Carbohydrate Polymers 93 (2013) 466–472

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

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

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

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ARTICLE INFO

Article history:
Received 8 October 2012
Received in revised form 8 November 2012
Accepted 5 December 2012
Available online 26 December 2012

Keywords:
Xyloglucan
Oxygen barrier
Packaging
Periodate oxidation
Cellulose derivatives

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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http://dx.doi.org/10.1016/j.carbpol.2012.12.041

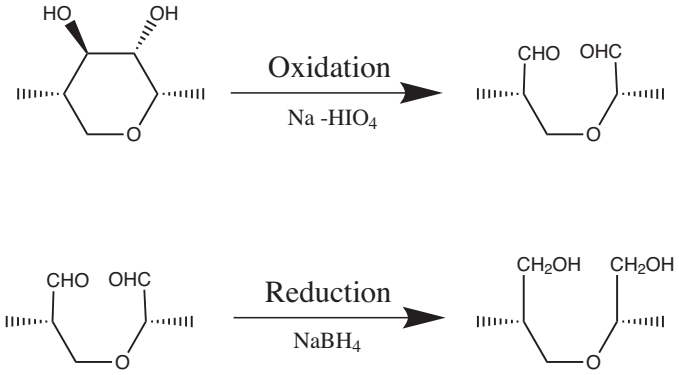

Fig. 1. Schematic representation of periodate oxidation and subsequent reduction of pyranose rings with vicinal diol groups.

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).

Standard solutions of glucose, xylose and galactose were used for calibration.

2.3.4. Enzymatic hydrolysis

Enzymatic hydrolysis of XG and modified XG samples to resolve into component oligosaccharides were performed using cellulase from *Trichoderma reesei* (EC 3.2.1.4) (Sigma Aldrich). About 80 mg of XG and modified XG samples were dissolved in 8 ml of 50 mM sodium acetate buffer (pH = 5.0) in glass vials. 8 mg of enzyme was added to different solutions and stirred for 24 hr at 37 °C. The enzyme reaction was terminated by increasing the temperature to 90 °C and kept stirring for half an hour. The resulting solutions were filtered through glass fiber filter paper (Whatman GF/A) and passed the filtrate through 0.45 μ PTFE syringe filters. The final filtrate was freeze dried.

MALDI-TOF-MS: matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was performed on Ultraflex MALDI-TOF workstation (Bruker Daltonics, Bremen, Germany) equipped with a nitrogen laser (337 nm) and operated in positive reflector mode. About 2 mg of enzyme hydrolyzed samples were dissolved in 1 ml of MilliQ water and 3 μL of sample solution was mixed with 6 μL of matrix (5 mg of 2,5-dihydroxy benzoic acid in 0.5 ml acetone) and spread over a MALDI-TOF plate (Bruker Daltonics) and air-dried. The ions were accelerated with a laser power of 21 kV.

2.4. Characterizations for dXG films

2.4.1. Tensile properties

The mechanical properties of conditioned films were measured using an Instron 5944 tensile testing machine in tensile mode with a 50 N load cell. The specimens were thin rectangular strips (30 μm × 5 mm) and the gauge length was 40 mm. The stress–strain curves of specimen samples were recorded at room temperature and 50% RH at a strain rate of 10% min^{-1}. Young's modulus (E) was determined from the slope of the low strain region in the vicinity of 0.05% strain. Yield stress was calculated as the intersection of the tangent of the initial elastic region and the following plastic region.

2.4.2. Water sorption

A dynamic vapor sorption (DVS) instrument from Surface Measurement Systems was used to determine the water sorption isotherm under different humidity atmospheres. XG and modified XG samples were first dried in the DVS cell, and then the relative humidity (RH) in the DVS cell was increased in steps from dry state up to 95%. The samples were weighed in different humidity atmospheres when the steady state point was reached.

The moisture content (M) at a particular RH level was calculated on a dry (or total weight) basis, as indicated by the formula below:

$$M = \frac{W_w - W_d}{W_d} 100\% \quad (1)$$

where M is the moisture content (%) of material, W_w is the weight of the sample in the DVS cell when the water content has reached steady state condition, and W_d is the weight of the dried sample.

2.4.3. Dynamic mechanical thermal analysis (DMTA)

DMTA measurements were performed on a dynamic mechanical analyzer (TA Instruments Q800) operating in tensile mode. Typical sample dimensions were 20 mm × 5 mm × 0.03 mm. The measurement frequency and amplitude were kept at 1 Hz and 15 mm, respectively. A temperature scan was made in the range 25–300 °C at a heating rate of 3 °C min^{-1} under ambient atmosphere.

Table 1
Carbohydrate composition of XG and modified XG samples. Data are reported as mmols of carbohydrates/100 mg of sample. Designations dXG30, dXG60 and dXG120, refer to time in minutes for periodate treatment.

Samples	Glucose	Galactose	Xylose
XG	0.269	0.088	0.203
dXG30	0.271	Nil	0.023
dXG60	0.263	Nil	0.004
dXG120	0.231	Nil	0.005

2.4.4. Thermo gravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was conducted on a Mettler Toledo TGA/SDTA851 instrument. The samples were heated from 25 °C to 500 °C, using a heating rate of 5 °C min^{-1}, in a N_2 flow of 50 ml/min.

2.4.5. Oxygen permeability

The oxygen transmission rate (OTR) measurements were performed with Oxygen Permeation Analyser (Systech 8001, Systech Instruments Ltd., UK) at 23 °C using 100% oxygen as test gas. Tests were done in dry condition and at 50%RH. The active area of measurement was 5 cm^2 by using a steel mask.

3. Results and discussion

3.1. Periodate oxidation and subsequent reduction

XG was rapidly oxidized at room temperature to form dialdehyde XG, which was evidenced by a strong aldehyde absorption peak at 1720 cm^{-1} in FTIR spectra (see Fig. S2 in SI). The viscosity of the solution increased significantly during the course of the reaction and stirring was hindered by the gelatinous nature of the solution after 30 min. of reaction. The resulting aldehyde groups were reduced to alcohols by the use of $NaBH_4$. The reduction of the aldehyde groups was complete with no characteristic carbonyl absorption peak at 1720 cm^{-1} in the modified XG samples.

The effect of oxidation on carbohydrate composition of XG and modified XG samples is presented in the carbohydrate analysis, see Table 1. The amount of glucose in dXG30 sample remained almost constant whereas a 2% decrease for dXG60 and a 14% decrease for dXG120 samples were observed. The reduction in glucose content of dXG120 samples could be the result of the cleavage of a few glucopyranose rings during oxidation. Meanwhile the oxidation of the galactose and xylose residues on the side chains wascompleted after only 30 min of reaction. The galactose and xylose residues on the side chains are thus favored for oxidation compared to the glucose residues on the main chain. The mechanism of regioselectivity is not completely understood. One reason for the preferential oxidation is the availability of the pendant side sugar residues compared to the glucose on the main chain. Moreover, the vicinal —OH groups of the β-(1→4)-linked D-glucopyranoses main chain is in *trans* state, which is kinetically less favorable for periodate oxidation than the predominant *cis* conformations observed in side galactose and xylose residues.

The effect of oxidation on the structure of xyloglucan was monitored with MALDI-TOF-MS analysis. The mass spectrum of xyloglucan oligosaccharides (XGOs) obtained by enzymatic hydrolysis of XG and modified XG samples are presented in Fig. 2. The mass peaks at m/z values of 1409.2, 1247.2 and 1085.2 corresponds to the XGO structures of XLLG, XXLG or XLXG and XXXG, which have molecular mass of 1386.5, 1224.4 and 1062.4 Da, respectively (see Fig. S1 in SI). All XGOs were oxidized during periodate treatment with none of the original XGOs present in the final product in all oxidation conditions. Carbohydrate analysis revealed that 10% of original xylose residues were preserved in dXG30 sample. However the intensity of these XGOs with xylose was too low to record

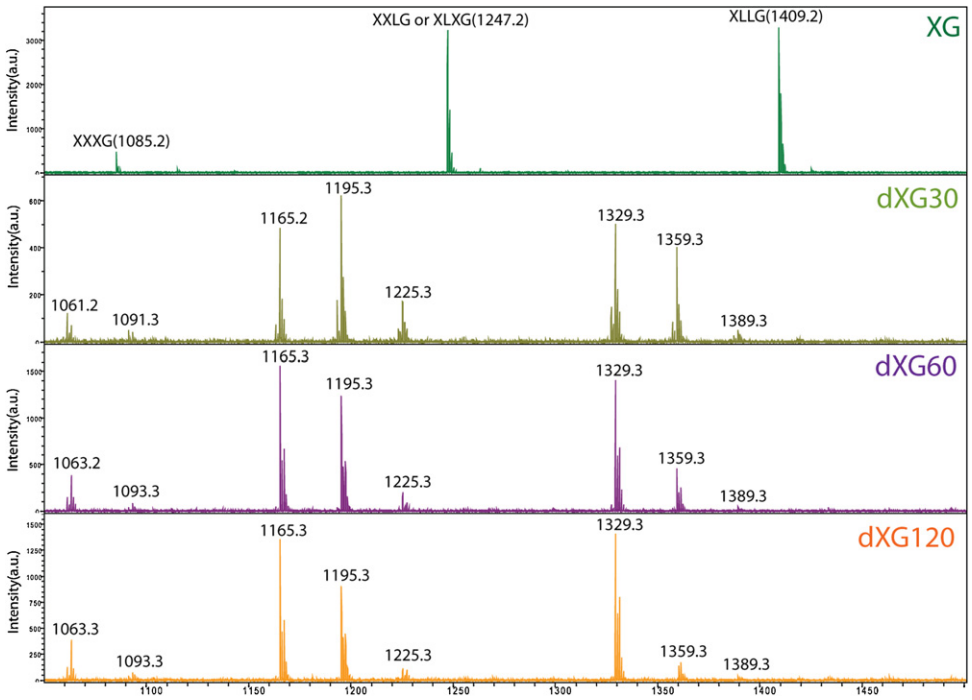

Fig. 2. MALDI-TOF-MS of xyloglucan oligosaccharides obtained by enzyme digestion of native XG and modified XG (m/z values include atomic weight of Na^+ counter ion). Designations dXG30, dXG60 and dXG120, refer to time in minutes for periodate treatment.

in MALDI spectrum. The constituent oligosaccharides on the side chains of XG were opened with different degree of oxidation. The modified products were identical in all samples except for the products obtained for dXG30 sample where m/z value of modified XXXG oligosaccharides are different from the corresponding values for dXG60 and dXG120 samples. The anticipated chemical structures of modified XGOs as conceived from MALDI-TOF-MS spectra are presented in SI Table S1. The m/z value of 1063.3 and 1093.3 for XXXG of dXG60 and dXG120 samples points to the fact that oxidation also occurred at one of the four glucose residues, which resulted in an increase of the m/z value by 2 units. On the other hand, no oxidation at glucose groups was detected for the dXG30 sample and the resulting m/z value was recorded at 1061.2 and 1091.3. This verifies the carbohydrate analysis discussed earlier, where the amount of glucose remained constant for dXG30 sample, and a slight decrease in glucose content was observed for dXG60 and dXG120 samples (Table 1).

Thus it is concluded from the structural characterization of modified XG using MALDI-TOF that homogeneous and selective oxidation occurred on side carbohydrate chains during periodate oxidation. The cellulose backbone of XG was well preserved for oxidation time up to 30 min. of reaction, whereas a few glucose residues on cellulose backbone were oxidized for dXG60 and dXG120 samples. A representative schematic sketch of these structures is presented in Fig. 3.

3.2. Properties of dXG films

3.2.1. Mechanical properties

The typical stress-strain curves in tension for modified XG samples at 50%RH and 23 °C are depicted in Fig. 4(A) and property data are presented in Table 2. The dXG30 sample shows very high toughness (work to fracture, area under stress–strain curve). The modulus and yield strength decrease with increased oxidation time. This correlates strongly with, first, complete disappearance of galactose and significant reduction of xylose content (XG compared with dXG30, see Table 1). As the xylose content is then reduced (dXG30, compared with dXG60 and dXG120, see Table 1), yield strength and modulus drops even further. The oxidation opens the side groups and this results in a different spatial packing of chains compared with native XG. Also, the intermolecular interactions are influenced as well as molecular mobility. The trend in decreased yield strength with increased oxidation time is strong. Yielding in ductile amorphous polymers tend to be by shear yielding (Kinloch & Young, 1983). Removal of the pendant sugar rings appears to greatly facilitate this process. The native XG has a high molecular weight of the order of M_w = 1.2 MDa (PDI = 1.62), whereas for modified XGs: dXG30 = 0.77 MDa (PDI = 2.61), dXG60 = 0.31 MDa (PDI = 2.11) and dXG120 = 0.57 MDa (PDI = 2.09). The molecular weights of all modified XG substrates were fairly high due to the short oxidation time used. In contrast, periodate oxidation of cellulose requires longer time in ambient conditions and is always accompanied by severe depolymerization so that the final product has inferior properties compared to commercial polymers (Painter, 1988).

Water was reported to act as a plasticizer in native XG films (Kochumalayil et al., 2010). The moisture sorption isotherms (Fig. 4(B)) reveals that modified XGs are less hygroscopic than XG. The moisture uptake at 50%RH is up to 60% lower than native XG. Side sugar oxidation reduces moisture adsorption at the molecular level although the precise mechanism is unclear. Increased strain to failure for modified XGs can then best explained by the internal plasticization effects from the opened side groups rather than moisture plasticization. Continued oxidation opens some glucose rings

Table 2
Mechanical properties of modified XG using data obtained from tensile tests at 23 °C and 50%RH (values in parentheses are standard errors). Designations dXG30, dXG60 and dXG120, refer to time in minutes for periodate treatment.

Sample	Tensile strength (MPa)	Strain to failure	Elastic modulus (MPa)	Yield stress (MPa)
XG	78 (8.6)	5.7 (3.6)	4597 (164)	72 (5.4)
dXG30	37 (3.9)	33 (11.2)	1084 (141)	28 (0.8)
dXG60	17 (1.7)	50 (4.2)	333 (24.9)	7.6 (0.3)
dXG120	20 (2.2)	46 (14)	291 (68.3)	6.9 (2.5)

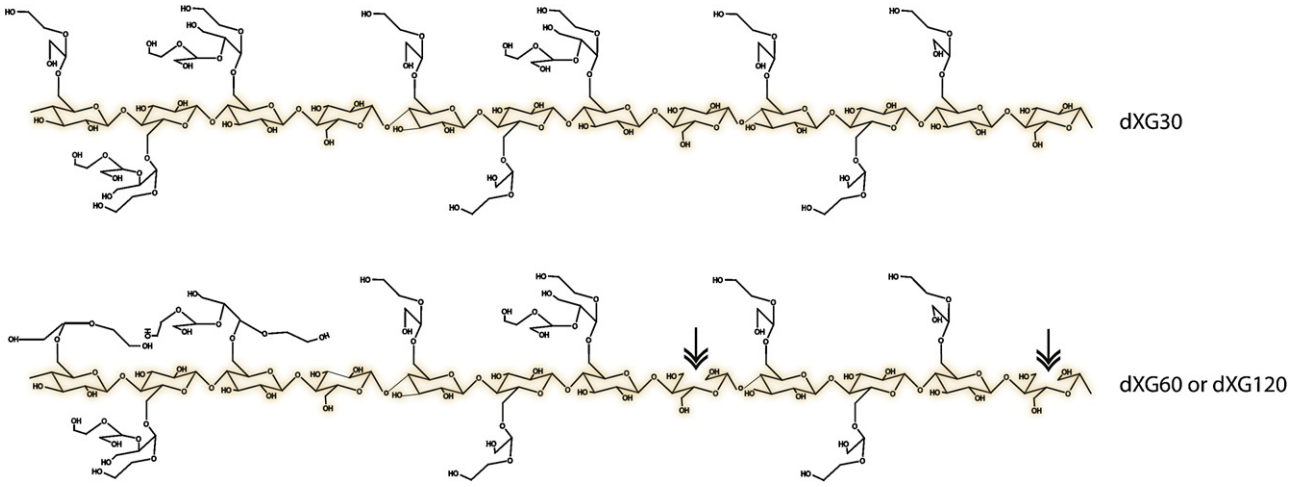

Fig. 3. Schematic of modified XG structures, as deduced from MALDI-TOF-MS and carbohydrate analysis. Designations dXG30, dXG60 and dXG120, refer to time in minutes for periodate treatment.

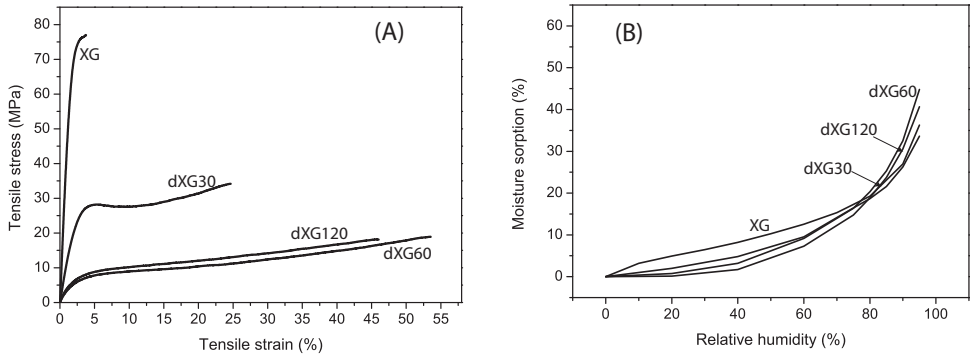

Fig. 4. (A) Typical tensile stress–strain curves for xyloglucan films conditioned at room temperature and 50%RH (B) Moisture sorption isotherms for native XG and modified XGs. Designations dXG30, dXG60 and dXG120, refer to time in minutes for periodate treatment.

in the main cellulose backbone, resulting in decreased strength and modulus for dXG60 and dXG120 samples, whereas the tensile strain to failure is increased. The structural characterization with MALDI-TOF-MS and carbohydrate analysis discussed in preceding sections support the observations.

3.2.2. Thermal properties

The dynamic mechanical properties of XG and modified XGs as a function of temperature are presented in Fig. 5.

The native XG has a Tg of the order of 275 °C. The modification reduces the glass transition temperature of native XG to 167 °C for dXG30, where all galactose and a significant part of the xylose have disappeared in the carbohydrate analysis (Table 1). The Tg is reduced to around 145 °C for dXG60 and dXG120 samples (Fig. 5), where all xylose has disappeared in carbohydrate analysis (Table 1). These reductions in Tg are very significant from a thermal processing point of view. The decrease in Tg is a consequence of the opening of pendant sugar rings. It results in perturbations in the spatial packing of modified XG chains, changes in intermolecular interactions and increased molecular mobility.

The native XG has very high thermal stability compared to other hemicelluloses (Bergström et al., 2012; Yang, Yan, Chen, Lee, & Zheng, 2007), whereas the modified XG samples have even higher thermal stability than XG (see the TGA results in SI Fig. S3). In inert N_2 atmosphere, XG shows maximum degradation at around 300 °C, whereas modified XGs degrade with a maximum at around 320 °C. In fact, modified XGs were showing thermal stability similar to cellulosic materials where the pyrolysis occurs in 315–400 °C with maximum weight loss at about 350 °C (Alen, Kuoppala, & Oesch, 1996; Yang et al., 2007). This can be considered as an indirect confirmation of the largely preserved cellulose backbone in modified XG samples.

3.2.3. Oxygen barrier properties

This is a very significant property for packaging applications. The permeabilities of modified XGs in comparison with XG are given in Table 3.

Oxygen permeability of modified XG is somewhat higher than for native XG in the dry state, whereas it is significantly lower than for commercial barriers in use today, such as PVOH. The oxygen permeability of a material depends on solubility of oxygen in the material and diffusion of the oxygen molecules in the material. This in turn depends on the polarity and free volume of the material (Comyn, 1985; Miller & Krochta, 1997). The chain packing in XG

Table 3
Oxygen permeability ($cm^3\ \mu m/[m^2\ day]\ kPa^{-1}$) of XG and modified XG films. Designations dXG30, dXG60 and dXG120, refer to time in minutes for periodate treatment.

Sample	Oxygen permeability $cm^3\ \mu m/[m^2\ day]\ kPa$ (dry, 23 °C)	Oxygen permeability $cm^3\ \mu m/[m^2\ day]\ kPa$ (50%RH, 23 °C)
XG	0.081	2.16
dXG30	0.152	1.96
dXG60	0.126	0.60
dXG120	0.129	0.52
PVOH	0.384	–

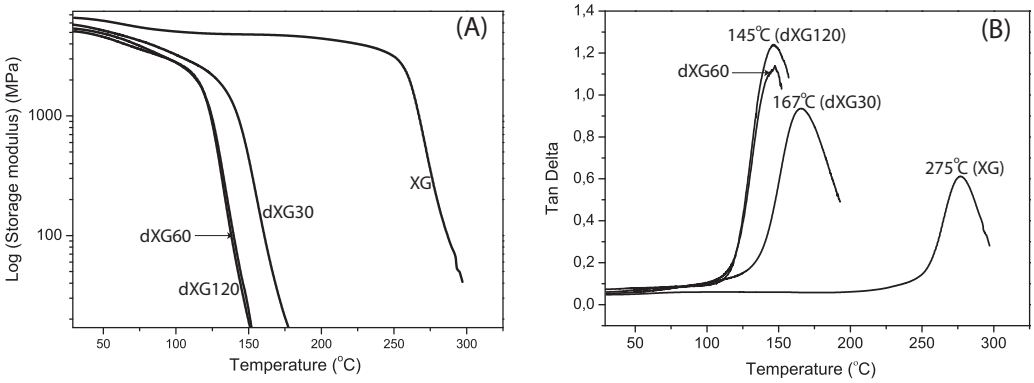

Fig. 5. Storage modulus (E') and tan δ at 1 Hz as a function of temperature for XG and modified XG with different oxidation times. Designations dXG30, dXG60 and dXG120, refer to time in minutes for periodate treatment.

was significantly altered as a result of the opening of side groups. This is reflected in increased oxygen permeability of modified XGs compared to XG. On the other hand, the oxygen barrier property of modified XGs was markedly improved at 50%RH. The main reason is that modified XGs have reduced moisture uptake compared with XG. Moisture adsorption is detrimental to the oxygen barrier performance of many hydrophilic polymers at high RH since intermolecular interactions between polymer chains are reduced due to the presence of moisture. In summary, the highly advantageous oxygen permeability of XG is improved at 50%RH for modified XG samples making this novel biopolymer an interesting candidate for packaging applications. The largely preserved cellulose backbone is important as is the reduced moisture adsorption compared with XG.

4. Conclusions

Xyloglucan is an interesting polysaccharide biopolymer of high molar mass from tamarind seed waste, with excellent mechanical and gas barrier performance. The high Tg of around 275 °C limits the potential for thermal processing. In the present study, the side sugars of XG were regioselectively opened using a simple chemical route to form modified XG with the cellulose backbone largely preserved. Almost all side carbohydrate residues were completely oxidized within 30 min of reaction by an equimolar amount of periodate added. The Tg of the resulting material was reduced by more than 100 °C as the pendant sugar rings on the side chains were transformed. More importantly, the oxygen permeability was improved at 50%RH, primarily due to reduced moisture adsorption compared with native XG. Moreover, at 30 min oxidation time the resulting material showed a superior combination of mechanical properties and oxygen barrier performance compared with petroleum-based polymers used in current industrial applications.

The present study provides detailed data on the changes in chemical structure of XG due to the modification scheme, and shows correlations between these structural changes and reductions in Tg, modulus and yield strength. The achievement of regioselective modification with largely preserved cellulose backbone is highly significant, since this leads to favorable physical properties. The present polymers are a new form of cellulose derivative where the XG origin means that the use of strong solvents can be avoided.

Acknowledgements

We gratefully acknowledge the funding for J. Kochumalayil by Biofiber Materials Centre (BiMac Innovation, http://www.bimacinnovation.kth.se), and Q. Zhou and L.A. Berglund by Wallenberg Wood Science Center (WWSC, http://wwsc.se/). The authors thank Prof. T. Morooka from Kyoto University, Japan for fruitful discussions.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2012.12.041.

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