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Adapting wood hydrolysate barriers to high humidity conditions

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ABSTRACT

The incorporation of layered silicates in bio-based barrier films resulted in lower water vapor permeability, and significantly lowered oxygen permeability at a relative humidity (RH) as high as 80%, with reduced moisture sensitivity of the wood hydrolysate (WH) based films. The applicability of WH based films was accordingly extended over a wider relative humidity condition range. Crude aqueous process liquor, the WH, was extracted from hardwood and utilized as a feed-stock for films without any upgrading pretreatment, yet producing superior oxygen barrier performance compared to partially upgraded WH and highly purified hemicelluloses. Films composed of crude WH and either one of two types of naturally occurring layered silicates, montmorillonite (MMT) or talc, as mineral additives, were evaluated with respect to oxygen and water vapor permeability, morphological, tensile and dynamic thermo-mechanical properties. Films with an oxygen permeability as low as 1.5 (cm^3 μm)/(m^2 day kPa) at 80% RH was achieved.

1. Introduction

Nowadays, there is a real need for the development of competitive bio-based and environmentally friendly packaging materials. A bio-based and abundant feedstock, that may be revalued as a useful and profitable side product in future biorefinery oriented wood processing industries, is the family of hemicelluloses, since they are readily released to and possible to recover from process liquors (Dahlman, Lindblad, Parkaas, Albertsson, & Edlund, 2009). Such hemicelluloses, more or less purified, have been shown to exhibit excellent oxygen barrier properties rendering them suitable for use as coatings, layers or films in food-packaging applications (Edlund, Ryberg, & Albertsson, 2010; Hansen & Plackett, 2008; Hartman, Albertsson, Lindblad, & Sjoeberg, 2006; Yaich, Edlund, & Albertsson, 2012; Ryberg, Edlund, & Albertsson, 2011). However, previous studies have recognized two major drawbacks of hemicelluloses that limit their use in high volume packaging applications: high production costs to obtain the highly purified form and their inherent strongly hydrophilic character (Hartman, Albertsson, & Sjoeberg, 2006; Persson, Nordin, Zacchi, & Jönsson, 2007; Willför, Sundberg, Tenkanen, & Holmbom, 2008). Highly purified hemicellulose films are typically poor water vapor barriers and the oxygen barrier properties deteriorate at high relative humidity. To circumvent this, a number of attempts based on chemical modification of hemicellulose have been reported (Söderqvist & Albertsson, 2004), including grafting more hydrophobic entities such as benzyl (Hartman, Albertsson, Lindblad, et al., 2006), fatty acids (Peroval et al., 2003) and polylactic acid (PLA) (Saadatmand, Edlund, & Albertsson, 2011), resulting in a reduced hydrophilicity and eventually a lower water vapor permeability of the functionalized hemicellulose based films and coatings. However, this process will interfere with the oxygen barrier performance of chemically modified hemicellulose films and coatings (Hartman, Albertsson, & Sjoeberg, 2006). The low oxygen permeability of the hemicelluloses is related to the densely packed structure arising from the high cohesive energy between macromolecular chains (Edlund, Yu, Zhu Ryberg, Krause-Rehberg, & Albertsson, 2012; Ryberg et al., 2011; Townrow, Kilburn, Alam, & Ubbink, 2007). Hydrogen bonds between the hydroxyl groups contribute significantly to the density of the structure (Ibn Yaich, Edlund, & Albertsson), and bulk chemical modification of the hemicelluloses will inevitably alter the matrix packing ability. Furthermore, excessive purification and/or chemical modification of hemicelluloses will definitely reduce the economic and environmental benefits of using such a natural material resource.

Utilization of crude or slightly purified hemicellulose rich wood hydrolysates (WH) is economically much more feasible. It was recently shown that less purified WH resulted in barrier films and coatings with similar or even superior oxygen barrier performance in comparison to those made from extensively purified hemicelluloses (Dahlman et al., 2009; Edlund et al., 2010; Ibn Yaich et al., 2012; Ryberg et al., 2011). Furthermore, the presence of

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hydrophobic lignin fragments may reduce the hydrophilicity of the system. Nevertheless, the good oxygen barrier properties of WH are most evident in a relative humidity not higher than 50% (Ryberg et al., 2011). Therefore, for efficient use in packaging the WH based material has to be laminated between two layers of conventional thermoplastics such PE or PP, providing the water vapor moisture barrier (Albertsson & Edlund, 2011), maintaining a partial dependence of the packaging industry on non-renewable petroleum derived material.

A key question for large scale packaging utilization of hemicellulose based products is to reduce their water sensitivity without compromising their oxygen barrier properties, economic competitiveness and carbon neutrality of the final product. In that perspective, we propose to incorporate natural layered silicates as mineral additives into WH formulation films or coatings using a simple and environmentally friendly process. Montmorillonite MMT and talc were selected as additives, being naturally occurring abundant silicate minerals. Since they are not chemically modified, these mineral additives have a much reduced carbon foot print and low price. Both MMT and talc belong to the layered silicate family (Brown, 1984). The layered silicates are available on the market; they come in different and versatile chemical structures, sizes and shapes, and are abundant and inexpensive. Therefore, by selectively incorporating an adequate mineral additive into the WH formulations, one can widen the range of properties.

The mixing of layered silicates with polymeric materials is an established approach; mineral additives in general have been extensively used as fillers and reinforcement for paper (Griggs, 1988) and commodity polymers such PP and PE (Wypych, 2010). In the last decades, there has been an increased interest in using silicate particles with reduced size and high aspect ratio to maximize their performance and efficiency as reinforcement additives (Ray & Okamoto, 2003). Nevertheless, one should note that the production of nanoparticles in general is usually accompanied with high energy production costs as well as some concerns about hazards implication that could occur due to the nano-size of the particles (Alvarez-Chavez, Edwards, Moure-Eraso, & Geiser, 2012).

Research on layered silicate/polysaccharide systems has predominantly been carried out using highly purified polysaccharides as matrices, for example starch (Zeppa, Gouanve, & Espuche, 2009), chitosan (Darder, Colilla, & Ruiz-Hitzky, 2003), pectin (Vartiainen, Tammelin, Pere, Tapper, & Harlin, 2010) hemicellulose (Uenlue, Guenister, & Atici, 2009) and cellulose (Ho, Ko, Zimmermann, Geiger, & Caseri, 2012; Liu & Berglund, 2012; Liu, Walther, Ikkala, Belova, & Berglund, 2011), generally resulting in enhanced barrier, mechanical, thermal and fire retardant performance of polysaccharides. However, the production of highly purified polysaccharides in general requires time-consuming delignification, sorption, enzymatic or solvent-extraction steps and/or chromatographic techniques resulting in a high impact on the environment, low yield and increased energy and production costs. Therefore, utilization of polysaccharides in less fractionated states, such as crude WH, a byproduct of the forestry industry, would be desirable from both economic and environmental points of view. This becomes even more interesting when considering the fact that the crude WH has shown performance superior to upgraded counterparts and the highly purified hemicellulose in terms of oxygen barrier properties, thereby meeting or even exceeding the performance requirements for a food packaging film (Ibn Yaich et al., 2012).

Our aim was to design adapted WH barrier films that perform with preserved integrity and as competitive oxygen barriers under the challenging humidity conditions prevailing in real food packages. This is achieved through the incorporation of naturally occurring mineral additives, giving rise to green and low cost, yet high performance WH-based barrier films where the good oxygen barrier properties are maintained even at high relative humidities and where the water vapor permeability is reduced. Herein, film formulations were prepared according to an environmentally friendly and facile protocol, from a crude hardwood derived WH that was generated as side product in the hydrothermal treatment of aspen and birch. Chemically non-modified montmorillonite MMT and talc were used as mineral additives. The effect of the type and content of mineral additive on the barrier, morphological, dynamic thermo-mechanical and tensile properties of the films will be reported.

2. Experimental

2.1. Materials

The hardwood hydrolysate used in this work was a side product of the hydrothermal treatment of wood and kindly provided by Södra Cell AB, Sweden. The hydrothermal treatment is an old technique that has gained increasing interest recently, as a prehydrolysis step in Kraft cooking for producing dissolving pulp, that is mainly used in textile industry (Saadatmand, Edlund, Albertsson, Danielsson, & Dahlman, 2012). The WH was produced from birch mixed with a small fraction of aspen wood chips by hydrothermal treatment in a batch reactor. The wood chips were steamed for 45 min at 100 °C, and then hot water was added until a liquid-to-wood ratio of 6:1 (volume/weight) was reached. The temperature of the mixture was ramped up to 160 °C at a rate of 1 °C min^{-1}, and maintained at 160 °C for 1 h. The process water fraction was removed from the mixture and this wood hydrolysate (WH) was centrifuged for 2 min at 4000 rpm to remove insoluble residues. The centrifuged WH was subsequently lyophilized and stored dry. The WH has an average molecular weight (M_w) of about 2100 g/mol, a polydispersity index value of 3.3 and contained mostly *O*-acetyl-4-*O*-methylglucuronoxylan with a degree of acetylation of 0.26 (Ibn Yaich et al., 2012).

Carboxymethyl cellulose (CMC) sodium salt with a medium viscosity of 400–1000 mPa.s, 2% in H_2O (25 °C) and having 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 previous work (Edlund et al., 2010), showing that films comprising a softwood hydrolysate and 40% (w/w) CMC had very low oxygen permeability (OP) values and good mechanical properties.

Sodium montmorillonite (Closite Na+) denoted MMT and magnesium silicate talc (Finntalc C10) were used as mineral additives. MMT with an exchange capacity of 92 meq/100 mg was obtained from Southern Clay product. Magnesium silicate talc, a product of Mondo minerals B.V, Finland had a hydrophobic nature with a median particle size of 2.3 μm.

2.2. Film preparation

Films were formulated and samples were labeled as shown in Table 1. A typical film was prepared according to the following protocol: first, a specified amount of layered silicate was dispersed in deionized water to obtain a concentration of 1% (w/w) suspension using an ultrasonic homogenizer (Sonics Vibra-cell) for 20 min with an amplitude of 40%, resulting in a very stable suspension. Without ultrasonic homogenization, the talc particles aggregate and float on the water surface due to their hydrophobic character. In contrast, MMT readily forms a very stable suspension due to the negative surface charge. The WH and CMC were dissolved separately in 15 mL portions of deionized water by mixing on a shaking board at a shaking rate of 200 min^{-1} for at least 3 h. Once the CMC was completely dissolved, the layered silicate suspension

Table 1
Compositions used for film preparation based on a crude hardwood hydrolysate (WH) with additional co-components carboxymethyl cellulose (CMC), montmorillonite (MMT) or talc.

Composition % (w/w)				
Films	CMC	WH	MMT	Talc
WH-0	40	60	0	0
WHT-1	40	59	0	1
WHT-2.5	40	57.5	0	2.5
WHT-5	40	55	0	5
WHT-10	40	50	0	10
WHT-20	40	40	0	20
WHM-1	40	59	1	0
WHM-2.5	40	57.5	2.5	0
WHM-5	40	55	5	0
WHM-10	40	50	10	0
WHM-20	40	40	20	0

was added dropwise to the CMC solution under vigorous stirring. Subsequently, the obtained CMC/layered silicate suspension was sonicated for an additional 5 min in an ice bath to enhance the dispersion and exfoliation of the layered silicate. The WH solution was then slowly added to the CMC/layered silicate suspension. The final suspension was stirred overnight on the shaking board and poured into a polystyrene petri dish with an inner diameter of 8.7 cm (area of 60 cm^2) and left to dry at 50% relative humidity (RH) and at 23 °C until constant weight was reached (approximately 3 days). The thickness of the films varied between 0.1 and 0.2 mm.

2.3. Characterization

2.3.1. Oxygen permeability (OP)

OP was determined according to the ASTM standard D3985-02 (ASTM American Society for Testing and Materials) using a Mocon Oxtran 2/20 (Modern Controls, Minneapolis, MN) 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 aluminum foils with a circular exposed area of 5 cm^2. The thickness was measured with a Mitutoyo micrometer and taken as the mean value of five individual measurements. At least two specimens were tested for each film type.

2.3.2. Water vapor permeability (WVP)

WVP was assessed according to the ASTM standard E96/E96M-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 in between aluminum foils 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 kept at 23 °C and 50% RH and weighed by the use of a scale (accurate to 0.001 g) two or three times a day, continuously for 3 days. Two individual tests were done for each sample. WVP was calculated according to the following equation, where ΔP represents the difference in water vapor partial pressure across the film.

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

2.3.3. 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 1 day before being cut into rectangular specimens according to the ASTM D 638 standard (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 operating at a rate of 4 mm min^{-1} and with an initial grip distance of 20 mm.

2.3.4. Dynamic mechanical thermal analysis (DMTA)

Experiments were carried out on a Q800 DMA analyzer (TA Instruments, USA) in tension mode. The typical sample dimensions were: thickness 0.1–0.2 mm, length 25 mm and width 5 mm. Samples were equilibrated at 25 °C for 5 min and heated to 320 °C with a heating rate of 3 °C min^{-1} and a frequency of 1 Hz and the distance between clamps was around 15 mm.

2.3.5. Scanning electron microscopy (SEM)

A Hitachi S-4800 scanning electron microscope, operated at 1 kV, was used to capture secondary electron images of the film cross-sections. The films were immersed in liquid nitrogen, fractured and the surface of cryo-fractured films was examined without any electrically conductive coatings.

3. Results and discussion

Crude aqueous process liquor, a wood hydrolysate (WH), was obtained as a discarded side product from hydrothermal treatment of birch and aspen wood chips. The WH was not subjected to membrane filtration or any other upgrading pretreatments but used as the major feedstock for the preparation of all renewable and low-cost oxygen barrier films. The WH was mixed with CMC, a water soluble and high molecular weight polysaccharide co-component, and either montmorillonite MMT or talc in their natural forms as mineral additives. The CMC, renewable-based and commercially available at a reasonable cost, was selected due to its ability to form strong secondary bonds with the oligo- and polysaccharides in the WH thereby generating a densely packed matrix, and contributing positively to the mechanical performance of the films (Edlund et al., 2010). The chemically non-modified montmorillonite MMT and talc were selected on the basis of their barrier enhancement capabilities, availability and price.

The WH was mainly composed of oligo- and polysaccharides (~86% (w/w)) together with ~6% (w/w) lignin, while water, ash and extractives were present in very small amounts. Since the WH was derived from a mixture of birch and aspen, the main hemicellulose constituent was *O*-acetyl-4-*O*-methylglucuronoxylan, a branched polysaccharide with 4-*O*-methyl glucuronic acid side groups attached to the backbone of xylose repeating units. The xylose units are acetylated to a degree of 0.26 per monosaccharide (Ibn Yaich et al., 2012).

A facile and environmentally friendly water based film processing technique was adopted, taking advantage of the water solubility of both WH and CMC together with the fact that layered silicate particles are easily dispersible using a simple ultrasonification pre-treatment. The layered silicate content was varied from 0 to 20% (w/w), while the content of the CMC co-component was fixed to 40% (w/w), based on the encouraging results of previous work, showing that films comprising 40% (w/w) CMC had excellent oxygen permeability values and good mechanical performance (Edlund et al., 2010). The processing conditions adopted were purposely chosen to yield WH based films with homogeneously distributed layered silicate particles, while limiting the energy input as no heating was used throughout the preparation procedure.

3.1. Oxygen and water-vapor-barrier performance of films

In the food packaging industry, oxygen and water vapor permeability of the packaging material are key factors defining the

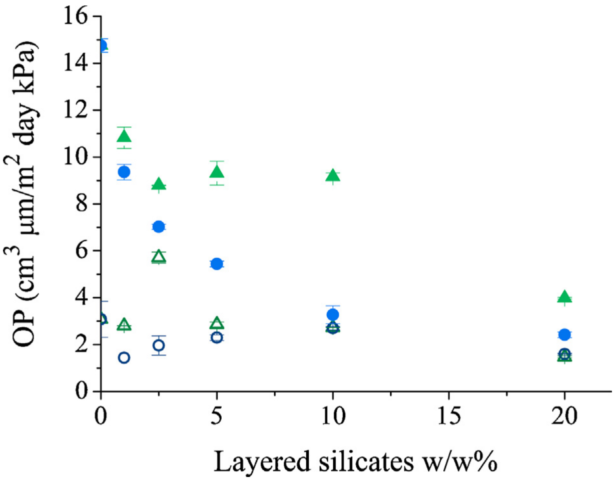

Fig. 1. Oxygen permeability (OP) of wood hydrolysate based films with different layered silicate content: WHM film with montmorillonite at a relative humidity RH of 50% (○) and 80% RH (●), WHT film with talc at a 50% RH (△) and 80% RH (▲). Data are presented as the mean values of at least two measurements from two separate samples.

shelf-life of the contained product. Accordingly, the oxygen permeability (OP) and water vapor permeability (WVP) properties of WH based films with different layered silicates and contents were assessed, as shown in Figs. 1 and 2, respectively. The incorporation of layered silicate, regardless of its type, had a small effect on the OP values at 50% RH, as the WH-0 films without any layered silicate added already have very low OP values. However, a dramatic change in OP was observed at 80% RH. At such humid conditions, absorbed water molecules from the surrounding environment act as plasticizers, increase the free volume in the material and cause the WH-0 film oxygen barrier properties to deteriorate. The incorporation of layered silicates was very effective as the OP at 80% RH dropped from approximately 15 cm^3 µm/m^2 day kPa for the pristine WH-0 to values as low as 1.5 cm^3 µm/m^2 day kPa for composite films containing 20% (w/w) of the mineral additive. This is a factor of 10 better than ever managed before for WH based films. Moreover, this is better by factors 280, 10 and 8 than high density polyethylene (HDPE), polyethylene terephthalate (PET) and ethylene vinyl alcohol copolymer (EVOH), respectively (Miller & Krochta, 1997). WH based films containing montmorillonite MMT (WHM) systematically showed lower OP than films containing talc (WHT). The MMT particles have a higher aspect ratio and adopt a preferential orientation parallel to the film surface as proven by SEM and presented in Fig. 3, thus offering a higher capability to extend the diffusion oxygen path length through the film matrix as elaborated later in this section. The OPs of WHM films reach values as low as 0.62 and 1.49 cm^3 µm/m^2 day kPa at 50 and 80% RH, respectively. WHT films reach OPs of 1.48 and 3.98 cm^3 µm/m^2 day kPa at 50 and 80% RH, respectively. A similar trend was observed for WVP, despite the relatively high standard deviations at low amounts of added layered silicates, which is due probably to the fact that at low additive contents even small fluctuations in the specimen composition or structure could lead to a noticeable deviation in performance. The water vapor barrier performance increased with increasing layered silicate content. The incorporation of 20% (w/w) MMT or talc resulted in a decrease of 68% and 40% in the WVP, respectively. A similar approach of incorporation of layered silicate was also adopted for other biopolymers such us biodegradable polyesters (Sanchez-Garcia & Lagaron, 2010) chitosan (Rhim, Hong, Park, & Ng, 2006), soy and wheat gluten proteins (Kumar, Sandeep, Alavi, Truong, & Gorga, 2010; Olabarrieta, Gaellstedt, Ispizua, Sarasua, & Hedenqvist, 2006) and cellulose (Ebina & Mizukami, 2007; Liu & Berglund, 2012) which resulted in improvements in either WVP or OP.

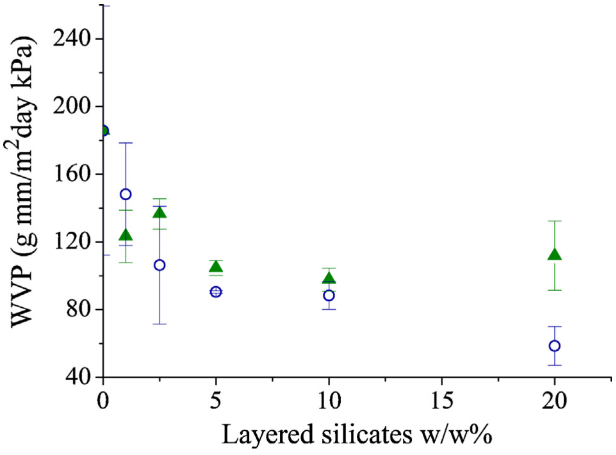

Fig. 2. Water vapor permeability (WVP) at 100/50% RH gradient of wood hydrolysate based films with different layer silicate content: WHM films with montmorillonite (○) and WHT films with talc (▲). Data are presented as the mean values of at least two measurements from two separate samples.

This reductions in OP and WVP is related to the plate-like geometry and the highly compact crystalline structure of layered silicates, acting as a physical barrier against the permeation of oxygen and water molecules through the matrix even at higher RH conditions, lengthening the travel path of the permeates by making it more tortuous. In addition, WH and CMC properties, such as thermal transition temperatures, free volume and molecular mobility are changed in the presence of layered silicates, further reducing the permeability. It is noteworthy that the reduction in the WVP also contributes to the reduction in OP by reducing amount of water in the system leading to the preservation of the inherent good barrier performance of WH and CMC.

3.2. *Morphology of films*

To better understand the relationship between morphology and barrier performance, cryogenically fractured surfaces of the prepared films were examined by SEM. The SEM images of some representative WH films containing different amounts of layered silicates are compared in Fig. 3 and in supplementary information (Fig. S1). WH-0 films without layered silicates show a smooth, compact and void free morphology. SEM images of WHM samples with MMT indicate that the MMT particles are well dispersed and uniformly distributed across the cross-section and oriented preferentially parallel to the film surface. The images of WHT samples with talc on the other hand, show clearly that talc particles are uniformly distributed across the cross-section of the films, however they are poorly dispersed, thus fewer in number and larger in size when compared to the MMT. Furthermore, because of their low aspect ratios, it was difficult to assess whether or not the talc particles adopt a preferential orientation. As estimated from the SEM images, the typical thickness of the MMT and talc particles is in the range of 60 nm and 1500 nm, respectively.

X-ray diffraction results presented in supplementary information (Fig. S2) show that WH-0 and all WHM films reveal no distinct crystalline peaks, whereas WHT films display a sharp peak at 9.3°. WH based films are hence amorphous. Furthermore, the absence of the MMT diffraction peaks in 5° to 40° region for WHM films suggests that MMT platelets are either exfoliated as in the case of WHM-1, WHM-2.5 and WHM-5 or intercalated as in the case of WHM-20, where the MMT d0 0 1 peak was shifted slightly below 5° for 2θ angles. This suggests that the WH, CMC and/or water were able to intercalate into the MMT gallery,

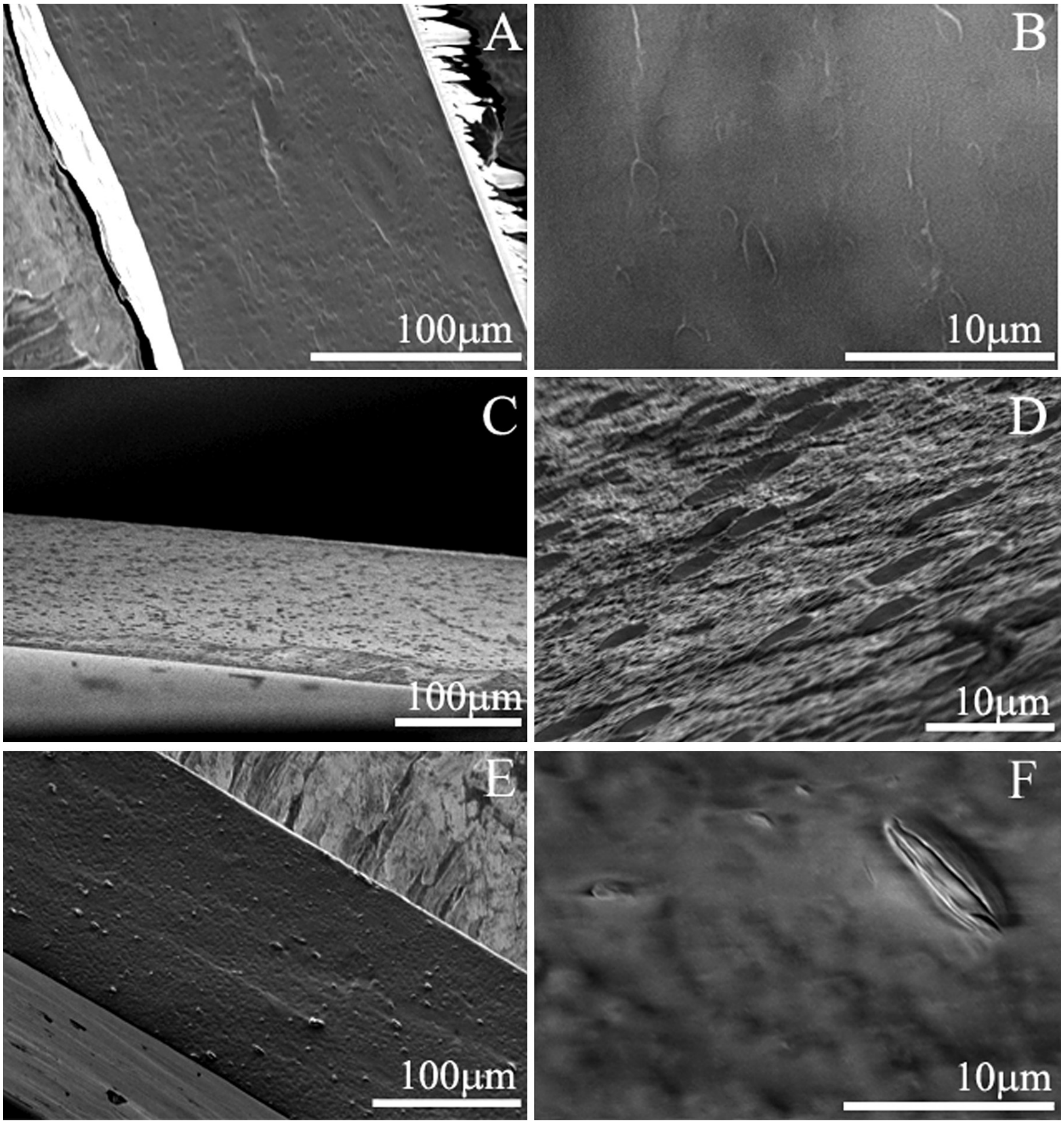

Fig. 3. SEM images of cross-sectional surfaces of cryo-fractured WH films: WH-0 film without layered silicates at magnifications 500× in (A) and 5000× in (B), WHM-5 film with 5% (w/w) montmorillonite at magnifications 300× in (C) and 3000× in (D), WHT-20 film with 20% (w/w) talc at magnifications 350× in (*E*) and 5000× in (F).

enlarging the interlayer spacing between the MMT platelets and reducing the periodicity. Further assessment with AFM, shown in supplementary information (Fig. S3), of the lamellar structure of MMT particles in the water suspension prior mixing with CMC and WH shows that MMT particles have a thickness less than 2 nm. This is in agreement with the XRD that showed that MMT particles are in exfoliated state at lower MMT loading. On the other hand, WHT film diffraction patterns reveal distinct diffraction peaks originating from the talc particles, indicating that the interlayer spacing of talc particles did not change upon mixing with other film constituents.

3.3. Dynamical mechanical performance of films

To better elucidate how incorporation of layered silicates into the WH formulation resulted in a better barrier performance, we need to study the interaction between the layered silicates and other components. Dynamical mechanical thermal analysis (DMTA), is an interesting technique in this respect, being sensitive to the response of structural changes on a molecular level that characterize the thermo-mechanical behavior of the films as well as the interaction between the films' individual components.

As seen in Fig. 4, two thermal transitions were observed. The first one at 195–206 °C originates from the α-relaxation of WH and the second one around 246–258 °C originates from the α-relaxation CMC. Noteworthy, the tan δ peak of the pure CMC was shifted from 277 °C to 251 °C, closer to the maximum tan δ of the WH, when these two components were mixed together, which indicates a good interaction between the CMC and the WH. This is in good agreement with the previously reported observation based on Hansen's solubility parameter calculations, positron annihilation lifetime spectrum (PALS) and OP measurements all indicating that CMC has a strong molecular affinity to WH, giving rise to a dense molecular packing and a low oxygen permeability (Ibn Yaich et al., 2012; Ryberg et al., 2011). Although, the incorporation of layered silicate particles into the WH based films leads to

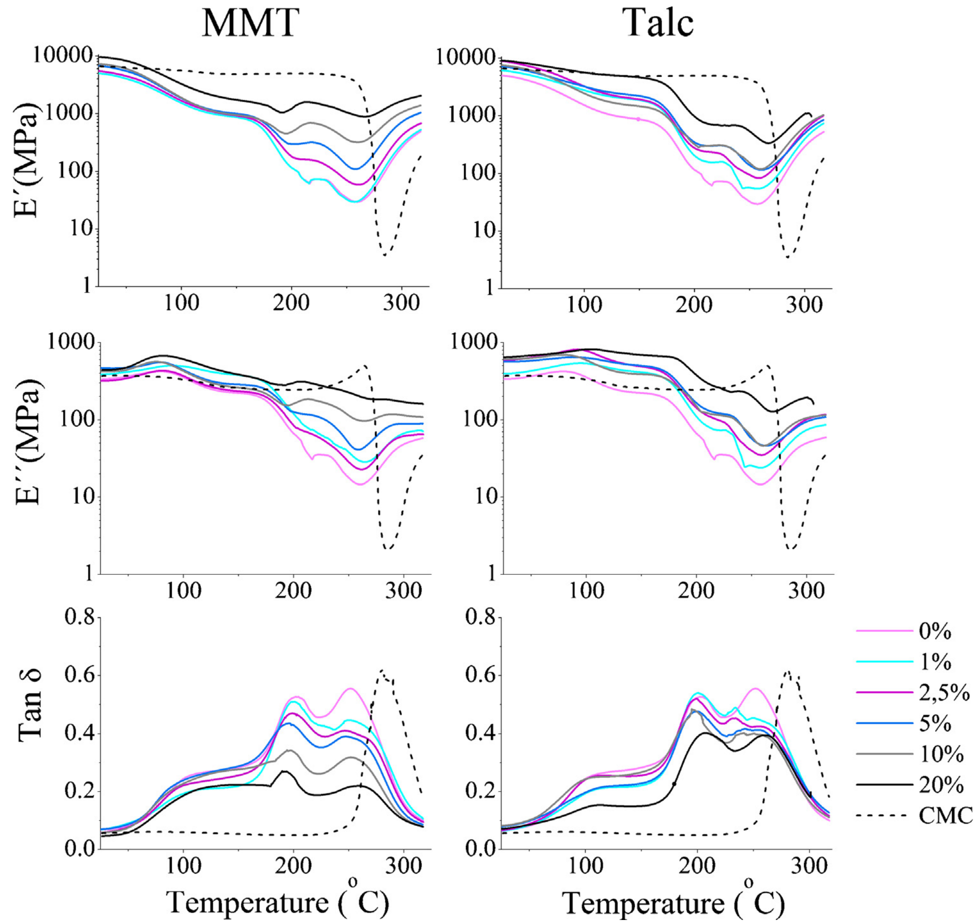

Fig. 4. DMTA curves of the storage modulus E', loss modulus E'' and tan δ versus temperature for pure WH based films, pure CMC, and WH films containing 1, 2.5, 5, 10 and 20% (w/w) MMT or talc. Data are presented based on one measurement.

a system with an apparently higher storage modulus E', the different films have different thicknesses (presented in Table 2) and therefore some of WH-based films with layered silicates may not be necessarily stiffer than the films without layered silicate. An increase of the layered silicate content lifts and straightens the storage modulus–temperature curves, demonstrating the reinforcing effect of layered silicates. Furthermore, there are slight shifts of both thermal transition tan δ peaks toward lower temperatures with talc incorporation at loading 1–10% (w/w). However at higher talc loading, 20% (w/w), both thermal transitions tan δ peaks shift back to higher temperatures exceeding the WH tan δ peak temperature. A rather similar behavior is observed for WHM, but at 20% (w/w) MMT loading only the second thermal transition tan δ peak shifts back to a higher temperature while the first thermal transition continues shifting to lower temperatures. The tan δ shifts to higher temperatures at higher layered silicates loading suggest that the mobility of WH and CMC chains is reduced, which either could be due to adsorption in case of talc or due to intercalation in case of MMT, which is in agreement with XRD data and SEM observations.

To compare the effect of the two types of layer silicates on the thermo-mechanical behavior of the WH-based films, storage modulus E' and tan δ versus temperature of WH films without any layered silicates added and composite films containing similar amount 20% (w/w) of either MMT (WHT-20) or talc (WHM-20) are shown in Fig. 5. Below 60 °C, both (WHT-20) and (WHM-20) have almost the same E'. Starting from 60 °C, there is a slight decrease in E' associated with a molecular relaxation of low molecular weight components. This decrease is steeper for the film containing MMT

Table 2
Tensile properties of WH based films, pure CMC as well as WH films containing 1, 2.5, 5, 10 and 20% (w/w) montmorillonite MMT (WHM) or talc (WHT).

	Average thickness (mm)	Tensile strength (MPa)	Strain-to-break (%)	*E*-modulus (GPa)
CMC	0.09	77.3 ± 5.2	7.9 ± 2.3	3.2 ± 0.7
WH-0	0.17	67.6 ± 10.5	4.7 ± 1.0	2.9 ± 0.1
WHM-1	0.13	66.5 ± 11.2	3.8 ± 0.7	2.5 ± 0.9
WHM-2.5	0.18	62.5 ± 17.5	2.6 ± 0.9	3.3 ± 0.2
WHM-5	0.16	61.1 ± 10.9	2.3 ± 0.2	3.6 ± 0.4
WHM-10	0.16	63.3 ± 15.3	2.1 ± 0.5	3.5 ± 0.5
WHM-20	0.14	66.9 ± 10.5	2.2 ± 0.3	3.9 ± 0.3
WHT-1	0.14	65.8 ± 6.9	3.1 ± 0.2	3.0 ± 0.5
WHT-2.5	0.12	72.2 ± 8.9	4.3 ± 0.3	2.4 ± 0.5
WHT-5	0.20	67.7 ± 6.7	3.0 ± 0.2	3.1 ± 0.4
WHT-10	0.14	61.0 ± 15.3	2.4 ± 0.4	3.9 ± 1.2
WHT-20	0.10	77.6 ± 2.4	3.6 ± 0.4	3.6 ± 0.5

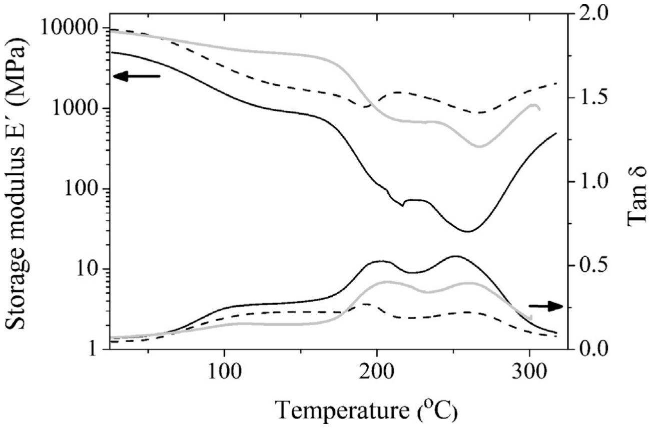

Fig. 5. DMTA curves of the storage modulus E' and tan δ versus temperature for WH based films: WH film without layered silicates (black line), WHT-20 composite film with 20% (w/w) talc (gray line), and (WHM-20) composite film with 20% (w/w) montmorillonite MMT (dashed line). Data are presented based on one measurement.

than for films with talc, although the MMT particles have a much larger specific surface area, higher aspect ratio, and stiffness than talc. This observation indicates that the WH and CMC chains have a higher interfacial adhesion to talc than to MMT which restricts the molecular motion, thereby improving thermal stability. This is reasonable considering the ionic repulsive forces between the negatively charged MMT and the carboxylate ions on both CMC and 4-*O*-methyl glucuronic acid side chain groups in the WH hemicellulose, making the adsorption of the macromolecular chains less favorable and weakening the stress transfer to MMT particles.

3.4. Tensile performance of films

The uniaxial tensile mechanical performance of pure CMC, WH based films with and without layered silicates was examined. The tensile data presented in Table 2 reveal that the addition of both talc and MMT results in a slight decrease in the tensile strain as well as an increase in the Young's modulus which is in agreement with the results obtained by DMTA measurements. On the other hand, the tensile strength values did not show any clear trend when varying the amount of layered silicate content, fluctuating around 70 MPa. This is due probably to the fact that the tensile strength depends on additional failure mechanisms and to the difference in the films thicknesses. Furthermore, WH-0 already has a high tensile strength at room temperature which makes the effect of the layered silicates less obvious than for other bio-based polymer/layered silicate systems where the matrices are initially much softer (Nedi, Di Maio, & Iannace, 2012; Zhu & Wool, 2006).

Table ST1 in the supplementary information shows the moisture uptake and density values of the WH based films. There are differences in density and moisture between the different WH films but there is no clear trend that correlates the variation in the barrier and mechanical performance with the incorporation of layered silicates.

In summary, the introduction of layered silicates into the WH based films did bring significant improvements in terms of OP, WVP and the thermo-mechanical properties. Consequently, WH based films with layered silicates have a low and stable oxygen barrier performance over a wide range of RH conditions demonstrating the potential of these materials to be used as oxygen barrier layers in multilayer food packaging materials. The improvement in the water vapor resistance of WH based films with layered silicates is particularly important as it can lead to a reduction in both the package weight and the use of petroleum based polymers conventionally used for their water vapor barrier property, as the WH based layer with layer silicates would act as a barrier for both oxygen and water vapor.

Beside these functional benefits, WH based films in general have major environmental benefits. Unlike other renewable resources based polymers such as PHA, PLA, and thermoplastic starch that are produced from agricultural products, the WH has been produced solely from forest resources that neither compete with food production in terms of agricultural land and resources nor require much fertilizers and toxic pesticides during its growing period. In addition, no organic solvent is used during the WH production cycle.

Furthermore, the WH based layer could be very advantageous when it comes to disposal of multilayer packages. Since WH and CMC are water soluble, the WH based layer may readily come apart from the rest of the package upon simple water immersion, thus facilitating the individual recycling of the different layers. The different components of WH based layer could be recovered, recycled or landfilled in principle without any potential impact on the environment.

All together, this could make WH based film one of the greener, affordable and most sustainable oxygen barrier alternatives to fossil derived oxygen barrier materials currently in use in the food packaging industry.

4. Conclusions

We have taken the next step and customized the wood hydrolysate (WH) barrier films that are already good oxygen barriers to make them even better barriers at extra high RH and demonstrated that these WH based films are a factor 10 better in terms of oxygen barrier performance than what was previously reported. This was achieved through the incorporation of naturally occurring layered silicates as mineral additives using a simple and green water based procedure. Films were prepared from a crude WH without further upgrading, recovered as a side stream product of hydrothermal treatment of a mixture of birch and aspen and containing mainly *O*-acetyl-4-*O*-methylglucuronoxylan. Formulations of WH together with CMC and either montmorillonite MMT or talc were prepared and the addition of both MMT and talc had a major impact on the film performance. The MMT, having a higher aspect ratio, being better dispersed across films cross section, and preferentially oriented parallel to the film surface direction, resulted in films with higher water and oxygen barrier performance. On the other hand talc particles, being non-charged on the surface and thus having better interfacial adhesion with WH and CMC yielded films with a better thermo-mechanical performance. These developed WH based materials may also be used as coatings, or as barrier layers in multilayer packaging materials, accordingly increasing the package competitiveness in terms of performance, cost and environmental foot print.

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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.2012.10.079.

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