Application of Carboxyl-functionalized Epoxy Resin in the Leather Tanning Process

by

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Abstract

Chrome tanning is widely used in the tanning process; however, it can cause environmental pollution. Leather tanned with epoxy resin was considered as a more environmentally friendly process, but it takes as long as five days for reaction, and results in poor performance of leather. The aim of the present study was to tan leather collagen with a carboxyl-functionalized epoxy resin, which was thought to be an eco-friendly tanning process and the reaction time was shortened to 12h. The reaction between carboxyl-functionalized epoxy resin and leather collagen can be divided into two stages, the reaction of epoxy group with leather collagen and the reaction of carboxyl group with leather collagen. The influences of tanning conditions (medium pH, epoxy resin amount and reaction time) on the properties of tanned leather were also discussed. In the first stage, the epoxy group was reacted with leather collagen in basic conditions. The results showed that the carboxyl-functionalized epoxy resin could better penetrate into the leather fibers when the pH value was 8.5, and the best effect of tanned leather collagen was found using reaction condition of pH 7.0. In the second stage, it was the reaction of carboxyl group to leather collagen in acid conditions, and the best effect was found under the condition of pH was 3.5. Meanwhile, it provided a better tanning effect when the carboxyl-functionalized epoxy resin amount was 6% and the reaction time was 12h. The chrome-less tanning process that carboxyl-functionalized epoxy resin combination with 3% chrome was studied. The results showed that the hydrothermal stability and strength properties of leather tanned by carboxyl-functionalized epoxy resin with 3% chrome were close, even superior, to those of the leather produced by conventional chrome tanning with 8% chrome.

Introduction

It is well known that chrome tanning is the most widely used tanning process in the industry, because it brings about highest hydrothermal stability and excellent strength properties for leather than any other single tanning material.[1] But the chrome tanning sometimes generates certain hazardous substances which are cytotoxic to human health and pollute environment.[2-3] With the improvement of environment realization and the change of consumption concept and manufacture patterns, the world industry is keen to take on greener or cleaner approaches to leather processing. Therefore, the researchers are compelled to explore eco-friendly products and processes for the alternative chrome tanning. [4]

Epoxy resins are important industrial polymers that widely used in many major industries such as coating, adhesive, civil engineering and casting due to the high reactivity of epoxy group.[5-6] Studies on leather tanned with epoxy resin have been reported in the literature since the 50's.[7] However, the epoxy resin as tanning agent gave the leather a poor performance with a low shrinkage temperature and was reversible.[8-9] Meanwhile, it was found in most studies that epoxy tanning agent required a high reaction temperature near to 50°C, a long reaction time as long as five days and a large amount of epoxy resin of 50% on the weight of the wet hide.[10] Therefore, until now the use of epoxide resins or compounds in leather tannage has not been comprehensively studied.

In the tanning process, the carboxyl has an important functional group, which can react with leather collagen through the hydrogen bond and improve the thermal stability. In addition, complexation could take place between carboxyl with chromium.[11-12]

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Luan *et al* reported that the polymers containing carboxyl groups on the end can forms lots of firm chemical bonds and a multi-sites-cross-linked structure with collagen fibers.[13] In the Pan's work, they found that the shrinkage temperature of wet-white sheepskin tanned with PMAA-SiO_2/P can reach 76°C, which is similarly due to the carboxyl groups based copolymer matrix provide possibilities for a new tanning system through covalent bonding with the collagen fiber.[14] In previous work, we prepared a carboxyl-functionalized epoxy resin.[15] In the present work, the carboxyl-functionalized epoxy resin was applied in pickled goat leather tanning process to study the application properties. Above all, the reaction conditions between the carboxyl-functionalized epoxy resin and leather collagen was studied.

Material and Methods

Material

Allyl glycidyl ether (AGE) was received from Sloan Materials Science and Technology Limited Company, Hangzhou, China. Methacrylic acid (MAA) was provided by TianJin Fuchen Chemical Reagent Factory, TianJin, China. Ammonium persulphate (APS) was purchased from HongYan Rergent Hedong District, TianJin, China. Sodium bisulfate ($NaHSO_3$) was obtained from Tianjin Tianli Chemical Reagent Corporation Limited, China. All other chemicals used for leather processing were commercial grade and purchased from local suppliers, which were generally used in the leather industries. The tests were carried out using pickled hides at pH 3.2.

Methods

Synthesis of the Carboxyl-functionalized Epoxy Resin

The preparation of carboxyl-functionalized epoxy resin has been reported in previous work.[15] In general, the sodium bisulfate solution was poured into a 250 mL three-neck-flask equipped with a digital agitator and a reflux condenser in a water bath, continuous stirring at 350 rpm. When the system was heated up to 60°C, the monomer mixture (AGE and MAA) and Ammonium persulfate solution were drop wise added within 1.5 h. The polymerization could continue for 4h. Then, the pH value was measured at 8.5 when the system was cooled to room temperature.

Tanning methodology

(1) Tanning process of carboxyl-functionalized epoxy resin Pickled hide strips (8 cm×5cm, pH 3.5) were soaked in NaCl (8%) solution in conical flasks(100mL), placed in a thermostatic vibrating water bath. Several experimental variables were examined: tanning agent amount, pH, and time. After 2 h immersion in this chemical solution at 25°C, the pH of the reaction system was adjusted using Na_2CO_3/$NaHCO_3$ solution. Most of the crosslinking reactions were carried out at 25°C, followed by diluted formic acid solution to adjust pH.

(2) Chrome-less tanning process of carboxyl-functionalized epoxy resin under the optimal condition between carboxyl-functionalized epoxy resin and leather collagen, the chrome-less tanning process with carboxyl-functionalized epoxy resin combination together with 3% chrome was studied.

Testing and Characterization

Shrinkage Temperature

The shrinkage temperature of tanned leather samples was determined according to the IULTCS official testing method IUP16 using a shrinkage tester (MSW-YD4, Sunshine Electronic Research Institute of Shaanxi University of Science and Technology, China). The rate of heating was maintained at 2°C/min.

Thickness Increment Ratio

The thickness increment ratio of tanned leather samples was determined using a digital leather thickness tester (MH-YDI, Sunshine Electronic Research Institute of Shaanxi University of Science and Technology, China). And the thickness increment ratio was calculated as the following equation:

$$\text{the thickness increment ratio (\%)}=(T_1-T_0)/T_0\times 100 \quad (1)$$

Where T_0 is the thickness before tanning and T_1 is the thickness after tanning process.

Mechanical Properties

Mechanical properties mainly including tensile strength, elongation at break and tear strength of the leather samples were measured by a universal testing machine (AI-3000) following the standard ISO 3376-1976.

Softness

The leather softness was determined by a softness tester following the standard procedures ST 300, each value reported was an average of three samples.

Enzymatic Degradation

The leather samples were placed in 500mL flasks with 0.05M phosphate buffer solution (pH 7.6), the flasks were placed in a water bath oscillator at 37°C for 4 ~ 8h to get the sample wetted thoroughly. Trypsin (1ml) from bovine pancreases (109003.8 units/g, 1 g/l solution), was added and sampling interval. The reaction was stopped by trichloroacetic acid solution (0.4M), then washed 3 times with distilled water, dried and weighed.

Chrome Content in Leather and Waste Water

The chrome content in leather and wastewater were estimated following a specific procedure (IUC 8, 1998).

Calculation

Thickness Increment Ratio

The thickness increment ratio was the thickness changes during the tanning process, it was calculated as the following equation:

the thickness increment ratio (%)= $(T_1\text{-}T_0)/T_0\times 100$ (1)

Where T_0 is the thickness before tanning and T_1 is the thickness after tanning process.

Enzymatic Degradation

The enzymatic degradation was the changes in weight of partially degraded samples (Zuriaga-Agustí *et al*., 2015), it was calculated using the following equations:

the degradation rate = $(m_1\text{-}m_0)/m_0\times\mathbf{100\%}$ (2)

Where m_0 is the original quality of leather and m_1 is the quality of leather after drying.

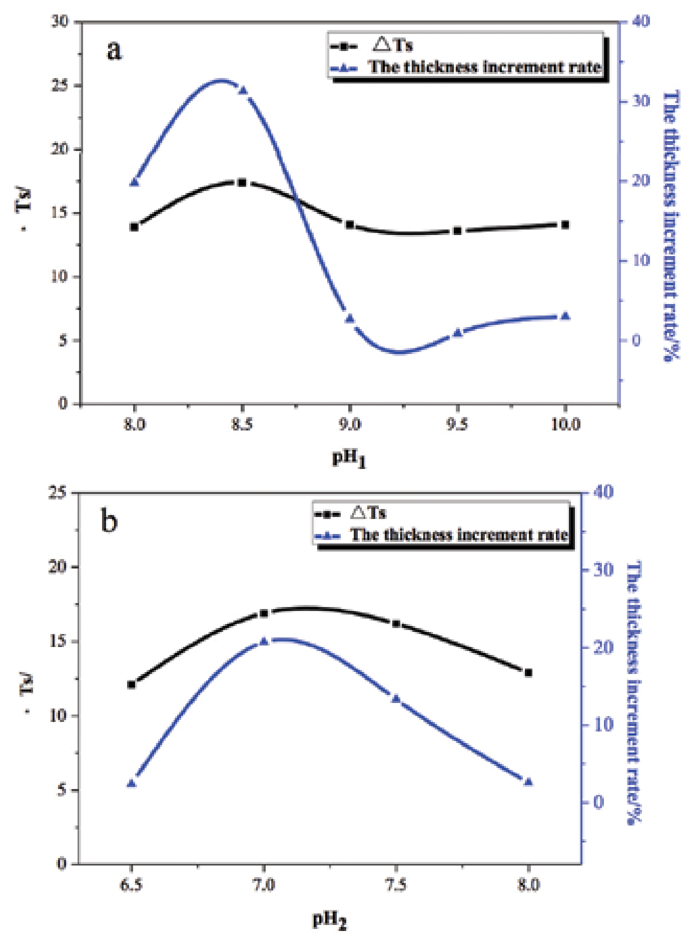

Figure 1. The effect of pH value in the first tanning stage: a-permeation pH (pH_1); b-reaction pH (pH_2)

Results

Tanning Conditions of Carboxyl-functionalized Epoxy Resin

pH

The reaction between carboxyl-functionalized epoxy resin and leather collagen can be divided into two stages, which were reaction of epoxy group and carboxyl group with leather collagen respectively. Generally, the medium pH value was an important factor that affected the tanning effects. In the first stage, the epoxy group was reacted with leather collagen in basic conditions. [16] As shown in the Figure 1, the ΔTs (the shrinkage temperature of leather collagen relative to that of leather collagen before tanning) and the thickness increment rate shows a highest value when the medium pH (pH_1) adjusted to 8.5. After that, both the ΔTs and the thickness increment rate were decreased with the pH value increased. When the medium pH(pH_2) adjust to 7.0, the value of ΔTs and the thickness increment rate were the highest. The results indicated that carboxyl-functionalized epoxy resin could penetration into pelt perfectly when the pH

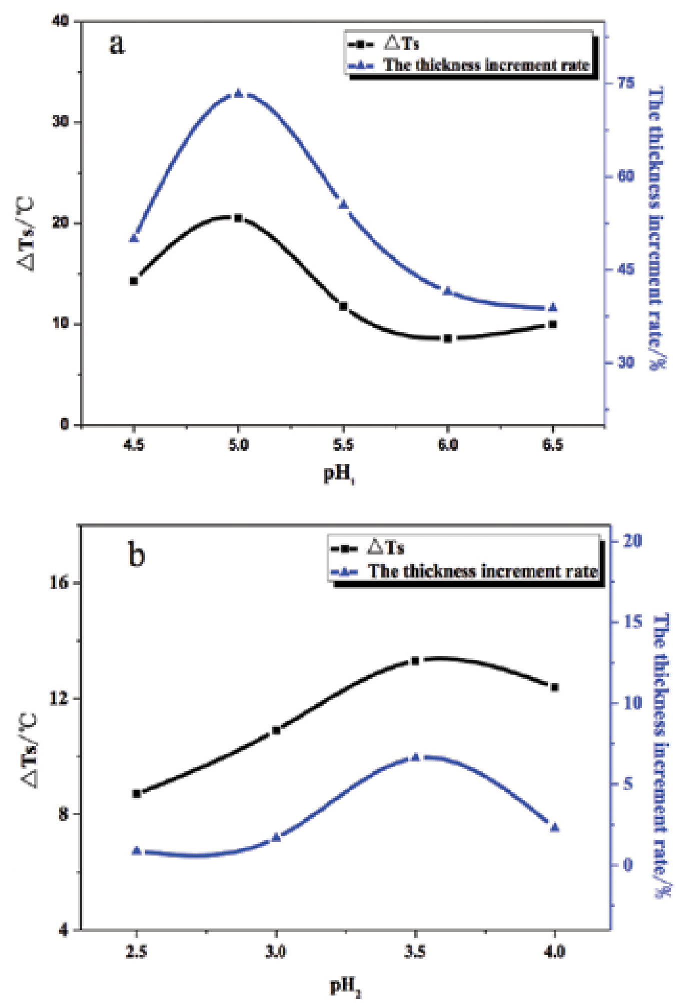

Figure 2. The effect of final pH value in the second tanning stage: a-permeation pH (pH_1); b-reaction pH (pH_2)

value was 8.5, and the drastic interaction between epoxy group in carboxyl-functionalized epoxy resin and NH_2 in collagen side chains occurred at pH 7.0.

In the second stage during the tanning process, it was the reaction of carboxyl group to leather collagen in acid conditions. As shown in the Figure 2, the ΔTs and thickness increment rate of leather increased with the penetration pH and final pH enhanced. However, when the pH was too high, the ΔTs and thickness increment rate of leather could have decreased because the reaction between carboxyl group and leather collagen occurred dominantly on the leather collagen surface and led to the grain too rough. From the results of Figure 2, the most appropriate penetration pH (pH_1) was 5.0 and the final pH (pH_2) was 3.5.

The amount of Tanning Agent

The amount of tanning agent was also one of the factors that affect the tanning results. As one could see from the Figure 3,

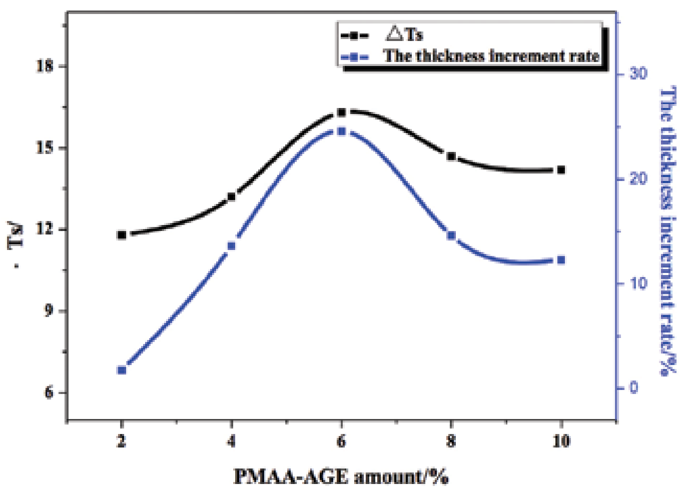

Figure 3 The effect of PMAA-AGE amount.

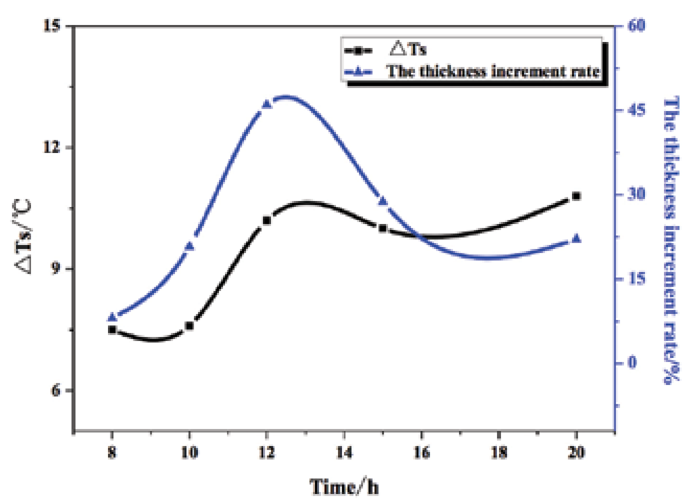

Figure 4. The reaction time of the first tanning stage.

when the amount of carboxyl-functionalized epoxy resin was 6%, a significant rise in ΔTs and thickness increment rate could be caused. However, when the amounts of carboxyl-functionalized epoxy resin were higher than 6%, the value of ΔTs and thickness increment rate fallen away, which was thought to be associated with increasing levels of pendant (i.e. single-point) attachment occurred, rather than crosslinking (i.e. multipoint) combination taken place.[17]

The commercial epoxide resins required a long reaction period as long as 5 days, however, carboxyl-functionalized epoxy resin had shown highest reactivity due to the synergistic effect of epoxy group and carboxyl group, with it crosslinking reaction can be completed in 12 h (Figure 4).

Chrome-less Tanning Results

SEM Topography of the Leather

The microstructures of the resulting leather were analyzed through SEM analysis. It is necessary to study the arrangement of fibers, which have a great contribution to the study of the thickening rate and shrinkage temperature of leather. The scanning electron photomicrographs of the transverse section and longitudinal section of leather were shown in Figure 5. Apparently, we could see from the SEM, after chrome-less tanning process containing polymer, no matter transverse section or longitudinal section, collagen fiber bundles were well-dispersed compared with those of the conventional chrome tanned, that meant such materials could penetrate into the collagen fiber inside and then form electrostatic or intermolecular and intermolecular cross-linking, which leads to the result that the thermal stability, softness as well as thickness ratio of the leather have been improved dramatically. These properties give the leather with a good handle.

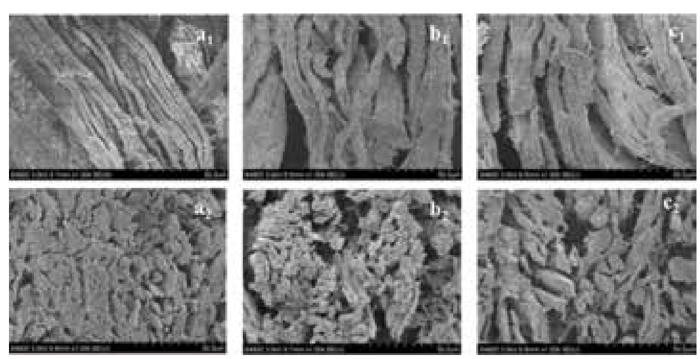

Figure 5. SEM of leather transverse and longitudinal section after different tanning process (a_1. transverse section under conventional tanning process; a_2. longitudinal section under conventional tanning process; b_1. transverse section under 3% chrome tanning process; b_2. longitudinal section under 3% chrome tanning process; c_1. transverse section under 3% chrome-less tanning process; c_2. longitudinal section under 3% chrome-less tanning process)

Physical Properties

As Figure 6 shown, the shrinkage temperature of the leather tanned with chrome-less tanning process was 114.1°C, while the shrinkage temperature of the leather tanned with 3% chrome was 87.6°C. The results suggested that the carboxyl-functionalized epoxy resin could effectively improve the hydrothermal stability, because the epoxy group and carboxyl group could react with the groups in the leather collagen chain and increased the cross-linking degree. Also, the thickness increment rate of the leather tanned with chrome-less tanning process was much larger than that of the leather tanned with 3% chrome. When the carboxyl-functionalized epoxy resin was used in pre-tanning, it was penetrated the collagen fibers and expanded the collagen fiber bundle, fibrils and collagen molecules, so that the leather thickening rate was increased.

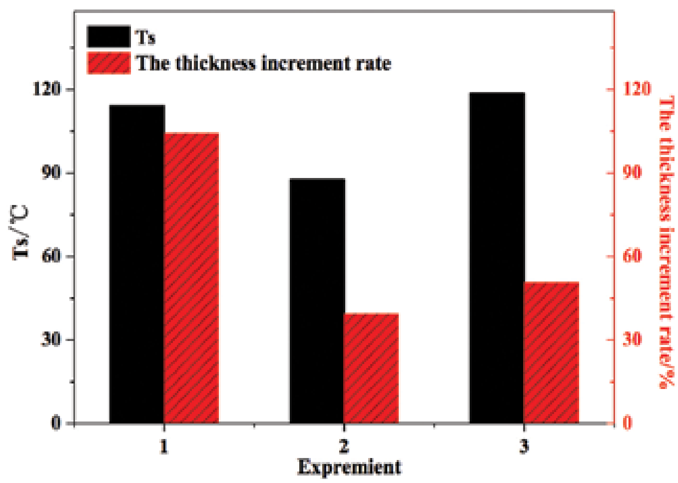

Figure 6. Shrinkage temperature and the thickness ratio of crust leather by different tanning. (1, chrome-less tanning; 2, 3% chrome tanning; 3, conventional chrome tanning)

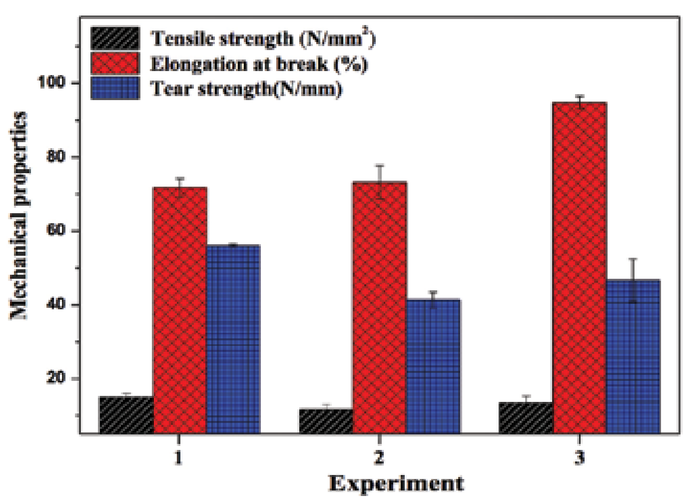

Figure 7. Mechanical properties of crust leather by different tanning. (1, chrome-less tanning; 2, 3% chrome tanning; 3, conventional chrome tanning)

Compared with that of the leather tanned by conventional chrome tanning process, the shrinkage temperature was equal, but the thickness increment rate was superior.

Mechanical Properties

The mechanical properties of the leather tanned by different process were shown in the Figure 7. The tensile strength and tear strength of the leather tanned with chrome-less process were higher than that of 3% chrome tanned leather and conventional chrome tanned leather. Although the elongation at break of chrome-less tanned leather was lower than the conventional chrome tanned leather, it met ISO standards for garment leather. It appeared that the formation of crosslinks with the addition of the carboxyl-functionalized epoxy resin could endow the tanned

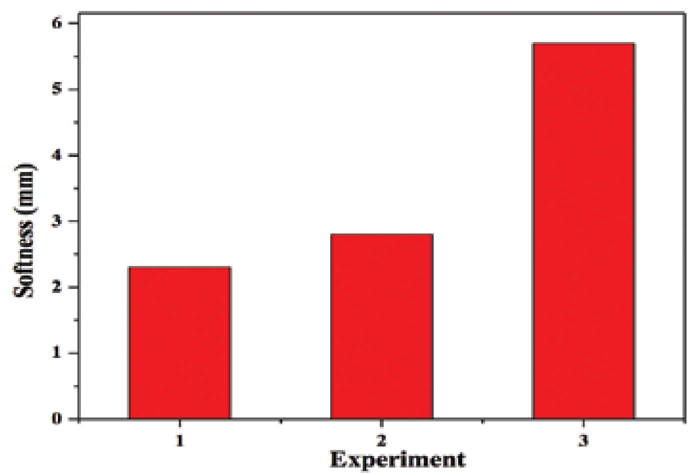

Figure 8. Softness of crust leather by different tanning. (1, chrome-less tanning; 2, 3% chrome tanning; 3, conventional chrome tanning)

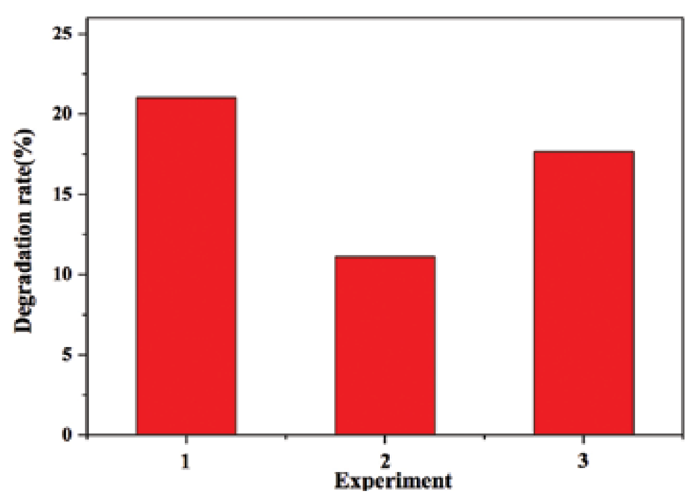

Figure 9. Degradation rate of crust leather by different tanning. (1, chrome-less tanning; 2, 3% chrome tanning; 3, conventional chrome tanning)

leather with favorable mechanical properties.

Softness

The softness of the resulting leathers tanned by different process is shown in the Figure 8. Compared with the leather that tanned by conventional chrome tanning process, the softness of the leather tanned by chrome-less tanning and 3% chrome tanning process was quite different, since the polar groups are exist in the carboxyl-functionalized epoxy resin, when it was used in the tanning process, such polar groups can form strong intermolecular and intramolecular crosslink that decrease the flexibility of carboxyl-functionalized epoxy resin, this further influenced the softness of crust leather and the flexibility of leather fiber, which was also consistent with the physical and mechanical properties.[18]

Enzymatic Degradation

Figure 9 reported the enzymatic degradation rate of crust leather by different tanning process. Compared with the 3% chrome tanning and conventional chrome tanning, the degradation rate of crust from chrome-less tanning process had improved significantly, it meant that the carboxyl-functionalized epoxy resin tanned pickled goat leather enhanced the enzymatic degradation rate of crust leather. Meanwhile, the carboxyl-functionalized epoxy resin was used in the pre-tanning process, the composites penetrated the interior of leather fiber, and improved the dispersion of collagen fibers, which more conducive to the infiltration of pancreatic into the collagen fibers, the pancreatic was better able to break down collagen fibers, lead to the improvement of the enzymatic degradation rate. The significant differences in the enzymatic stability offered by carboxyl-functionalized epoxy resin could be due to the effectiveness of the epoxy resin exhibiting interaction with collagen through multiple inter and intramolecular crosslinks. [19-20]

Chrome Content in Leather and Waste Water

Table I showed the chrome content in wastewater and crust leather with different tanning process. Obviously, the amount of chrome presented in the wastewater of chrome-less tanning was less than that in the waste water of 3% chrome tanning and conventional chrome tanning. The leather tanned by chrome-less tanning has a higher chrome content than other tanning process. The carboxyl groups of carboxyl-functionalized epoxy resin maybe enhanced the chromium uptake. It meant that pre-tanning with carboxyl-functionalized epoxy resin could increase the fixation of chrome and reduced the pollution of the environment.

Table I

Amount of chrome load in wastewater and crust leather with different tanning process.

Tanning process	1	2	3
The chrome content in wastewater /mg.L^{-1}	683.14	992.83	3026.31
The chrome content in crust leather /%	2.30	2.14	5.38

Note: 1, chrome-less tanning; 2, 3% chrome tanning; 3, conventional chrome tanning

Conclusions

In this research, carboxyl-functionalized epoxy resin was applied to pickled hide collagen, the optimum conditions of processing were achieved as follows: the amount of carboxyl-functionalized epoxy resin was 6%, the optimum penetrate pH and reaction pH were 8.5 and 7.0, respectively, and the reaction should continue 12 h in the first tanning stage. Meanwhile, the optimum penetrating pH and final pH were 5.0 and 3.5, respectively in the second tanning stage. The hydrothermal stability and physical- mechanical properties of leather tanned by carboxyl-functionalized epoxy resin with 3% chrome were close to those of the conventional chrome tanned leather, it was thought to be an eco-friendly tanning process.

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