Carbohydrate Polymers 117 (2015) 346–354

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Enhanced formability and mechanical performance of wood hydrolysate films through reductive amination chain extension

Anas Ibn Yaich, Ulrica Edlund, Ann-Christine Albertsson*

Fiber and Polymer Technology, Royal Institute of Technology (KTH), Teknikringen 56, SE-100 44 Stockholm, Sweden

ARTICLE INFO

Article history:
Received 23 June 2014
Received in revised form
16 September 2014
Accepted 18 September 2014
Available online 5 October 2014

Keywords:
Wood hydrolysate
Xylan
Reductive amination
Oxygen barrier
Packaging
Film

ABSTRACT

An *O*-acetyl-4-*O*-methylglucuronoxylan-rich wood hydrolysate (WH), generated by the hydrothermal treatment of hardwood, was chain extended using di- and tri-functionalized amino chain extenders through reductive amination. Chain extension was achieved via facile one- or two-step syntheses. The carbohydrate chain extension efficiency, molecular weights, and branching patterns were determined through a combination of SEC, 1HNMR, FTIR and elemental analysis. The mild reaction conditions enabled an increase in the molecular weight while preserving the initial structures of the hemicelluloses. The chain extension strategy developed in this study was demonstrated to significantly improve the formability and mechanical performance of WH films, allowing for the water-casting production of coherent films with higher ratios of WH – 70–85% (w/w) – and reducing the need for co-components. Chain-extended WHs produced stronger and more ductile films than corresponding formulations prepared from unmodified WH. Films made from ethylenediamine chain-extended WH mixed with 30% (w/w) carboxymethyl cellulose showed a tensile strength of 62 MPa and a strain-to-failure of 3.3%. Additionally, chain-extended WHs produced films with an oxygen permeability as low as 0.2 cm^3 μm m^{-2} day^{-1} kPa^{-1} at 50% RH.

1. Introduction

Wood-derived hemicelluloses have attracted increasing interest as renewable and non-edible raw materials for the production of sustainable food-packaging barriers due to their desirable properties, such as very low gas permeability, water solubility, biodegradability, non-toxicity and abundance(Hansen & Plackett, 2008; Hartman, Albertsson, & Sjöberg, 2006; Hartman, Albertsson, Söderqvist-Lindblad, & Sjöberg, 2006). Furthermore, wood-derived hemicelluloses can potentially be recovered in large quantities as by-products from many forestry industrial processes (Albertsson, Voepel, Edlund, Dahlman, & Söderqvist-Lindblad, 2010; Li, Saeed, Jahan, Ni, & van Heiningen, 2010; Thornton, Ekman, Holmbom, & Örså, 1994). To implement materials derived from hemicellulose-rich biomass in the food-packaging sector, several challenges need to be overcome, not the least of which the high production cost associated with obtaining highly purified hemicelluloses. Other challenges are inherent hydrophilicity and brittleness, the latter typically rendering hemicelluloses unable to alone form coherent free-standing films with satisfactory mechanical properties.

Hemicelluloses are generally extracted from wood or holocellulose by alkali treatments (i.e., kraft pulping or hot or cold alkali extractions), resulting in the cleavage of *O*-acetyl and other side groups; rigorous or prolonged alkali treatment will lead to further degradation of the main chain by peeling reactions (Timell, 1967). The resulting unbranched hemicelluloses – regardless of type or source – are characterized by poor water solubility and high tendencies to form aggregates and irreversibly readsorb onto cellulose fiber surfaces due to their increased capability of intermolecular hydrogen bonding (Danielsson, Kisara, & Lindström, 2006; Dervilly-Pinel, 2004; Simkovic et al., 2014). On the other hand, hemicelluloses with partially preserved acetylated and branched native structures can be found in aqueous process liquors – wood hydrolysates (WHs) – generated by hydrothermal treatment or other neutral-acidic extraction processes (e.g., thermomechanical pulping, steam explosion, pre-hydrolysis, microwave treatments) (Palm & Zacchi, 2003). These hemicelluloses show good solubility in certain polar solvents such as water, which is considered to be of utmost importance in view of sustainable industrial applications. Many green production technologies in use today, or in the development pipeline, including water-based coating and casting as well as various green chemical modifications, rely on the aqueous solubility of the base material.

It is also becoming apparent that large-scale isolation of highly purified hemicelluloses from these forestry process liquors

* Corresponding author.
E-mail address: aila@kth.se (A.-C. Albertsson).

http://dx.doi.org/10.1016/j.carbpol.2014.09.067
0144-8617/

is neither an economical nor environmentally viable approach. The laborious sequential purification, involving solvent-extraction, delignification, enzymatic steps and/or chromatographic techniques, necessary to completely separate the dissolved or dispersed, and strongly interacting, wood components make the production of highly purified hemicelluloses a low-yield and costly process that demands large amounts of solvents and energy and may also generate considerable amounts of waste (Albertsson et al., 2010; Persson, Nordin, Zacchi, & Jönsson, 2007; Willför, Sundberg, Tenkanen, & Holmbom, 2008). Conversely, the utilization of crude or less purified hemicelluloses or a hemicellulose-rich WH, whereby a reasonable amount of lignin and other water-soluble wood components are purposely preserved, provides a technically more viable and economically feasible strategy (Albertsson et al., 2010; Dahlman et al., 2009; Edlund, Zhu Ryberg, & Albertsson, 2010).

Recently, we demonstrated that free-standing films can be produced by solvent casting of aqueous formulations made from mixtures of WHs and a high-molecular-weight co-components such as carboxymethylcellulose (CMC) (Edlund et al., 2010; Ibn Yaich, Edlund, & Albertsson, 2012), microfibrillated cellulose (MFC) (Saadatmand, Edlund, Albertsson, Danielsson, & Dahlman, 2012), or chitosan (Edlund et al., 2010). The presence of a fair amount of lignin in the WH does not necessarily pose a problem, in fact it has been shown that lignin have strong interaction with hemicelluloses, which results in good compatibility between the different constituents within WH as well as within film formulations (Zhu Ryberg, Edlund, & Albertsson, 2012). WH-based films performed as well or even superior to analogous films based on highly purified hemicelluloses. The formulations contained no low-molecular-weight plasticizers but were favored by a co-component content on the order of 40% (w/w) or above during the formation of continuous and coherent free-standing films with good mechanical properties. This behavior is explained by the relatively short and stiff nature of the hemicellulose chains, being the principal component of the WH, which does not favor the formation of a sufficient number of chain entanglements that will ensure the transmission of the covalent bond strength and the formation of continuous films. Means for overcoming this difficulty can be categorized into three distinctive yet complementary approaches: (i) limiting hemicellulose degradation by controlling the extraction conditions (pH, temperature, time) (Saadatmand et al., 2013; Song, Pranovich, & Holmbom, 2011); (ii) fractionation through different industrially viable routes (ultrafiltration, diafiltration, ethanol precipitation) to accumulate the higher-molecular-weight fraction (Ibn Yaich et al., 2012); or (iii) increasing the hemicellulose molar mass and/or the molecular mobility via chemical or enzymatic post-treatments (Hartman, Albertsson, & Sjöberg, 2006; Hartman, Albertsson, Söderqvist-Lindblad, et al., 2006; Kochumalayil & Berglund, 2014; Kochumalayil, Zhou, Kasai, & Berglund, 2013; Laine et al., 2013; Mikkonen, Schmidt, Vesterinen, & Tenkanen, 2013; Oinonen, Areskogh, & Henriksson, 2013; Persson, Dahlman, Albertsson, & Edlund, 2012; Zhu Ryberg, Edlund, & Albertsson, 2013).

Many hemicellulose chemical modification methods have been reported in the literature, most of which rely predominantly on the large amount of synthetically available hydroxyl groups present in hemicellulose structures when seeking to introduce thermoplastic, gel, hydrophobic, or film-formability characteristics and/or new functionalities (Edlund & Albertsson, 2012; Hansen & Plackett, 2008; Maleki, Edlund, & Albertsson, 2014; Simkovic et al., 2014). However, many inherent properties of hemicelluloses, including gas permeability, swelling, solubility, and biodegradability, are dependent on a subtle balance between hydroxyl, acetyl and other natural pendant groups (Fonseca Silva, Habibi, Colodette, & Lucia, 2011; Heikkinen et al., 2013; Ibn Yaich et al., 2012). It has, for example, been shown that the high oxygen barrier performance of hemicelluloses, similarly to that of other polar polymers, arises from dense chain packing, low free volume and high cohesive energy density, all of which are largely due to the strong inter-chain hydrogen bonding between the hydroxyl groups on the carbohydrate backbone (Zhu Ryberg, Edlund, & Albertsson, 2011). Thus, the aforementioned chemical modifications might interfere with native features, such as oxygen barrier properties. Moreover, activation of hydroxyl groups in aqueous reactive media is usually conducted at alkaline or acidic pH levels and/or quite high temperatures, which once again, causes degradation and reduction of the polysaccharide chain length. Other chemical modification routes involve an extensive use of non-renewable solvents and reagents, and depending on the degree of substitution and the size of the substituents, the introduced petroleum-derived, synthetic components might represent a predominant percentage of the overall so-called "hemicellulose derivatives" (Hansen & Plackett, 2011; Hartman, Albertsson, & Sjöberg, 2006; Hartman, Albertsson, Söderqvist-Lindblad, et al., 2006; Heinze & Daus, 2011; Söderqvist-Lindblad & Albertsson, 2004; Zhong, Peng, Yang, Cao, & Sun, 2013). Therefore, the advantage gained, in terms of sustainability, of using such material in large-scale food-packaging applications is questionable.

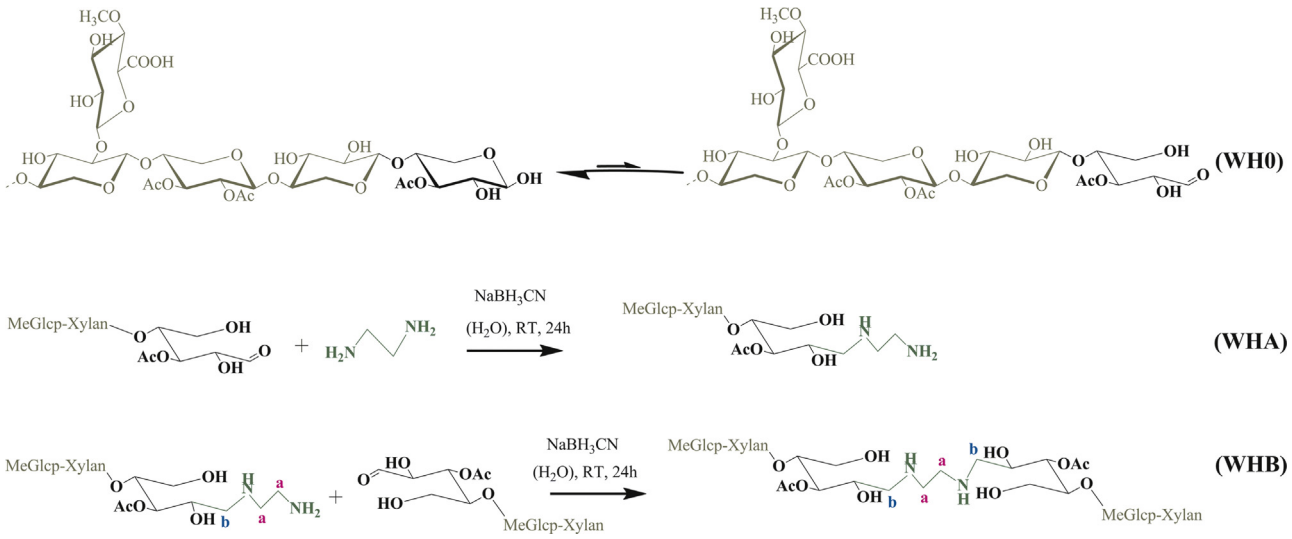
As an alternative to the classic hydroxyl-mediated modifications of hemicelluloses, we propose herein a different approach using the ring-opened aldehyde at the reducing end of each hemicellulosic chain as a reactive center for attaching very small amounts of multifunctional amino coupling agents through reductive amination chemistry, thereby connecting the hemicellulose chains in a head-to-head configuration. Reductive amination is a common tool used in carbohydrate chemistry to anchor different types of amino-functionalized entities to saccharide structures (Brumer, Zhou, Baumann, Carlsson, & Teeri, 2004; Dalpathado, Jiang, Kater, & Desaire, 2005; Daus, Elschner, & Heinze, 2010; Guerry et al., 2013). The possibility of conducting the reaction in aqueous media and under mild conditions together with the strategy's simplicity, robustness and high selectivity makes this type of chemistry fit the green requirements of hemicellulose-rich WH modification perfectly.

Our goal is to develop oxygen barrier films with a much higher content of hardwood hydrolysate (WH) and better film-forming and mechanical properties than those of films prepared from unmodified WH, concurrently reducing the need for a carboxymethylcellulose (CMC) co-component. This aim was achieved by increasing the molecular weight of the *O*-acetyl-4-*O*-methylglucuronoxylan hemicelluloses present in the WH via reductive amination using di- and tri-functional amine coupling agents while retaining the WH initial structure and functionalities without cross-linking.

2. Experimental

2.1. Materials

The hardwood hydrolysate (WH) used in this work was produced from birch wood chips (Södra Cell AB), as described in our previous paper (Saadatmand et al., 2013). Briefly, 2 kg of wood chips (94% dry) was subjected to a sequence of two hydrothermal treatments in a laboratory circulation digester. Each treatment was performed for 60 min at 155 °C, with a 6:1 ratio of total deionized water to wood. The total process water fraction collected from each treatment was then subjected to membrane filtration (ultrafiltration + 2 diafiltration processes) through ceramic membranes with a 10,000 g/mol cutoff purchased from Orélis. Finally, the obtained retentate phase, herein denoted wood hydrolysate (WH0), was



Scheme 1. (i) *O*-acetyl-4-*O*-methylglucuronoxylan (MeGlc*p*-Xylan) reducing-end hemiacetal in equilibrium with the ring-opened aldehyde, (ii) MeGlc*p*-Xylan amine functionalization and (iii) head-to-head chain extension of MeGlc*p*-Xylan.

lyophilized and stored dry until use. The WH0 carbohydrate and lignin composition is given in Table ST1 (Supplementary information) and was determined as previously described (Saadatmand et al., 2013) using ion-exchange chromatography analysis, which was performed after an acid hydrolysis of the WH and removal of the Klason lignin.

A 2% carboxymethyl cellulose (CMC) sodium salt solution in H_2O (25 °C) with a medium viscosity of 400–1000 mPa.s and a degree of substitution of 0.6–0.9 (CAS number: 9004-32-4) was used as received from Sigma-Aldrich. CMC was selected as a co-component in WH-based film formulations following the encouraging results of our previous studies (Edlund et al., 2010), which indicated that films containing a WH and 40% (w/w) CMC exhibited very low oxygen permeability (OP) values and good mechanical properties. Hydrochloric acid (HCl) 50% (Sigma-Aldrich), tris(2-aminoethyl)amine 96% (Sigma-Aldrich), ethylenediamine (≥99.5%) (Fluka), sodium cyanoborohydride ($NaBH_3CN$) 95% (Fluka), ethanol (99.5%, VWR BDH Prolabo), and dimethyl sulfoxide-*d*6 (DMSO-*d*6) (CIL Cambridge Isotope) were used without further purification.

2.2. Two-step chain extension

Chain extension of *O*-acetyl-4-*O*-methylglucuronoxylan chains present in WH was conducted via a two-step process (Daus et al., 2010) as illustrated in Scheme 1. First, the functionality was attached to *O*-acetyl-4-*O*-methylglucuronoxylan (MeGlc*p*-Xylan) chains through reductive amination. WH0 (3.0 g) was dissolved in 20 mL deionized water, and 1,2-ethylenediamine (0.34 g) was added. Thereafter, the pH was adjusted to 6.0 using a 1 M HCl aqueous solution, and $NaBH_3CN$ (188 mg) was added. The reaction was allowed to proceed for 24 h at room temperature, and the produced end-group-modified MeGlc*p*-Xylan denoted as WHA was recovered by ethanol precipitation, washed three times with ethanol, and finally dried under reduced pressure at room temperature. In a second step, WHA (1.0 g) and WH0 (1.0 g) were dissolved in 20 mL deionized water, and $NaBH_3CN$ (115 mg) was added. The reaction mixture was stirred at room temperature for 24 h, and the produced head-to-head chain extension of MeGlc*p*-Xylan denoted WHB was recovered by ethanol precipitation, washed three times with ethanol, and finally dried under reduced pressure at room temperature.

Table 1
The coupling agent/WH feed ratios used to produce single-step chain-extended WH samples.

Sample name	1,2-Diaminoethane *mg/(g WH)*	Sample name	Tris(2-aminoethyl) amine *mg/(g WH)*
WH0	0	–	–
WHN2a	21.4	WHN3a	34.8
WHN2b	7.1	WHN3b	11.6
WHN2c	5.4	WHN3c	8.7
WHN2d	2.7	WHN3d	4.4
WHN2e	1.8	WHN3e	2.9
WHN2f	1.3	WHN3f	2.2

2.3. Single-step chain extension

A series of chain-extended WHs with different molecular weights was prepared via a one-pot reaction by changing the coupling agent content and/or number of functionalities. Samples were denoted as shown in Table 1 according to both the functionality and the amount of coupling agent used, i.e., WHN2x denotes samples derived from a di-functional chain extender (1,2-diaminoethane), whereas WHN3x denotes samples derived from a tri-functional chain extender (tris(2-aminoethyl)amine). The reactions were performed in a similar manner to that of the two-step procedure. For each experiment, WH0 (0.25 g) was dissolved in 2 mL deionized water, and either ethylenediamine (1.3–21.4 mg/gWH) or tris(2-aminoethyl)amine (2.2–34.8 mg/gWH) was added. Thereafter, the pH was adjusted to 6 using a 1 M HCl aqueous solution, and $NaBH_3CN$ (15.7 mg) was added. The reaction was allowed to proceed for 48 h at room temperature, and the final product was recovered by ethanol precipitation, washed three times with ethanol, and finally dried under reduced pressure at room temperature and analyzed by aqueous SEC.

Two reactions selected from the previous series of single-step chain extension reactions, namely WHN2f and WHN3d, were scaled up by a factor of 12 (3.0 g of WH0), providing a sufficient amount of material for film production and subsequent tensile and oxygen barrier testing.

2.4. Film preparation

A series of free-standing films made from blends of either unmodified WH, denoted WH0 herein, or chain-extended WH (WHB,

WHN2f and WHN3d) together with CMC (15–30% (w/w)) was prepared by casting from an aqueous solution. Typically, the WH and CMC were dissolved separately in 15 mL deionized water by mixing on a shaking board at a shaking rate of 200 min^{-1} for at least 3 h. Once the CMC and WH were completely dissolved, the solutions were combined, and the mixture was stirred for another 12 h and then poured into a polystyrene Petri dish with an inner diameter of 8.7 cm (area of 60 cm^2); the mixture was left to dry at 50% relative humidity (RH) and 23 °C until a constant weight was reached (approximately 3 days).

2.5. Instruments and methods

2.5.1. Elemental analysis

The nitrogen content was determined in duplicate for unmodified (WH0), modified (WHA) and chain-extended (WHB) hydrolysates, according to the standard method Dumas with a Carlo Erba NA 1500 instrument. All analyses were performed by Mikro Kemi AB, Uppsala Sweden.

2.5.2. NMR

^{1}HNMR spectra were recorded at 400 MHz on a Bruker DMX-400 nuclear magnetic resonance spectrometer with Bruker software. DMSO-*d*6 was used as the solvent, and spectra were recorded in sample tubes with an outer diameter of 5 mm. MestReNova Lite software was used for data processing.

2.5.3. FT-IR Fourier transform infrared spectrometry

Fourier transform infrared spectrometry (FT-IR) was carried out on a Perkin-Elmer Spectrum 2000 FTIR (Norwalk, CT) with an attenuated total reflectance (ATR) crystal accessory (Golden Gate) from Graseby Specac LTD (Kent, England). All spectra were calculated using 16 individual scans at a resolution of 2 cm^{-1} over the range 4000–600 cm^{-1} with corrections made for atmospheric water and carbon dioxide.

2.5.4. SEC

Size exclusion chromatography (SEC) with 10 mM NaOH as the mobile phase was utilized to determine the molecular weights and molar-mass distribution of different wood hydrolysate samples. The analyses were performed on a Dionex Ultimate-3000 HPLC (Dionex, Sunnyvale, CA, USA) system equipped with a Waters 410 refractive index (RI) detector (Waters, Milford, MA, USA), three PSS Suprema columns (300 × 8 mm^2, 10 μm particle size) with pore sizes of 30 Å, 1000 Å and 1000 Å connected in series, a guard column (50 × 8 mm^2, 10 μm particle size), an LPG-3400SD gradient pump, and a WPS-3000SL autosampler. A conventional calibration method was created using Pullulan standards with a narrow molecular weight distributions ranging from 342 to 708,000 g/mol (PSS, Germany). The measurements were conducted at 40 °C at a flow rate of 1 mL/min, and the RI signal and UV absorbance at 280 nm were monitored. PSS WinGPC Unity software version 7.2 was used to process the data. Before injection, samples were dissolved at room temperature in a 10 mM NaOH aqueous solution and filtered (0.45 μm, Millipore).

2.5.5. Oxygen permeability (OP)

OP was determined according to ASTM standard D3985-02 (ASTM American Society for Testing and Materials) using a Mocon Oxtran 2/20 (Modern Controls, Minneapolis, USA) equipped with a coulometric sensor. Samples were conditioned at 50% or 80% RH and 23 °C for 3 days. The samples were cut and sealed between sheets of aluminum foil with a circular exposed area of 5 cm^2. The thickness was taken as the mean value of five individual measurements performed with a Mitutoyo micrometer. At least two specimens were tested for each film type.

2.5.6. Water vapor permeability (WVP)

WVP was assessed according to the ASTM standard E 96/E 96 M-05 (ASTM International: West Conshohocken, 2005). Aluminum cups were used for wet-cup tests. Films were conditioned for at least 1 week at 50% RH and 23 °C prior to analysis, and the thickness of each sample was measured by a micrometer (Mitutoyo). The conditioned films were cut and sealed between sheets of aluminum foil with a circular exposed area of 5 cm^2 and then mounted and sealed to the top of the aluminum cup filled with 25 mL distilled water. The water-loaded cup covered with the aluminum sealed film was stored at 50% RH and 23 °C and weighed using a scale (accurate to 0.001 g) two or three times a day, continuously for 3 days. Two individual tests were performed for each sample. WVP was calculated according to the following equation, where ΔP represents the difference in water vapor partial pressure across the film.

$$\text{WVP} = \frac{\text{film thickness (mm)} \times \text{weight loss (g)}}{\text{exposed area (m}^2\text{)} \times \text{time (day)} \times \text{pressure difference } \Delta P \text{ (kPa)}}$$

2.5.7. Tensile testing

To minimize the generation of micro-cracks during sample preparation, films were first conditioned at 100% RH in a desiccator containing deionized water at 23 °C for 4 h before being cut into rectangular specimens according to ASTM standard D638 (ASTM International, 2008) and conditioned for 1 week at 50% RH. For each film, a minimum of five specimens were tested to break using an Instron universal materials testing machine equipped with a 500-N load cell operated at a rate of 4 mm min^{-1} and with an initial grip distance of 20 mm.

3. Results and discussion

The production of oxygen barrier films containing high proportions of hardwood hydrolysate (WH) without compromising their mechanical, barrier and water-solubility properties was achieved by increasing the chain length of the hemicelluloses present in the WH. Facile one- or two-step chain extension of WH carbohydrate chains is achieved through reductive amination. Generally, high-molecular-weight polysaccharides exhibit better film-forming and mechanical properties as a result of the chains' enhanced ability to intertwine and form physical entanglements (Rinaudo, 2008).

Our previous work (Saadatmand et al., 2013) on the pilot-scale hydrothermal treatment of hardwood showed that the molecular weight of the recovered WHs was strongly affected by the duration of the treatment and by the recovery procedure. WH with the highest molar mass (weight-average molecular weights $M_w \approx 6500$ g/mol), denoted WH0 herein, was obtained with the shortest hydrothermal treatment time (60 + 60 min), followed by one ultrafiltration and two diafiltration upgrading pretreatments. The upgraded WH0 consisted of a large share of poly- and oligosaccharides, mainly *O*-acetyl-4-*O*-methylglucuronoxylan, together with 23% (w/w) lignin (Saadatmand et al., 2013). In the present work, WH0 hemicelluloses chains were coupled head to head in a two-step process via reductive amination, using 1,2 ethylenediamine as the coupling agent, as illustrated in Scheme 1. The chain-extended WH, denoted WHB, was then characterized and compared to the WH0 in terms of solubility, film-forming ability, and mechanical and oxygen barrier properties. To further make the suggested chain-extension strategy greener and more industrially friendly, we also conducted both amine functionalization and

Table 2
Tensile properties, oxygen permeability (OP) at 50% and 80% relative humidity (RH), and water vapor permeability (WVP) of WH0- and WHB-based films containing 15%, 20% and 30% (w/w) carboxymethyl cellulose (CMC).

	Tensile strength (MPa)	Tensile strain-to-break (%)	E-modulus (GPa)	OP50% RH ($cm^3\ \mu m\ m^{-2}\ day^{-1}\ kPa^{-1}$)	OP80% RH ($cm^3\ \mu m\ m^{-2}\ day^{-1}\ kPa^{-1}$)	WVP ($g\ mm\ m^{-2}\ day^{-1}\ kPa^{-1}$)
WH0-15CMC	–[a]	–[a]	–[a]	–[a]	–[a]	–[a]
WH0-20CMC	–[a]	–[a]	–[a]	–[a]	–[a]	–[a]
WH0-30CMC	4 ± 1	0.2 ± 0.1	2.7 ± 0.3	–[a]	–[a]	–[a]
WHB-15CMC	41.3 ± 14.7	2.5 ± 0.6	2.2 ± 0.3	4.4 ± 0.2	14.9 ± 0.2	79.2 ± 2.3
WHB-20CMC	51.2 ± 9.7	2.9 ± 0.7	2.5± 0.2	2.6 ± 0.1	10.6 ± 0.1	82.6 ± 2.9
WHB-30CMC	59.8 ± 1.8	4.9 ± 0.5	2.3 ± 0.3	2.5 ± 0.0	13.4 ± 0.1	79.7 ± 2.8

[a] The formulation did not form a coherent film.

coupling reactions in a one-pot, single-step process without isolating the intermediates. The molecular weight of the resulting WHs was tuned by varying the type and the amount of the coupling agent used.

3.1. WH barrier and mechanical performances

Hemicellulose-based films and coatings generally exhibit excellent oxygen barrier properties at low relative humidity. For instance, films based on arabinoxylan together with 40% (w/w) glycerol and sorbitol as a plasticizer exhibit OPs of 7.4 and 4.7 $cm^3\ \mu m\ m^{-2}\ day^{-1}\ kPa^{-1}$, respectively (Mikkonen et al., 2009). Likewise, films made from purified *O*-acetylated galactoglucomannan and 35% (w/w) CMC) exhibit an OP as low as 1.28 $cm^3\ \mu m\ m^{-2}\ day^{-1}\ kPa^{-1}$ (Hartman, Albertsson, & Sjöberg, 2006; Hartman, Albertsson, Söderqvist-Lindblad, et al., 2006). Recently, OP values of 0.3 and 2.5 $cm^3\ \mu m\ m^{-2}\ day^{-1}\ kPa^{-1}$ were obtained for a film made from a partially upgraded softwood hydrolysate and crude hardwood hydrolysate together with 50% (w/w) and 40% (w/w) CMC, respectively (Edlund et al., 2010; Ibn Yaich, Edlund, & Albertsson, 2014). Low molecular weights and/or high intra- and intermolecular interactions require large amounts of additives such as plasticizers or co-components in hemicellulose-based formulations to form films with acceptable mechanical performance.

In the present work, we chose to limit the content of CMC added to the WH-based films to a maximal value of 30% (w/w). CMC was selected as a co-component following the encouraging results obtained in previous studies showing that films made from WH and CMC exhibited very low OP values and good mechanical performance (Edlund et al., 2010). The effects of varying the CMC content on the film formability of WH0- and WHB-based films was explored following the casting and drying of aqueous solutions of WH0 and WHB with 0%, 5%, 10%, 15%, 20% and 30% (w/w) CMC. For unmodified WH, i.e., WH0, at least 30% (w/w) CMC is needed to form cohesive films, whereas WHB can form a continuous free-standing film with only 15% (w/w) CMC. All films with lower CMC contents i.e., WH0-CMC [0–20% (w/w)] and WHB-CMC [0–10% (w/w)], fractured into small pieces either during drying or the handling step.

The tensile and barrier properties of the produced WH-based films are summarized in Table 2. The films created using WH0 and 30% (w/w) CMC were clearly the weakest, with a tensile strength value reaching only 3.8 MPa. Already before performing the tensile experiments, it was evident that WH0-30CMC yielded brittle and fragile films, whereas the chain-extended WHB-based films were stronger and more flexible, even with a much lower CMC content. The WHB-based films exhibited tensile strengths ranging from 41 to 59 MPa. These values are more than one order of magnitude greater than those obtained for the WH0-based films. Interestingly, films prepared from WHB with 30% (w/w) CMC exhibited a tensile strain-to-break as high as 4.9%, much higher than what has been previously reported (Saadatmand et al., 2013) for films prepared from WH0 with 67% (w/w) CMC, for which a tensile strain-to-break of 4.0% was obtained.

Unlike in previous studies utilizing internal or external plasticizers (Hartman, Albertsson, & Sjöberg, 2006; Hartman, Albertsson, Söderqvist-Lindblad, et al., 2006; Laine et al., 2013; Mikkonen et al., 2009), in which improvement in the ductility of hemicelluloses was often obtained at the expense of gas barrier properties, herein, as presented in Table 2, all WHB-based films exhibited oxygen permeability (OP) values well below the upper limit of what is considered to be characteristic of a good oxygen barrier (38.9 $cm^3\ \mu m\ m^{-2}\ day^{-1}\ kPa^{-1}$) at both 50% and 80% RH (Miller & Krochta, 1997). The high barrier performance of the WHB-based films reflects the dense molecular packing and the strong inter-molecular interaction between the film components. Furthermore, water vapor permeability values ranging from 79 to 82 ($g\ mm\ m^{-2}\ day^{-1}\ kPa^{-1}$) were reasonable considering the large amount of hydrophilic polysaccharides used. It is noteworthy that these results are approximately 50% lower than those we previously reported for crude WH-based films with 40% (w/w) CMC in which the crude WH contained much less lignin (6% (w/w)) (Ibn Yaich et al., 2012). This finding demonstrates that lignin plays a positive role in reducing the moisture sensitivity of WH-based films.

3.2. Hydrolysate chain extension

Chain-extended WHB was prepared by reductive amination coupling of *O*-acetyl-4-*O*-methylglucuronoxylan (MeGlc*p*-Xylan) present in WH0 with 1,2 ethylenediamine, as reported in Scheme 1. This procedure involved two steps. In the first step, amine-modified MeGlc*p*-Xylan (WHA) was prepared by reacting MeGlc*p*-Xylan with an excess of 1,2 diaminoethane, forming an intermediary imine that was subsequently reduced to a more stable secondary amine with sodium cyanoborohydride ($NaBH_3CN$). The reaction was carried out in water (pH = 6) at room temperature for 24 h. $NaBH_3CN$ is a weak reducing agent that can act selectively toward imine groups in the presence of a wide variety of other functional groups, such as carbonyl, carboxyl, and unsaturated structures (Clayden, Greeves, Warren, & Wothers, 2001). In the second step, the resulting amine-terminated MeGlc*p*-Xylan chains (WHA) were then coupled to a nearly equivalent amount of MeGlc*p*-Xylan reducing-end aldehydes (WH0) via a reductive amination procedure similar to that applied in the first step. As expected, WHA and WHB are readily soluble in both water and dimethylsulfoxide (DMSO), suggesting that no crosslinking occurred.

To confirm the success of the chain extension reaction, unmodified WH0, amine-functionalized WHA and chain-extended WHB were characterized by aqueous SEC. Fig. 1 illustrates the SEC traces of the three different samples, and Table 3 summarizes their corresponding average molecular weights and dispersity indices. WHB showed a weight-average molecular weight M_w of 10,600 g/mol and a number-average molecular weight M_n of 4100 g/mol, which is approximately 1.6 and 1.5 times higher than the M_w and M_n of WH0 respectively, clearly indicating that a reductive amination coupling

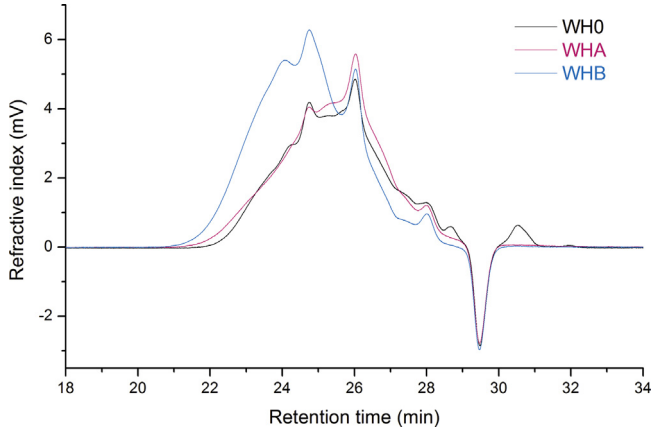


Fig. 1. Alkaline aqueous SEC traces of wood hydrolysate (WH0); 1,2-diaminoethane-functionalized wood hydrolysate (WHA) and chain-extended wood hydrolysate (WHB).

Table 3
Average molecular weights, dispersity indices ($Đ$) and nitrogen contents for wood hydrolysate (WH0), 1,2-diaminoethane-functionalized wood hydrolysate (WHA) and chain-extended wood hydrolysate (WHB).

	M_n (g/mol)	M_w (g/mol)	$Đ$	N% (w/w)
WH0	2700	6600	2.5	b.l.[a]
WHA	2900	7000	2.5	1
WHB	4100	10,600	2.6	0.7

[a] b.l: Below detection limit of the instrument.

occurred. However, the increase is still lower than the theoretical value of 2 expected when using a di-functional coupling agent. The difference between the experimental and theoretical molecular weight can be attributed to several possible factors. These include the broad dispersity of WH0, the fact that the non-carbohydrate components of WH0 were not chain-extended, and the difficulty of performing the coupling reaction under strict stoichiometric balance (i.e., NH_2/HCO molar ratio). Furthermore, the molecular weight of WHA was slightly higher than that of WH0, which was expected considering the fractionation effect of ethanol precipitation during the purification steps. The possibility of a limited coupling reaction between unmodified MeGlc*p*-Xylan and amine-terminated MeGlc*p*-Xylan cannot be ruled out, in spite of the large excess of 1,2 diaminoethane used at this stage. The amount of nitrogen, determined based on elemental analysis, was used to calculate the amount of coupling agent introduced into WHA and WHB, taking into account that the coupling contained two amino groups. The analysis showed nitrogen contents of 1% (w/w) and 0.7% (w/w) for WHA and WHB, respectively, which corresponds roughly to 3% (w/w) of 1,2 ethylenediamine introduced into WHB and 4.3% (w/w) introduced into WHA.

The WH0, WHA and WHB chemical structures were further assessed by ^{1}HNMR, as shown in Fig. 2. All samples showed a typical pattern of overlaid peaks in the 5.6–3.2 ppm region, corresponding to the xylan backbone and 4-*O*-methylglucuronic acid side-chain protons. In addition, the peak arising from the *O*-acetyl pendant groups at ~2 ppm was identified in all WH samples, indicating that the hemicelluloses preserved their initial acetylated structures through the entire chain-extension process. The reductive amination reactions gave rise to new signals in the 2.6–2.9 ppm region, stemming from the —CH_2— groups of both 1,2 ethylenediamine and the ring-opened xylose units at the chains' reducing ends, referred to as (a) and (b), respectively, in Scheme 1 and Fig. 2. These data further support the results of SEC and elemental analysis, confirming the successful chain extension.

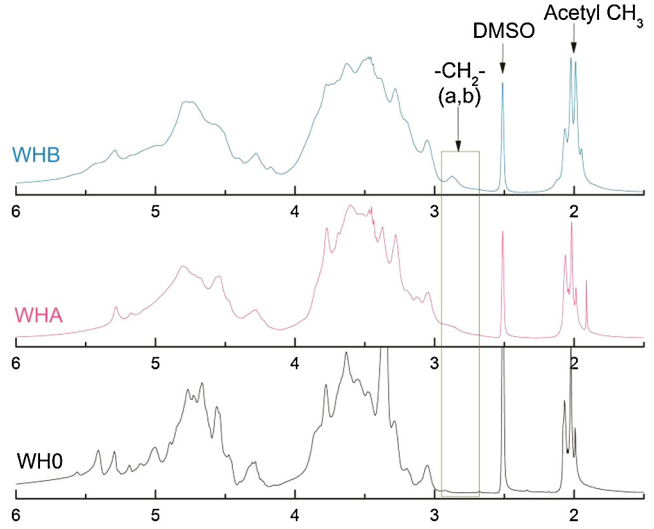


Fig. 2. ^{1}HNMR spectra of wood hydrolysate (WH0); 1,2-diaminoethane-functionalized wood hydrolysate (WHA) and chain-extended wood hydrolysate (WHB) in DMSO.

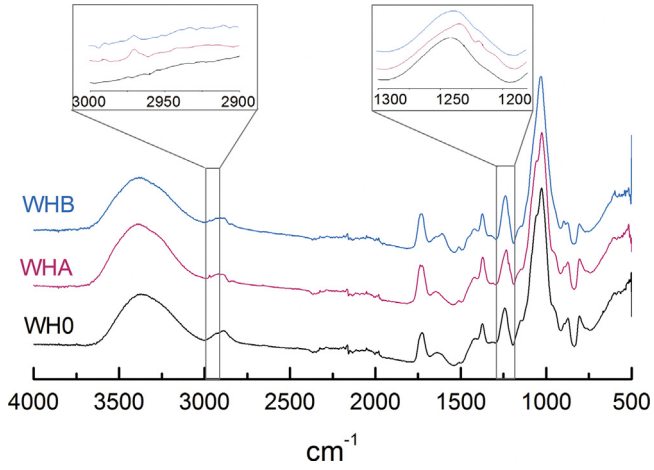


Fig. 3. FTIR spectra of wood hydrolysate (WH0); 1,2-diaminoethane-functionalized wood hydrolysate (WHA) and chain-extended wood hydrolysate (WHB).

The FT-IR spectra of WH0, WHA and WHB are shown in Fig. 3, where the differences between the three spectra are highlighted in the inserts. The reductive amination of WH0 gave rise to a new peak, shown in the WHA spectrum at 1217 cm^{-1} and ascribed to the C—N stretching of primary amines, together with another low-intensity peak at 2970 cm^{-1} attributed to the aliphatic CH_2 of the coupling agent. The other characteristic peaks of the primary and secondary amines at 3300–3400 cm^{-1} and 1378 cm^{-1}, respectively, could not be distinguished in the spectra due to the overlap with the broad O-H bands. The disappearance of the primary amine C—N stretching peak in the WHB spectrum further suggests a successful coupling reaction between unmodified MeGlc*p*-Xylan and amine-terminated MeGlc*p*-Xylan. Apart from the introduced amine-related peaks, the three spectra were identical, suggesting no major modifications of the WH's initial acetylated carbohydrate backbone in the reductive amination reactions. The occurrence of bands at approximately 1610 cm^{-1} and 1423 cm^{-1} assigned to the COO^- group, respectively, indicates the presence of 4-*O*-methylglucuronic acid side groups. A sharp peak at 1734 cm^{-1} is ascribed to C=O stretching corresponding to the acetyl and carbonyl groups in MeGlc*p*-Xylan (Marchessault & Liang, 1962). In addition, two bands at 1511 cm^{-1} and 1320 cm^{-1} characteristic

Table 4
Average molecular weights and dispersity indices (Đ) of wood hydrolysate (WH0), 1,2-diaminoethane chain-extended wood hydrolysate WHN2a–WHN2f and tris(2-aminoethyl)amine chain-extended wood hydrolysate WHN3a–WHN3f.

	M_n (g/mol)	M_w (g/mol)	Đ
WH0	2700	6600	2.5
WHN2a	2500	6800	2.7
WHN2b	2900	7800	2.6
WHN2c	3000	8000	2.6
WHN2d	4000	12,200	3.0
WHN2e	4200	12,300	2.9
WHN2f	4300	12,500	2.9
WHN3a	2800	7800	2.7
WHN3b	3400	8700	2.6
WHN3c	3900	9500	2.5
WHN3d	4900	13,300	2.7
WHN3e	4600	13,000	2.8
WHN3f	4500	12,700	2.8

of lignin associated with hemicellulose were observed (Sun & Tomkinson, 1999). Once again, these data, in agreement with the ^{1}HNMR results, confirm that the hemicelluloses maintained their original branched and acetylated structure throughout the entire chain-extension process.

3.3. Single-step chain extension

From a scaling-up perspective, we aimed to simplify the chain-extension reaction of *O*-acetyl-4-*O*-methylglucuronoxylan in the WH by reducing the number of steps from a two- to a one-pot reaction and reducing the number of purification steps as well as the associated chemical waste.

Among all of the reaction parameters, the relative concentrations of the amine and the hemicellulose reducing-end aldehyde are critical in determining the chain-extension efficiency and thus the molecular weight of the final product. A chain-extended WH with maximum molecular weight will result if the number of amine sites and the number of aldehyde active sites are properly balanced. Furthermore, the number of functional amine groups per coupling agent molecule dictates the maximum number of hemicellulose chains that can be attached together.

In view of the foregoing discussion, a series of chain-extended WHs was prepared in a single-step reaction, using di- and tri-functionalized amino coupling agents in different amounts. The efficiency and progress of the chain-extension reactions were determined via SEC analysis. The SEC data for the unmodified and chain-extended WH samples are summarized in Table 4. The molecular weights of most chain-extended samples were higher than those for unmodified WH0, and for many samples, these values even exceeded the molecular weight achieved by the two-step chain-extension process. The highest increase in the WH molecular weight (M_w = 13300 g/mol) was obtained for WHN3-d containing not more than 0.44% (w/w) tris(2-aminoethyl) amine. WH samples extended with the di-functionalized coupling agent reached a maximum M_w of 12,500 g/mol when using 1.3 mg of 1,2-diaminoethane per gram of WH0.

Based on the average molecular weight data, WHN2f and WHN3d were selected as the most favorable candidates from the single-step 2-diaminoethane and tris(2-aminoethyl)amine chain-extended WHs, respectively, to be scaled up, used for the film-forming, mechanical and oxygen barrier tests and allow for a comparison with their two-step counterpart (WHB).

Accordingly, aqueous formulations of WHN2f and WHN3d with 0%, 15% and 30% (w/w) CMC were cast and dried. We observed that neither of the two WHs was able to form without the addition of CMC. WHN2f, like WHB, forms a continuous free-standing film with only 15% (w/w) CMC. The WHN3d-based film containing 15% (w/w) CMC cracked into pieces during the drying step, some of which were large enough to prepare tensile test specimens. WHN3d containing 30% (w/w) CMC on the other hand did form a continuous and cohesive film.

The tensile properties of the WHN2f- and WHN3d-based films are summarized in Table 5. Interestingly, the WHN2f-based films were stronger than their WHN3d counterparts, although both WHs exhibited nearly the same apparent molecular weight as measured by SEC. This finding indicates that the architecture of the molecular chains also plays an important role in determining the physical properties of the WH material. The WHN2 and WHB, which exhibit longer and linear chains, can more easily intertwine and entangle with neighboring chain molecules than WHN3, which exhibits a star-shaped structure with three shorter arms.

Furthermore, WHN2f-15CMC and WHN2f-30CMC exhibited tensile strengths of 35 and 62 MPa, respectively. These values are within the same range as the tensile strengths for the WHB-15CMC and WHB-30CMC films (Table 2). The similarities in tensile strength are reasonable given the similarities in molecular structure and the small difference in molecular weight between the film components. The WHN2f-15CMC films were still more brittle, showing a slightly higher OP than the films containing 30% CMC. Examination of the WHN2f-15CMC and WHN2f-30CMC films surfaces by scanning electron microscopy (SEM) did not reveal any notable morphological difference between these two films as shown in Figs. S1 and S2 (Supplementary information). The lowest OP value at 50% RH was observed for WHN2f-30CMC, having an OP as low as 0.2 $cm^3\ \mu m\ m^{-2}\ day^{-1}\ kPa^{-1}$.

In summary, a robust and environmentally friendly method was adopted for the preparation of chain-extended WH. The reaction was conducted in water at pH 6 at room temperature and was robust to the presence of lignin and other WH components. The chain extension of the WH did give rise to significant improvements in terms of film formability or ductility for the WH-based films. Consequently, films with higher WH contents could be produced. Furthermore, the chain-extension process did not cause any major degradation or alteration of the hemicellulose structure. Thereby, the inherent water solubility, low viscosity and oxygen barrier properties of the WH were preserved. The possibility of conducting the chain-extension reaction in a single-step process with very low amounts of coupling agent (<1% (w/w)) was demonstrated, making this approach even more interesting from both industrial and environmental perspectives. Furthermore, we conducted reductive amination with $NaBH_3CN$ as a reducing agent to provide an initial proof of concept. Other mild reducing agents such as

Table 5
Tensile properties and oxygen permeability (OP) at 50% relative humidity (RH) of WHN2f-6- and WHN3d-4 based films containing 15% and 30% (w/w) carboxymethyl cellulose (CMC).

	Tensile strength (MPa)	Tensile strain-to-break (%)	E-modulus (GPa)	OP 50% RH ($cm^3\ \mu m\ m^{-2}\ day^{-1}\ kPa^{-1}$)
WHN2f-15CMC	35.4 ± 3.2	1.2 ± 0.0	3.7 ± 0.4	5.9 ± 0.1
WHN2f-30CMC	62.5 ± 7.6	3.3 ± 0.5	2.7 ± 0.2	0.2 ± 0.1
WHN3d-15CMC	15.9 ± 1.6	1.3 ± 0.1	1.9 ± 0.2	–[a]
WHN3d-30CMC	36.6 ± 8.5	1.9 ± 0.4	2.4 ± 0.3	1.7 ± 0.7

[a] Did not form a large continuous film.

($(CH3)_2NHBH_3$), $NaBH(OAc)_3$ could also be employed (Dalpathado et al., 2005).

The single-step chain extension reaction could potentially be applied to WH process liquors prior to recovery and upgrading pretreatment (ultrafiltration, diafiltration or ethanol precipitation), which might also lead to an increase in the yield of the high-molecular-weight fraction that can be recovered from these liquors because the separations in all these techniques are carried out mainly based on differences in the solutes' molecular size.

4. Conclusions

A *O*-acetyl-4-*O*-methylglucuronoxylan-rich wood hydrolysate (WH) derived from hardwood was successfully chain extended via a water-based reductive amination reaction, using amino-functionalized coupling agents. The film formability and tensile properties of the films based on chain-extended WH are far superior to those of their counterparts based on unmodified WH and containing equal amounts of co-component (CMC), particularly in terms of tensile strength and strain-to-break. Consequently, free-standing continuous films with a WH content as high as 85% (w/w) were produced. The produced films exhibit excellent oxygen barrier performance, with permeability values as low as 0.2 $cm^3\ \mu m\ m^{-2}\ day^{-1}\ kPa^{-1}$ and 10.6 $cm^3\ \mu m\ m^{-2}\ day^{-1}\ kPa^{-1}$ at 50% and 80% relative humidity, respectively. The chain-extension process was also performed in a single step and facile one-pot reaction, thus rendering this approach greener and more applicable for industry. Utilization of a minor amount of coupling agent as low as 0.13% (w/w) was sufficient to double the molecular weight of the WH.

Acknowledgments

The authors gratefully acknowledge VINNOVA (Project number 2009-04311) and Tetra Pak Packaging Solutions AB for their financial support. Dr. Margaretha Söderqvist-Lindblad at Södra Innovation AB is thanked for kindly providing the wood chips. Lidija Glavas is acknowledged for helpful discussion.

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.2014.09.067.

References

Albertsson, A.-C., Voepel, J., Edlund, U., Dahlman, O., & Söderqvist-Lindblad, M. (2010). Design of renewable hydrogel release systems from fiberboard mill wastewater. *Biomacromolecules*, *11*(5), 1406–1411.

Brumer, H., Zhou, Q., Baumann, M. J., Carlsson, K., & Teeri, T. T. (2004). Activation of crystalline cellulose surfaces through the chemoenzymatic modification of xyloglucan. *Journal of the American Chemical Society*, *126*(18), 5715–5721.

Clayden, J., Greeves, N., Warren, S., & Wothers, P. (2001). *Organic chemistry*. New York, NY: Oxford University Press.

Dahlman, O., Söderqvist Lindblad, M., Parkås, J., Albertsson, A. -C., & Edlund, U. (2009). Utilization of a wood hydrolysate. EP 2067793 / WO 2009068525 A1.

Dalpathado, D. S., Jiang, H., Kater, M. A., & Desaire, H. (2005). Reductive amination of carbohydrates using $NaBH(OAc)_3$. *Analytical and Bioanalytical Chemistry*, *381*(6), 1130–1137.

Danielsson, S., Kisara, K., & Lindström, M. E. (2006). Kinetic study of hexenuronic and methylglucuronic acid reactions in pulp and in dissolved xylan during kraft pulping of hardwood. *Industrial & Engineering Chemistry Research*, *45*(7), 2174–2178.

Daus, S., Elschner, T., & Heinze, T. (2010). Towards unnatural xylan based polysaccharides: Reductive amination as a tool to access highly engineered carbohydrates. *Cellulose*, *17*(4), 825–833.

Dervilly-Pinel, G. (2004). Investigation of the distribution of arabinose residues on the xylan backbone of water-soluble arabinoxylans from wheat flour. *Carbohydrate Polymers*, *55*(2), 171–177.

Edlund, U., & Albertsson, A.-C. (2012). SET-LRP goes green: Various hemicellulose initiating systems under non-inert conditions. *Journal of Polymer Science Part A: Polymer Chemistry*, *50*(13), 2650–2658.

Edlund, U., Zhu Ryberg, Y. Z., & Albertsson, A.-C. (2010). Barrier films from renewable forestry waste. *Biomacromolecules*, *11*(9), 2532–2538.

Fonseca Silva, T. C., Habibi, Y., Colodette, J. L., & Lucia, L. A. (2011). The influence of the chemical and structural features of xylan on the physical properties of its derived hydrogels. *Soft Matter*, *7*(3), 1090–1099.

Guerry, A., Bernard, J., Samain, E., Fleury, E., Cottaz, S., & Halila, S. (2013). Aniline-catalyzed reductive amination as a powerful method for the preparation of reducing end-clickable chitooligosaccharides. *Bioconjugate Chemistry*, *24*(4), 544–549.

Hansen, N. M. L., & Plackett, D. (2008). Sustainable films and coatings from hemicelluloses: A review. *Biomacromolecules*, *9*, 1493–1505.

Hansen, N. M. L., & Plackett, D. (2011). Synthesis and characterization of birch wood xylan succinoylated in 1-n-butyl-3-methylimidazolium chloride. *Polymer Chemistry*, *2*(9), 2010.

Hartman, J., Albertsson, A.-C., & Sjöberg, J. (2006). Surface- and bulk-modified galactoglucomannan hemicellulose films and film laminates for versatile oxygen barriers. *Biomacromolecules*, *7*, 1983–1989.

Hartman, J., Albertsson, A.-C., Söderqvist-Lindblad, M., & Sjöberg, J. (2006). Oxygen barrier materials from renewable sources: Material properties of softwood hemicellulose-based films. *Journal of Applied Polymer Science*, *100*, 2985–2991.

Heikkinen, S. L., Mikkonen, K. S., Pirkkalainen, K., Serimaa, R., Joly, C., & Tenkanen, M. (2013). Specific enzymatic tailoring of wheat arabinoxylan reveals the role of substitution on xylan film properties. *Carbohydrate Polymers*, *92*(1), 733–740.

Heinze, T., & Daus, S. (2011). Xylan and xylan derivatives—Basis of functional polymers for the future. In P. A. Williams (Ed.), RSC polymer chemistry series. Renewable resources for functional polymers and biomaterials (pp. 88–129).

Ibn Yaich, A., Edlund, U., & Albertsson, A.-C. (2012). Wood hydrolysate barriers: Performance controlled via selective recovery. *Biomacromolecules*, *13*(2), 466–473.

Ibn Yaich, A., Edlund, U., & Albertsson, A.-C. (2014). Adapting wood hydrolysate barriers to high humidity conditions. *Carbohydrate Polymers*, *100*, 135–142.

Kochumalayil, J., & Berglund, L. (2014). Water-soluble hemicelluloses for high humidity applications—Enzymatic modification of xyloglucan for mechanical and oxygen barrier properties. *Green Chemistry*, *16*, 1904–1910.

Kochumalayil, J. J., Zhou, Q., Kasai, W., & Berglund, L. A. (2013). Regioselective modification of a xyloglucan hemicellulose for high-performance biopolymer barrier films. *Carbohydrate Polymers*, *93*(2), 466–472.

Laine, C., Harlin, A., Hartman, J., Hyvärinen, S., Kammiovirta, K., Krogerus, B., et al. (2013). Hydroxyalkylated xylans—Their synthesis and application in coatings for packaging and paper. *Industrial Crops and Products*, *44*, 692–704.

Li, H., Saeed, A., Jahan, M. S., Ni, Y., & van Heiningen, A. (2010). Hemicellulose removal from hardwood chips in the pre-hydrolysis step of the kraft-based dissolving pulp production process. *Journal of Wood Chemistry and Technology*, *30*(1), 48–60.

Maleki, L., Edlund, U., & Albertsson, A.-C. (2014). Unrefined wood hydrolysates are viable reactants for the reproducible synthesis of highly swellable hydrogels. *Carbohydrate Polymers*, *108*, 281–290.

Marchessault, R. H., & Liang, C. Y. (1962). The infrared spectra of crystalline polysaccharides. VIII. Xylans. *Journal of Polymer Science*, *59*(168), 357–378.

Mikkonen, K. S., Heikkinen, S., Soovre, A., Peura, M., Serimaa, R., Talja, R. A., et al. (2009). Films from oat spelt arabinoxylan plasticized with glycerol and sorbitol. *Journal of Applied Polymer Science*, *114*, 457–466.

Mikkonen, K. S., Schmidt, J., Vesterinen, A.-H., & Tenkanen, M. (2013). Crosslinking with ammonium zirconium carbonate improves the formation and properties of spruce galactoglucomannan films. *Journal of Materials Science*, *48*(12), 4205–4213.

Miller, K. S., & Krochta, J. M. (1997). Oxygen and aroma barrier properties of edible films: A review. *Trends in Food Science and Technology*, *8*, 228–237.

Oinonen, P., Areskogh, D., & Henriksson, G. (2013). Enzyme catalyzed cross-linking of spruce galactoglucomannan improves its applicability in barrier films. *Carbohydrate Polymers*, *95*(2), 690–696.

Palm, M., & Zacchi, G. (2003). Extraction of hemicellulosic oligosaccharides from spruce using microwave oven or steam treatment. *Biomacromolecules*, *4*(3), 617–623.

Persson, J., Dahlman, O., Albertsson, A., & Edlund, U. (2012). Modification of the mechanical and thermal properties of birch xylan by lactide-grafting. *Nordic Pulp Paper Journal*, *27*(3), 518–524.

Persson, T., Nordin, A., Zacchi, G., & Jönsson, A. (2007). Economic evaluation of isolation of hemicelluloses from process streams from thermomechanical pulping of spruce. *Applied Biochemistry and Biotechnology*, *136-140*

Rinaudo, M. (2008). Main properties and current applications of some polysaccharides as biomaterials. *Polymer International*, *57*(3), 397–430.

Saadatmand, S., Edlund, U., Albertsson, A., Danielsson, S., & Dahlman, O. (2012). Prehydrolysis in softwood pulping produces a valuable biorefinery fraction for material utilization. *Environmental Science and Technology*, *46*, 8389–8396.

Saadatmand, S., Edlund, U., Albertsson, A.-C., Danielsson, S., Dahlman, O., & Karlström, K. (2013). Turning hardwood dissolving pulp polysaccharide residual material into barrier packaging. *Biomacromolecules*, *14*(8), 2929–2936.

Simkovic, I., Kelnar, I., Uhliariková, I., Mendichi, R., Mandalika, A., & Elder, T. (2014). Carboxymethylated-, hydroxypropylsulfonated- and quaternized xylan derivative films. *Carbohydrate Polymers*, *110*, 464–471.

Song, T., Pranovich, A., & Holmbom, B. (2011). Effects of pH control with phthalate buffers on hot-water extraction of hemicelluloses from spruce wood. *Bioresource Technology*, *102*(22), 10518–10523.

Sun, R. C., & Tomkinson, J. (1999). Physicochemical characterization of hemicelluloses from steamed aspen and birchwood. *International Journal of Polymer Analysis and Characterization*, *5*(2), 181–193. DOI 10.1080/10236669908014183.

Söderqvist-Lindblad, M., & Albertsson, A.-C. (2004). Chemical modification of hemicelluloses and gums. In D. Severian (Ed.), *Polysaccharides* (pp. 491–508). London: CRC Press.

Thornton, J., Ekman, R., Holmbom, B., & Örså, F. (1994). Polysaccharides dissolved from norway spruce in thermomechanical pulping and peroxide bleaching. *Journal of Wood Chemistry and Technology*, *14*(2), 159–175.

Timell, T. E. (1967). Recent progress in the chemistry of wood hemicelluloses. *Wood Science and Technology*, *1*, 45–70.

Willför, S., Sundberg, K., Tenkanen, M., & Holmbom, B. (2008). Spruce-derived mannans—A potential raw material for hydrocolloids and novel advanced natural materials. *Carbohydrate Polymers*, *72*(2), 197–210.

Zhong, L., Peng, X., Yang, D., Cao, X., & Sun, R. (2013). Long-chain anhydride modification: A new strategy for preparing xylan films. *Journal of Agriculture and Food Chemistry*, *61*, 655–661.

Zhu Ryberg, Y. Z., Edlund, U., & Albertsson, A.-C. (2011). Conceptual approach to renewable barrier film design based on wood hydrolysate. *Biomacromolecules*, *12*(4), 1355–1362.

Zhu Ryberg, Y. Z., Edlund, U., & Albertsson, A.-C. (2012). Retrostructural model to predict biomass formulations for barrier performance. *Biomacromolecules*, *13*(8), 2570–2577.

Zhu Ryberg, Y. Z., Edlund, U., & Albertsson, A.-C. (2013). Innovative approaches for converting a wood hydrolysate to high-quality barrier coatings. *ACS Applied Materials & Interfaces*, *5*(16), 7748–7757.