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Biomass derived oligosaccharides for potential leather tanning

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The global demand for renewable and affordable feedstocks, combined with the worldwide targets for reducing carbon emissions, is the driving force behind a breakthrough in resource revolution and GreenTech innovations [1]. Owing to the vast reserves and short growing cycle, utilizing lignocellulosic biomass as an alternative to petroleum and environmentally friendly feedstock to furnish bioenergy and biomaterials is key to building a more sustainable future. Lignocellulose mainly contains three biopolymers, i.e., cellulose, hemicellulose and lignin. Over the centuries, utilization of lignocellulose has crossed its possible molecular scale ranging from 10^{1} m, as the original matrix, to 10^{-10} m, as a monomeric molecule. Apart from directly using raw lignocellulose beyond the micron-grade scale (e.g., building and furnishing materials), depolymerization and structural modification can endow lignocellulose-derived molecules with smaller molecular dimensions and distinct functional groups, which can be further converted into a broad spectrum of chemicals with diverse industrial applications [2]. However, the selective production of a particular chemical or group of chemicals is very challenging due to the complex original structure of lignocellulosic biomass. Instead, mixed reaction products are produced, requiring complex and costly separation procedures to obtain specific fine chemicals with high purity. In comparison, detaining the biomass depolymerization/fractionation process at the early reaction stages offers new cost-effective opportunities. Notably, utilizing the mixed oligomers with widely distributed molecular sizes produced during partial biomass depolymerization eliminates the separation/purification stages and can be considered one of the most promising opportunities for lignocellulose biorefining at the industrial level. Herein, we discuss the recent applications of oligosaccharide derivatives from lignocellulosic biomass as a mixture for green leather tanning.

Leather tanning involves crosslinking between the tanning agent and the active groups (amino and carboxyl groups) in the collagen matrix, aiming to improve the dispersion and fixation of the collagen fibers. The oxygen-containing groups and the widely distributed molecular size of the oligosaccharides benefit to be adopted as tanning agent via structure modification [3]. Considering the polyhydroxy structures of oligosaccharides, aldehyde group-rich oligosaccharide derivatives can be produced through oxidization. Once these species are synthesized, a robust crosslinking network is weaved via forming multisite Schiff base structures between the aldehyde group in the oligosaccharides and the amino group in the collagen fibers [4, 5]. For example, biomass-derived aldehyde (BDA) tanning agents were prepared through periodate oxidation of sodium carboxymethyl cellulose (CMC) and sugarcane bagasse, in which the C2–C3 bond of the

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glucose unit was selectively cleaved to form 2,3-dialdehyde CMC [6, 7]. Even though the sustainable BDA exhibits acceptable tanning capabilities, BDA tanning lowers the electropositivity of the tanned leather. Therefore, the further uptake and fixation of conventional anionic post-tanning chemicals are inhibited, leading to final leather with undesirable mechanical and organoleptic properties. More recently, a terminal aluminum tanning treatment combined with a BDA tanning agent was proposed. Utilizing this strategy, a robust crosslinking network was formed via Al(III) bonding with an excess of oxygen-containing functional groups in the BDA, post-tanning materials and collagen fibers. Consequently, the as-prepared leather products showed similar properties to those produced with the conventional Cr tanning procedure [8].

In addition to as the tanning agent themselves, oligosaccharides can also be used as masking agents for chrome-free metal tanning (e.g., Al, Zr and Ti salts) due to their abundant oxygen-containing groups. Here, oligosaccharides coordinate with chrome-free metal ions in advance, promoting their penetration into the leather matrix for further crosslinking reactions. The non-coordination end with multiple oxygen-containing groups can resist the precipitation of metal ions when chrome-free metals occupy these coordination positions. Besides, modified by degradation and oxidation, the molecular weight distribution and the functional groups in oligosaccharide derivatives can be adjusted for diverse coordination with chrome-free metals to enhance their masking effects. Following this strategy, starch and its derivatives were modified by H_2O_2 oxidation to prepare oxidized oligosaccharides as masking agents [9]. Thereinto, carbonyl and carboxyl groups were formed in the oligosaccharides for the coordination with a Zr salt, remarkably improving its tanning effect, as well as the physical and mechanical properties of the crust leather. Life cycle assessment (LCA) was applied to compare the environmental impacts of a chrome tanning system (CTS) and an Al–Zr-oxidized starch tanning system (CFMTS). The much lower greenhouse gas emissions, the non-living resource consumption and the carcinogenic effect of CFMTS demonstrated it as an environmentally friendly and sustainable tanning technology [10]. Inspired by the features offered by the starch-based oligosaccharides with satisfactory masking performance, exploring stale grain or non-grain lignocellulose for green masking agents is supposed to be practically viable.

Cellulose and hemicellulose are the most abundant components within lignocellulosic biomass, accounting for more than 50 wt% of the material. Unlike starch, cellulose and hemicellulose, with more hydrogen bonds, have more compact structures. Especially for cellulose, complicated inter- and intra-molecular hydrogen networks among the glucose chains bring about crystalline structures. Therefore, hemicellulose and cellulose are hard to be degraded into oligosaccharides, and using catalysts has been widely adopted to break the hydrogen bonds and the glycosidic linkages. Recently, a 'Trojan horse strategy' for developing an Al-oligosaccharides complex tanning agent was proposed via an $AlCl_3$-catalyzed cellulose depolymerization. The dual function of $AlCl_3$ was fully utilized [11]. On the one side, $AlCl_3$ was used to efficiently catalyze cellulose depolymerization into oligosaccharides, where Cl^- was responsible for disrupting the hydrogen bonding and dissembling the glucose

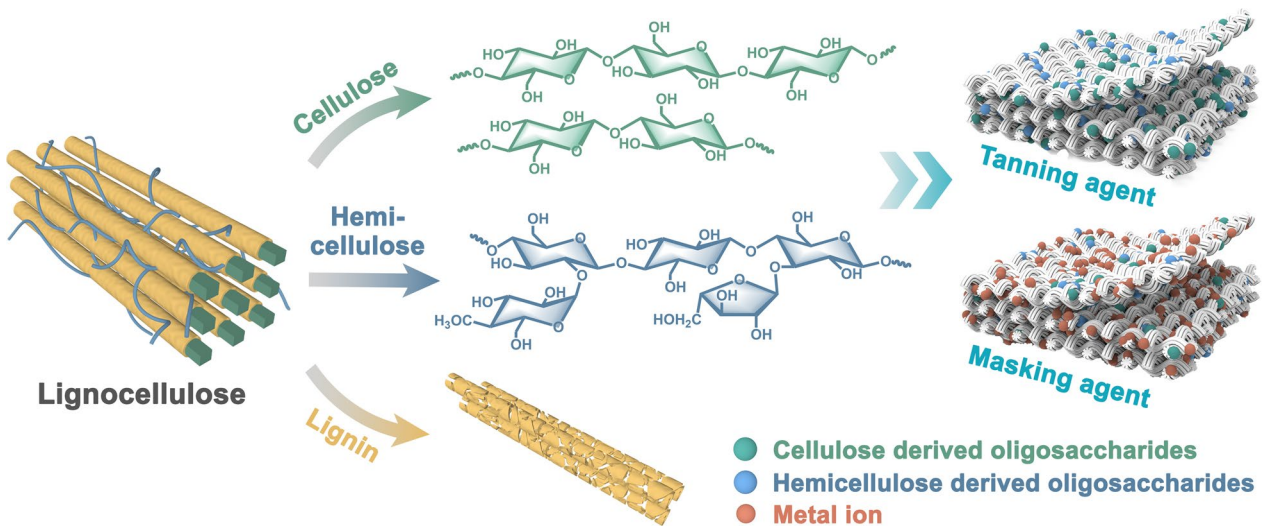

Fig. 1 Utilization of the oligosaccharides from lignocellulose for leather tanning

chains, and the acidic property of the catalysts contributed to cleaving the glycosidic bonds. On the other side, the water-soluble Al-oligosaccharides complex could be used as an environmentally friendly tanning agent without separating the catalyst or products. Combining with H_2O_2 oxidation, the distribution of the oxygen-containing groups was adjusted; assisted by extracting the non-carbohydrate products using an organic solvent, part of the undesirable and colored byproducts were removed [12]. These techniques further improved the tanning performance of the complex tanning agents. Similarly, hemicellulose in biomass (e.g., bamboo and corncob) could also be degraded by $AlCl_3$ or $ZrOCl_2$, in situ generating Al/Zr-oligosaccharides complexes that can serve as tanning agents [13].

In conclusion, based on the hierarchical structure of the collagen fibers, oligosaccharides with abundant active oxygen-containing groups and widely distributed molecular weights can be employed as tanning agents or masking agents for green leather tanning. These options entirely use the structural features of oligosaccharides and expand the application fields of biomass-derived chemicals (Fig. 1).

Author contributions

ZJ, WD, JR and BS conceived the idea. ZJ drafted the manuscript. All authors edit and approved the final manuscript. All authors read and approved the final manuscript.

Declarations

Competing interests

The authors have not disclosed any competing interests.

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