Carbohydrate Polymers 201 (2018) 549–556

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Effect of structure features of polysaccharides on properties of dialdehyde polysaccharide tanning agent

Wei Ding[a,c], Ya-nan Wang[a,b,*], Jianfei Zhou[a], Bi Shi[a,b]

[a] National Engineering Laboratory for Clean Technology of Leather Manufacture, Sichuan University, Chengdu 610065, PR China
[b] Key Laboratory of Leather Chemistry and Engineering (Sichuan University), Ministry of Education, Chengdu 610065, PR China
[c] Guangdong Dymatic Fine Chemicals, Inc., Foshan 528305, PR China

ARTICLE INFO

Keywords:
Polysaccharide
Crystallinity
Dialdehyde polysaccharide
Molecular weight
Tanning

ABSTRACT

Sodium alginate (SA), tara gum (TG), starch (ST) and cyclodextrin (CD) were oxidized to dialdehyde polysaccharides (DAPs) using equivalent sodium periodate. The effects of polysaccharide structure features on aldehyde group content, molecular size and tanning performance of DAPs were investigated. Each DAP had abundant aldehyde groups (> 7 mmol/g) for fur tanning in the experimental conditions, and DAP with higher aldehyde group content was obtained when polysaccharide with lower molecular weight and linear chain was used. Lower crystallinity and β-(1→4) glycosidic linkage of polysaccharide benefited its degradation. Compared with dialdehyde ST (M_w > 150,000) and dialdehyde CD (M_w < 500), DAPs prepared from β-(1→4)-linked amorphous SA and TG had moderate molecular sizes (M_w 15,000–30,000) and exhibited satisfactory penetrability and crosslinking reactivity in collagen fiber network, and thus performed more favorable tanning properties in terms of higher shrinkage temperature and whiteness of fur. This suggests the suitability of *β*-(1→4)-linked amorphous polysaccharides for preparing dialdehyde tanning agents.

1. Introduction

As one kind of abundant and renewable biopolymers, polysaccharides have been widely used for a long time in the fields of food, clothing, and papermaking (Eliasson, 2004; Stanković, Popović, & Poparić, 2008; Ververis, Georghiou, Christodoulakis, Santas, & Santas, 2004). Apart from these traditional applications, some of the polysaccharides have extensive industrial relevance with functional materials in their chemically modified forms (García-González, Alnaief, & Smirnova, 2011; Lin, Huang, & Dufresne, 2012). As an important modified polysaccharide, dialdehyde polysaccharide (DAP) prepared by periodate 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 (Du et al., 2016; Hu et al., 2014; Leite et al., 2016; Mu, Guo, Li, Lin, & Li, 2012; Skopinska-Wisniewska, Wegrzynowska-Drzymalska, Bajek, Maj, & Sionkowska, 2016; Zhang et al., 2018).

Based on the crosslinking reaction between aldehyde groups in DAP and amino groups in collagen, we have used oxidized sodium alginate, a typical DAP, to significantly enhance the thermal stability and dispersion degree of collagen fiber (Ding, Zhou, Zeng, Wang, & Shi, 2017). Accordingly, DAP 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 (Yu, Wang, Ding, Zhou, & Shi, 2017). It is known that both the crosslinking reactivity and penetrability of a tanning agent play decisive roles in its tanning effect since the skin/hide collagen matrix has finite thickness (Covington, 2009). Therefore, the aldehyde group content, molecular weight and spatial structure of DAP will inevitably affect its tanning performance in the three-dimensional hierarchical structure of skin/hide.

Polysaccharides are a class of carbohydrates whose molecules contain various linked monosaccharide units. The differences in structure parameters of polysaccharides, such as primary structure, molecular size, spatial conformation, chain entanglement and stiffness, could profoundly influence their crystallinity, hydrophilicity, solubility and chemical stability (Yalpani, 1999), and further affect the reactions between polysaccharides and oxidants. For instance, the oxidation degree of sodium hypochlorite oxidized starch could vary greatly with the amylose/amylopectin ratio of starch (Kuakpetoon & Wang, 2006). Besides, different types of glycosidic linkages may exhibit diverse chemical stabilities and cleavage reactivities, which would endow oxidized polysaccharide with different molecular weights. Our previous work

* Corresponding author at: National Engineering Laboratory for Clean Technology of Leather Manufacture, Sichuan University, Chengdu 610065, PR China.
E-mail address: wangyanan@scu.edu.cn (Y.-n. Wang).

https://doi.org/10.1016/j.carbpol.2018.08.111
Received 24 April 2018; Received in revised form 25 August 2018; Accepted 25 August 2018
Available online 27 August 2018

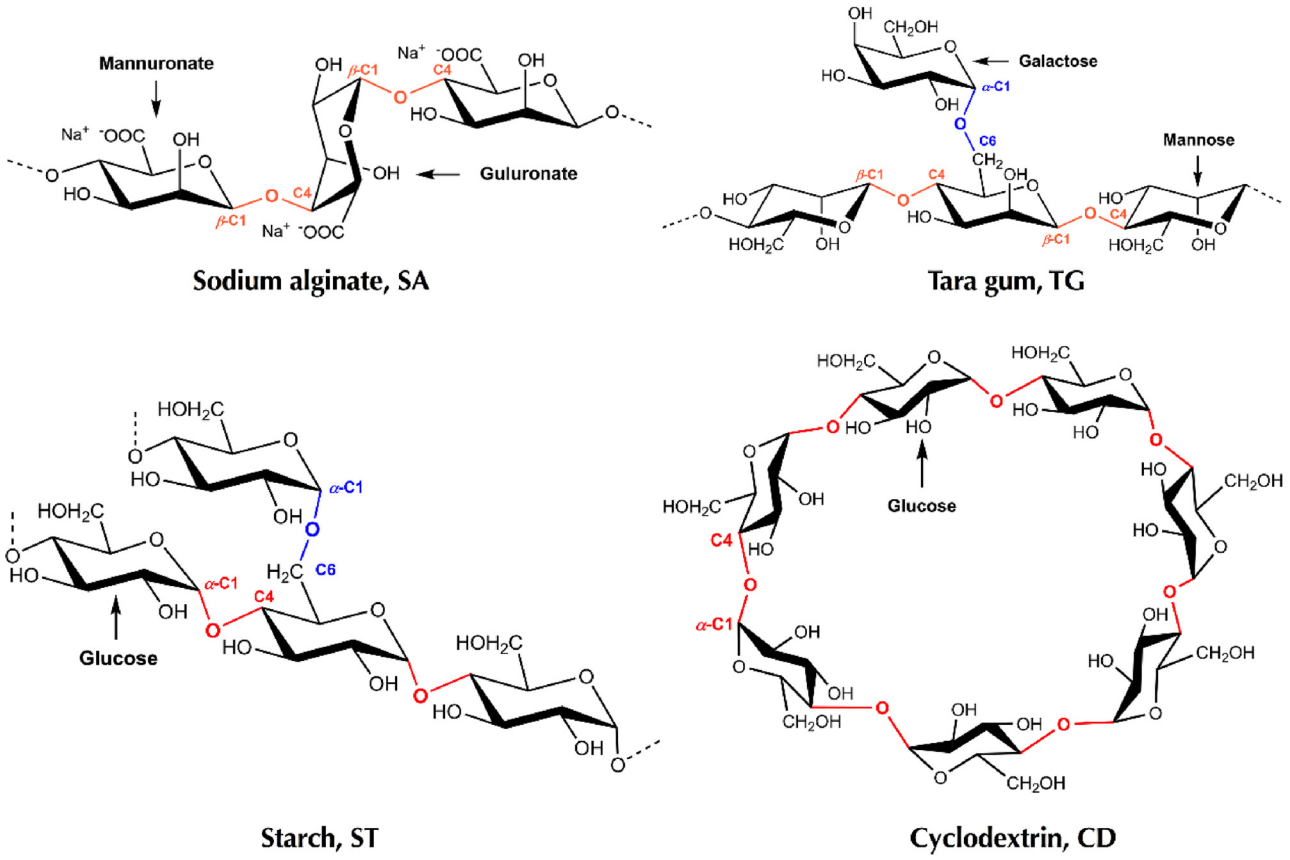

Fig. 1. The chemical structures of the selected polysaccharides.

has demonstrated that lower molecular weight of oxidized sodium alginate resulted in higher thermal stability and better dispersion degree of collagen fiber (Ding et al., 2017). Therefore, the aim of this research is to explore the effect of structure features of polysaccharide on the oxidation degree and molecular size of DAP, so that we can select desirable polysaccharide for the preparation of tanning agent with favorable tanning performance.

In the present work, four typical polysaccharides varying in structures and molecular weight (sodium alginate, tara gum, starch and cyclodextrin, shown in Fig. 1) were oxidized to DAPs with equivalent sodium periodate under the same conditions. The structural parameters of DAPs, including aldehyde group content, molecular weight, crystallinity and particle size, were determined. Then a comprehensive comparison of their tanning properties on sheep fur was conducted to clarify the relationships between the polysaccharide features and the tanning properties of DAPs.

2. Materials and methods

2.1. Materials

Sodium alginate (SA, the mannuronate/guluronate (M/G) ratio was 1.02, the viscosity of a 2% (w/v) solution at 25 °C was 419 mPa s), starch (ST, content of amylose was 28.3%), β-cyclodextrin (CD), sodium periodate and ethanediol were of analytical grade and purchased from Chengdu Kelong Chemical Co., Ltd. (Chengdu, China). Tara gum (TG) was of food grade and supplied by Datian food additive Co., Ltd. (Zhengzhou, China). The viscosity of a 2% (w/v) TG solution at 25 °C was 475 mPa s. Pickled sheep fur was supplied by Zhejiang Zhonghui Fur & Leather Co., Ltd. (Tongxiang, China). The other chemicals used in sheep fur tanning were of analytical grade.

2.2. Preparation of DAPs

10.0 g polysaccharide (SA, TG and CD) was dispersed in 500 mL distilled water and dissolved thoroughly, respectively. 10.0 g ST was added into 500 mL distilled water and gelatinized at 90 °C for 10 min, and then cooled to room temperature. Next, sodium periodate in a mole ratio of 0.8 (sodium periodate/monomeric unit) was added into the polysaccharide solution/mixture under prolonged magnetic stirring in the dark at room temperature. After oxidation for 24 h, the reaction was terminated by equimolar ethylene glycol to sodium periodate under stirring for 0.5 h. Then the solution was filtered, and the filtrate containing DAP was collected and lyophilized into powdery sample for further analysis.

2.3. Characterization of polysaccharides before/after oxidation

2.3.1. Fourier transform infrared (FT-IR) spectroscopy

The Fourier transform infrared (FT-IR) spectra of SA, TG, ST, CD and their oxidized products (DAPs) were recorded using FT-IR spectrometer (Nicolet iS10, Thermo Scientific, USA). Samples were pressed as KBr pellet and measured in the range of 400–4000 cm^{-1} at room temperature, using 32 scans and a resolution of 4 cm^{-1}.

2.3.2. Nuclear magnetic resonance (NMR) spectroscopy

The spectra of SA, TG, ST and CD were performed at a solid state on an Agilent 600 MHz DD2 spectrometer at a resonance frequency of 150.81 MHz. The ^{13}C NMR spectra of lyophilized DAPs samples were gained on a Bruker Avance III 400M NMR spectrometer using D_2O as solvent at a concentration of 42 mg/mL.

2.3.3. Analysis of aldehyde group of DAPs

Potentiometric titration by the hydroxylamine hydrochloride/