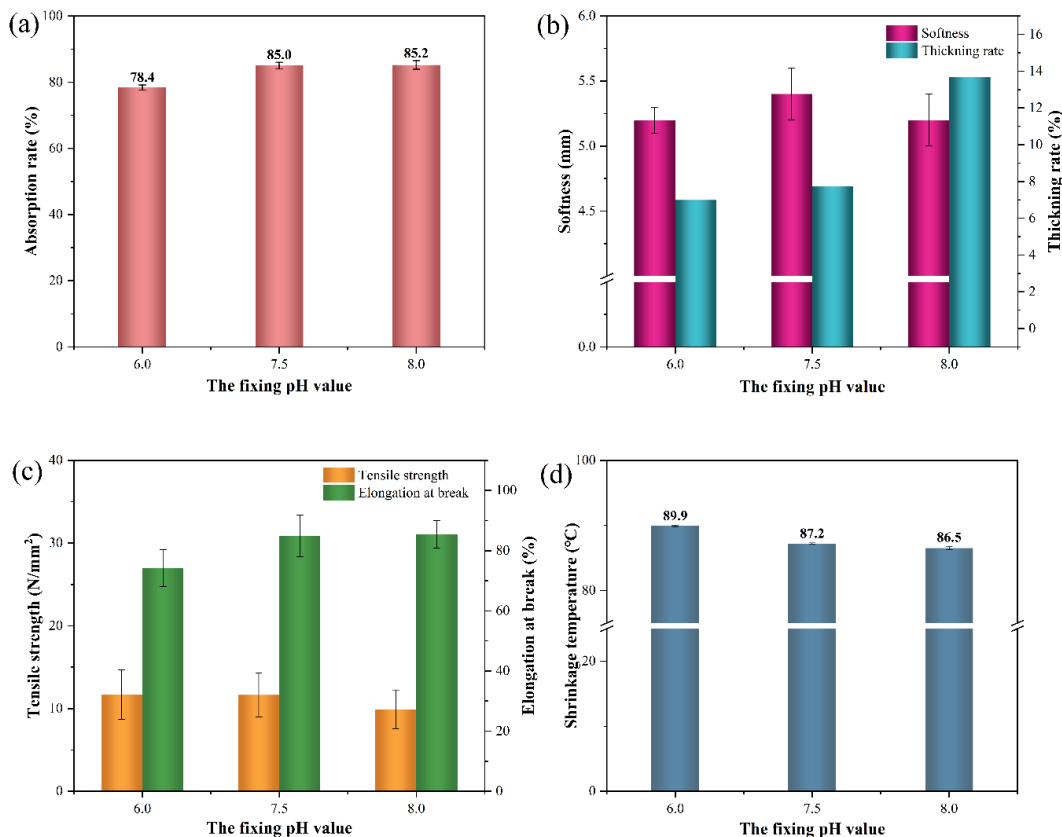


Figure 4. (a) Absorption rate of APE at different fixing pH; (b) Thickening rate and softness, (c) Tensile strength and elongation at break, (d) T_s of SATL leather fatliquored with APE at different fixing pH values

before APE treatment (10.1 N/mm²), their tensile strength changed slightly. While compared with the elongation at break of untreated leather (49.0%), their elongation at break increased sharply. This can also be attributed to the lubrication function of APE. Briefly, after APE was well-dispersed inside the collagen fibers and well-bonded with fiber chains, the flexible long alkyl chains in APE could stretch the intermolecular spacing and enhance the relative slippage between collagen fibers,²⁰ thus significantly improving the extensibility of leather. Furthermore, the elongation at break of leather obtained at the fixing pH of 7.5 and 8.0 is very close, and both of them are higher than that of leather obtained at the fixing pH of 6.0, which indicated that the fixing pH of 7.5 is sufficient to ensure the excellent flexibility of leather.

T_s , that reflects the hydrothermal stability of leather, is one of the most important indicators for leather performance. Unfortunately, compared with the T_s of untreated leather, the T_s decreased slightly with the increase of fixing pH. This was mainly because the APE deposited in the gaps between collagen fibers increased the chain spacing between collagen molecules, thus weakened the cross-linking degree of collagen fiber networks.^{21,41} In addition, the higher absorption rate of APE, the lower the T_s . However, it is worth mentioning that the T_s of SATL, as a chrome-free tanned leather, is still acceptable after fatliquoring.

To sum up, under the condition of the fixing pH of 7.5 and the initial pH of 4.0, the electrostatic attraction between APE and SATL leather as well as the aggregation and deposition of APE due to its amphoteric characteristics can be fully utilized to balance the filling effect and softening effect, so that APE can be well dispersed and absorbed, the physical and mechanical properties of SATL leather can be significantly improved. It can be speculated that there is almost no obvious negative impact on the cross-linking network after APE treatment.

3.2.2 Effect of initial pH value at the beginning of fatliquoring

In Schemes 4, 5 and 6, the organoleptic status and physico-chemical features of SATL leather fatliquored at different initial pH value of fatliquoring are studied and shown in Figure 5. It can be observed that under the premise of keeping the fixing pH at 7.5, the highest APE absorption rate (86.2%), softness (5.8 mm), thickening rate (8.1%), as well as elongation at break (86.2%) were obtained when the initial pH was 4.0 (Scheme 4). This phenomenon can be explained as follows. In Scheme 5 and Scheme 6 with the initial pH of 5.0 and 6.0 respectively, during the whole fatliquoring process, APE was positively charged, while the SATL leather was negatively charged (Figure 3a). Therefore the strong electrostatic attraction between SATL and APE might lead to excessive combination of fatliquoring agent on the leather surface in the initial stage, blocking the subsequent penetration of APE into the middle layer of

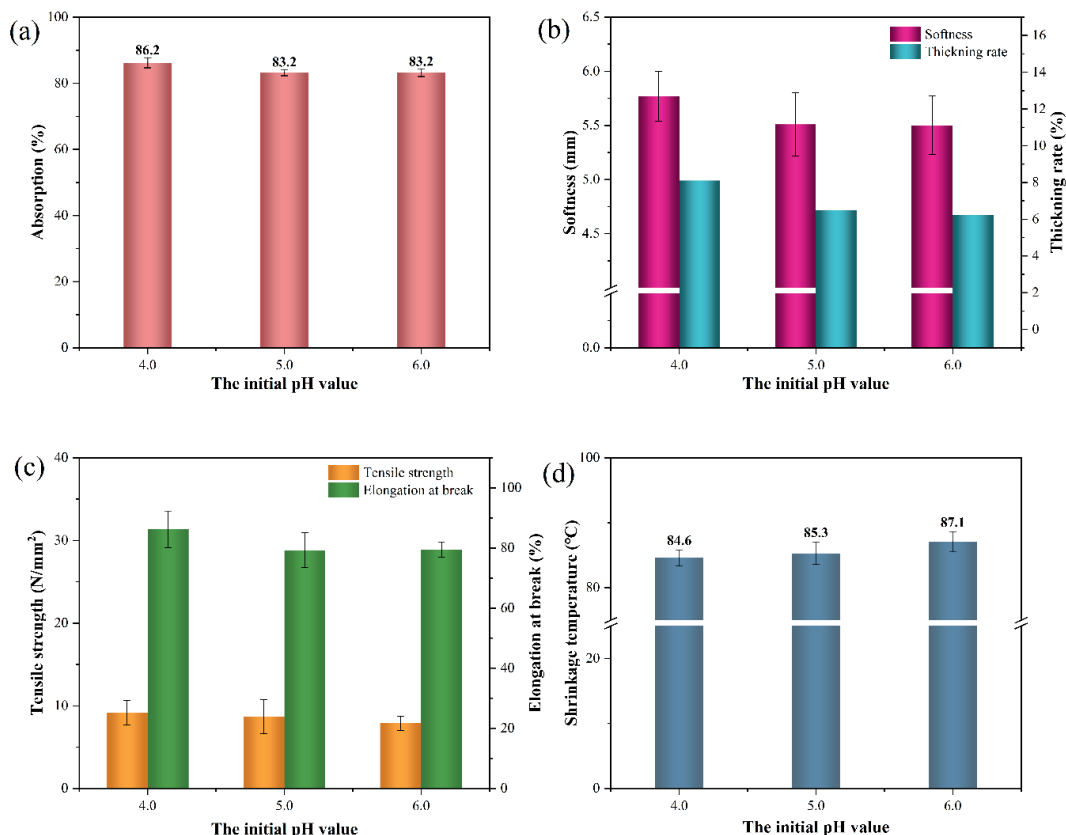


Figure 5. (a) Absorption rate of APE at different neutralization pH; (b) Thickening rate and softness, (c) Tensile strength and elongation at break, (d) T_s of SATL fatliquored with APE at different pH values before fatliquoring.

leather, which means that more APE accumulated on the surface of leather, while less APE lubricated the collagen fiber networks inside leather, finally resulting in greasy feeling and inferior mechanical properties.¹⁸ On the contrary, the strategy of first penetration and then combination used in Scheme 4 (the same as Scheme 2) allowed enough APE to penetrate and combine in the leather to play a role in lubrication, thus obtaining better physical and mechanical properties. The lowest T_s (84.6°C) of fatliquored leather in Scheme 4 is also an indirect evidence of preferable lubrication effect. In addition, the T_s of fatliquored leather in Scheme 6 is higher than that in Scheme 5, although they have almost the same APE absorption rate (83.2%), suggesting more combination of APE on the leather surface.

3.2.3 Interaction mechanism model between amphoteric polymer and silicic acid tanned leather

According to the above research results, when the initial pH at the beginning of fatliquoring is 4.0 and the fixing pH at the end of fatliquoring is 7.5, the optimal fatliquoring effect can be achieved, in which the amphoteric characteristics of SATL and APE play a crucial role. Therefore, a possible interaction mechanism between SATL leather and amphoteric polymer is proposed and illustrated in Figure 6. As mentioned above, SATL is a silicic acid-modified collagen fiber matrix with a pI of 4.62, while APE rich in active groups has a pI of 8.22. When adjusting the initial pH to 4.0, the SATL leather and

APE are both positively charged, allowing APE to penetrate easily into SATL with the help of mechanical action and its own surface activity and small particle size. Then, in order to maximize the use of the difference between the pI of APE and SATL to enhance the electrostatic interaction between them, the pH value of the bath liquid was adjusted to 7.5. In the meantime, the site binding between amphoteric polymer in APE and collagen can be realized, that is, the quaternary ammonium group and sulfonic acid group in amphoteric polymer are combined with the amino- and carboxyl groups in collagen fibers through ionic bonds respectively, while its tertiary amino groups mainly formed hydrogen bonds with collagen fibers and three-dimensional silica network in SATL. Moreover, the long alkyl chains in amphoteric polymer are arranged outward and distributed between collagen fibers, which plays a lubricating role. Besides, the aggregation of particles inside APE is also conducive to the absorption and filling effect of APE. Consequently, the flexibility and extensibility of silicic acid-modified collagen network are strikingly improved, and SATL leather is softer and more flexible macroscopically.

What's striking is that the pH adjustment mode for fatliquoring in this work is completely opposite to that in the process of fatliquoring chrome tanned leather. For chrome tanned leather, the neutralization pH and fixing pH are generally 6.0 and 4.0 respectively. This is mainly owing to the higher pI of chrome tanned

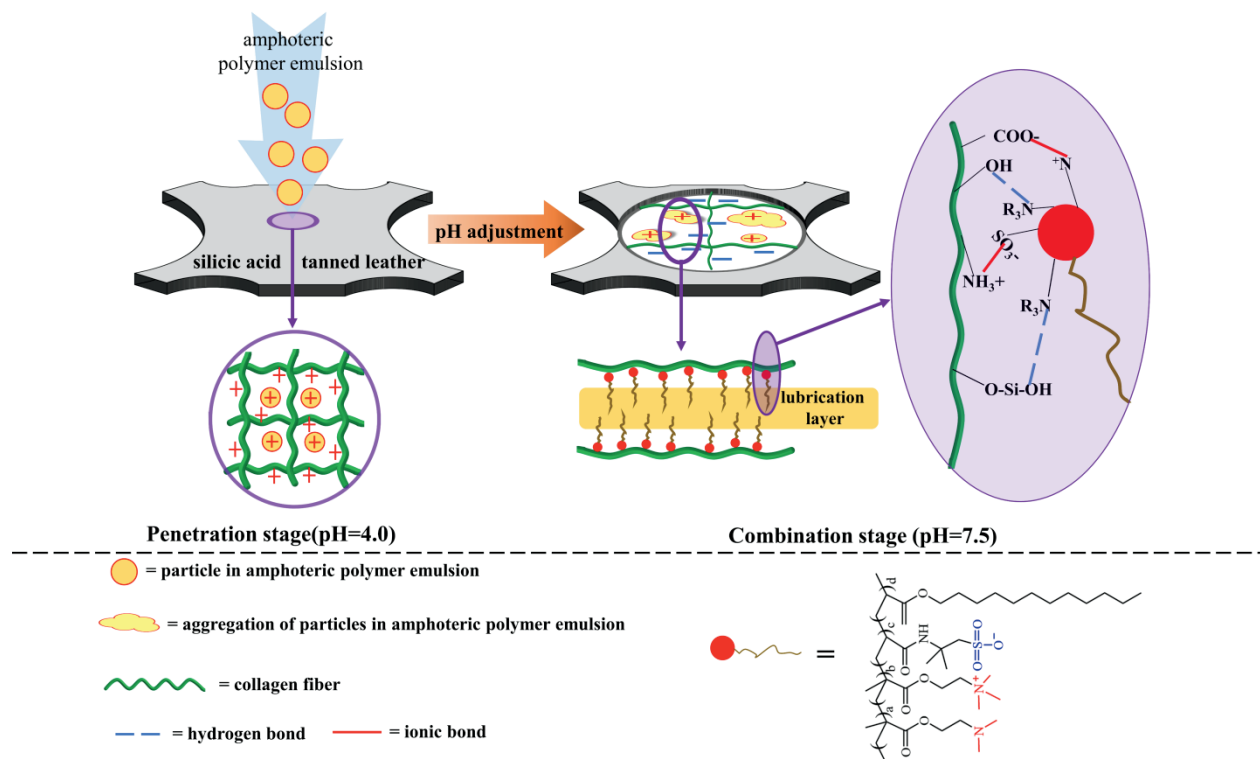


Figure 6. Schematic illustration of the interaction mechanism between amphoteric polymer and silicic acid-tanned leather

leather (between 7.0 to 8.0) as well as the use of anionic fatliquoring agent. That is, the electrostatic interaction between chrome tanned leather and anionic fatliquoring agent is weakened when the initial bath pH is neutralized to 6.0, and then strengthened when the bath pH is adjusted to 4.0 at the end of fatliquoring, so as to achieve the same purpose of penetration first and then combination. It is worth mentioning that these two pH adjustment strategies are different in form, but both of them essentially regulate the surface charge state of leather and fatliquoring agent by changing the environmental pH, thus controlling the mass transfer and combination of fatliquoring agent in leather.

3.3 Adaptability of amphoteric fatliquoring agent to the SATL leather

After understanding the interaction mechanism of amphoteric polymer and silicic acid-modified collagen fiber matrix and obtaining the optimal initial pH and fixing pH, we compared the fatliquoring effects of APE and COAPE, and also compared with a counterpart anionic commercial polymer fatliquoring agent, further explored whether the amphoteric fatliquoring agent was suitable for the fatliquoring process of SATL leather, and designed in Schemes 7, 8 and 9. The physical properties of SATL leather treated with different fatliquoring agents are summarized in Table III.

Table III shows that SATL treated with COAPE exhibits the highest tensile strength, elongation at break, softness and thickening rate. Compared with APE, COAPE contains castor oil, which can assist

the filling and lubrication of long alkyl chains, thus obtaining better physical properties. Notably, the absorption rate of the anionic commercial fatliquoring agent is sharply lower than that of APE and COAPE. This is mainly attributed to the fact that there are only anionic groups in the commercial fatliquoring agent, which is detrimental to combination with the relatively electronegative SATL leather. Consequently, poor absorption leads to the lowest tensile strength, elongation at break and thickening rate of SATL treated with commercial fatliquoring agent. In contrast, APE and COAPE, two amphoteric emulsions with abundant cationic groups ($-NR_2$, N^+), have high positive charge, so they have excellent affinity with SATL leather. What's more, the highest absorption rate of COAPE (90.5%) indicates that the application of COAPE can reduce the chemical residue in fatliquoring wastewater, thus alleviating the subsequent waste management. Intriguingly, the T_s value of SATL treated with commercial fatliquoring agent dropped the most, despite the fact that only a small amount of the commercial fatliquoring agent was absorbed to lubricate the collagen fibers. It may have stemmed from the weak interaction of commercial fatliquoring agent and SATL leather caused by the "de-tanning" action, whereas the multi-point combination between APE/COAPE and SATL leather can offset the partial "de-tanning" action.

Since the SATL leather is light white, the color change, especially yellowing, will significantly affect its practical application.⁴² Thus, the color difference (ΔE) and yellowness difference (Δb^*) of leathers before and after aging were evaluated and recorded in Table III. The ΔE values of unfatliquored and fatliquored leathers are all

quite tiny, which are all less than the minimum color difference of 1.5 that can be distinguished by the naked eye,⁴¹ indicating that silicic acid tanned leather has excellent light fastness, and the addition of APE, COAPE and commercial fatliquoring agent has little negative effect on it. The satisfactory yellowing resistance of untreated leather and all fatliquored leathers was further identified according to the Δb^* values. The effects of APE, COAPE and the commercial fatliquoring agent on the favorable light fastness and yellowing resistance of SATL leather can be ignored.

Moreover, the morphology of untreated and treated collagen fibers with APE, COAPE and the commercial fatliquoring agent was observed by SEM at different magnifications (Figure 7), and their pore diameter distributions were tallied in Figure 8. During the fatliquoring process, the separation of collagen fiber bundles is mainly related to the supporting and lubricating functions of fatliquoring agents.⁴³ As shown in Figure 7a1 and a2, the collagen fibers of untreated SATL leather arranged compactly, whereas

the SATL leathers treated with APE, COAPE and the commercial fatliquoring agent all exhibited loose structure (Figure 7b1-d1, b2-d2). Particularly, it can be observed that the adhesive collagen fiber bundles were opened up and separated into smaller bundles, which was consistent with the increase of smaller pores (Figure 8). This evidently proves that these three fatliquoring agents could penetrate into the collagen fiber and lubricate them, thus imparting the SATL leather good flexibility. Moreover, collagen fibers treated by COAPE were looser than the other two treatments, presenting the best filling and lubrication effect.

Overall, the above results clearly prove that COAPE is more suitable for the fatliquoring process of SATL leather than anionic commercial fatliquoring agent, since COAPE can not only greatly improve the physical and mechanical properties, especially softness and elongation at break, but also facilitate the realization of clean technological process for SATL, a chrome-free tanned leather.

Table III
Physical properties of SATL leather treated with different fatliquoring agents

Fatliquoring agent	Untreated	APE	COAPE	Anionic commercial polymer fatliquoring agent
Absorption rate (%)	-	82.7	90.5	63.2
Tensile strength (N/mm ²)	7.9±1.0	11.0±0.5	11.6±1.3	9.0±0.5
Elongation at break (%)	53.2±5.8	83.1±6.8	95.5±7.1	70.4±5.5
Softness (mm)	4.1±0.2	5.7±0.3	6.5±0.3	6.3±0.3
Thickening rate (%)	-	7.3	7.8	5.5
Ts (°C)	90.6±1.1	87.0±0.6	86.5±0.5	85.0±1.3
ΔE	0.3	0.3	0.4	0.3
Δb^*	0.2	0.2	0.2	0.2
Average pore diameter (μm)	11.3	8.1	8.7	9.3

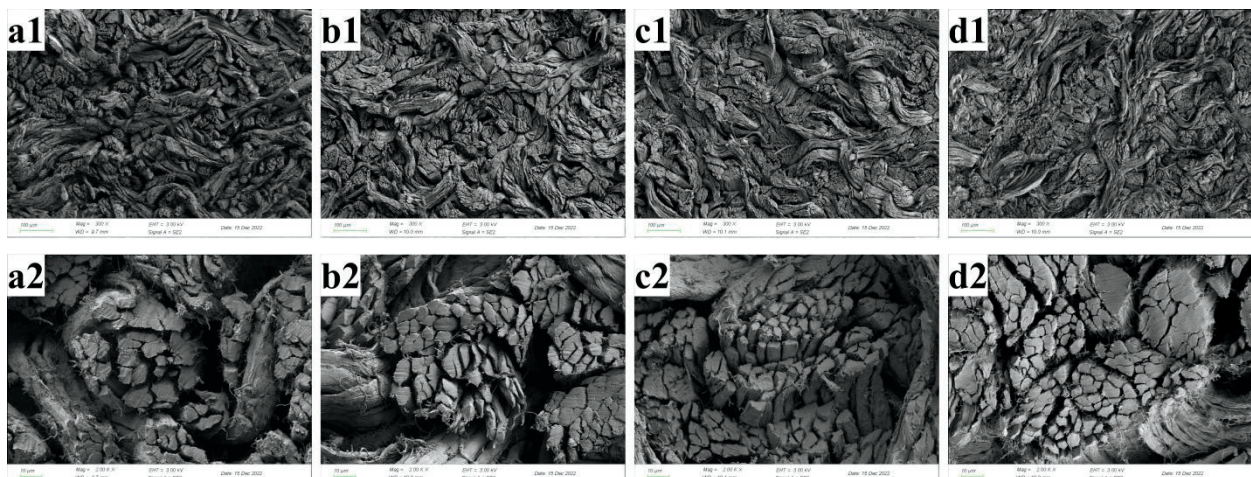


Figure 7. SEM images of SATL leather: (a1) unfatliquored, (b1) APE fatliquored, (c1) COAPE fatliquored and (d1) commercial fatliquoring agent fatliquored; (a2-d2) were the corresponding high magnification of SEM images of corresponding leathers, respectively

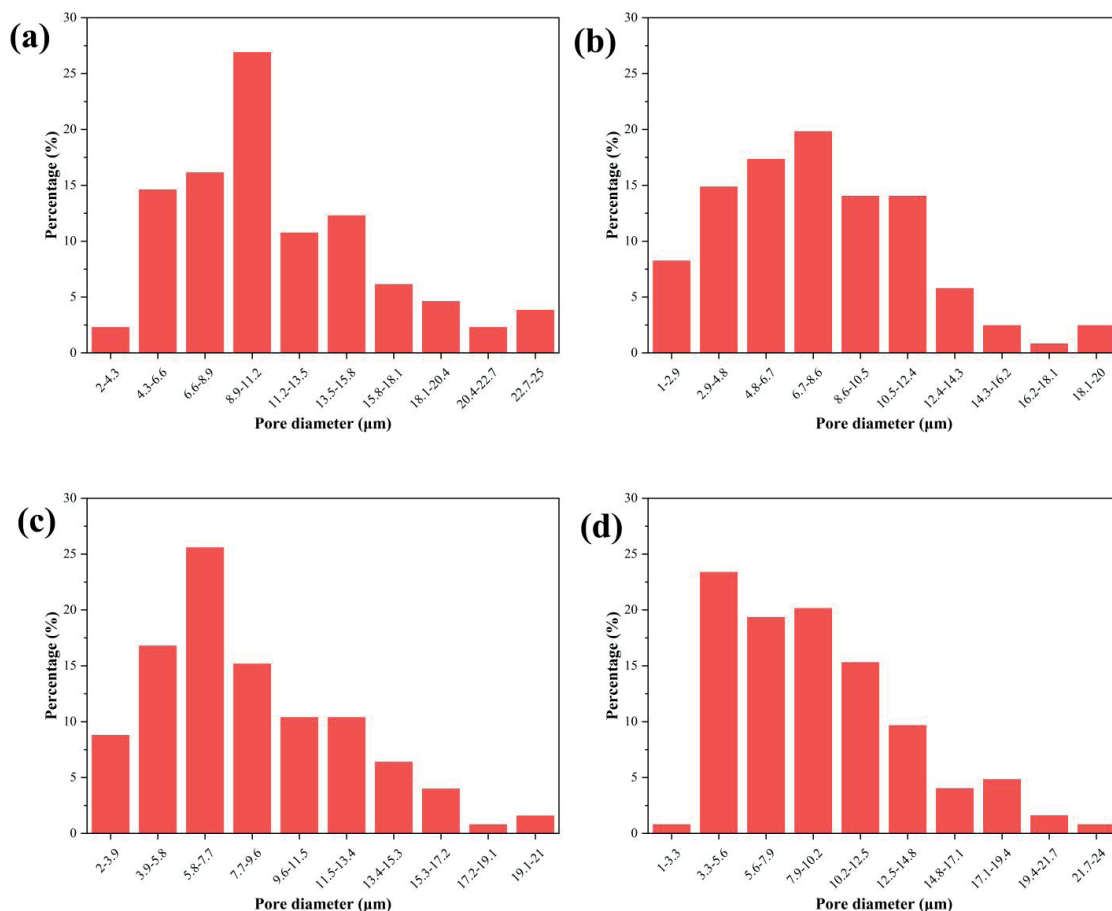


Figure 8. Pore size distribution of SATL leather: (a) unfatliquored, (b) APE fatliquored, (c) COAPE fatliquored, and (d) commercial fatliquoring agent fatliquored

4. Conclusion

In this work, an amphoteric polymer emulsion APE was successfully synthesized. The structure of amphoteric polymer was confirmed by FT-IR and XPS characterization. The measurement of surface tension, zeta potential and particle size identified the amphiphilic structure as well as amphoteric nature of APE with a pI of 8.22, which performed obvious aggregation behavior near pI. The interaction between amphoteric polymer and silicic acid-modified collagen fibers can be easily controlled by adjusting the pH value of the fatliquoring bath. When the initial pH value at the beginning of fatliquoring is 4.0, the same surface charge state is conducive to the penetration of APE emulsion particles into SATL leather. Attractively, when the fixing pH at the end of fatliquoring is 7.5, the synergistic effect of the electrostatic interaction between APE and collagen fibers and the aggregation effect of APE particles makes them reach the best combination state, and site binding occurs in the form of hydrogen bonds and ionic bonds, thus forming a molecular layer on the surface of collagen fibers, which isolated and lubricated the collagen fibers. Subsequently, the APE emulsion was compounded with castor oil as an amphoteric fatliquoring agent (COAPE) and

applied to silicic acid tanned leather (SATL). Compared with those of the SATL treated with the anionic commercial fatliquoring agent, the mechanical and physical properties of the COAPE-treated SATL leather and the absorption rate of fatliquoring agent were greatly improved, demonstrating that the amphoteric fatliquoring agent is more compatible with SATL leather. Therefore, this work provides a viable strategy for the fatliquoring process of SATL leather, thus facilitating to promote the practical application of silicic acid-based tanning technology, and also provides some theoretical support for the application of amphoteric polymers in natural collagen-based materials.

Acknowledgements

This research was supported by the National Natural Science Foundation of China (No. 21376153), the Fundamental Research Funds for the Central University of China. The authors would thank Jinwei Zhang (College of Biomass Science and Engineering, Sichuan University) for his great help during conducting the leather tanning and fatliquoring process.

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