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Isolation, characterization and valorization of hemicelluloses from *Aristida pungens* leaves as biomaterial

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ABSTRACT

Aristida pungens, a perennial grass widely distributed on the Algerian arid regions, may potentially be the source of raw cell wall material to promote a local development in North Africa. Hemicelluloses, the main matrix cell wall polymers of this species were isolated from leaves with 14% KOH aqueous solution, characterized and converted as plastic material. The extraction procedure yielded two hemicellulose fractions (A and B) accounting for 3.5 and 10.1% of the starting leaf material, respectively. GC and ^{13}C NMR showed the presence of xylose as the main component with arabinosyl residues. Both analyses indicate that hemicelluloses from *A. pungens* leaves are arabinoxylans. Arabinoxylans were transformed into hydrophobic plastics by grafting of lauroyl chloride. The resulting materials were characterized by FT-IR and ^{1}H NMR spectroscopies, with both mechanical and thermogravimetric analysis.

1. Introduction

Most of the polymers used in plastic industry come from petroleum. Originally, plastics like polyethylene, polypropylene, polystyrene and polyvinyl chloride were produced abundantly as they met several criteria such as weak cost, solidity, flexibility and resistance to microorganism degradation. However, due to the exhaustion of petroleum reserves and pollution generated by the destruction of synthetic plastics, the design of new biodegradable plastics with organic polymers from renewable resources is needed to promote sustainable development.

Biodegradable plastics can be made from proteins, lipids, polysaccharides or combination of these compounds (Gontard & Guilbert, 1994). The most commonly used polysaccharides are cellulose and starch, but other polymers from plant and algal cell walls (pectins, carraghenans and alginates), tree exudates (arabic gum), seeds (guar gum) or bacterial production (xanthan and gellan gum) are also suited (Krochta, Baldwin, & Nisperos-Carriedo, 1994). Interestingly, the use of hemicelluloses as raw material for the production of potentially biodegradable plastics has not been as extensively studied as cellulose and starch despite their abundances and structural diversities (Gabrielii & Gatenholm, 1998; Gabrielii, Gatenholm, Glasser, Jain, & Kenne, 2000; Kayserilioğlu, Bakir, Yilmaz, & Akkaş, 2003; Höije, Gröndahl, Tømmeraas, & Gatenholm, 2005).

Hemicelluloses are a family of heteropolysaccharides that can be extracted from plant tissues either by water and/or aqueous alkali (Gabrielii et al., 2000; Whistler, 1993). Depending on the phylogeny, the hemicelluloses can be glucans, xyloglucans, xylans, arabinoxylans, mannans, gluco- or galactomannans with different substitution motifs. It is well admitted that hemicelluloses from Poaceae have a (1 → 4)-β-D-xylopyranosyl backbone with different branching patterns consisting of mono-, di- and tri-saccharide side chains composed of xylopyranosyl, arabinofuranosyl, and/or galactopyranosyl units. In addition, these arabinoxylans can also be substituted with D-glucuronopyranosyl and/or its 4-*O*-methyl derivative (Verbruggen, Beldman, & Voragen, 1998; Ebringerova & Heinze, 2000). Finally, the fine structure of arabinoxylans greatly varies among plant species and even among organs or tissues (Rantanen et al., 2007).

Aristida pungens (Poaceae) is a perennial grass, growing in the dry regions of North Africa with leaves as tall as one meter. Whereas its extensive root system prevents sand erosion, leaves are valuable sources of forage and pulp (Béchet, Nedjraoui, & Djebaili, 1982). To ensure the survival of this species, leaves must be cut every 2 or 3 years. To date, a minor part of this raw material is either used to feed cattle or to produce art craft, most of the

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remaining plant material is to date unexploited. Thus, investigations aiming to increase the value of such plant residue are important.

In this work, we chose to focus on *A. pungens* hemicelluloses extracted from leaves although cell walls are also composed of other components. To the best of our knowledge, this is the first report on the characterization of hemicelluloses from this species. In addition, we also investigated the thermal and mechanical properties of plastic materials produced by fatty acylation of these natural polymers.

2. Experimental

2.1. Plant material

Leaves of *A. pungens* (Poaceae) were harvested in El-Kheiter, located in the west Algerian mountains, cut into small fragments, dried in an oven at 50 °C for 72 h and finally ground to a fine powder.

2.2. Extraction of hemicelluloses

The scheme for hemicellulose extraction from the *A. pungens* leaves is shown in Fig. 1. Leaf powder (20 g) was refluxed twice with a chloroform–methanol (150/150 ml) mixture for 14 h, treated with ethanol for 2 h at room temperature, and finally with boiling ethanol for 2 h. The insoluble cell wall residue recovered by filtration with nylon mesh was then dried at 50 °C for 48 h.

Cell wall material was sequentially treated under stirring; (i) in water for 2 h at room temperature; (ii) in boiling water for 2 h; (iii) in 1% aqueous ethylenediamine tetraacetic acid (EDTA) pH 6.8 at 80 °C for 4 h. To each step, extracts were collected by filtration, precipitated by addition of 3 volumes of 95% ethanol, centrifuged, resuspended in water and dialyzed against distilled water to obtain the room temperature water-soluble polysaccharides (RTW-SP), hot water-soluble polysaccharides (HW-SP) and EDTA-soluble polysaccharides (EDTA-SP).

The remaining insoluble residue was then treated with 1% NaOH in 70% ethanol solution at 80 °C for 2 h to solubilize lignins (Gabrielii et al., 2000). The weight loss was defined as NaOH–EtOH lignin. The NaOH–EtOH soluble polysaccharides (NaOH–EtOH SP) were recovered by precipitation of the extract with 3 vol. ethanol. Finally, the insoluble residue was treated with 14% KOH aqueous solution for 14 h at room temperature. After filtration, the extract was acidified to pH 5–6 by addition of glacial acetic acid. Upon acidification, a precipitate was formed and recovered by centrifugation to yield hemicellulose A. The supernatant was concentrated under reduced pressure, dialyzed against distilled water and precipitated with ethanol (3 vol.) resulting in a fraction named hemicellulose B. The alkali insoluble residue was oven dried.

2.3. Chemical analyses of the cell wall fractions

2.3.1. Colorimetric assays

Total carbohydrate and uronic acid contents were estimated by the phenol sulfuric acid (Dubois, Gilles, Hamilton, Rebers, & Smith, 1956) and the *m*-hydroxybiphenyl methods (Blumenkrantz & Asboe-Hansen, 1973), respectively.

2.3.2. Gas chromatography

Hemicellulosic fraction B (1 mg) was pre-hydrolyzed with 500 μl trifluoroacetic acid 2 N for 4 h at 80 °C and air dried. Then, the samples (100 μg) were incubated with 250 μl of anhydrous methanol–HCl 0.5 M for 20 h at 80 °C under nitrogen. After drying under nitrogen flow, the methyl-glycosides were acetylated (Zanetta, Timmerman, & Leroy, 1999), and the glycoside derivative mixture was analysed by gaz chromatography on a Varian 3900 apparatus equipped with a CP Sil 5-CP column (0.53 mm × 50 m, fused silica, Varian) and a flame ionization detector. Nitrogen was used as carrier gas (5.5 psi) and the oven temperature program was as follow: started at 150 °C for 10 min, rose to 200 °C at 0.8 °C/min, maintained at 200 °C for 7 min, increased to 240 °C at 5 °C/min and finally kept at 240 °C for 20 min. Monosaccharides were identified by comparison of their retention times with authentic standards and quantified by reference to lysine used as internal standard.

2.4. Plastic preparation from hemicelluloses

The method was adapted from described by Satgé et al. (2002). Briefly, pooled hemicelluloses A and B (3 g, 0.023 mol of anhydroxylose unit) were solubilized in 150 ml of 8% (w/v) LiCl/DMAc for 1 h at 90–100 °C. Polymers were then acylated for 1 h at 90–100 °C, under stirring, by addition of lauroyl chloride (6 equiv per anhydroxylose unit, 0.143 mol, 30.9 ml) using 3 equiv of DMAP (2 equiv, 0.046 mol, 5.6 g) as basic catalyst. The acylated polysaccharides were recovered by precipitation with methanol (450 ml) and recovered by filtration. The product was purified by successive solubilisations/precipitations in CH_2Cl_2 and methanol, respectively, and finally converted into plastic by casting.

2.5. Spectroscopic analysis

FT-IR spectroscopy was carried out with a FT-IR Bruker Vector 22 apparatus equipped with a diamond ATR accessory.

NMR spectroscopy was performed to analyze both hemicelluloses and plastics. For analysis of hemicellulosic fraction, ^1H NMR spectra were recorded at 75.5 MHz, using a Bruker DPX 300 Avance spectrometer with samples dissolved in DMSO-d_6 (^1H NMR) using tetramethylsilane (TMS) as internal standard. ^{13}C NMR spectra were acquired on a Bruker Avance 400 spectrometer with a 5 mm-BBO probehead (^{13}C 100.67 MHz). Spectra were recorded at 353 K in DMSO-d_6 and TMS was used as internal standard (δ ^{13}C at 0).

For hemicellulosic-based plastic films, ^1H NMR spectra were recorded with samples dissolved in $CDCl_3$ (^1H NMR) using tetramethylsilane (TMS) as internal standard, and were useful for the calculation of the degree of substitution (DS; number of fatty chains grafted per anhydroglucose units). These spectra can be divided into three parts: carbohydrate protons between 2.75 and 5.50 ppm, fatty chain methylene protons between 1.20 and 2.32 ppm and fatty chain methyl protons at 0.89 ppm. Hemicellulose ester DS was determined according to the following formula:

$$\mathrm{DS} = \frac{8 \times (I_{\mathrm{CH_3}})}{3 \times I_{\mathrm{C}} + I_{\mathrm{CH_3}}}$$

with I_{CH_3} corresponding to methyl protons integration and I_C as carbohydrate protons integration.

2.6. Mechanical properties

Uniaxial tensile tests were performed with plastic films cut into dumbbell-shaped samples with a thickness ranging from 0.31 to 0.41 mm. Tensile velocity was fixed at 1 mm/min. Data were the mean of 13 replicates.

2.7. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed using a Setaram TG-DTA 92 apparatus. Samples (15–20 mg) were heated from 20 to 400 °C at 5 °C/min rate. Degradation temperature (T_d) was

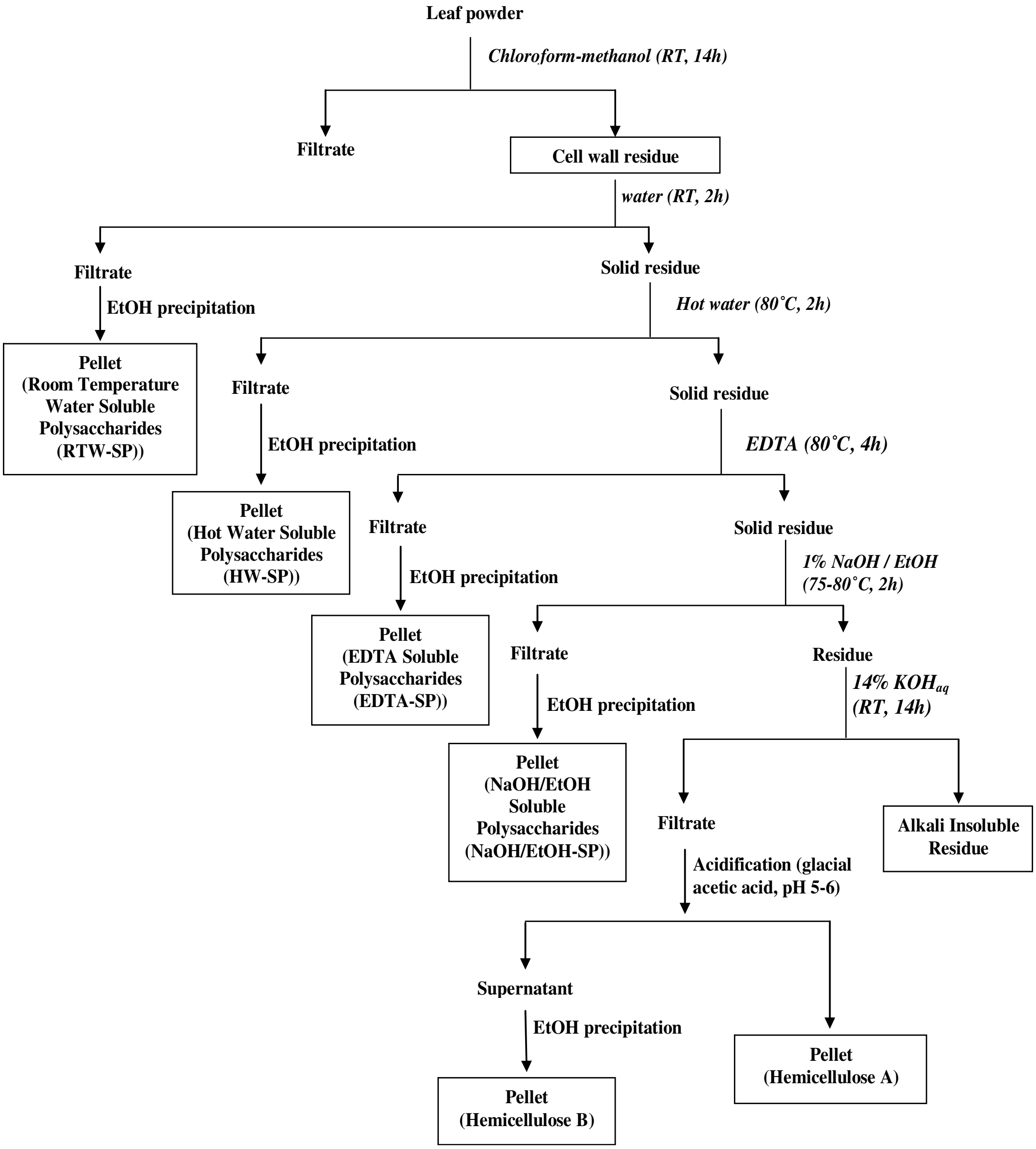

Fig. 1. Protocol for sequential extraction of cell wall polymers from *Aristida pungens* leaves (RT, room temperature).

determined by the loss of 0.5% of the material initial weight during the heating process.

3. Results and discussion

3.1. Recovery and characterization of extractible polysaccharides

Pre-treatment with organic solvents is often used to remove liposoluble components such as waxes and pigments. This treatment yielded an insoluble cell wall residue (67% of the initial leaf powder).

Recovery and sugar composition of extracted polysaccharides are reported in Table 1. Polysaccharides from RTW-SP, HW-SP, and EDTA-SP accounted for 4.1% of dry matter leaves. Monosaccharide compositions of the three extracts showed 15–39% GalA indicating that RTW-SP, HW-SP and EDTA-SP were GalA-rich pectic material which have been proposed recently as side chains of rhamnogalacturonan1 (Vicken et al., 2003). In addition, they are also enriched in Xyl*p* (35–47%) and Ara*f* (11–19%). Undoubtedly, in grasses most of the xylosyl and arabinosyl residues are constituent of hemicelluloses (Hatfield, 1989). Therefore, it appears that a low amount of hemicelluloses were extracted with treatments normally used to solubilize pectins. Finally, most of the glucose detected in those extracts may be related to the mixed β-(1 → 3),(1 → 4)-linked glucans found transiently during the development of Poaceae (Buckeridge, Rayon, Urbanowicz, Tiné, & Carpita, 2004).

Delignification treatment (1% NaOH in 70% EtOH) also solubilized 0.9% of polysaccharides related to the starting leaf material. Xyl (56.5%) and Ara (17%) being the major monosaccharides detected, some arabinoxylans appear to be co-extracted during this process. These data are in accordance with those found in literature (Ford, 1986; Dusterhöft, Posthumus, & Voragen, 1992), suggesting that arabinoxylans were covalently linked with lignins. Moreover, it was also reported that up to 8% of the total hemicelluloses from different oat tissues were lost during sodium chlorite delignification (Buchala, Fraser, & Wilkie, 1972). Pectic polymers were also present since their monosaccharide

Table 1
Yields and monosaccharide compositions of the extractible cell wall polysaccharides

Fraction	Yield[a]	Monosaccharide composition (mol%)							
		Rha	Ara	Xyl	Glc	Gal	Man	GalA	GlcA	MeGlcA
RTW-SP	2.9	4.3	18.9	47.2	6.8	7.2	–	15.6	nd	nd
HW-SP	0.7	2.6	15.1	37.3	7	5.4	–	32.6	nd	nd
EDTA-SP	0.5	1.9	11.2	34.9	6.9	5.9	–	39.2	nd	nd
NaOH/EtOH-SP	0.9	4.0	17.0	56.5	3.7	2.1	–	16.7	nd	nd
Hemicellulose A	3.5	1.8	9.3	82.6	2.9	–	tr	3.4	nd	tr
Hemicellulose B	10.1	4.1	23.1	68.1	1.8	2.5	tr	0.3	nd	tr

(RTW-SP, room temperature water-soluble polysaccharides; HW-SP, hot water-soluble polysaccharides; EDTA-SP, EDTA-soluble polysaccharides; NaOH/EtOH-SP, NaOH/EtOH soluble polysaccharides).

[a] Yield expressed as % from starting leaf powder (dry weight); nd, not detected; tr, traces i.e., < 0.5%; Rha, rhamnose; Ara, arabinose; Xyl, xylose; Glc, glucose; Gal, galactose; Man, mannose; GalA, galacturonic acid; GlcA, glucuronic acid; MeGlcA, 4-*O*-methyl-glucuronic acid.

markers, GalA and Rha were detected (16.7% and 4.0%, respectively).

Preliminary data using a three step procedure for hemicellulose extraction with 4, 14 and 24% KOH aqueous solution have recovered 53.9, 31.2 and 14.9% of the total hemicelluloses, respectively. From those results, and in order to minimize the losses, a one step extraction with 14% KOH was carried out. Two hemicellulosic fractions were separated: hemicellulose A (3.5% of the dry starting leaf material) being soluble in KOH only at pH higher than 10, and hemicellulose B (10.1% of the dry starting leaf material) remaining soluble in KOH upon acidification with glacial acetic acid. As shown in Table 1, the major monosaccharidic units in hemicelluloses A and B were D-xylose (ca. 82.6 and 68.1%, respectively) and L-arabinose (9.3 and 23.1%, respectively). These data suggested that hemicelluloses extracted from *A. pungens* leaves are mainly arabinoxylans (AX) since glucuronic acid and 4-*O*-methyl-glucuronic acid were not detected or as traces.

FT-IR spectrum of total hemicelluloses is shown in Fig. 2a. It displays typical bands of xylans between 1125 and 1000 cm^{-1} (Sun, Tomkinson, Ma, & Liang, 2000), and in the anomeric region (700–950 cm^{-1}), a sharp band at 897 cm^{-1} characteristic of β-glycosidic linkages between sugar units (Kayserilioğlu et al., 2003; Kačuráková, Capek, Sasinková, Wellner, & Ebringerová, 2000). It confirms that the polysaccharide backbone is built up of β-linked xylose units. The strong band at 1037 cm^{-1} was associated with the C–O, C–C stretching or C–OH bending in hemicelluloses (Sun, Lawther, & Banks, 1996). Another band assigned to hemicelluloses also appeared at 1370 cm^{-1} (Xiao, Sun, & Sun, 2001). The presence of arabinosyl side chains is characterized by a band at 1168 cm^{-1}, corresponding to the C–O–C vibrations in the anomeric region of hemicelluloses (Xiao et al., 2001). The band at 1410 cm^{-1} indicates the presence of carboxylate groups. The lack of signal at 1745 cm^{-1} for the acetyl and uronic ester groups of the hemicelluloses indicates that the alkali treatment completely saponified these ester bonds from the hemicelluloses (Sun & Sun, 2002). The strong signals in the region 2900–3300 cm^{-1} are associated with the stretching vibrations of CH groups and OH (Sun & Tomkinson, 2002).

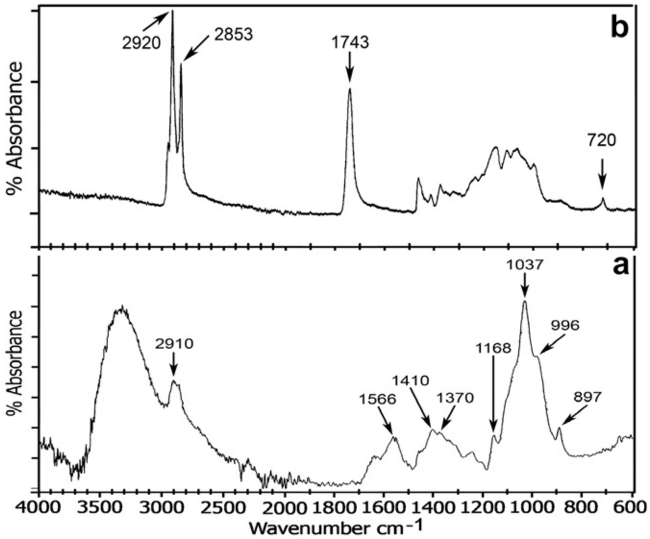

Fig. 2. FT-IR spectra of native (a) and esterified (b) arabinoxylans.

^{13}C NMR spectrum of the total hemicellulosic fraction, illustrated in Fig. 3, confirmed that hemicelluloses are arabinoxylans. Indeed, the strongest signals at 102.8, 76.6, 75.0, 73.6 and 64.3 ppm are assigned to the C–1, C–4, C–3, C–2 and C–5 of the (1 → 4)-linked β-D-Xyl*p* units, respectively. Signals at 108.3, 87.0, 81.5, 78.8 and 62.9 ppm are characteristics for C–1, C–4, C–2, C–3 and C–5 of the α-L-Ara*f* residues, respectively (Chaikumpollert, Methacanon, & Suchiva, 2004). Specific ^{13}C NMR signals of 4-*O*-methyl-glucuronic acid at 181.6 ppm (C-6) and 59.7 ppm (4-*O*-methoxyl groups) were not detected.

Based on the monosaccharide composition (Table 1), comparison of the Ara/Xyl molar ratios of the two hemicellulose fractions (A and B) was estimated to 0.1 and 0.3, respectively. It may indicate that hemicellulose B was more branched than hemicellulose A. This is in accordance with previous reports showing that weakly substituted xylans were less soluble (Chaikumpollert et al., 2004; Bendahou, Dufresne, Kaddami, & Habibi, 2007). The final alkali resistant material accounted for 25.2% of the dry starting leaf material.

3.2. Synthesis and characterization of plastic materials from extracted hemicelluloses

Hemicellulose modification was carried out in homogeneous medium, according to our previous work on other polysaccharides such as cellulose and inulin (Joly et al., 2006; Grandtner et al., 2005). For this preliminary study, one plastic was synthesized by reacting lauroyl chloride with native hemicelluloses dissolved in LiCl/DMAc. DMAP was used as basic catalyst to prevent the hydrolysis of the polysaccharide by hydrochloric acid released during the reaction. The fatty acylated polysaccharide was isolated by its selective precipitation, converted into film by casting, analyzed by classical spectrometric methods and characterized for its thermal and mechanical properties.

FT-IR spectrum of lauroylated hemicelluloses (Fig. 2b) shows evidence of fatty acylation introduced onto the polysaccharide by the chemical reaction, and by the presence of the band at 1743 cm^{-1} characteristic of carbonyl ester. Moreover, the band observed at 720 cm^{-1} is indicative of a sequence of at least four consecutive CH_2 characteristic of the grafted fatty acid chains. By comparison with the spectrum of total hemicelluloses (Fig. 2a), we noticed a concomitant disappearance of the band at

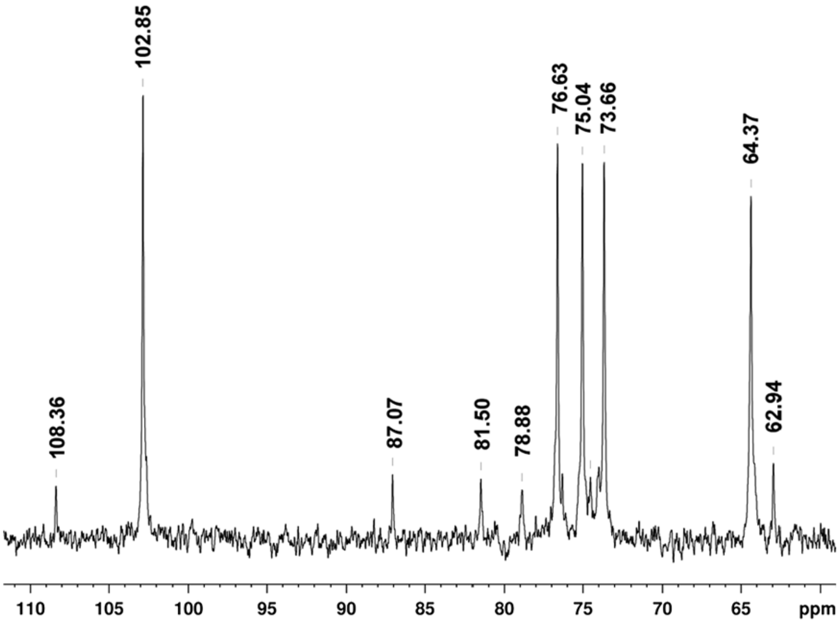

Fig. 3. ^{13}C NMR spectra of hemicelluloses.

3300 cm^{-1}, characteristic of hydroxyl groups, and an intensity increase of the bands at 2853 and 2920 cm^{-1}, typical of the stretching of the C–H bonds of alkyl chains (Joly, Granet, Branland, Verneuil, & Krausz, 2005). The fact that OH typical band at 3300 cm^{-1} disappeared indicated that almost every hydroxyl groups of the starting hemicelluloses were functionalized by fatty acid chains.

As FT-IR spectrometry, ^{1}H NMR spectroscopy was used to confirm the grafting of the lauroyl chains onto the arabinoxylan, with the appearance of the signals of fatty acid protons at 0.89 ppm (terminal CH_3, t, 3 H), at 1.26 ppm ($(CH_2)_8$, m, 16 H), at 1,60 ppm (CH_2 in β position of carboxylic function, m, 2 H) and at 2.32 ppm (CH_2 in α position of carboxylic function, t, 2 H), and anhydroxylose protons between 3.0 and 5.0 ppm. ^{1}H NMR spectrum was also useful to determine the degree of substitution (DS) of hemicellulose esters, calculated according to the ratio of integration of glycosidic and fatty chain protons (Satgé et al., 2002). This DS value is 1.9 (considering the isolated hemicellulose as a xylosidic homopolymer) and confirmed the previous interpretation of FT-IR analysis, i.e., that almost every hydroxyl groups were substituted.

3.3. Thermal properties of hydrophobic film

Thermogravimetric analysis (TGA) is one of the most convenient methods to determine general degradation characteristics of materials under pyrolysis and combustion (Sun & Tomkinson, 2002). This analysis included a precise study of the weight loss during programmed exposure of plastic films to raising temperatures. Degradation temperatures of native hemicellulosic polysaccharide and hemicellulose-based plastic were observed at 250 and 185 °C, respectively. This weight loss was attributed to decarboxylation, dehydration, and oxidation of hemicellulosic macromolecules (Sun, Fang, Tomkinson, & Jones, 1999). By comparison, TGA of cellulose esters with DS equals to 1.7, 1.9 and 2.4 exhibited lower degradation temperature, i.e., 160 °C (Satgé, Granet, Verneuil, Branland, & Krausz, 2004).

3.4. Mechanical properties of hydrophobic films

Analyses of the hydrophobic film tensile properties showed a tensile failure stress around 6 MPa, a tensile strain level of 29% and an elastic modulus of 100 MPa. These mechanical properties are lower than the ones obtained with commodity plastics such as polyethylene or polypropylene (Table 2). Nevertheless, by comparison with a casted film obtained from barley husk arabinoxylans (Höije et al., 2005), our esters are more deformable but less resistant. Moreover, failure strain level is more important for glucuronoarabinoxylan esters than arabinoxylan esters, so the glucuronoarabinoxylan ester films are more ductile (Moine, Gloaguen, Gloaguen, Granet, & Krausz, 2004). On the other hand, we noted that the mechanical properties of Poaceae-extracted-hemicellulose esters are similar to those of cellulose laurate with a DS of 2.4 (Satgé et al., 2002). Finally, mechanical properties of poaceae-based plastic films are closely related to those obtained with low-density polyethylene (Fontanille & Gnanou, 2002).

Table 2

Comparison of mechanical properties of *A. pungens* arabinoxylan (AX) ester plastic film with other bio-based films and commodity plastics

	Polysaccharide-based films			Petroleum-based plastics			
	AX laurate (DS 1.9)	AX (barley husks)	Cellulose laurate (DS 2.4)	LDPE	PP	PET	PVC
E[a](GPa)	0.1	2.9	0.085	0.1–0.3	2.2–2.4	2–4	2.5–4
σ_R[b] (MPa)	6	50	10.6	5–25	130–300	190–260	25–70
ε_R[c] (%)	29	2.5	36	100–700	>50	60–165	60

[a] Elastic modulus.

[b] Tensile failure stress.

[c] Tensile strain level; DS, degree of substitution; LDPE, low-density polyethylene; PP, polypropylene; PET, polyethylene terephthalate; PVC, polyvinyl chloride.

4. Conclusion

In this study, we have characterized the hemicellulosic fractions of *A. pungens* as arabinoxylans. We have also succeeded in converting these polysaccharides into plastic films. In regard of their mechanical properties, our films are not with sufficient qualities to permit direct industrial application. In order to fit both industrial needs and environment requirements, an outmost modification in the film manufacture would be the replacement of liquid-based reaction with solvent-free ones. To conclude, our results are very promising in the perspective of substituting petroleum-based plastics with bio-based plastics, and giving a new opportunity to valorize plant material from emerging countries. We are now working on the introduction of such bio-based materials into petrochemical plastics to see their influence on properties and biodegradability of commodity plastics.

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