Study on tanning effect of tapioca dialdehyde starch combined with titanyl sulfate

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Abstract

As a kind of dialdehyde polysaccharide, dialdehyde starch is widely used in leather tanning. Titanium tanning agent is also considered as a potential tanning agent. However, the tanning effect of dialdehyde starch and titanium tanning agent is not ideal. In this study, a system of dialdehyde starch with different aldehyde group contents was prepared by the oxidation of tapioca with sodium periodate. The highest aldehyde content of tapioc can reach 93.17%. The molecular weight of dialdehyde starch decreased, while their aldehyde group content increased withincreasing dosage of sodium periodate. The degradation products of dialdehyde starch with different molecular weight were obtained by degradation. Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to study the effect of composite tannery of degradation products of dialdehyde starch and titanium sulfate. Under the experimental conditions, the leather was tanned with dialdehyde starch degradation products, and then the leather was re-tanned with titanyl sulfate. The effect of single tanning of dialdehyde starch degradation products and combined tanning with titanium oxide sulfate on the tanning effect of sheep skin was investigated. The results show that the tannability of leather can be improved by combining disaldehyde-degradation products with titanyl sulfate.The shrinkage temperature of DAS combined with titanium oxide sulfate increased by 9℃ compared with that of DAS alone. The dispersion and fixation degree of collagen fiber network of leather tanned by the combination of degraded DAS and titanium-oxysulfate were the highest, and the tanning effect was the best.

Keywords: Tapioca, Dialdehyde starch, Titanyl sulfate, Tanning

1. Introduction

Dialdehyde polysaccharides have been widely used as greencross-linking agents in various biomaterials due to their high reactivity, excellent biocompatibility, and low cytotoxicity[1-3]. Derived from natural polysaccharides, this type of crosslinkercan avoid

deleterious effects arising from some cytotoxic crosslinking agents such as glutaraldehyde[4]. As an importan tmodified polysaccharide, dialdehyde starch (DAS) prepared byperiodate oxidation has been previously exploited as a kind of green crosslinker for protein or polypeptides due to its environmental friendliness, low toxicity and feasible crosslinking reactivity[5]. Accordingly, starch is also supposed to be a green crosslinker for leather/fur (called tanning agent) because leather/fur is regarded as a collagen fiber matrix. This will be conducive to relieving the increasing environmental and social pressure caused by conventional chrome tannage in leather/fur industry[6].

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). Therefore, the development of sustainable chromefree tanning agents has become the focus of international leather researchers in academia and industry[7]. In leather industry, dialdehyde starch oxidized by sodium periodate can be used as a crosslinker for stabilizing collagen as well as leather tanning process. DAS as ligand in zirconium tanning was widely applied.

In the present work, DAS was prepared using sodium periodate as oxidant. The effects of oxidant dosage on the oxidation degree (DAS aldehyde group content) of DAS were investigated. The structure and properties of DAS was characterized by Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD) measurement and Scanning electron microscope (SEM) observations. Then the performance of DAS as ligand in titanium tanning was evaluated.

2. Material and Methods

2.1 Materials

Topioca(water content 11.08%), $NaIO_4$(99.5%), $CuSO_4 \cdot 5H_2O$, NaOH, H_2SO_4, Na_2CO_3, methylene blue, $C_4H_4O_6KNa \cdot 4H_2O$ and $TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$. The reagents used for analysis were of analytical grade, and the chemicals used for leather processing were commercial products.

2.2 Preparation of dialdehyde tapioca

64 g topioca was dispersed in sodium periodate in a mole ratio of 0.2, 0.4, 0.6, 0.8, 1.0, 1.1and 1.2 (sodium periodate/monomeric unit). Then pH adjusted to 3.5. The reaction was conducted under stirring at 40℃ for 4 h in the dark. After dialdehyde, the starch is repeatedly cleaned with distilled water and anhydrous ethanol about 7-8 times. After being dried in a blast dryer at about 40℃ for about 48 hours, dialdehyde tapioca was obtained and stored away from light[8].

2.3 Determination of dialdehyde content

Weigh 0.15-0.20g of starch product in a conical bottle and add 10ml of standard sodium hydroxide solution with a molar concentration of 0.25mol/L. After the oscillating conical bottle is fully dissolved, it is rapidly oscillated in a 70℃ water bath for 2min,

and then cooled with cold water for 1min. Add 15ml of 0.125mol/L standard sulfuric acid solution to shake the conical bottle and add black powdered activated carbon about half a teaspoon, continue to shake rapidly.Then the mixed solution was extracted and filtered to obtain clear solution. Phenolphthalein indicator was used again. Finally, with 0.25mol/LNaOH, acid-base titration operation (triple parallel titration)[9]:

$$DAS\% = \frac{C_1V_1 - 2C_2V_2}{M(1-X)/160} \times 100\%$$

where C_1 represents the usage concentration of sodium hydroxide solution; V_1 is the volume of sodium hydroxide solution to be consumed; C_2 represents the concentration of sulfuric acid solution; V_2 is volume of sulfuric acid solution to be consumed; M represents the weigh the quality of the starch product sample; X is moisture content of starch product sample; 160 represents the relative molecular weight of the basic unit of starch after dialdehyde.

2.4 Degradation of dialdehyde tapioca

A certain amount of cassava dialdehyde starch with a known aldehyde group content of about 30%, 60%, 90% was weighed respectively, and a certain amount of distilled water and sulfuric acid were added to stir evenly. The degradation reaction was carried out at 70℃, 80℃ and 90℃, respectively.The predetermined reaction time is long, the temperature is lowered to about 40℃, the pH of the degradation solution is adjusted to about 6 using saturated sodium carbonate solution, and the discharge material is stored away from light.

2.5 Determination of DE value of dialdehyde tapioca hydrolysate

The DE value of the degradation solution was measured by Lane-Eynon constant titration method. The DE value is often used to express the sugar content of starch sugars, that is, the percentage of reducing sugars in the solution expressed by the basic monosaccharides of glucose. The degradation degree of dialdehyde starch was indicated by DE value.

2.6 Fourier transform infrared (FT-IR) spectroscopy

The FT-IR spectra of native starch, DAS-30% and DAS-90% were recorded in the range from 400 to 4000 cm^{-1} using FT-IR spectrometer (Nicolet 6700, Thermo Scientific, USA) with a resolutionof 2 cm^{-1}.

2.7 X-ray diffraction (XRD) measurement

X-ray diffraction patterns of native starch, DAS-30% ,DAS-60% and DAS-90% were recorded using a Cu-Kα wide-angle X-ray diffractometer (XRD,Philips X'Pert Pro-MPD, Netherlands). The scattered radiation was detected in the angular range of 5-60° (2θ).

2.8 Tanning processes

300% of water (based on the weight of pickled sheep fur) and 60 g/L of sodium chloride (based on the volume of water, the same below) were put into the drum. After running for 5 min at room temperature, a piece of pickled sheep fur was put into the drum and then tanned by 15%DAS (based on the weight of pickled sheep fur). After running for 4 h, the pH of tanning liquor was adjusted to 7.8–8.0 with 12 g/L sodium bicarbonate in four times at an interval of 15 min. The drum kept running for 4 h at 30 °C and then stood for 12 h for the sufficient crosslinking between DAS and collagen fiber. Cut a small piece of skin to measure the shrinkage temperature The resultant tanned sheep fur was finally washed by running water at room temperature for 10 min. Adjust pH to 1.8-2.0 with 10% sulfuric acid, add 4% titanium oxysulfate and run for 4h. Cut a small piece of skin and measure the shrinkage temperature again.

2.9 Scanning electron microscope (SEM) observations

The morphologies of collagen fiber and crosslinked collagen fiber were observed using SEM (JEOL, JSM-7500F, Japan). Samples were fixed on the conductive adhesive, sputter coated with gold, and then observed with an accelerating voltage of 5 kV.

3. Results and Discussion

3.1 Aldehyde group content

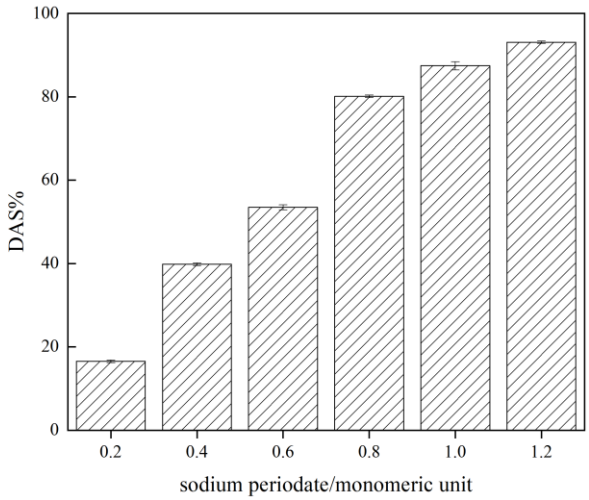

Fig. 1 Aldehyde group content of tapioca dialdehydestarch

The hydroxyl groups on C2 and C3 of the repetitive unit of polysaccharide can be oxidized to two aldehyde groups by sodium periodate[10], which provide the chemical structural basis for fur tanning. As shown in Figure 1, the dialdehyde content of tapioca increased as the molar ratio of sodium periodate to tapioca monomer increased.When the content of sodium periodate in the reaction solution increases, the probability of collision between molecules in the unit volume of solution will also increase, and the probability of hydroxyl in starch will be oxidized to aldehyde group. Therefore, the more sodium periodate is used, the higher the dialdehyde content of tapioca after oxidation, and the dialdehyde content can reach up to 93.17%.

3.2 DE value

Table 1

DE value of dialdehyde starch hydrolysate

DAS/%	Experiment condition	DEg/100g
30	60℃5h	9.87
30	70℃5h	15.12
30	80℃5h	20.56
60	60℃5h	10.23
60	70℃5h	15.47
60	80℃5h	20.14
90	60℃5h	10.14
90	70℃5h	16.12
90	80℃5h	20.34

DE value is the increase of reducing sugar in solution, the greater the degree of degradation of cassava starch, the smaller the molecular weight.The dialdehyde content of 30%, 60% and 90% respectively decreases to different molecular weights at different temperatures, and the measurement results of DE values are described in Table 1.Under the same experimental conditions, the higher the degradation temperature, the higher the DE value, and the smaller the molecular weight of the degradation products.

3.3 FT-IR spectroscopy

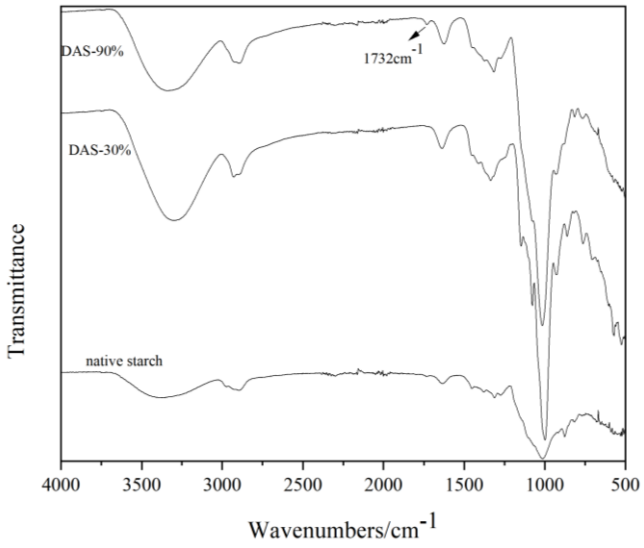

Fig. 2 FTIR Spectrum of native Starch and DAS

It is observed in Figure 2 that the vibration absorption peak of the carbonyl group is not obvious at first when the starch oxidation degree is relatively low. However, when

the dialdehyde content of cassava dialdehyde starch was increased to a certain extent, the small and weak peak and the vibration absorption peak of normal aldehyde functional group C-O bond were obviously observed at 1732cm^{-1}.

3.4 X-ray diffraction (XRD)

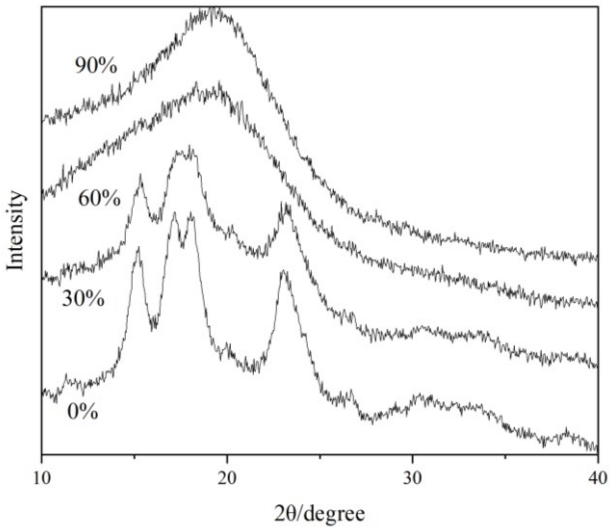

Fig. 3 XRD of tapioca starch and dialdehyde starch

As shown in Figure 3, at 2θ of 15.24°, 17.12, 18.04 and 23.04, tapioca raw starch had diffraction peaks, showing typical A-type starch crystal morphology. The intensity of various diffraction peaks decreased with the increase of tapioca starch dialdehyde content. More than 60% of the tapioca dialdehyde starch internal crystals are completely destroyed, becoming a common amorphous structure.

3.5 Tanning experiment

Shrinkage temperature (Ts) is the commonest quoted measurement of hydrothermal stability of leather/fur. As shown in Figure 4, when DAS is tanned alone, the shrinkage temperature increases with the high content of dialdehyde. This is because the aldehyde group can bind to the amino group in the collagen, and the binding ability of collagen is stronger when the content of aldehyde group is increased. The shrinkage temperature of DAS combined with titanium-oxysulfate was higher than that of DAS alone. The shrinkage temperature of DAS-30% was 72.4℃ when tanned alone, and 81.4℃ when tanned with DAS-30% and titanium oxysulfate, which was increased by 9℃. The shrinkage temperature of the degraded DAS combined with titanium oxide sulfate was slightly higher than that of the undegraded DAS and titanium oxide sulfate.This is because titanium oxide sulfate, when used as tanning agent, mainly interacts with guanidine group and amino group, and the aldehyde group in DAS promotes the binding ability of titanium tanning agent and amino group. The degraded DAS is more conducive to the combination tanning with titanium oxysulfate due to its smaller molecular weight.

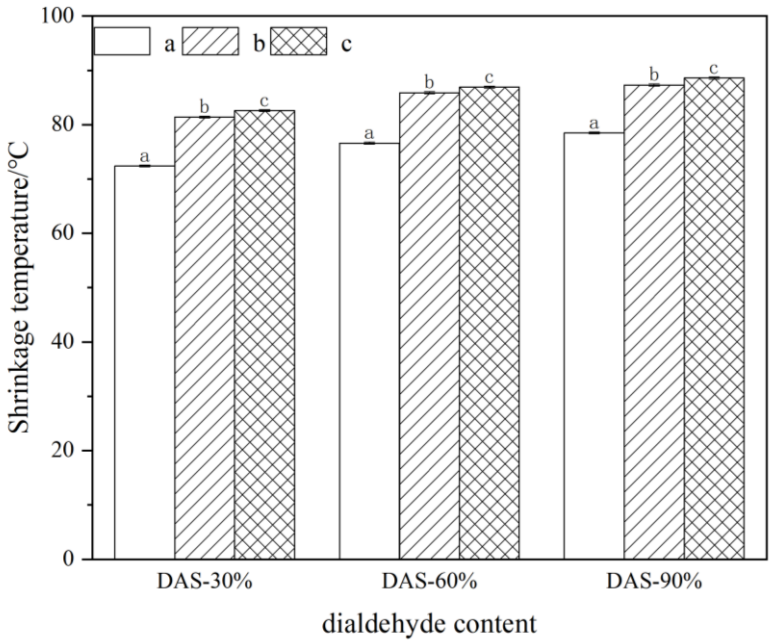

Fig. 4 Shrinkage temperature of tanned leather: (a) DAS; (b)DAS-titanyl sufate; (c) degraded DAS-titanyl sufate

3.6 SEM

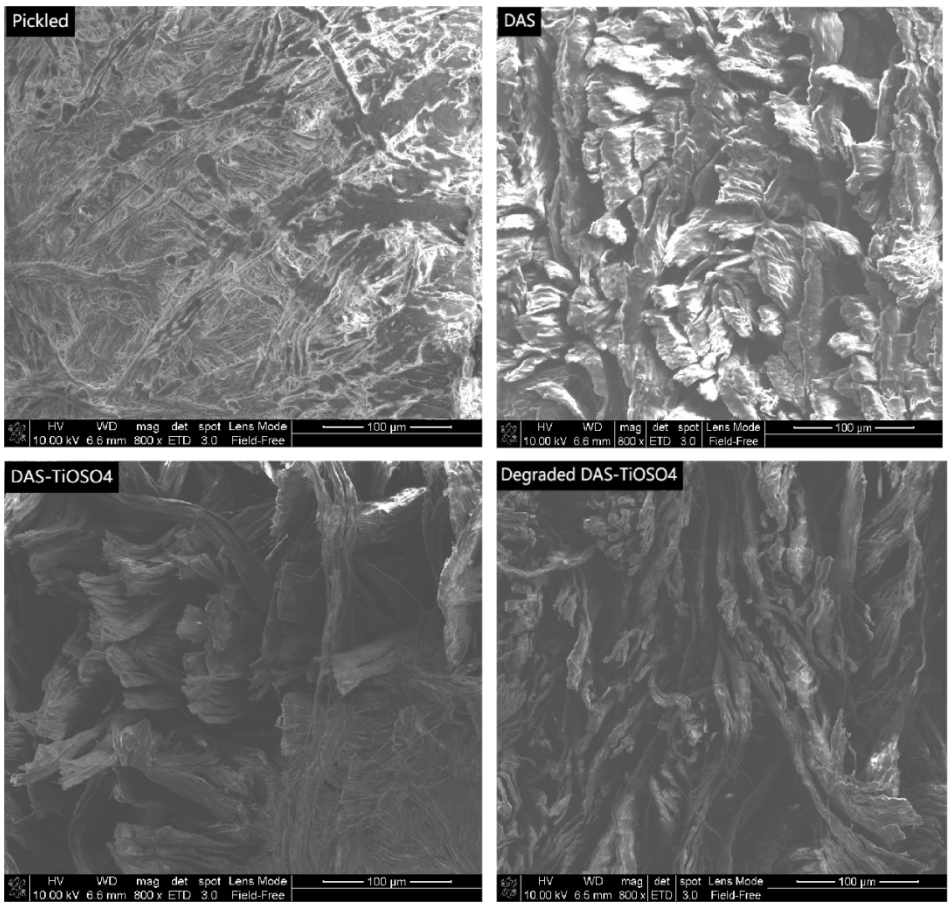

Fig. 5 SEM images of the cross section of pickled and tanned leather.

Figure 5 shows the morphologies of cross section of DAS tanned furs. Higher extent of dispersion and fixation of collagen fiber network indicates better tanning effect. Compared with the morphology of raw collagen fiber, the DAS or DAS-$TiOSO_4$ crosslinked collagen fiber appeared to be less compact and sticking. Among them, the best fiber dispersion is the leather tanned by the combination of degraded DAS and titanium oxide sulfate.Therefore, SEM further proved that the combined tanning of degraded DAS and titanium-oxysulfate showed better crosslinking properties on collagen fibers. This is consistent with the law of shrinkage temperature.

4. Conclusion

Dialdehyde tapioca starch with different contents of dialdehyde was prepared by sodium periodate oxidation and degraded by inorganic acid to obtain dialdehyde tapioca starch with different contents. The shrinkage temperature of tanned leather can be obviously increased by using dialdehyde tapioca starch and its degradation solution as ligands of titanium tanning agent. The shrinkage temperature of DAS combined with titanium oxide sulfate increased by 9℃ compared with that of DAS alone, and the shrinkage temperature of degraded DAS combined with titanium oxide sulfate increased by 10.2℃ compared with that of DAS alone. The content and degradation degree of aldehyde group play an important role in leather making performance. The higher the content of aldehyde group, the greater the degradation degree and the better the tannage effect. In general, this work allows us to understand the effect of dialdehyde starch on the properties of titanium tanning agent, which is beneficial to the application of dialdehyde starch and titanium tanning agent in chromium-free tanning technology and the sustainable development of fur industry.

5. Acknowledgements

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