

REVIEW

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# Application of amphoteric polymers in the process of leather post-tanning

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## Abstract

With the characteristics of controllable charge and environmental friendliness, amphoteric polymers can be used in post-tanning process to solve the problems that arise during leather making and are caused by the low absorption rate of single-charge chemicals, incompatibility with new tanning methods, and complex operation process. In this review, the structure, performance, and preparation of amphoteric polymers are reported. Then, the charge change of collagen during different tanning and pH treatments is introduced. Finally, the application and development of amphoteric polymers during the post-tanning process of leather making are discussed. This review has certain guiding significance to the preparation and application of amphoteric polymers for tanning system.

**Keywords:** Amphoteric polymer, Leather making, Post-tanning, Research and application, Progress

## 1 Introduction

Tanning is one of the oldest industries in human history. During the tanning process, raw hides are transformed into leather that can be directly used through complex treatment and cross-linking modification [1]. The post-tanning section of leather making directly determines the wearability and color style of finished products, which is a key step after tanning. The main component of raw skin is collagen, which has amphoteric properties and controllable charge because it contains both acidic and basic groups [2–4]. During leather making, both chemicals and pH affect the charge of collagen. Chemicals consume acidic and basic groups of collagen, and the added chemicals carry a certain amount of charge. At the same time, the changed pH of the bath can make collagen deviate from its isoelectric point (pI) region [5, 6]. Different substances diversely affect collagen. The use of a single charged material to interact with collagen may cause many problems such as excessive surface binding, poor

permeability, low absorption of the subsequent same-charge substance, poor compatibility, and complex process [7–10]. In comparison, apart from having the functional properties of single-charge material, amphoteric polymer can also adjust its charge with a change in the structure and pH to meet the requirements of collagen. Its main characteristics are as follows: (1) regulation of collagen charge; (2) provision of synergistic effect for the absorption of matching chemicals; (3) process simplicity; and (4) possession of good environmental compatibility and low irritation [11–13]. Therefore, the development of amphoteric polymers for leather making is essential for the research on leather making chemicals. Our group has successfully developed several excellent amphoteric chemicals for leather making, such as an amphoteric polyurethane retanning agent with an aldehyde removal function, an amphoteric collagen-based retanning agent with a filling function, and an amphoteric polymer fatliquoring agent that is based on ionic liquid. On the basis of our previous studies, this paper reviews the structure and properties of amphoteric polymers, amphoteric properties of collagen fibers, and the research status of amphoteric polymers during post-tanning.

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## 2 Structure, properties, and synthesis methods of amphoteric polymers

### 2.1 Structure and properties of amphoteric polymers

Amphoteric polymers contain both anionic and cationic groups in the same molecular structure [14]. Therefore, it has the characteristics of pI, good compatibility, adjustable molecular charge, and low toxicity [15–18]. Amphoteric polymers can be classified in different ways. One of the classifications is based on the structural characteristics of polymers, the skeleton structure, and the types of anionic and cationic groups [19].

According to the structure of main skeleton, amphoteric polymers can be divided into carbon skeleton, hetero skeleton, and elemental organic skeleton. The skeleton structures of carbon chain amphoteric polymers are composed of carbon atoms. The skeletons of polyolefin are more common such as a polymethacrylamide framework [20], polymethacrylate skeleton [21], polyethylene pyridine skeleton, and acrylamide and maleic anhydride copolymer skeleton [22]. In addition to carbon atoms, there are oxygen, nitrogen, phosphorus, sulfur, and other heteroatoms in the main skeleton structure of heterochain amphoteric polymers, including polyurethane and polyester amphoteric polymers. Some of the natural polymers also belong to this type including polypeptide skeletons [23, 24] and phosphatidyl choline [25, 26]. Elemental organic amphoteric polymers are semi-organic polymers. The main molecular skeleton is mainly composed of inorganic elements or metal atoms; however, the side groups are mostly organic groups such as amphoteric hydrotalcite organic polymers. The introduction of polymer frameworks with different structural types and properties greatly enriched the properties of amphoteric polymers.

The positive charge centers of amphoteric polymers are mainly nitrogen, phosphorus, and sulfur atoms, which can form cations of quaternary ammonium, quaternary phosphonium, and sulfonium salts. Among them, the most common one is nitrogen atom, which can be divided into pH-insensitive and pH-sensitive types according to the functional groups formed by nitrogen atom. The charge amount of pH-insensitive nitrogen atoms does not change in a wide range of pH such as the quaternary amino group in betaine amphoteric polymers. Because in the outermost layer of nitrogen atom four electrons form covalent bond with outer electron of carbon atom respectively and one electron is lost, the quaternary amino group always has a stable positive ion, in which nitrogen atom transfer electrons difficultly with the change of pH. The charge amount of pH-sensitive nitrogen atom changes with the pH environment, such as primary amino group, secondary amino group and tertiary amino group in polypeptide molecules, in which the nitrogen atoms can get or lose

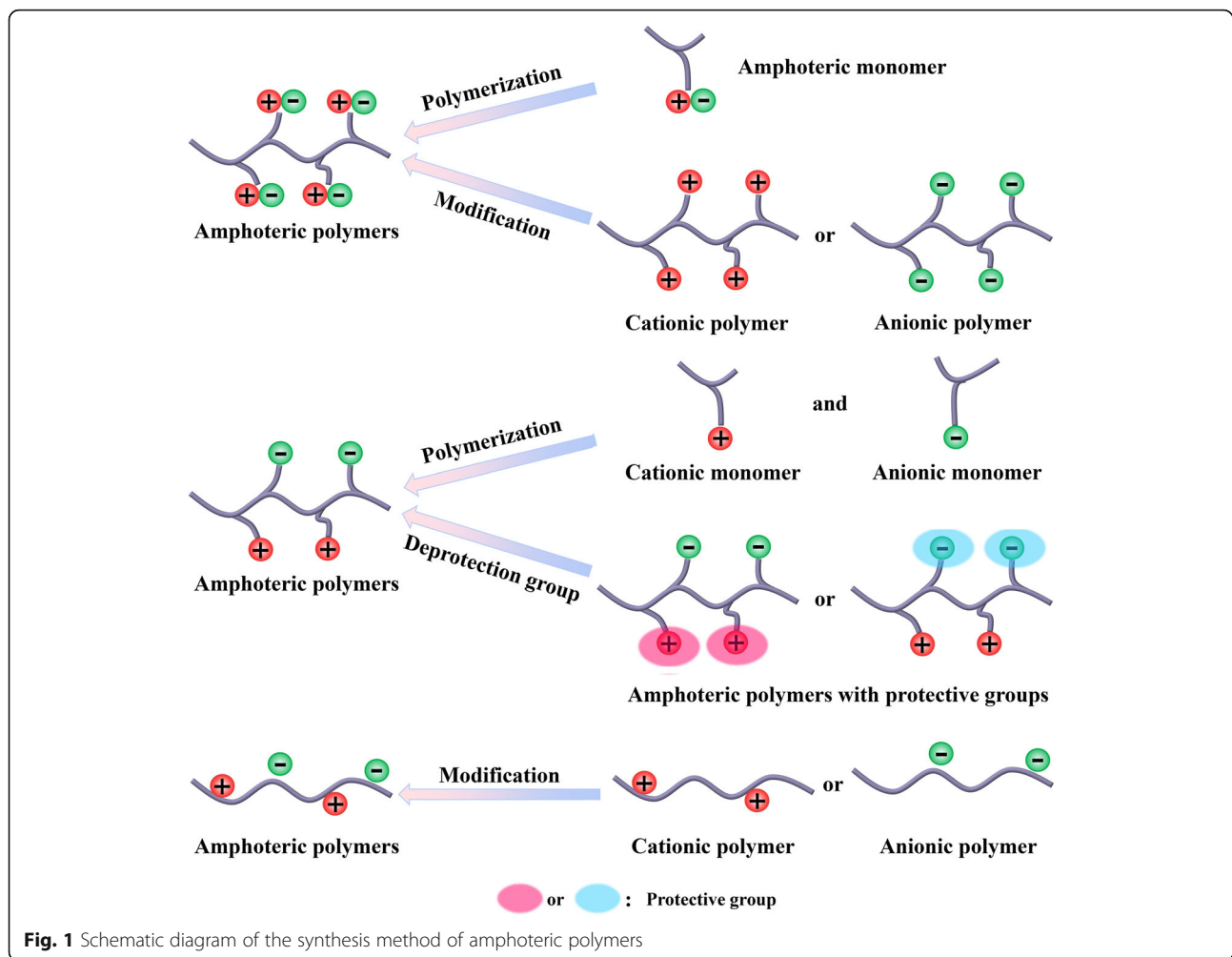
electrons. Negative charge centers are loaded on negatively charged acidic groups such as carboxylic acid, sulfonic acid, sulfuric acid, sulfite, and phosphate groups [14]. Different amphoteric polymers can be constructed by pairwise combination of different positive and negative charge centers [27].

### 2.2 Synthetic methods of amphoteric polymers

Amphoteric polymers can be synthesized by monomer polymerization or polymer molecular modification. The approaches can be divided into direct and indirect synthesis. The former refers to the preparation of amphoteric polymers by the polymerization of amphoteric small molecule monomers or the copolymerization of anionic monomers and cationic monomers. The common amphoteric monomers are acrylamide betaine, methacrylate betaine, and vinylpyridine betaine [22]. The main polymerization method is radical polymerization. In recent years, reactive controlled radical polymerization has been widely used in the synthesis of amphoteric polymers such as atom transfer radical polymerization (ATRP) and reversible addition fragmentation chain transfer (RAFT) radical polymerization. Such as, Skinner et al. [28] prepared amphoteric block copolymers via ATRP method, in which phosphorylcholine and choline phosphate methacrylate were used as monomers and a difunctional poly (propylene oxide) was used as macroinitiator. Ohno et al. [29] successfully grafted amphoteric polymer brushes onto a glass substrate via RAFT. In this surface grafting polymerization, methacrylic acid and 2-(dimethylamino) ethyl methacrylate were used as monomers, (n-butylsulfanylthiocarbonylsulfanyl-2-methyl propionic acid) was used as free chain transfer agent and (4,4'-azobis (4-cyanopentanoic acid)) was used as initiator. The latter refers to the method of modifying the main chain or side chain of polymer molecules by introducing anion and cation groups. In some studies, chloroacetic acid has been used to quaternary ammoniate the tertiary amine group of the polymer to obtain amphoteric polymer with a carboxyl betaine structure. Amphoteric polymers can also be obtained by click chemistry reactions [30] between the sulfhydryl groups of zwitterion and alkene or alkyne functional groups of polymers. In addition, polymer precursors with protective groups can be prepared to obtain amphoteric polymers by deprotection (Fig. 1).

## 3 Amphoteric properties of collagen after tanning

The pI of crust leather is an important index of its amphoteric properties, at which the total number of positive and negative charges in leather are equal. It directly affected the charge of leather in different pH and the choice of chemical and technology during leather making. Leather is a polymer matrix with a three-

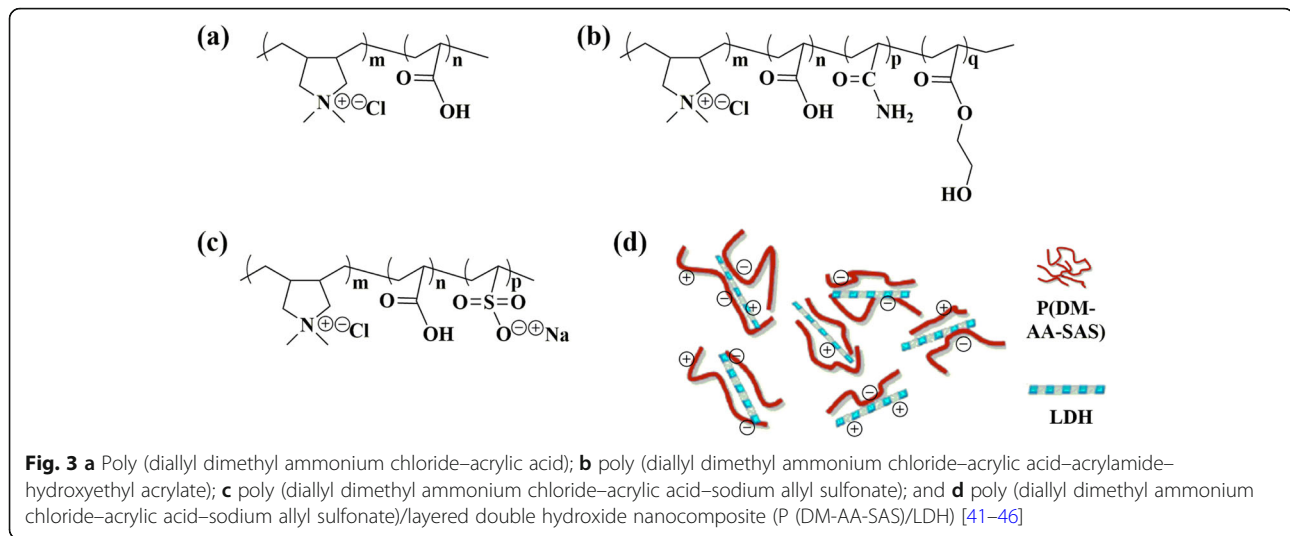


dimensional network structure woven by collagen fibers. Collagen fiber is not only the main component of leather but also a typical amphoteric polymer. The amino group on the side chain of basic amino acid residue and the carboxyl group on the side chain of acid amino acid residue in collagen can bind or release hydrogen ions ( $H^+$ ) and even ionize in aqueous solutions, which results in the collagen fiber with positive or negative charges [31, 32]. During the process of leather making, chemicals can interact with collagen matrix. Chemicals can consume the acidic and/or basic groups of collagen. Furthermore, the added materials have a certain amount of charge, which will also affect the pI of leather. Figure 2a shows the mechanism of action between several tanning agents and polar groups in collagen fibers and the pI of leather after tanning [33, 34].

The pI of pickled skin is 5.4, which is attributed to the hydrolysis of the peptide bond of collagen and deamidation of asparagine and glutamine residues. The chrome tanning agent is mainly coordinated with the carboxyl group in skin collagen, and the metal chromium

complex is cationic. Therefore, the pI (7.2) of chrome-tanned leather was increased. The pI of vegetable-tanned leather is 4.6. This occurs because the vegetable tanning agent is the polyphenol polymer; thus, the hydroxyl group in the molecule can combine with the amino group of collagens by hydrogen bond. The pI of syntan-tanned leather is 4.2. In the preparation of syntan, sulfonation is often used to modify polyphenols to improve its combinability and water solubility. Sulfonic acid group of syntan can combine with the collagen amino group by an ionic bond, which increases the negative charge in the skin. Aldehyde tanning agent covalently combines with amino groups in collagen, which makes the pI of the tanned skin 4.8. In the newly developed white wet leather without chrome, the pI of F-90-tanned white wet leather is 4.5. F-90 is a modified product of cyanuric chloride and contains chlorine atom, which can be covalently bonded with amino groups in collagen. The amphoteric tanning agent TWT can consume amino groups in collagen fibers through aldehyde groups, but its amino groups can increase the number of

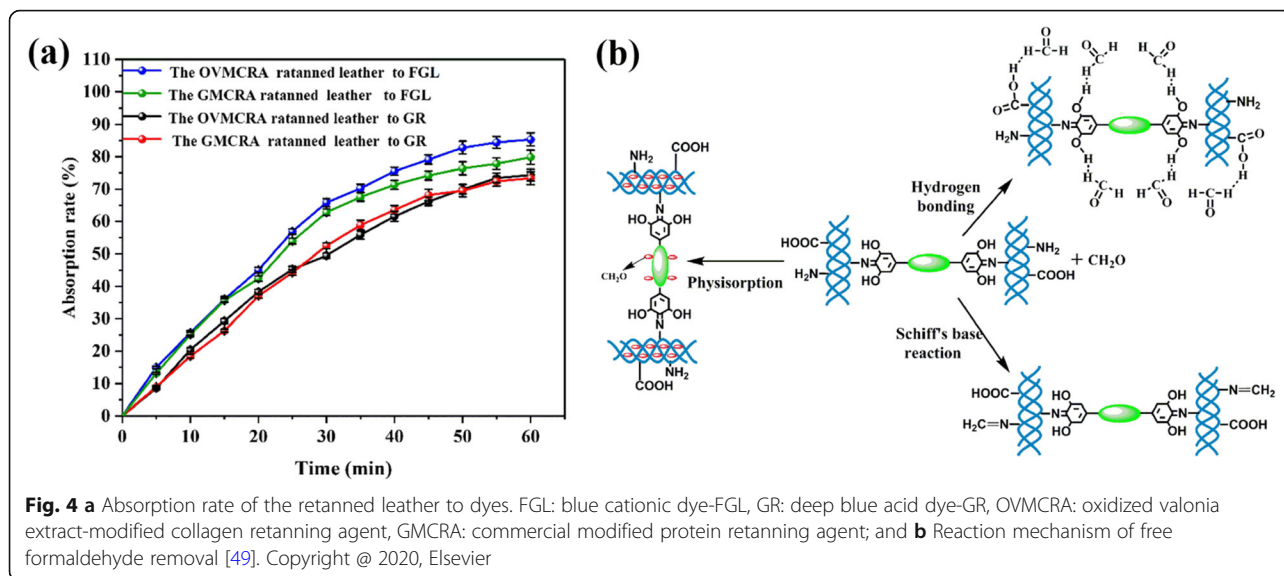




molecule was weak in combination with chrome-tanned leather. To further improve the tanning effect of the polymer, a polyampholytic polymer retanning agent was prepared by introducing acrylamide and hydroxyethyl acrylate. After being applied to chromed leather, the dyeing depth (K/S value) of dyed leather sample is increased by 50.8%. Then amphoteric polymers with sulfonic groups were synthesized, which could inhibit the expansion of naked leather. The amphoteric polymer/hydroxalcite nanocomposites with an organic–inorganic framework structure were prepared by introducing layered double hydroxides (LDH), which could further improve the absorption of anionic materials during the post-tanning process of leather to obtain leather with substantial darkening, different color, and softness. The introduction of zwitterions increased the positive charge of leather and the application of the amphoteric retanning agent improved the dyeing performance of chromed leather. These characteristics are obtained because of the electrovalence and hydrogen bonding interactions between carboxyl and sulfonic anions and quaternary amino cations in amphoteric polymers with collagen. Moreover, the selection of biomass materials provides a method for the sustainable development of leather [47]. Lv et al. [48] have synthesized an amphoteric retanning agent via the copolymerization of biomass material chitosan with methacrylic acid and acrylamide and applied it to the leather retanning process. In addition to good dyeing properties, zwitterions and chitosan have excellent antibacterial properties.

The manufacturing technology of organic chrome-free ecological leather is an important direction for the sustainable development of the leather industry. However, the positive charge of tanned white wet leather is weakened, and the absorption rate of traditional anionic dyeing and finishing materials is reduced, which affects the

quality of finished leather. The amphoteric structure has both positive and negative charges, which provide a feasible solution for solving the aforementioned problems. Our group [49–51] uses polyurethane as the skeleton structure to synthesize functional retanning agents. One is the combined amphoteric retanning agent containing an aldehyde group, which is produced by introducing 2, 4-dihydroxybenzaldehyde. The other is an amphoteric retanning agent with an aldehyde removal function, which is produced by introducing chromotropic acid and collagen. Then, they were applied to vegetable, F-90, and aldehyde tanned leather. It was observed that the K/S of leather surface after retanning and dyeing was higher than that of leather with an acrylic resin retanning agent. The dye absorption rate of vegetable leather reached 90.00%, and the free formaldehyde removal rate of formaldehyde reached 80.95%. To leather retanned by acrylic resin, the dye absorption rate of vegetable leather was only reached 85.00%, and the free formaldehyde removal rate of formaldehyde reached 1.40%. The properties of chrome-free tanned leather were improved, and the types of matching chemicals were enriched. To further promote the green development of leather chemicals, a new type of biomass amphoteric leather retanning agent with the function of reducing free formaldehyde was prepared by hydrolyzed collagen and oxidized tannin extract as raw materials [52]. It can improve the absorption of cationic and anionic dyes in vegetable-tanned leather (Fig. 4a). At the same time, the amphoteric amino group in collagen can capture formaldehyde via the Schiff base reaction; carboxyl group can also bind a certain amount of formaldehyde through van der Waals force and hydrogen bonding, and the pore structure of collagen can also physically adsorb formaldehyde (Fig. 4b). This information provides guidance for the research on chrome-free tanning matching chemicals.



**Fig. 4 a** Absorption rate of the retanned leather to dyes. FGL: blue cationic dye-FGL, GR: deep blue acid dye-GR, OVMCRA: oxidized valonia extract-modified collagen retanning agent, GMCRA: commercial modified protein retanning agent; and **b** Reaction mechanism of free formaldehyde removal [49]. Copyright © 2020, Elsevier

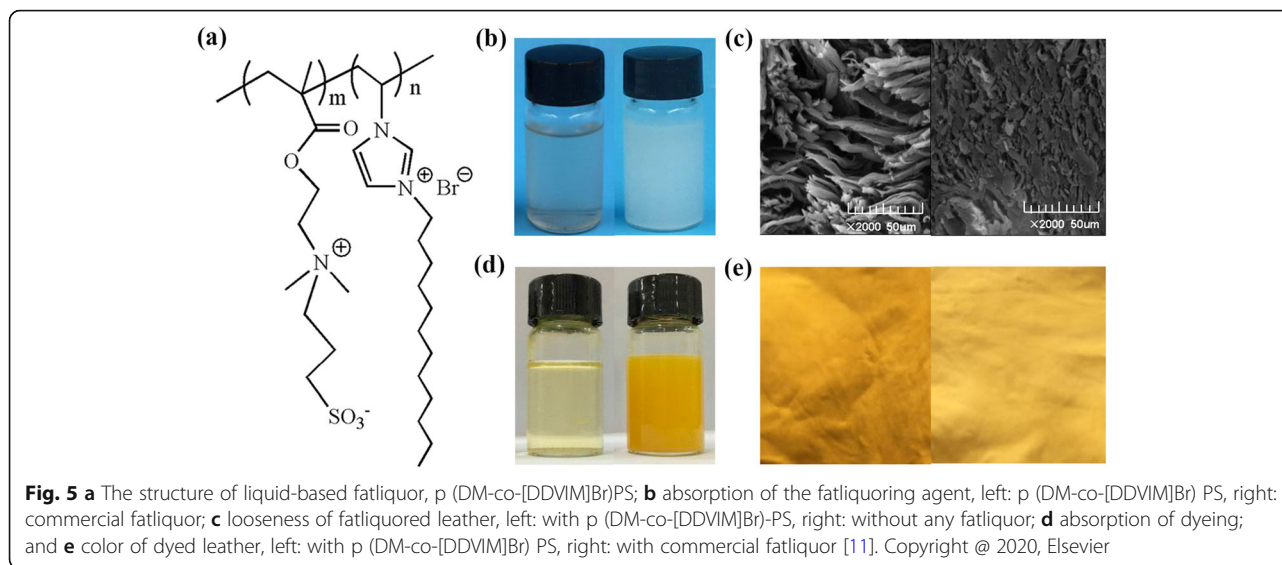
#### 4.2 Fatliquoring agent

Fatliquor is one of the key chemicals to determine the quality of resulted leather. Most amphoteric fatliquors have amphiphilic structures with hydrophilic ionic groups and hydrophobic alkyl long chains. Their surfactants and emulsifying power can wrap oil into the leather interior. At the same time, amphoteric properties can promote the combination of amphoteric fatliquor and collagen fiber. Lv et al. [53] prepared amphoteric fatliquor used the cheap rapeseed oil as raw material, which was partially amidated with ethylenediamine to introduce the amino group and polymerized with acrylic acid to introduce carboxyl group. The results showed that the flexibility of fatliquored leather samples and the absorption rate of fatliquor were higher than those of commercial products. Zheng et al. [54] have obtained a new amphoteric fatliquoring agent in three steps. The first step is to esterify fatty acids with diethanolamine. Diethanolamine can provide cation and combined with anion to form amphoteric polymer. Then, the resulting product is reacted with maleic anhydride and finally sulfonated. Janardhanan et al. [55] prepared a novel amphoteric surfactant diethylamino lauryl itaconic acid ester by mixing diethylamine and dodecyl itaconate anionic polymerizable surfactant. It was determined that they had deeper penetration and better fatliquoring performance when it was applied to leather. To further adapt to the development of the tanning system, our group [11] used free radical polymerization to synthesize the amphoteric polymer surfactant that was based on ionic liquid. The fatliquoring agent which named as p (DM-co-[DDVIM]Br) PS was synthesized from 1-dodecyl-3-vinylimidazole bromide [DDVIM] Br, dimethylaminoethyl methacrylate (DM) and 1,3-propanesultone as monomers. Using zwitterions and good

solvent properties of ionic liquids, the fatliquoring agent prepared by mixing the amphoteric polymer surfactant with oil had an absorption rate of 99.26%, loose leather fibers, and high softness. The obtained results showed that the binding affinity between collagen and dyes was improved during the fatliquoring process. The dye absorption rate was 99.01%. The fatliquoring and dye solutions were clear and considerably better than those of an anionic fatliquor on the market (Fig. 5). Therefore, our study helps to improve the absorption rate of anionic post-tanning materials, reduce the pollution caused by the use of chrome tanning agent, and provide a new way for clean production of leather industry. Except carboxyl group, the phosphate group is also the conventional anionic group in the amphoteric polymer, which has a better binding force with leather and makes the resulted leather have an excellent mercerizing and oil moistening feeling [56]. Our group [57] has further synthesized amphoteric phosphate surfactants using polyphosphoric acid as a phosphorylating agent. The surface tension of phosphate ester surfactant is better than that of dodecyl trimethyl ammonium bromide and sodium lauryl sulfate owing to the mutual attraction between zwitterions. It can be used during leather fatliquoring. Amphoteric fatliquor can improve the binding force with collagen fiber through its zwitterionic properties and promote the absorption of fatliquor to make softer leather.

#### 4.3 Other materials

In addition, amphoteric polymers are essential during the dyeing process. Ballús et al. [58] have added amphoteric dyeing auxiliaries in leather dyeing and determined that these amphoteric dyeing auxiliaries can considerably improve the dye uptake. Luo et al. [59] have synthesized amphoteric polymer additives by the radical



copolymerization of methacrylic acid, sodium methallyl-sulfonate, and diallyl dimethyl ammonium chloride using ammonium persulfate. The application of amphoteric polymer additives during the absorption of dyes and fatliquors in chrome-free leather shows that they have a strong auxiliary absorption capacity. The absorption rate of dyes and fatliquors is  $> 96\%$ .

## 5 Conclusions and prospects

During the post-tanning process of leather making, the selection of suitable amphoteric polymer materials based on the structural characteristics of collagen fibers in different tanning processes can meet the processing requirements of different leather samples and also give the resulted leather excellent properties. In addition, it is an important way for the clean production of leather. The research directions of amphoteric polymers for post-tanning of leather can be performed on the basis of the following aspects.

### 5.1 Development of amphoteric polymers with different structures for leather making

The current structure of amphoteric polymers used in leather making is mainly the polyethylene skeleton structure with low variety and single performance. Thus, there is a need to develop more amphoteric polymers with different skeleton structures and anions and cations. For example, leather waste collagen, which is an amphoteric polymer, can be applied in leather processing through modification. However, the previous modification method was mainly through the Schotten-Bauman reaction, which used irritant raw materials and produced salts and volatile organic compounds. Therefore, the green method can be used to endow the collagen more functional characteristics, which allows the

recycling of waste leather and increasing the variety of amphoteric polymers to be applied in leather post-tanning materials. What's more, Phosphate ester group, which is one of the functional amphoteric leather chemicals, can increase the absorption rate of chemical used in leather making and improve the fullness and handle of leather.

### 5.2 Study on the interaction mechanism between amphoteric polymers and leather

Although the effect of amphoteric substances on leather properties has been reported, there are few systematic studies on the interaction mechanism and structure–activity relationship between amphoteric polymers and leather. Therefore, it is suggested that the influence of amphoteric polymers with different pI, skeleton structure, and anionic ions on leather structure and properties should be systematically studied to explore the structure–activity relationship between amphoteric polymers and leather properties. In addition, the influence of amphoteric polymer on the charge of leather with different pI can be explored under different pH conditions. By conducting the aforementioned studies, the mechanism of the interaction between amphoteric polymers and leather can be revealed to guide the development and application of amphoteric polymers.

### 5.3 Exploration of characterization methods

The current detection methods of amphoteric polymers and their application performance in leather mostly refer to the detection methods in other fields, which have the following drawbacks: i.e., poor applicability of detection instruments, complexity of sample preparation and detection methods, and high detection result errors. It is necessary to explore the detection method with higher

matching and simpler process such as the charge of amphoteric polymer changes with pH, distribution of amphoteric polymer in leather without special elements, and detection of pI of solid materials.

#### 5.4 Clean application process of amphoteric materials in post-tanning

Ionic properties enable amphoteric post-tanning materials to be applied in the processing of crust with different pI in a wider pH range. For example, the amphoteric fatliquor with a higher pI can achieve higher absorption rate without the acid-adding process after fatliquoring. Therefore, it is worthy to optimize the tanning process of amphoteric materials to simplify the traditional post-tanning process, reduce the use of chemicals, and promote clean leather production.

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#### Authors' contributions

XW contributed to the investigation, funding acquisition and conceptualization. SS designed the frame, collected the data and wrote the original draft. XZ added a corrective to the manuscripts. PG corrected the grammar. XL contributed to the investigation and the guidance of professional knowledge. CL typeset picture. ML collated references. All authors read and approved the final manuscript.

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#### Competing interests

The authors declare that they have no competing interests.

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