Journal of Cleaner Production 175 (2018) 199–206

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Desirable retanning system for aldehyde-tanned leather to reduce the formaldehyde content and improve the physical-mechanical properties

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ARTICLE INFO

Article history:
Available online 22 December 2017

Keywords:
Polyacrylic acid
Gemini polyurethane surfactant
Complex retanning system
Aldehyde-tanned leather
Physical-mechanical property
Formaldehyde content

ABSTRACT

The aim of the present work is to provide a new retanning system for aldehyde-tanned leather, which can improve the physical-mechanical property of resultant leather and reduce the formaldehyde content in the resultant leather. This new retanning system consists of polyacrylic acid and gemini polyurethane surfactant, which are not harmful to human. The physical-mechanical property of leathers treated with different retanning system was analyzed, and the fiber structure of leather treated with the new complex retanning system was observed; the effects of some factors on the physical-mechanical property and formaldehyde content of leathers were studied, which were the hydrophobic chain length of gemini polyurethane surfactant, the offer percentage of retanning agent and the pH condition of retanning process. The results showed that the complex retanning system had better retanning effect, and the physical-mechanical property and formaldehyde content of leathers would be affected by above factors. When the hydrophobic chain length was eight and the offer percentage was 6%, the retanning effect was the best, and the thickening rate was 8.5%, the elongation and tear strength increased by 14.5% and 18.4%, respectively. At the same time, the reduction rate of formaldehyde content was 30.0%. Notably, when the value of pH decreased to 2.7 in the retanning stage, the reduction rate of formaldehyde content could increase to 39.3%. This retanning system had better retanning effect, which indicated that it would be helpful to the clean production of leather and the development of environmental protection. In addition, the work provided a good alternative to solve the other formaldehyde problems in our life.

1. Introduction

Leather productions can be seen everywhere in our life, which become a kind of life necessities. The process of raw hides into leathers is achieved mainly through tanning, which can improve the stability of fiber structure by introduction of additional cross-links (Yao et al., 2017). Chrome tanning agent is the most commonly used in all of the tanning agent (Nashy et al., 2012), which can endow leather high thermal stability, physical-mechanical property, excellent soft touch and good anticorrosive property (Silambarasan et al., 2015; Ramamurthy et al., 2014).

As the development of society and the improvement of people living standard, the environmental protection requirements of resultant leathers and their production process become more severe. The conventional chrome tanning process gives only about 60–70% w/w chromium uptake and the remaining is discharged into wastewater (Jia et al., 2016), which may convert into hexavalent chromium in some case (Liu et al., 2016). Hexavalent chromium will cause menace to the health of persons (Kolomaznik et al., 2008). Therefore, the tanning agents without chrome are studied and used to reduce the chrome pollution.

Vegetable and aldehyde are the usual organic tanning agents. Compared with the vegetable tanning agent, which is time consuming, work intensive, more expensive and low quality

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https://doi.org/10.1016/j.jclepro.2017.12.058
0959-6526/

product (Krishnamoorthy et al., 2013), the aldehyde tanning agent is cleaner and cheaper. Nowadays, the modified glutaraldehyde is usually used in the chrome-free tanning. Nevertheless, compared with the interaction between chrome and leather collagen,the combination of modified glutaraldehyde with leather collagen is weaker (Lin and Zhang, 2000; Onem et al., 2017), the physical-mechanical properties of resultant leather cannot satisfy the requirements of product standards. And the industrial grade modified glutaraldehyde (hydroxymethyl glutaraldehyde) will decompose under certain conditions to release formaldehyde, which was human carcinogen (List et al., 2016). For these two reasons, the aldehyde tanning agents are not used widely in practical industrial production, which are usually used with other compounds in leather tanning process (Krishnamoorthy et al., 2012; Kumar et al., 2009).

As far as we know, retanning process is one of important steps in leather manufacturing process to improve the physical-mechanical properties of leathers. Different retanning agent, such as polyacrylic acid, vegetable tannin, polyurethane can give the resultant leather different performance (Zarlok et al., 2017). At the same time, many functional groups can react with formaldehyde, such as amino group (Forro et al., 2016), phenolic hydroxyl group (Zhang et al., 2017), and so on. Some polyphenols compounds have been used to reduce the formaldehyde content in leather treated with aldehyde compounds. In the experiments of Marsal et al. (2017), the leather retanned with formaldehyde resin was further retanned by polyphenols vegetable compound, which guaranteed that the formaldehyde content of resultant leather was maintained below 16 mg/kg. In the study of Bayramoğlu (2013), the formaldehyde content of resultant leather decreased at appreciable level by adding the grape seeds extracts or powder at the retanning process. However, their works only decreased the formaldehyde content of leather treated aldehyde compounds in tanning or retanning process, and they did not obtained a retanning system for aldehyde-tanned leather which not only decreased the formaldehyde content also improved the physical-mechanical property. Up to now, few retanning systems for aldehyde-tanned leather had been reported to achieve the two goals simultaneously.

In this paper, in order to decrease the formaldehyde content and improve the physical-mechanical property of leather tanned with modified glutaraldehyde, we studied the property of leather retanned with the complex of polyacrylic acid and gemini polyurethane surfactant. Gemini polyurethane surfactant with high surface activity could facilitate polyacryic acid to permeate into the fiber. At the same time, gemini polyurethane surfactant and polyacryic acid would form polymer complex existing in fiber steadily by the intermolecular hydrogen bonding under low pH condition. Additionally, gemini polyurethane surfactant containing amide groups could react with formaldehyde to decrease the formaldehyde content in resultant leather, and the polymer complex could form strong interaction with collagen to improve the physical-mechanical properties of resultant leather. Therefore, this new complex retanning system could be beneficial to the development of aldehyde tannage and the clean production of leather.

2. Materials and methods

2.1. Materials

Acrylic acid (AA, AR, Aladdin Reagent), 1,2-Epoxyoctane (96%, Aladdin Reagent), 1,2-Epoxydodecane (95%, Aladdin Reagent), 1,2-Epoxyhexadecane (80%, Aladdin Reagent), isophorone diisocyanate (IPDI, AR, Aladdin Reagent), dibutyltin dilaurate (AR, Aladdin Reagent), potassium hydroxide (KOH, AR, Kelong Reagent, China) and ammonium persulfate (AR, Aladdin Reagent) were used as received. Methoxy poly(ethylene glycols) with molecular weight of 550 g/mol (mPEG, AR, Aladdin Reagent) was dried in 80 °C vacuum for 12 h before using.

The pickled goat skins were purchased from the market of Sichuan. The commercial grade chemicals employed in the process were those normally used in leather industry except the retanning agent. SWA, NL-20, JM, JMK, FS-90, DF were supplied by Sichuan Dowell Science and Technology Inc (Chengdu, China). And SWA is a kind of industrial-grade wetting dispersant composed of complex surfactants; NL-20 is a kind of anionic light-resistance retanning material; JM is a kind of sulphonated fatliquoring agent; JMK is a kind of sulphited fatliquoring agent; FS-90 is a kind of lecithin fatliquoring agent; DF is a kind of sulphited neatfoot oil sulphited. Modified glutaraldehyde was supplied by Wuhan Organic industry, and the formaldehyde content was 283.1 mg/L measured with acetylacetone coloration method. The dosages of the chemicals were all based on the weight of pickled pelts. Tap water was used all through the process of leather. In addition, the analytically pure chemicals and ultrapure water were used to analyze the formaldehyde content.

2.2. Methods

2.2.1. Synthesis of polyacrylic acid (PAA)

First, 20 g AA was added into the beaker with 20 g water, and the solution was stirred uniformly. Then, the potassium hydroxide aqueous solution was added dropwise into the solution to adjust the pH value to 4.0–4.5. Meanwhile, 50 g water and 0.2 g ammonium persulfate were placed in a 200 mL three-neck flask equipped with a mechanical stirrer, which was placed in a thermostat water bath at 80 °C. 5 mL prepared AA solution was slowly added into the three-neck flask every 15min. The reaction was kept another 30min when all the AA solution was added, and polyacrylic acid (PAA) solution was obtained. PAA was freeze-dried for two days before using, and the solid content was 100%. At the same time, the number-average molecular weight (M_n) and polydispersity index (PDI) of PAA measured by gel permeation chromatography (GPC) were 8065 and 14.79, respectively.

2.2.2. Synthesis of gemini polyurethane surfactants (PUG)

The synthesis route of PUGs is shown in Scheme 1. The composite formula is presented in Table 1, which contains main reactants. 0.1 mol epoxy alkyl and 0.1 mol mPEG were added into a 100 ml three-necked flask equipped with a stirrer, and potassium hydroxide corresponding to equal mole of epoxy group was added. Under the high speed stirrer, the mixture was heated up to 80 °C and maintained for 15 h in a thermostat water bath. 0.05 mol IPDI and 0.2 g dibutyltin dilaurate were added into the three-necked flask, and the reaction was kept for 3 h. The product was obtained. PUG was synthesized without solvent, and the solid content was 100%. The M_n and PDI of PUG (represented by PUG-8) measured by GPC were 700 and 1.43, respectively. At the same time, the surface tensions of PUG-8, PUG-12 and PUG-16 at the critical micelle concentration, measured by static surface tensiometer, were 33.8 mN/m, 30.1 mN/m and 35.4 mN/m, respectively.

2.2.3. Processing of leathers

The pickled local goat skins were chosen as the raw materials in this experiments. In order to make sure the same fiber woven status, the raw material was cut into two piece with the same size (200 mm × 150 mm) along the spine. For comparison, the one piece was treated with retanning agent and the other piece was not. The process recipe and formula of the raw materials are shown in Table 2.