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Mechanisms of Zn(II) binded to collagen and its effect on the capacity of eco-friendly Zn-Cr combination tanning system

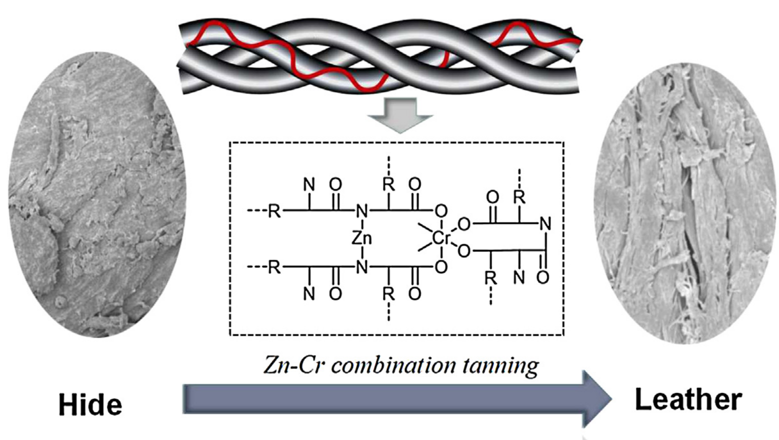
Shan Cao[a,b], Bing Liu[c], Baozhen Cheng[d], Fuping Lu[a], Yanping Wang[b], Yu Li[a,*]

[a] College of Biotechnology, Tianjin University of Science and Technology, Tianjin, 300457, PR China
[b] College of Food Engineering and Biotechnology, Tianjin University of Science and Technology, Tianjin, 300457, PR China
[c] Room L1.42 Gorlaeus Laboratory, Leiden, The Netherlands
[d] College of Material Science and Chemical Engineering, Tianjin University of Science and Technology, Tianjin, 300457, PR China

HIGHLIGHTS

- Less-chrome tanning by zinc pretanning for tannery is a first report.
- Mechanisms of Zn(II) binded with collagen were explored to optimize tanning process.
- Evaluation of the wet-blue from combination tanning show the availability and utilization of this method.

GRAPHICAL ABSTRACT



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ABSTRACT

The eco-friendly combination tanning process has been developed to reduce chromium in existing researches, which is based on zinc tanning agents. This can be considered as a less-chrome substitute for current tanning process. To gain deeper understanding of the binding mechanisms of zinc-collagen interaction, which are affected by tanning pH, experiments have been carried out. Analysis in this paper reveals how chemical bonds from the collagen's main function groups combine with zinc. XPS and NIR data was analyzed for further understanding of where the zinc binding sites lie on collagen fibers at different pH. The results indicate that high pH is helpful to amino-binding sites while low pH promotes carboxyl-binding sites on collagen fibers. Furthermore, from the effect of Zinc-chrome combination tanning, we can see that the new method reduces the chromium dosage in tanning process compared to the conventional chrome tanning method.

1. Introduction

Environmental pollution is the main problem of leather industry due to enormous solid and liquid wastes. Among the solid wastes

* Corresponding author at: 415#, College of Biotechnology, Tianjin University of Science and Technology, Tianjin, 300457, PR China.
E-mail addresses: cs1988@foxmail.com, cs1988@tust.edu.cn (Y. Li).

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pollutants, the chromium containing tannery shavings are of major concern. The cost of processing one metric ton of rawhide produces is generating 200 kg of tanned waste leather and 250 kg of non-tanned waste on average [1]. Although traditional practice to dispose chrome shavings is landfilling, restrictions imposed on the disposal of chromium bearing waste in many parts of the world is extremely stringent [2]. At present, almost all the countries including the developing countries have introduced the pollution control standard similar to developed countries such as United States, European Union and others. In view of the seriousness of environmental issues, researchers are compelled to eco-friendly products and alternative chrome tanning processes [3].

Inorganic tannins, such as chromium, aluminum, titanium, iron and zirconium, are widely applied. They can improve the viability and also the resistance to chemical, thermal and microbiological corrosion of leather products [4]. Besides, organic tannins such as aldehyde, high molecular weight vegetable tannins and synthetic tannins are able to be used for tanning. However, the complicated waste treatment processes are the limit and disadvantage of the known tannins [5], furthermore, the expensive disposal of leather scraps is another complicated problem [6]. Therefore, combination tanning methods, such as the chrome-less and chrome free combination tanning process, are considered as suitable solutions to overcome the problems from single tanning processes [7]. The tanning agent chosen for combination tanning should not only satisfy the environmental requirements but also not introduce any color to the leather [8]. Accepted as inexpensive and eco-friendly materials, zinc can be considered as an ideal potential tanning agents to turn hide into leather.

Zinc plays an essential role in biochemical processes [9], and many results show that zinc enhances the stability of collagen. As we all known, collagen is the major component of the hide, which plays the role of supporting structure. Osorio presented that perhaps zinc is a potent competitive inhibitor of matrix metalloproteinase, and it creates metal-activated switches to increase the dentin collagen stability [10]. Rosenberg found that cartilage oligomeric matrix protein can bind to collagen I/II and procollagen I/II, and the interaction is dependent on the divalent cations Zn^{2+} [11]. In a $3d^{10}$ system, zinc can readily accommodate all kinds of building blocks such as linear chain, zigzag chains, ladder structure and square grid [12], and it's particularly suited for the construction of coordination polymers and networks as chromium in tanning process.

Zinc was first noticed for the tanning property when it was used as deliming agents, it showed an obvious shrinkage temperature increase after zinc treatment [13]. The past researches found vegetable-zinc combination tannage can provide a higher shrinkage temperature [14]; tanning agents based on aluminum-zinc combination can increase the shrinkage temperature of leather over 90 °C [15] Using the chrome-zinc tanning agent, the exhaustion of chromium has been increased to above 90%. Leather processed with the chrome-zinc tanning agent shows the zinc imparts tremendous physical strength and enhances the grain smoothness of the leather [16]. Hence, Zinc is potential to be applied as a candidate for combination tanning agent, to replace the single chromium tanning. It's significant to have the researches on the field of characteristics and mechanism of interaction between zinc and collagen.

In previous study, we expounded the mechanisms of Cr binded to collagen by using ultraviolet-visible and near infrared reflectance spectrophotometer (UV–vis-NIR) [17], because of NIR spectroscopy has a high sensitivity to the slight changes in the N—H 1st overtone peak of amino groups ($—NH_2$) and the O—H 1st overtone peak of carboxyl groups (—COOH) in collagen [18]. Moreover, the effects of single zinc tanning [19] and combination Zn-Ti tanning were also explored [20]. Based on that, the binding sites of collagen and zinc are studied in this paper. Influences of pH on the reactivity of amino group and carboxyl group of collagen with zinc are fully revealed. Furthermore, the characteristics of Zinc-chromium tanning system were analyzed, which is a guidance of a new discovery on eco-friendly combination tanning methods.

2. Experimental methods

2.1. Materials

Collagen fiber (CF) was prepared from bated goat pelts according to the method described in the literature (Ma et al., 2015). Different collagen fibers, such as CF, deaminated collagen fiber (DACF) and decarboxylated collagen fiber (DCCF), were used for experimental trials. The raw material of pickled pelt processes from wet salted goat skin was used for tanning processing. The zinc solution (0.1 mol/L) was prepared by dissolving $ZnSO_4$ in distilled water, respectively. Chemicals used for experiments are all of chemical grade, and those used for analysis are of analytical grade (Jiangtian Chem. Co., Ltd, Tianjin, China).

2.2. Preparation of DACF and DCCF

2.2.1. Preparation of DACF

DACF was prepared by the reaction of CF and $NaNO_2$ in acid condition, which removes 40% to 50% amino groups on CF [21]. CF (50 g)was soaked with distilled water (100 mL) for 36 h, after which $NaNO_2$ solution (200 g/L, 250 mL) was added. The mixture was shaken for 1 h at 25 °C, followed by adding glacial acetic acid (42.6 g). The deamination was then performed for 24 h at 25 °C. The product was vacuum-filtrated, washed successively with distilled water (five times, 50 mL per time), and acetone aqueous solution (1:1, v/v; 10 min/time, three times). After dried at 40 °C for 48 h, DACF was obtained and stored at 25 °C, humidity of 65%.

2.3. Preparation of DCCF

DCCF was prepared by esterification, which removes 90% carboxyl groups on CF [22]. CF (30 g) was added to a mixture of methanol aqueous solution (2 mol/L, 750 mL) and concentrated hydrochloric acid (36.7%, 5.63 mL), and kept shaken for 24 h at 25 °C. The mixture was then neutralized to pH 7 with 40% (w/v) NaOH solution and kept shaken for 30 min. The product was filtrated, washed successively with distilled water (50 mL, five times), acetone aqueous solution(1:1, v/v; 10 min/time, three times). After dried at 40 °C for 48 h, DCCF was obtained, and stored at 25 °C with a humidity of 65%.

2.4. Analysis of pH influenced Zn(II)–collagen binding

2.4.1. Determination of precipitation pH of zinc tanning agent

Zinc solution (0.1 mol/L, 20 mL) was transferred to separate triangular flasks respectively. Standard NaOH solution (0.1 mol/L) was used to titrate the solutions (under continuous stirring) at a rate of 1 mL/min until precipitate was formed. The precipitation pH values of zinc were measured pH titrator (ZDJ-5, LEICI, China).

2.4.2. Tanning simulation experiments

CF, DACF and DCCF (0.5 g each) was tanned for 6 h with zinc solutions (0.1 mol/L, 25 °C, 10 mL). Reaction pH range was 1–5 with an increment of 0.5. After that the pH was raised to the precipitation pH of zinc with sodium carbonate aqueous solution (1:20, w/w). After basifying, the reaction mixture was kept shaken for another 12 h. Subsequently, the collagen fibers were vacuum filtrated, washed successively with distilled water (50 mL, five times), acetone aqueous solution(1:1, v/v; 10 min/time, three times). After