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Nanocomposite-based green tanning process of suede leather to enhance chromium uptake

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ABSTRACT

A nanocomposite-based green tanning process of suede leather was developed, which could be recognized as an eco-friendly chrome-less tanning process. In this study, nanocomposites were applied in tanning and retanning process during suede leather making. Effects of nanocomposites on shrinkage temperature, mechanical properties, softness, biodegradability of the leather samples were investigated; The resulting leather was characterized by scanning electron microscopy and atomic force microscopy; Effects of nanocomposites on the chromium load, biochemical oxygen demand, chemical oxygen demand in the wastewater were analysed. The results show that the addition of nanocomposites could endow the leather with high hydrothermal stability, biodegradability and softness; The mechanical properties of the leather treated with nanocomposites were close to those of the chrome-treated leather; The SEM and AFM indicated the resulting leather treated with nanocomposites contained well-dispersed fibrils and uniform fluff. Additionally, it was found that nanocomposites applied in the tanning and retanning processes brought better chromium uptake and reduction of chromium load in the wastewater. The ratio of biochemical oxygen demand and chemical oxygen demand in the wastewater was 0.37, which demonstrates that the effluent of less chrome combination retanning systems was more easily biodegradable than that of the chrome retanning process and the experimental process exhibited lowest chemical cost as compared to the chrome tanning process. Nanocomposites applied in the suede leather making process could improve the properties of the resulting leather and help to realize the cleaner production.

1. Introduction

Suede leather is composed of the reticular layer near the grain layer. In the reticular layer, the fibrils become very coarse and loose-woven (Deng, 2008), especially in the head and belly region, which leads to a significant decrease of strength of leather. Therefore, tanning is one of the important processes during suede leather production, which could form crosslink and then improve thermal stability and strength of leather. Chrome tanning bringing about better hydrothermal stability than any other tanning methods is widely used in leather making process. More than 90% of the global leather production is currently through chrome-tanning process (Li et al., 2009; Saadia et al., 2009). However, the uptake of chromium during the traditional chrome tanning process is only 65–75% (Ganesan et al., 2013; Sundarapandiyan et al., 2011), that is to say, 25–35% of the chromium remains in tanning liquor. A large quantities of chrome liquors discharged into the soil and water may cause serious pollution (García et al., 2013; Bonilla et al., 2010; Morera et al., 2011). In addition, the shortage of chrome in our country results in a sharp rise in leather costs. Therefore, how to reduce chrome waste to realize clean production becomes an important direction of the sustainable development of the leather industry.

Chrome-free tanning materials are considered as a suitable eco-friendly option for replacing chrome tanning agent such as polymers (Suparno et al., 2005; Sundar et al., 2002), vegetable tannins

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(Swarna et al., 2009), other metal tanning agents (Li and Wang, 2013), oil (Sundar et al., 2013), oxazolidine (Li et al., 2009) and unnatural amino acids (Krishnamoorthy et al., 2012), etc. However, all the above chrome-free tanning materials lead to excessive loading in the leather, which reduces its versatility to make different resulting products and also has low resource availability. Hence, chrome-less tanning is a green process for leather production, which can both improve thermal stability and mechanical properties and minimize the use and generation of hazardous substances.

With the rapid development of nanotechnology, nano materials, such as TiO_2 (Zhao et al., 2008), SiO_2 (Ma et al., 2008), Montmorillonite (MMT) (Ma et al., 2002, Bao et al., 2007 and 2008), ZnO (Li et al., 2011), are applied in the leather making process. Nano materials could penetrate into fibres inside with those small size and large specific surface area to improve the properties of resulting leather. Among them, ZnO has antibacterial property and ultraviolet resistance (zhou et al., 2008; Jiang et al., 2012). It is as a very important nano-material has attracted much attention in the leather field because of its outstanding characteristics. Additionally, In our previous study (Li et al., 2011), amphoteric vinyl-polymer/ZnO (PDM/ZnO) nanocomposites were prepared and then PDM/ZnO combined with 2.0% chrome tanning agent was applied in goat leather tanning process. The results indicate that the application properties improved in comparison with those of PDM.

In this research, the prepared nanocomposites (PDM/ZnO) combined a few chrome tanning agents were applied in suede leather making process to study the application properties and assess the environmental impact.

2. Experimental

Local Chinese calf skin by Wentai tannery, Shandong, China was used. Polymer/ZnO nanocomposite was prepared in our lab. Sodium chloride, sodium formate and sodium bicarbonate used were of commercial grade. Chromate B (33% basicity) from Brother Enterprises Holding co., Ltd, China was used as chrome tanning agent. Tap water was used all through the work.

2.1. Tanning and retanning process

Local calf skin was made in the beam-house operation as usual. After the skin was pickled in 10.0% NaCl for 15 min, and then tanned with 4.5% chrome (Chromate B, 33.0% basicity). After basification, the exhausted chrome bath showed a pH value of about 4.0. The resulting suede leather was washed with water and horsed up for 2 days to ensure the fixation of the chrome salts. After horsing up, the wet blue was retanned with 10% chrome and basified, which was as the conventional tanning and retanning process (Exp. 1). In the tanning process of the pickled pelt, 4.5% chrome was applied and 3.0% nanocomposites combined with 3.0% chrome were applied in the retanning process (Exp. 2). In the tanning process of the pickled pelt, 3.0% nanocomposites combined with 3.5% chrome were applied, and 2.0% nanocomposites combined with 3.0% chrome were applied in the retanning process (Exp. 3). During the tanning process, the weight of bated pelts is used as a measurement basis of chemicals and in the retanning process, the weight of wet blue is used as a measurement basis of chemicals.

2.2. Leather testing

The properties of the resulting leather were tested, such as shrinkage temperature, physical and mechanical properties, softness and biodegradation.

2.2.1. Shrinkage temperature

The leather samples were prepared by the mould, and then the shrinkage temperatures (Ts) of each tanned or retanned leather samples were determined by a shrinkage tester (MSW-YD4 Sunshine Electronic Research Institute of Shaanxi University of Science and Technology).

2.2.2. Physical and mechanical properties

The leather samples were cut in rectangular strips and conditioned under standard atmospheric conditions for 48 h prior to analysis of the mechanical properties. Physical and mechanical properties mainly including tensile strength and elongation at break of the leather samples were measured by a universal testing machine (AI-3000) following the standard ISO 3376-1976.

2.2.3. Softness and biodegradation

The leather samples were conditioned under standard atmospheric conditions for 48 h prior to analysis of the softness, which was determined by a softness tester following the standard procedures GT 303. The biodegradation of the resulting leather samples was observed by collagenase following paper previously reported in the literature (Di and Heath, 2009).

2.3. Morphological analyses

The microstructure of resulting leather was characterized by the atomic force microscopy and scanning electron microscopy.

2.3.1. AFM characterization

The leather samples were prepared through frozen section prior to the atomic force microscopy (AFM) analysis. The roughness of the grain surface of the resulting leather samples was observed by using AFM techniques.

2.3.2. SEM characterization

Prior to scanning electron microscopy (SEM) analysis on a SEM instrument, the grain surface and cross section of the resulting leather samples of about 3 mm thickness were freezing fractured, and the grain surface and cross section were coated with a thin layer of gold using a vacuum sputter at an acceleration voltage of 5 kV and then were observed by using SEM techniques.

2.4. Environmental impact assessments

The wastewater of tanning and retanning process containing a large number of pollutants has an impact on the environment and human. In this paper, The wastewater analysis includes chrome content in wastewater, biochemical oxygen demand and chemical oxygen demand.

2.4.1. Chrome content in wastewater

The chromium present in the wastewater was estimated following a specific procedure (IUC 8, 1998) after acid digestion of the wastewater sample.

2.4.2. Biochemical oxygen demand (BOD_5) and chemical oxygen demand (COD_{Cr})

The tanning liquor from the experimental processing was collected and analysed for COD_{Cr} and BOD_5 by using a standard procedure (APHA, 1995).

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