Preparation of highly-oxidized starch using hydrogen peroxide and its application as a novel ligand for zirconium tanning of leather

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ABSTRACT

A series of highly-oxidized starch (HOS) were prepared using H_2O_2 and a copper-iron catalyst as a desired ligand for zirconium tanning of leather. The effects of catalyst and H_2O_2 dosages, and reaction temperature on the oxidation degree (OD, represented as the amount of carbonyl and carboxyl groups derived) of starch were investigated. The OD reached 76.2% when oxidation was conducted using 60% H_2O_2 and 0.015% catalyst at 98 °C for 2 h. ^{13}C NMR and FT-IR illustrated carbonyl and carboxyl groups were formed in HOS after oxidation. GPC and laser particle size analyses indicated the decrease of HOS molecular size with increasing H_2O_2 dosage and OD. HOS with moderate OD and molecular weight was able to coordinate with zirconium and remarkably improve tanning process. Leather tanned by Zr complexes using HOS-60 (60% H_2O_2, Mn 3516 g/mol) as ligand presented considerably better physical and organoleptic properties than those of traditional Zr-tanned leather.

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1. Introduction

Starch, one of the most abundant polysaccharides in nature, is a glucose polymer composed of two polymeric units, amylose and amylopectin (Li, Prakash, Nicholson, Fitzgerald, & Gilbert, 2016). Besides food industry, starch can be widely used in various non-food industries, especially after modification. As an important type of modified starch, oxidized starch has better water solubility, film-forming and binding properties than the raw material (S.D. Zhang et al., 2015; Y. Zhang et al., 2015), ascribed to the oxidation process that converts hydroxyl groups into carbonyl/carboxyl groups. Oxidized starch has been commonly used in textile sizing, adhesive, paper coating and surface sizing (Salmi et al., 2016). In addition, it can also be used as a builder for detergents owing to its excellent capabilities for binding calcium and magnesium ions (Santacesaria, Trulli, Brussani, Gelosa, & Di Serio, 1994; Sheng et al., 2012). In leather industry, dialdehyde starch oxidized by sodium periodate can be used as a crosslinker for stabilizing collagen as well as leather tanning process (Jayakumar, Kanth, Rao, & Nair, 2015; Kanth et al., 2006).

Nowadays, leather industry is faced with rigorous environmental and social pressure due to the use of chrome tanning agent. The chrome-containing wastewater and solid waste may pose a potential risk to environment in terms of the conversion of Cr(III) into more toxic Cr(VI) (Chaudhary & Pati, 2016; Dixit, Yadav, Dwivedi, & Das, 2015; Scapel, Lamers, Matos, Baldasso, & Dettmer, 2016; Zhou et al., 2012). Therefore, the development of sustainable chrome-free tanning agents has become the focus of international leather researchers in academia and industry. Zirconium salt is regarded as a potential alternative to chrome tanning agent and has drawn renewed attention due to its relatively high tanning ability and low environmental risk (Cao, Zeng, Cheng, Zhang, & Liu, 2016; Sizeland, Wells, Edmonds, Kirby, & Haverkamp, 2016). However, traditional Zr-tanned leather has poor organoleptic properties, such as stiff handle and coarse surface. A generally accepted reason is that zirconium salt is very active to react with skin collagen fibers in the initial stage of tanning and thus precipitate on the leather surface, leading to the uneven distribution of Zr in leather and poor tanning performance (Ramasami, Sreeram, Rao, & Nair, 2000; Sundaram et al., 2000). Small molecular ligands with hydroxyl, carbonyl and carboxyl, such as lactic acid, citric acid and tartaric acid, have been used as masking agents in order to coordinate with Zr ion and reduce its reactivity (Madhan, Sundarrajan, Rao, & Nair, 2003; Sundarrajan, Madhan, Rao, & Nair, 2003). However, the improvement of organoleptic properties of leather is still limited. The

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possible reason is that the functional groups in these ligands are not enough to coordinate and stabilize the Zr complexes. In addition, Zr complexes may be too small to form macromolecular cooperating unit, resulting in insufficient crosslinking reaction between collagen fibers (Covington, Lampard, Hancock, & Ioannidis, 1998). On the other hand, ligands with too strong coordination ability probably hinder the reaction between Zr complexes and skin collagen, and ligands with too large molecular size may be difficult to penetrate and evenly distribute in leather. Hence, it is essential to design a ligand with more appropriate coordination effect and molecular size for zirconium tanning and further understand the structure-property relations of the ligand.

Abundant hydroxyl groups in starch, primarily in C-2, C-3 and C-6 positions of glucose unit, can be transformed into carbonyl and carboxyl groups by oxidation. Meanwhile, the molecular weight of oxidized starch can be regulated by oxidation through controlling the rupture degree of α-(1–4) glycosidic bond (S.D. Zhang et al., 2015; Y. Zhang et al., 2015). Therefore, oxidized starch seems to be an excellent choice for developing ligand of Zr complex due to its variable coordinating groups content and molecular size. Moreover, compared with synthetic organic ligands, starch-based ligand is supposed to be more sustainable, environment-friendly and economic due to the renewability, biodegradability and low cost of starch. Although starch oxidized by H_2O_2 has been extensively studied, most of the products had relatively low degree of oxidation (Wang, Chen, Zhao, Wang, & Wang, 2015; Wang, Poya et al., 2015; Zhou, Liu, Zhang, Chen, & Kong, 2016). An oxidized starch product with a higher degree of oxidation was obtained for preparing thermoplastic material (Zhang, Wang, Zhao & Wang, 2013). However, it may still be too large in molecular size to be used as a ligand of Zr complex. Actually the relationship between the oxidation degree and molecular weight of oxidized starch and its effect in zirconium tanning has not been clarified yet. Therefore, it is necessary to explore the structure-property relations of highly-oxidized starch (HOS) and prepare HOS with moderate coordinating groups and suitable molecular weight for zirconium tanning of leather.

In the present work, HOS was prepared using H_2O_2 as oxidant and copper/iron salts as catalyst. The effects of catalyst dosage, oxidation temperature and H_2O_2 dosage on the oxidation degree (OD, representing the amount of carbonyl and carboxyl groups) of HOS were investigated. The structure and properties of HOS was characterized by Fourier transform infrared (FT-IR) spectroscopy, nuclear magnetic resonance (NMR), gel permeation chromatography (GPC) and laser particle size analysis. Then the performance of HOS as ligand in zirconium tanning was evaluated.

2. Materials and methods

2.1. Materials

Corn starch (amylose content 28.3%), H_2O_2 (30%), $CuSO_4 \cdot 5H_2O$, $FeSO_4 \cdot 7H_2O$ and $Zr(SO_4)_2 \cdot 4H_2O$ were of analytical grade and purchased from Chengdu Kelong Chemical Co., Ltd (Chengdu, China). The reagents used for analysis were of analytical grade, and the chemicals used for leather processing were commercial products.

2.2. Preparation of HOS

Corn starch (40.0 g) and a certain amount of distilled water were gelatinized at 90 °C for 20 min in a 1000 mL three-neck flask. Then a combination of two metal salts ($CuSO_4 \cdot 5H_2O$ and $FeSO_4 \cdot 7H_2O$ in a mass ratio of 2:8, determined by preliminary investigation) with a dosage ranging from 0 to 0.1 wt% (based on the weight of starch, the same below) were introduced into the blend. After 3 min of intensive stirring, different amounts of H_2O_2 (10 wt%, 40 wt%,

60 wt%, 100 wt% and 140 wt%, respectively) and a certain amount of distilled water were added to form a blend of 400 mL. Then oxidation reaction was conducted at different temperatures (70–98 °C) for certain duration (1–4 h), and the products (HOS) were sampled from the reactor for determinations. The product oxidized by 10% H_2O_2 was labeled as HOS-10, and the product oxidized by 40% H_2O_2 was labeled as HOS-40, and so on.

2.3. Decomposition rate of H_2O_2

Decomposition rate of H_2O_2 was determined by iodometric titration according to the method described by Kingzett (1880). 2 mL HOS sample was mixed with 2 mL sulfuric acid (20%), 1.0 g potassium iodide and three drops of ammonium molybdate (30 g/L) in an iodine flask. The mixture was sealed and kept away from light for 10 min, and then was titrated with sodium thiosulfate (0.104 mol/L) using starch solution indicator (5.0 g/L, 3 mL). Gelatinized starch without H_2O_2 was used for the blank determination. The concentration of H_2O_2 in the sample was calculated as follows:

$$C(H_2O_2)(\text{mol/L}) = \frac{C(Na_2S_2O_3) \times (V_S - Na_2S_2O_3 - V_{B-Na_2S_2O_3})}{2 \times V_S} \quad (1)$$

where $C(Na_2S_2O_3)$ is concentration of sodium thiosulfate solution (0.104 mol/L), $V_{S-Na2S2O3}$ is the volume of $Na_2S_2O_3$ solution used for the sample titration (mL), $V_{B-Na2S2O3}$ is the volume of $Na_2S_2O_3$ solution used for the blank titration (mL) and V_s is the volume of sample (2 mL).

Decomposition rate of H_2O_2 was calculated by the initial and the final H_2O_2 concentrations of the blend. It should be mentioned that the initial H_2O_2 concentration was determined prior to the addition of the catalyst. Measurements were made in triplicate, and the results were presented as the means ± standard deviation.

2.4. Determination of oxidation degree (OD)

Oxidation degree (OD) of HOS was defined as the amount of carbonyl and carboxyl groups in per glucose unit. Carbonyl content of the samples was determined according to a hydroxyl amine method described by Smith et al. (1967). 5 mL sample solution and 50 mL distilled water were transferred into a 250 mL beaker and then heated to 40 °C. The pH was adjusted to 3.2 with 0.1 mol/L HCl solution. 60 mL hydroxylamine chloride solution (mixing 25.0 g hydroxylamine hydrochloride with 100 mL of 0.5 mol/L NaOH solution and diluting the compound to 500 mL) was then added. The blend was covered with aluminum foil and stirred in water bath at 40 °C for 4 h. After that, the excess hydroxylamine content was determined by a rapid titration to pH 3.2 with 0.098 mol/L HCl solution. It should be noted that carboxyl groups in HOS were not involved in the reaction. Moreover, 5 mL of 10% soluble starch solution (w/v) was used for a blank determination. The carbonyl content was calculated as follows:

$$\text{Carbonyl content}(\%) = \frac{C_{HCl} \times (V_{B-HCl} - V_{S-HCl})}{1000 \times 3 \times m/M} \times 100 \quad (2)$$

where C_{HCl} is the concentration of HCl solution (mol/L), V_{B-HCl} is the volume of HCl solution used for the blank titration (mL), V_{S-HCl} is the volume of HCl solution used for the sample titration (mL), m is the solid content of HOS in sample solution (0.5 g), M is the molar mass of glucose unit (162 g/mol), and 3 is amount of hydroxy group in a glucose unit.

Carboxyl content of the samples was determined was by a procedure described by Lukasiewicz (2012) with some modifications. The sample solution (5.0 mL) loaded on to a column (3.5 cm × 37 cm) filled with strong-acid cation exchange resin (Amberlite IR120, Sigma-Aldrich, USA), and was eluted with ultrapure water (250 mL for each sample) at a flow rate of 1.7 mL/min. The eluate was collected and titrated to pH 8.3 with 0.098 mol/L NaOH solution using