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Regioselective modification of a xyloglucan hemicellulose for high-performance biopolymer barrier films

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ABSTRACT

Biobased polymers such as starch and hemicelluloses from wood are of interest for packaging applications, but suffer from limitations in performance under moist conditions. Xyloglucan from industrial tamarind seed waste offers potential, but its Tg is too high for thermal processing applications. Regioselective modification is therefore performed using an approach involving periodate oxidation followed by reduction. The resulting polymer structures are characterized using MALDI-TOF-MS, size-exclusion chromatography, FTIR and carbohydrate analysis. Films are cast from water and characterized by thermogravimetry, dynamic mechanical thermal analysis, dynamic water vapor sorption, oxygen transmission and tensile tests. Property changes are interpreted from structural changes. These new polymers show much superior performance to current petroleum-based polymers in industrial use. Furthermore, this regioselective modification can be carefully controlled, and results in a new type of cellulose derivatives with preserved cellulose backbone without the need for harmful solvents.

1. Introduction

The packaging industry is a major consumer of the global plastic production. In food packaging, plastic films are used due to favorable cost, mechanical performance, gas barrier function toward oxygen, moisture and aroma, and compatibility with other structural components (Buchner et al., 2000; Halek, 1988). Oxygen barrier performance is sometimes the most critical parameter. Aluminum is often used as the oxygen barrier (Lange & Wyser, 2003; Leterrier, 2003). Over the past decades, synthetic polymers such as polyvinyl alcohol (PVOH), ethylene vinyl alcohol copolymer (EVOH), polyvinylidene chloride (PVDC) have successfully replaced some aluminum-based packaging solutions. In terms of cost, processability, functionality, lightweight, and transparency, these polymers are advantageous (Strupinsky & Brody, 1998). Although the packaging technology has gone through many developmental stages, virtually all oxygen barrier polymers in commercial use today have been in use since late 1970s (Lange & Wyser, 2003; Strupinsky & Brody, 1998). However due to strive toward increased use of renewable resources, the continued use of petroleum-derived plastics in packaging industry is challenged. Moreover, new legislations and increased social awareness for sustainable development gathers momentum in favor of biopolymers from renewable resources. There are strong technology developments in this area, most notably starch and polylactic acid (PLA), for packaging applications (Miller & Krochta, 1997). However, starch and PLA do not meet the critical oxygen barrier performance required in many food packaging applications. Recently, hemicelluloses have been considered as oxygen barrier materials (Edlund, Ryberg, & Albertsson, 2010; Hansen & Plackett, 2008), especially those derived from wood pulp. Their poor hygromechanical performance is a challenge. A candidate polymer, therefore, needs both mechanical and oxygen barrier performance for successful commercial applicability.

Among hemicelluloses, Kochumalayil et al. recently found xyloglucan (XG), a polysaccharide derived from tamarind (*Tamarindus Indica*) seeds to be a high performance engineering polymer due to its high molecular weight and structural features (Kochumalayil, Sehaqui, Zhou, & Berglund, 2010; Marais, Kochumalayil, Nilsson, Fogelström, & Gamstedt, 2012). Lab trials have demonstrated that XG has very low oxygen permeability of the order of 0.5–2.0 $cm^3\ \mu m\ m^{-2}\ d^{-1}\ kPa^{-1}$ at 23 °C and 50%RH. The chemical structure of XG is described by several authors (Gidley et al., 1991; Urakawa, Mimura, & Kajiwara, 2002), where XG has a cellulose backbone with β-(1→4)-linked D-glucopyranoses. Up to 75% of glucose residues are being substituted at *O*-6 with α-D-xylose and part of these xylose residues are further

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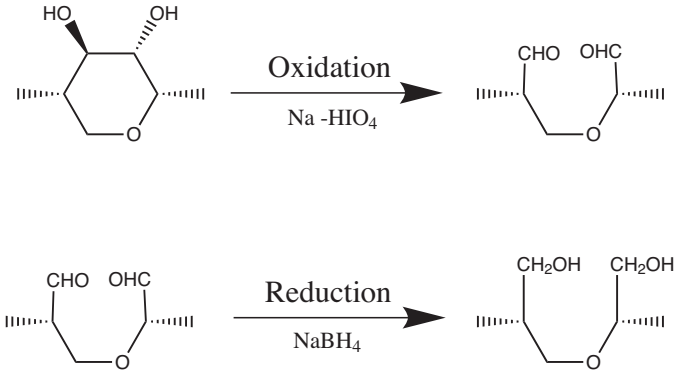

Fig. 1. Schematic representation of periodate oxidation and subsequent reduction of pyranose rings with vicinal diol groups.

substituted by β-D-galactose. The basic repeating unit of xyloglucan comprises four oligosaccharides which differ in the number and linkages of galactose residues. They are conveniently represented as XXXG, XLXG, XXLG, and XLLG in the molar ratio:1:0.42:2.08:6.20 (Urakawa et al., 2002), where X represents a Xyl*p*(α1→6)-Glc*p* unit, L represents a Gal*p*(β1→2)Xyl*p*(α1→6)Glc*p* unit, and G represents a Glc*p* residue (Fry et al., 1993; York, van Halbeek, Darvill, & Albersheim, 1990). When written sequentially, a β(1→4) linkage between the Glc*p* residues is implied, with the reducing end on the right. These oligosaccharides are represented in Fig. S1 in supporting information, SI.

The XG chains are self-aggregated in water solutions forming highly viscous solutions (Lang & Kajiwara, 1993; Picout, Ross-Murphy, Errington, & Harding, 2003). Though the polymer has shown excellent oxygen barrier performance of the order of commercial oxygen barriers, the high glass transition temperature (Tg) of around 260 °C makes thermal processing difficult. Sorbitol was reported to be a suitable plasticizer for XG with a Tg decrease of more than 100 °C with 40 wt% sorbitol addition (Bergström, Salmén, Kochumalayil, & Berglund, 2012). However, such large amount of plasticizer is undesirable in terms of material design and final properties.

In the present work xyloglucan is chemically modified in order to reduce the Tg. The chemical modification uses periodate oxidation of vicinal hydroxyl groups present on XG to form dialdehyde products with ring cleavage and subsequent reduction to dialcohols. The schematic of the oxidation and reduction reaction of a representative sugar moiety is presented in Fig. 1. The galactose and part of xylose rings have three consecutive —OH groups which upon periodate oxidation can consume two moles of periodate ions resulting in dialdehyde and a formic acid molecule (Bhagavan, 2002).

Periodate oxidation of cellulose and other polysaccharides are well known in organic chemistry and the oxidation reaction is commercially utilized to prepare dialdehyde starch (Jackson & Hudson, 1937; Kim, Kuga, Wada, Okano, & Kondo, 2000; Levine, Griffin, & Senti, 1959; Morooka, Norimoto, & Yamada, 1989). The present work is devoted to the chemical modification of XG macromolecule and investigates the structure–property relationship of these materials in the context of packaging applications.

2. Materials and methods

2.1. Preparation of modified XG (dXG)

Xyloglucan (XG) from tamarind seed kernel powder was acquired from Innovassynth technologies Ltd., India and further purified by removing the proteinous material by centrifuging a 0.5 wt% XG solution in water. The solution was then freeze dried to obtain pure XG for further experiments. 2 g of purified XG is dissolved in 100 ml water by heating at 60 °C for 1 h under continuous magnetic stirring. The oxidation and reduction steps were carried out in accordance with an earlier protocol reported for cellulose (Morooka et al., 1989). 3.6 g of sodium meta-periodate (an equimolar amount of periodate (Sigma Aldrich) for complete oxidation of carbohydrate rings present in XG) in 35 ml water was added to three different glass beakers containing the XG solution. The reaction was allowed to continue for 30 min, 1 h and 2 h for different solutions in dark conditions under magnetic stirring at room temperature. Gelation was observed even after 20 min of reaction. The excess periodate was decomposed by adding 2.5 ml of ethylene glycol. The solution is transferred to 1.2 l of methanol in a beaker to precipitate the dialdehyde XG. Methanol was decanted through a Nylon mesh by vacuum filtration. The precipitate is washed thrice with smaller amount of methanol and vacuum dried overnight. The dry precipitate was ground well and transferred to a beaker containing 80 ml of water.

4 g of sodium borobydride (Sigma Aldrich) was dissolved in 20 ml water and added dropwise to the beaker containing dialdehyde XG solution kept under magnetic stirring in an ice bath. The precipitate was completely dissolved after 1 h of stirring. The excess sodium borohydride was neutralized with 30% acetic acid. The solution was transferred to 1.4 l ice-cold methanol in a beaker and washed as described previously. The precipitate was kept under vacuum overnight. To purify further, the dried mass was dissolved in 50 ml distilled water and dialysed under running water for three days. It is again precipitated in methanol and dried under vacuum. The modified XG samples were designated dXG30, dXG60 and dXG120, the numbers denote time in minutes for periodate treatment.

2.2. Preparation of dXG films

0.5 g of modified XG samples and native XG sample were dissolved in 40 ml distilled water at 50 °C for 1 h under magnetic stirring. The resulting solutions were degassed under vacuum and the solutions were then spread over Teflon-coated Petri dishes and placed on an oven shelf at 35 °C. The dried films were peeled-off, and conditioned at 23 °C, 50%RH for two days.

2.3. Characterizations for dXG samples

2.3.1. Fourier transform infrared spectroscopy (FTIR)

FTIR was performed on a Perkin-Elmer Spectrum 2000 FTIR equipped with a MKII Golden Gate, Single Reflection ATR system from Specac Ltd., London, UK. The spectral range was 600–4000 cm^{-1}. The spectra were normalized, allowing a comparison between the spectra.

2.3.2. Size exclusion chromatography (SEC)

SEC measurements were made on a Waters 616 HPLC system equipped with a set of two PL aquagel-OH mixed 8 μm (300 mm × 7.5 mm) columns at 22 °C. The buffer (0.1 M $NaNO_3$ + 0.05 M NH_4OAc) at pH 4.5 was used as the eluent at a flow rate of 1 ml/min. Analyte detection and quantification were performed by a 410 differential refractometer (Waters Corp.). Pullulan polysaccharide standards (Polymer Laboratories) were used to calibrate the system over the Mw range 180–1,660,000.

2.3.3. Carbohydrate analysis

After acid hydrolysis to individual sugar molecules using 70% sulfuric acid (ASTM, 2003), the hydrolyzate were analyzed using high performance anion exchange chromatography equipped with Pulsed Amperometric Detector (HPAEC-PAD, Dionex ICS-3000).