This is the accept manuscript of the following article that appeared in final form in Industrial Crops and Products 47: 331-338 (2013),
which has been published in final form at https://doi.org/10.1016/j.indcrop.2013.03.031.
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DOI: https://doi.org/10.1016/j.indcrop.2013.03.031

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EFFECT OF DIFFERENT HEMICELLULOSES CHARACTERISTICS ON FILM FORMING PROPERTIES

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Abstract

Hemicelluloses are known to have good gas barrier properties makes them of interest to film applications. Corn cob, cotton waste, olive, apple tree pruning, pepper and chilli wastes were used as hemicelluloses sources for films production. Hemicelluloses were recovered from these wastes by direct alkaline extraction and raw material delignification. The hemicelluloses and their films were characterized using different analytical techniques (IR-ATR, TGA, DSC, HPLC, nitrobenzene oxidation, GPC, ^{13}C NMR, DMA). Hemicelluloses obtained by direct alkaline extraction produces brownish films (≤ 4.46% lignin, Mw = 30997-91796, Tg = 140-150 ºC). The presence of lignin and arabinose/xylose enhanced the film forming properties. Delignified hemicelluloses produced less coloured films (Mw = 17449-20180, Tg = 140-150 º C) and Ara/Xyl ratio improved film forming capacity although a possible cellulose contamination could be observed. This study demonstrated the suitability of different agricultural wastes for hemicelluloses recovery and their physico-chemical properties for first step film elaboration.

Keywords: Agricultural wastes, hemicelluloses, extraction, physico-chemical properties, film

1. Introduction

Hemicelluloses are known to have good gas barrier properties due to their ability to form a dense macromolecular network with low mobility, and their excellent oxygen barrier properties (Zhang et al., 2011) makes them of interest to packaging film applications. In the efforts to better utilization of natural resources and decrease of accumulation of non-degradable packaging waste, the usage of hemicelluloses extracted from agricultural residues for film production is an interesting emerging field. In addition hemicelluloses are extracted from renewable, low cost and worldwide available material.

Hemicelluloses constitute complex branched heteropolysaccharides, made up of pentoses (β-D-xylose, α-L-arabinose), and hexoses (β-D-mannose, β-D-glucose, α-D-galactose). The backbone chain is constituted mainly by xylose units, linked by β-1-4-glycosidic bonds where the hydroxyl groups of sugars can be partially substituted with arabinose, uronic acids (α-D-glucoronic, α-D-4-O-methylgalacturonic and α-D-galacturonic acids) and/or acetyl groups (Gírio et al., 2010). The physical characteristics of packaging films are greatly influenced by the chemical structure of the hemicelluloses, molecular weight, crystallinity and processing conditions (Bahcegul et al., 2012).

Höije et al. (2005) isolated high molecular weight arabinoxylans from barley husks to be used for the preparation of oxygen barrier films or coatings. The films made by water casting, were strong, stiff and rather brittle with similar material properties than those of Aspen glucuronoxylan films plasticized with 20% of sorbitol (Gröndahl et al., 2004).

The production and characterization of films from cotton stalk xylan was studied by Goksu et al. (2007) who observed that self-supporting continuous films could not be

produced using pure cotton stalk xylan; however, film formation was achieved using 8–14% (w/w) xylan without complete removal of lignin. Several studies of chemical and physical treatments of the hemicelluloses with the aim of induce desirable properties for novel materials production have also been reported (Sun et al., 2001; Ren et al., 2008; Fang et al., 1999a).

The aim of the present study was to evaluate the physico-chemical characteristics of hemicelluloses obtained from different agricultural residues with respect to their film forming capacities. The effect of the lignin (extracted together with hemicelluloses) on film properties was also analyzed. For different hemicelluloses extraction (with and without lignin), direct alkaline extraction and sequential treatment of raw material delignification followed by alkaline extraction were carried out. The delignification step was used to obtain lignin-free hemicelluloses to avoid contamination and relatively colored films production. The obtained hemicelluloses were characterized using various physical and chemical techniques.

2. Materials and Methods

2.1 Raw materials conditioning and characterization

Corn cobs, cotton waste, olive, and apple tree prunings, pepper and chilli wastes were collected from different places in north of Spain. All residues were conditioned to constant moisture, ground in a hammer mill and sieved to obtain 4 to 6 mm sized fractions. Ash; ethanol–toluene extractives; lignin were determined according to TAPPI T211 om-93, TAPPI T204 cm-97, and TAPPI T222 om-98, respectively (TAPPI Standards, 2007). α-holocellulose and α-cellulose were determined according to Wise et al.(1946) and (Rowell, (1983) respectively, and the hemicelluloses content was calculated as the difference between the holocellulose and cellulose contents.

2.2 Hemicelluloses extraction

For mild direct alkaline extraction, the raw material was mixed with 1% NaOH (w/w) using a solid:liquid ratio of 1:10 (w/w), for 24 h at room temperature without agitation to extract high molecular weight hemicelluloses. The liquor was separated from the solid phase by filtration through a sieve of 0.16mm mesh. The pH of the filtrate was adjusted with glacial acetic acid to 7. Lignin-hemicelluloses precipitates (L-H) were recovered using three volumes of ethanol. In the second extraction method, raw material delignification was performed before alkaline extraction, with the objective to obtain native hemicelluloses free of lignin. The raw materials were treated with sodium chlorite in acid solution, at 70 ºC for 20 h, according to the method described by Wise et al. (1946) for α-hollocellulose quantification. For this, 2.5 g of raw material was placed into 80 mL of distillate water and 0.5 mL of glacial acetic acid and 2.6 mL of sodium chlorite solution (25% w/w) were added every hour for 6-8 h, after which the solution was kept in the bath for 12 h. The hollocellulose was washed with distillate water and over dried at 100 ºC. After that, the hollocellulose fractions were subject to alkaline extraction according to Rowell (1983) for α-cellulose quantification. In this case, 17.5% of NaOH (w/w) was used to extract hemicelluloses from hollocellulose, obtaining an α-cellulose fraction as solid phase while lignin-free hemicelluloses (H) remained in the alkaline liquid phase. The liquor was neutralized with glacial acetic acid at pH = 7 and hemicelluloses were precipitated in three volumes of ethanol. All precipitated hemicelluloses (L-H and H) were oven dried at 50 ºC for 24 h.

2.3 Film production

Films were prepared via water casting, using precipitated hemicelluloses solubilized in distilled water at a concentration of 5 wt%. After 2 h of stirring with a magnetic stirrer, the solution was centrifuged for 2 min to remove insoluble particles. The insoluble fraction was oven-dried at 50 ºC and weighed to calculate the amount of

solubilised hemicelluloses. 60 mL of homogeneous solution was placed into a petri dish with a diameter of 13.5 cm. Films were dried at room temperature until they could be manually peeled from the dishes. The films were conditioned at 23 ºC and 50% RH in a climate-controlled chamber and the thickness was determined using a digital micrometer (No.293-521-30, Mitutoyo).

2.4 Hemicelluloses characterization

Fourier transform infrared spectroscopy (IR-ATR) was performed using a Nicolet Nexus 670 FT-IR spectrometer (Madison, Wisconsin USA) equipped with a single horizontal Golden Gate ATR cell (Specac, Kent, United Kingdom). The precipitates were analyzed in powder form and spectra were recorded using a spectral width ranging from 600 to 4000 cm^{-1}, with 2 cm^{-1} resolution and an accumulation of 20 scans.

Thermal degradation of the samples was studied by a TGA/SDTA 851 analyzer from Mettler Toledo. Samples of ~ 5 mg were heated from 25 to 600 ºC at a rate of 10 ºC/min, under a constant nitrogen flow.

The glass transition temperatures (Tg) of precipitated hemicelluloses were determined using a Mettler Toledo DSC 822 differential scanning calorimeter equipped with a Sample Robot TSO 801 RO. About 5–10 mg of sample sealed in perforated aluminium pans was used for each experiment, and nitrogen gas was purged at a flow rate of 10 mL/min. In order to remove interferences related to humidity, all samples were first heated to 110 ºC and maintained there for 10 min, cooled to 25 ºC and reheated to 225 ºC. All the scans were performed at a constant rate of 5 ºC min^{-1}.

Characterization, quantifications of sugars monomers, and Arab/Xyl ratio determinations were carried out in a high performance liquid chromatograph (HPLC) Jasco LC Net II /ADC equipped with a refractive index detector and a photodiode array

detector. A Phenomenex Rezex ROA HPLC column (300 mm x 7.8 mm) was used with mobile phase of 0.005 N H_2SO_4 prepared with 100% deionised and degassed water. The injection conditions were 0.35 mL/min of flow rate, 40 ºC and injection volume of 20 µL. High purity D(+) glucose, D(+) xylose, D(-) arabinose formic and acetic acids (Sigma-Aldrich) were used for establishment of calibration curves. For monomeric sugar quantifications and Arab/Xyl ratio determination, the precipitated hemicelluloses were hydrolysed with sulphuric acid at a concentration of 4% (w/w).

The percentage and chemical composition of the lignin associated in hemicellulosic fractions were determined by alkaline nitrobenzene oxidation using HPLC JASCO instrument equipped with an interface (LC-NetII/ADC) and a photodiode array detector. Fifty mg of sample were placed in a tube with 7 mL of 2 M sodium hydroxide solution and 0.4 mL of nitrobenzene and left at 175 ºC for 2.5 h. Successive extractions with 25 mL chloroform were performed, rota-evaporated and mixed with the mobile phase for analysis. A Teknokroma Mediterranean sea TR-010006 column (25 x 0.46 cm) was used and a solution of acetonitrile:water at a ratio of 1:8 with 1 % of acetic acid was used as mobile phase. The injection conditions were 0.5 mL/min of flow rate, 40 ºC and injection of 20 µL. Calibration was made using standards (Sigma-Aldrich) – of vanillic, syringic, ferulic and p-hydroxybenzoic acids, p-hydroxybenzaldehyde, vanillin, syringaldehyde, and acetovanillone.

The weight-average (M_w) and number-average (M_n) molecular weights and polydispersity (IP = M_w/M_n) of the different precipitated hemicelluloses dissolved at concentration of 2 g/L in distillate water, were determined by gel permeation chromatography (GPC) in a GPC Jasco LC-Net II /ADC equipped with a photodiode array detector and refractive index detector. The column was PL aquagel-OH MIXED-H

8 μm. The mobile phase was constituted by 0.005 N H_2SO_4 prepared with 100% deionised and degassed water at a flow rate of 0.6 mL/min, 40 ºC and injection volume of 20 μL. Calibration curve was made using Pullulan polysaccharides (Calibration kit SAC-10, Varian) with different molecular weights (between 180 and 805000 Da).

The chemical structure of the hemicelluloses was studied by solid-state nuclear magnetic resonance (^{13}C NMR) using a Bruker 400 WB Plus spectrometer. Spectra were collected using a 4-mm CP-MAS probe at a spinning of 10000 Hz. ^{13}C CPMAS spectra of solid samples were recorded for 12 h using the standard pulse sequence, at 100.6 MHz, a time domain of 2 K, a spectral width of 29 KHz, a contact time of 1.5 ms and an interpulse delay of 5 s.

2.5 Dynamic mechanical analysis (DMA)

A dynamic mechanical analyser (DMA) was used to study the α-relaxation (glass transition temperature, Tg) of films, storage modulus (E') and loss modulus (E'') as a function of temperature using Eplexor 100N GABO equipment. Data were collected at a heating rate of 2 ºC min^{-1} from 25 ºC to 180 ºC at frequency of 10 Hz. During the scans the sample was subjected to a static force deformation of 0.5% and a dynamic deformation of 0.1%.

3. Results and discussion

3.1 Composition of raw materials and hemicelluloses extraction yields

Composition of the raw materials (% on a dry basis and less than 2% of experimental error) and hemicelluloses extraction yields are shown in Table 1.

The hemicelluloses contents ranged from 26 to 36%. These percentages are comparable with those of barley straw (30%), wheat straw (29.70%), rice straw (35.10%) and maize stalks (26.70%) (Menardo et al., 2012). Pepper and chilli wastes demonstrated

the lowest lignin concentrations (12-16%) while in other raw materials, it was between 23-26%. In addition, the pepper, chilli, corn cob and cotton wastes demonstrated the highest cellulose concentration of 37-41%, while it was between 27-33% in other raw materials.

Hemicelluloses extraction yields varied from 3.97 to 10.78% when using the 1% NaOH (w/w) extraction process, while after delignification pretreatment, the extraction yields reached 47.66% to 82.34%.

3.2 Film production

The films obtained using precipitated lignin-hemicelluloses and lignin-free hemicelluloses are shown in Fig.1. The films obtained using precipitated hemicelluloses by 1% NaOH (w/w) extraction process were brownish, whereas the hemicelluloses obtained after delignification were transparent, although, in few days, they acquired a whitish-yellow appearance. The hemicelluloses obtained from corn cob, cotton waste, olive and apple tree pruning produced intact films, whereas pepper and chilli wastes hemicelluloses provided cracked films under the conditions used. The films obtained from corn cob (both brownish and whitish films) could be handled easily without causing apparent fractures. The thickness of brownish films was about 0.05 ± 0.01 mm while the thickness of the whitish films was slightly higher, 0.08 ± 0.02 mm. These differences could be explained by the different solubility of the hemicelluloses (Table 2).

3.3 Hemicelluloses characterization

Fourier transform infrared spectra of all precipitated hemicelluloses are shown in Fig.2. Bands at 3300-3400 cm^{-1} indicate OH stretching whereas those at 2930–2850 cm^{-1} are due to CH bond deformation of CH_2 and CH_3 groups, respectively. The intense peaks between 1650-1573 cm^{-1} might be due to the presence of water (Sun and Tomkinson,

2002) while the peak at 1408 cm^{-1} is due to the CH and OH bending (Sun et al., 2000). The presence of hemicelluloses was observed at 1034-1040 cm^{-1} originating from xylans and at 893 cm^{-1} from β-glycosidic bonds between sugars. The presence of arabinosyl side chains is indicated by low-intensity shoulders at 1160 cm^{-1} and at 990 cm^{-1} (Buranov and Mazza, 2010). Small peaks due to the presence of lignin, especially for the phenylpropane skeleton at 1520 cm^{-1}, C-H deformation combined with aromatic ring vibration at 1460 cm^{-1} (Boeriu et al., 2004) and syringyl ring breathing with C-O stretching at 1330 cm^{-1} were found in the precipitated lignin-hemicelluloses samples, represented by Fig.2a'. The band at 1244 cm^{-1} was assigned to C-O stretching (Sun et al., 2000). In Fig.2b', the weak peak observed at 1335 cm^{-1} in lignin-free hemicelluloses could be due to residual lignin or cellulose together with the bands observed at 1263 cm^{-1} (assigned to the -C-O-C- bond in the cellulose chain) (Mahato et al., 2009) and at 1015 cm^{-1} (Kacurakova et al., 2002), distinguishable more easily in pepper and cotton precipitated hemicelluloses.

The pyrolysis of hemicelluloses and cellulose occurred quickly, with the weight loss of hemicelluloses mainly occurring at 220–315 ºC and at 315–400 ºC for cellulose. However, lignin was more difficult to decompose, as its weight loss happened in a wide temperature range (from 160 to 900 ºC) (Yang et al., 2007). The thermal behaviour of obtained precipitated is shown in Fig.3. Three visible peaks are identifiable on the DTG curves (Fig.3a) of lignin-hemicelluloses samples. These hemicelluloses were stable up to 180 ºC, whereas the maximum weight loss rate due to the hemicelluloses degradation was observed between 275 and 290 ºC. Lignin-hemicelluloses obtained from corn cob demonstrated the highest maximum weight loss peak temperature at 290 ºC whereas for the other materials, the maximum lignin-hemicelluloses decomposition occurred at 275 ºC with a small shoulder at 250 ºC. The weight loss seen at 450 ºC is possibly due to lignin while the first peak is due to the water evaporation. The lignin-hemicelluloses

obtained from corn cob had 35% solid residue at 600 ºC while for the other materials solid residues, between 38-45% were obtained. The thermal behaviour of the lignin-free hemicelluloses is shown in Fig. 3b. The hemicelluloses maximum loss rate was observed at 205 ºC and at 275 ºC while the peak observed at 380 ºC could be due to cellulose decomposition. The absence of weight variation at the highest temperatures indicates the absence of lignin in these hemicelluloses, which is in agreement with the IR results. In the lignin-free hemicelluloses, the solid residue varied between 31-35% at 600 ºC. These results demonstrate that hemicelluloses degradation temperature did not changed significantly between the extraction processes.

DSC (Fig. 4a) revealed a clear endothermic signal in olive, pepper and chilli lignin-hemicelluloses precipitates due to the disintegration of intramolecular interaction and decomposition (Sun et al., 2003), whereas the endothermic peak had lower intensity in apple, cotton and corn cob lignin-hemicelluloses, suggesting that structures could have less hydrogen bonds, maybe caused by presence of substituents. The Tg values were observed around 140 ºC-150 ºC. Glass transition temperature of 167–180 ºC have been reported for wood xylans (Irvine, 1984). The Tg values demonstrated that the obtained films were brittle and therefore the usage of some plasticizers like sorbitol, glycerol or xylitol will improve their properties.

The characterization and quantification of monomeric sugars units, Arab/Xyl ratio, solubility and lignin content of the samples are shown in Table.2. The HPLC results confirmed that all precipitates consisted mostly of xylose units making up between 61.9 and 96.5% of the total sugars, followed by 1.6-25.5% and 3.5-29.5% of arabinose and glucose, respectively. Minor signals from galacturonic acid and those from the decomposition products, formic and acetic acid were observed. Among the L-H samples,

corn cob had the highest Ara/Xyl ratio (0.37) indicating the presence of branched arabinoxylan, followed by apple and olive tree pruning (0.14). Pepper and chilli waste demonstrated the lowest Ara/Xyl ratio, (0.07-0.09), whereas no arabinose monomer was detected in cotton L-H. According to these results, the lower endothermic peak observed in corn cob L-H by DSC (Fig.4a), could be related with its high Ara/Xyl ratio.

The highest water solubility for 5 wt% initial film formation (Table 2) was obtained using hemicelluloses after delignification (H), which was between 95-98%. Water solubility and plasticity increase with increasing arabinose substitution (Höije et al., 2008). The Arab/Xyl ratio was higher in L-H samples than H samples, but the solubility of hemicelluloses was lower (between 45.4-61.3%) probably affected by the presence of lignin.

The highest percentage of lignin was found in corn-cob L-H (4.66% of the precipitate), cotton waste L-H (1.20%) and olive tree pruning L-H (1.16%). Vanillin was the main product (from 88% to 100% (respect to total phenolics compounds detected) followed by small quantities of 4-hydroxybenzaldehyde and syringaldehyde. According to these results, the lignin presence could have a direct relation with the lower solubility of the L-H samples.

The weight-average (M_w) and number-average (M_n) molecular weights and polydispersity (Mw/Mn) of the hemicelluloses is given in Table 3. The GPC chromatograms showed two main peaks corresponding to two different molecular weight components. The hemicelluloses with higher M_w were obtained with 1% NaOH (w/w) extraction (L-H) of corn cobs, olive and apple tree prunings and cotton waste Mw = 91796-36684 (g/mol), providing continuous and self-supporting brownish films as shown in Fig.1. However, the weight-average molecular weight of L-H obtained from pepper

and chilli wastes were only 30997 and 31105 (g/mol), respectively, giving cracked films. The high molecular weight of the L-H samples could be due to the presence of lignin-xylan complexes (Jeffries, 1990). In fact, the higher lignin content observed in corn cob L-H (4.66%) could have enhanced its molecular weight besides its higher Xyl/Arab ratio (0.37). The molecular weight of H samples varied from 20180 to 17449 (g/mol).

Thus for L-H samples, the lignin presence (at least 1.16%) and then the higher Ara/Xyl ratio, enhanced film forming properties and the molecular weight was dependent of these factors. Among the H samples, with the exception of obtained film from cotton waste (where no arabinose but possible cellulose contamination was observed), the Arab/Xyl ratio enhanced the film forming capacity. Separation and purification technologies could be used to obtain more pure and defined molecular weight hemicellulose fractions (Egüés et al., 2012) to improve the thermal stability for thermoplastic products.

Based on the availability in Spain, acceptable hemicelluloses extraction yields and film formation capacities, cotton and corn cob waste might be the most promising residues to be used in packaging.

Solid state ^{13}C NMR spectra of lignin-hemicelluloses and lignin-free hemicelluloses obtained from corn cobs (Fig.5a and b), demonstrated the main 1,4-linked β-D-Xylp units signals at 102.5-102.9, 74.0-74.1, and 63.3-63.5 ppm, which are attributed respectively to C-1, C-3, and C-5 of the β-D-Xylp units. The carboxylic group of methyl galacturonic acid (MeGlcA) was identified at 180.3-180.8 ppm (Sun et al., 2004) in both precipitates whereas the peak observed at 172.4 ppm in lignin-hemicelluloses spectra could be due to the carbonyl group esterification of uronic acid residues (Ren et al., 2007). The strong signal observed at 25.26-26.93 in lignin-free hemicelluloses could be due to -

CH_3 in MeGlcA (Sun et al., 2000) or CH_3 in Ar-$COCH_3$ at 24.94 in lignin-hemicelluloses sample (Sun et al., 2004). The weak peak found at 175.7 in lignin-hemicelluloses could also have originated from C-6 of glucuronic acid residue in xylan (Fang et al., 1999b). The presence of arabinofuranosyl residues (at 109.0 (C-1), 86.4 (C-4), 80.4 (C-2), 78.3 (C-3), and 61.8 (C-5) ppm) or cellulose presence (at 60-70 (C-6), 70-81 (C-2, C-3, C-5), 81-93 (C-4), and 102-108 (C-1) ppm), could not be established unambiguously, due to overlapping signals. Only a peak around 87 ppm could be distinguishable in both spectra, which could correspond to C-4 of glucose or arabinose.

No clearly distinguishable ring signals indicative of lignin (between 100-160 ppm) were observed in both precipitates. However, in Fig.5a, it could notice weak signals referred to aromatic ring. The similar spectra between 1% NaOH soluble and delignified alkaline soluble hemicelluloses demonstrated that treatment of corn cob with both methods did not significantly change the macromolecular structure of these hemicelluloses. These results proved that the hemicelluloses obtained from corn cob contained a backbone of β-(1,4)-linked D-xylopyranosyls with arabinose and glucuronic acid as substituents, as demonstrated by IR, HPLC and ^{13}C NMR results.

3.4 DMA measurements

DMA measurements could only be carried out with corn cob hemicelluloses films as all the other films were too fragile. The corn cob lignin-hemicelluloses based film storage modulus (E'), reached values around 2800 MPa prior to reaching the glass transition temperature of 150 ºC (Fig. 6), which then it dropped rapidly. This result is in agreement with the Tg observed with the DSC measurement. The broad peak in tan δ at around 60 ºC is probably caused by initial movements of different chains during β-relaxation of the amorphous fraction.

4 Conclusions

Between L-H samples, isolated from agricultural residues by direct alkaline extraction, the lignin content is the most important characteristic for the film forming capacity following by Ara/Xyl ratio. In samples without lignin, Ara/Xyl ratio enhances the film formation capacity of hemicelluloses, although possible contaminations of cellulose have been observed. To improve thermal stabilities, Tg values and to obtain more defined molecular weight hemicelluloses, additional purification method as well as the usage of plasticizers need to be explored.

Acknowledgements

The authors are grateful for the financial support received from the Department of Education, Universities and Investigation of the Basque Government (Grant of I.E., ref BFI09.164), SAIOTEK program and Diputacíon de Gipuzkoa.

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List of tables:

Table 1. Compositions of raw materials (% on a dry basis, < 2% of deviation standard) and hemicelluloses extraction yields from 1% NaOH (w/w) extraction (< 1% of deviation standard) and delignification (< 4% of deviation standard).

Table 2. Percent of monosaccharides of total sugars as determined by HPLC, ratio of arabinose/xylose units (Ara/Xyl), solubility for 5 wt% film formation and lignin content of precipitated lignin-hemicelluloses, indicated as L-H and lignin-free hemicelluloses, indicated as H.

Table 3. Gel Permeation Chromatography (GPC) results of precipitated lignin-hemicelluloses, indicated as L-H and lignin-free hemicelluloses, indicated as H.

Table 1

	Ash	Ethanol-Toluene extractives	Klason lignin	Holocellulose	Cellulose	Hemicellulose	Hemicellulose extraction yield[a]	
							1% NaOH	Delignification
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
Corn cobs	2.10	1.68	23.19	67.34	37.92	29.42	4.65	78.26
Cotton waste	5.97	1.31	23.00	73.94	37.84	36.10	10.78	82.34
Aplee tree prunings	2.75	10.71	26.15	57.44	27.32	30.12	9.46	66.79
Olive tree prunings	3.01	3.86	23.97	60.83	33.61	26.54	3.97	77.09
Pepper waste	8.82	1.66	12.50	70.17	41.15	29.02	9.35	54.74
Chilli waste	7.82	2.18	16.20	71.18	38.12	33.06	6.92	47.66

[a]%: Percentage of precipitated sample respect to the raw material hemicelluloses content

Table 2

	Sample	Glucose (%)	Xylose (%)	Arabinose (%)	Ara/Xyl ratio	Solubility (%)[a]	Lignin content (%)[b]
Corn cobs	L-H	15.1	61.9	23.0	0.37	55.7	4.66
	H	3.1	85.6	11.3	0.13	98.00	nd[c]
Cotton waste	L-H	22.5	77.5	nd	-	45.4	1.20
	H	4.1	95.9	nd	-	95.5	nd
Aplee tree prunings	L-H	14.9	74.5	10.6	0.14	61.3	1.19
	H	3.5	96.5	7.72	0.08	95.0	nd
Olive tree prunings	L-H	29.5	61.8	8.7	0.14	48.8	1.16
	H	2.7	88.5	8.8	0.10	95.7	nd
Pepper waste	L-H	22.8	72.1	5.1	0.07	56.4	<1
	H	10.0	83.1	6.6	0.08	95.2	nd
Chilli waste	L-H	6.6	85.8	7.6	0.09	56.8	<1
	H	4.5	93.9	1.6	0.02	95.0	nd

[a] %: Weight percentage of sample solubilised in the film.

[b] %: Weight percentage of lignin content of the obtained hemicelluloses precipitates.

[c] nd = not detected.

Table 3

	Sample	M_w[a]	M_n[b]	IP[c]	(%)[d]
Corn cobs	L-H	91796	1801	3.3	77.9
	H	19332	1831	1.8	21.1
Cotton waste	L-H	36684	1716	1.6	73.0
	H	17779	1863	1.6	38.2
Aplee tree prunings	L-H	38125	431	1.7	68.4
	H	20180	1880	1.5	35.6
Olive tree prunings	L-H	39631	470	2.0	45.4
	H	18024	1850	1.3	31.0
Pepper waste	L-H	30997	1968	1.7	48.1
	H	17449	2036	1.6	41.4
Chilli waste	L-H	31105	1972	1.7	48.5
	H	18382	2023	1.8	45.0

[a] M_w: Weight-average molecular weight (g/mol).
[b] M_n: Number-average molecular weight (g/mol).
[c] IP: Polydispersity (Mw/Mn).
[d] %: Percentage of the higher fraction.

List of figures:

Figure 1: Films produced with lignin-hemicelluloses precipitates obtained from a) corn cobs, b) cotton waste, c) olive tree prunings, d) apple tree prunings, e) pepper waste, f) chilli waste, and lignin-free hemicelluloses precipitates from a') corn cobs, b') cotton waste, c') olive tree pruning, d') apple tree pruning, e') pepper waste and f') chilli waste, at 5 wt% of initial concentration.

Figure 2: Fourier transform infrared spectroscopy (IR-ATR), spectra of precipitated lignin-hemicelluloses (2a) and its expanded spectra (2a') and lignin-free hemicelluloses (2b) and its expanded spectra (2b') from: corn cobs, cotton waste, olive tree prunings, apple tree prunings, pepper waste and chilli waste.

Figure 3: Thermogravimetric analysis spectra of precipitated lignin-hemicelluloses (a) and lignin-free hemicelluloses (b) from: corn cobs, cotton waste, olive tree prunings, apple tree prunings, pepper waste and chilli waste.

Figure 4: Differential Scanning Calorimetry (DSC) of precipitated lignin-hemicelluloses (a) and lignin-free hemicelluloses (b) from: corn cobs, cotton waste, olive tree prunings, apple tree prunings, pepper waste and chilli waste.

Figure 5: Solid state ^{13}C NMR spectra of lignin-hemicelluloses (5a) and lignin-free hemicelluloses (b) obtained from corn cobs.

Figure 6: Dynamic Mechanical Analysis (DMA) curves of film obtained using lignin-hemicelluloses from corn cob, storage modulus (E'), loss modulus (E'') and tan δ.

Fig. 1

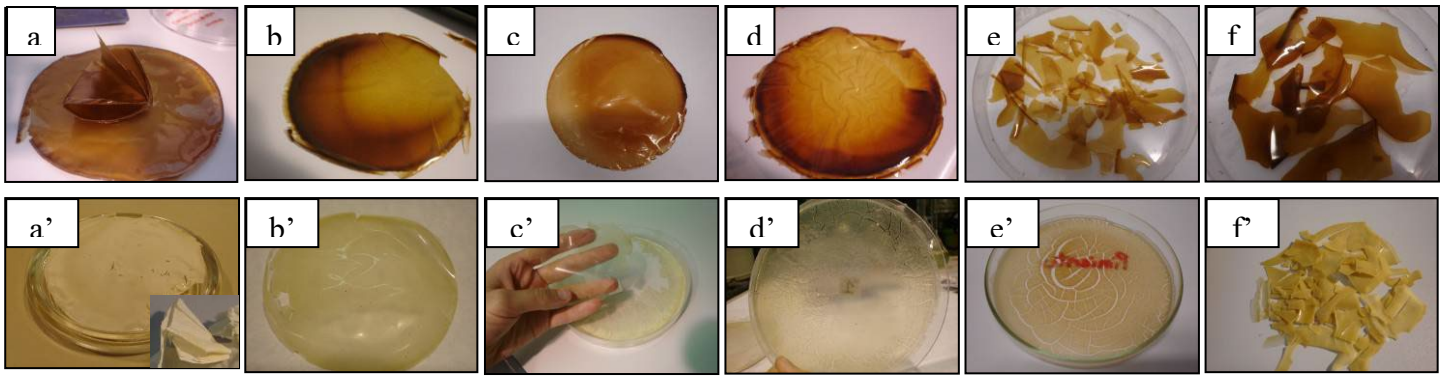
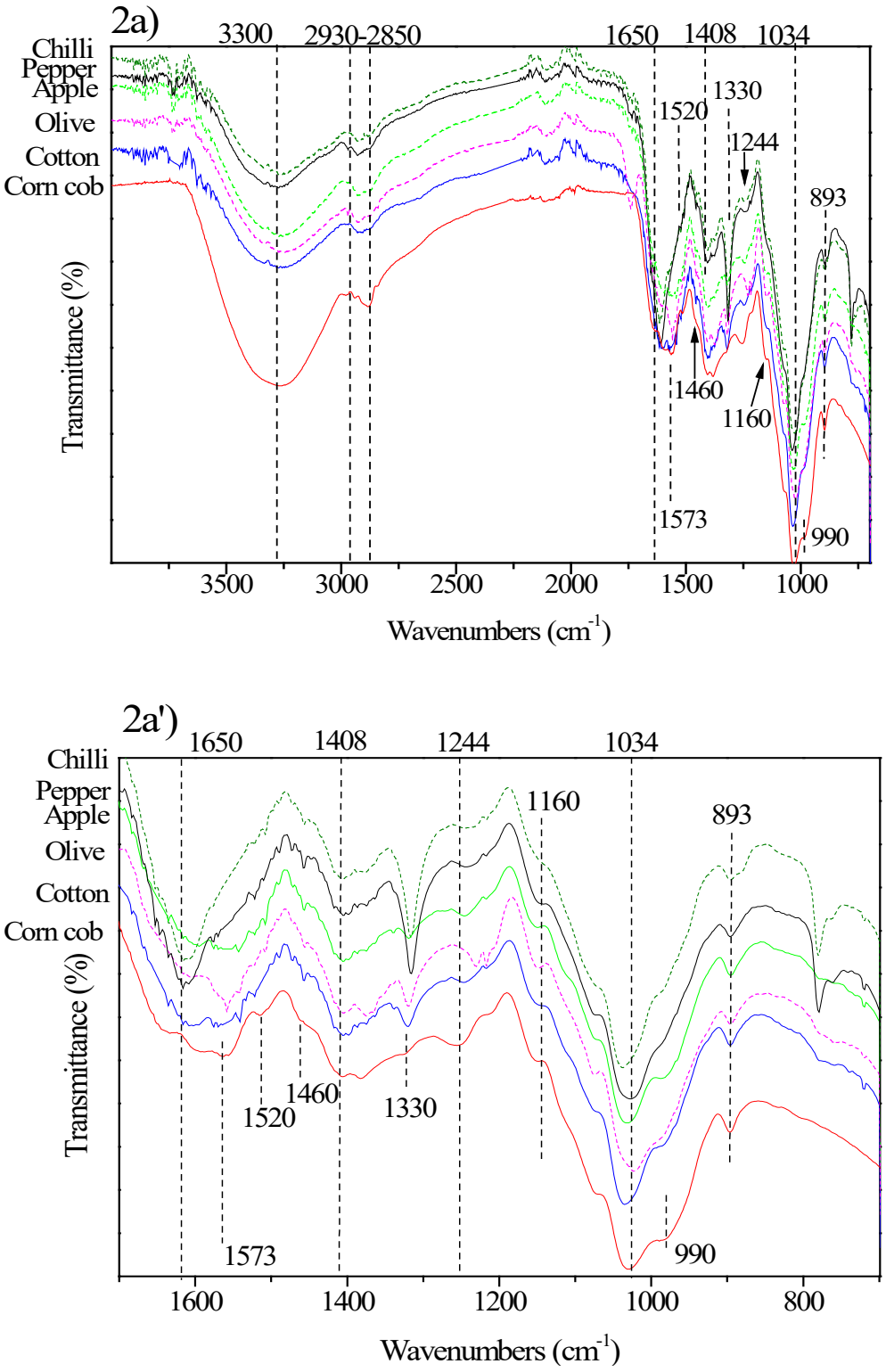
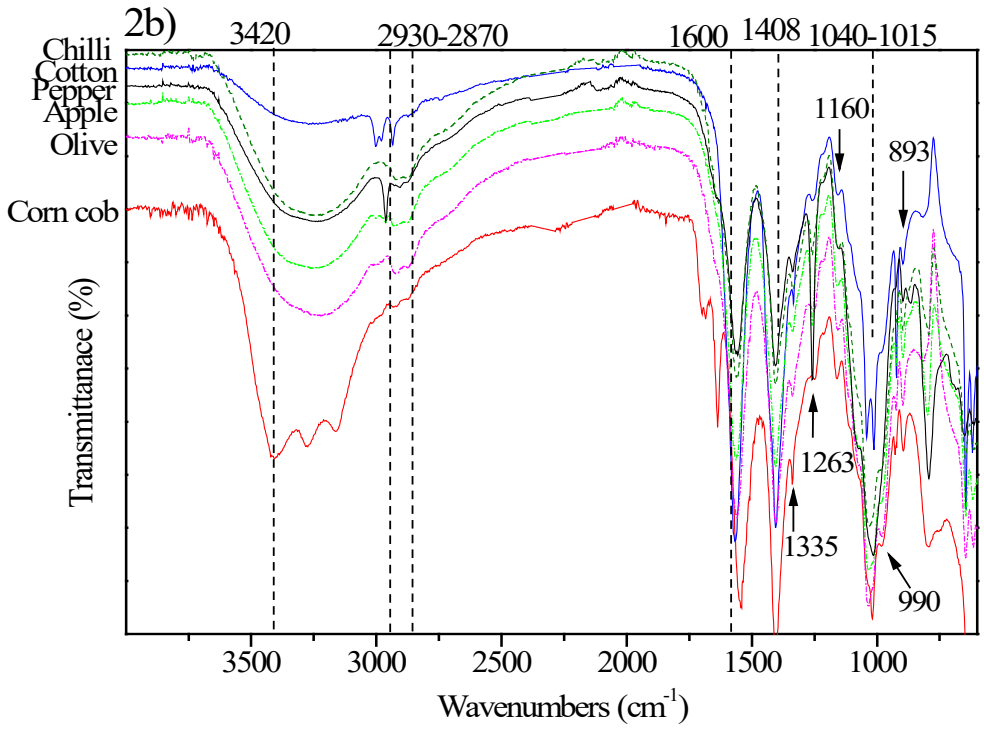


Fig. 2


2a)
3300
2930-2850
1650
1408
1034
1520
1330
1244
893
1460
1160
1573
990
Chilli
Pepper
Apple
Olive
Cotton
Corn cob
Transmittance (%)
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)
2a')
1650
1408
1244
1034
1160
893
1460
1520
1330
1573
990
Chilli
Pepper
Apple
Olive
Cotton
Corn cob
Transmittance (%)
1600
1400
1200
1000
800
Wavenumbers (cm-1)


2b)
3420
2930-2870
1600
1408
1040-1015
Chilli
Cotton
Pepper
Apple
Olive
Corn cob
1160
893
1263
1335
990
Transmittanace (%)
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)

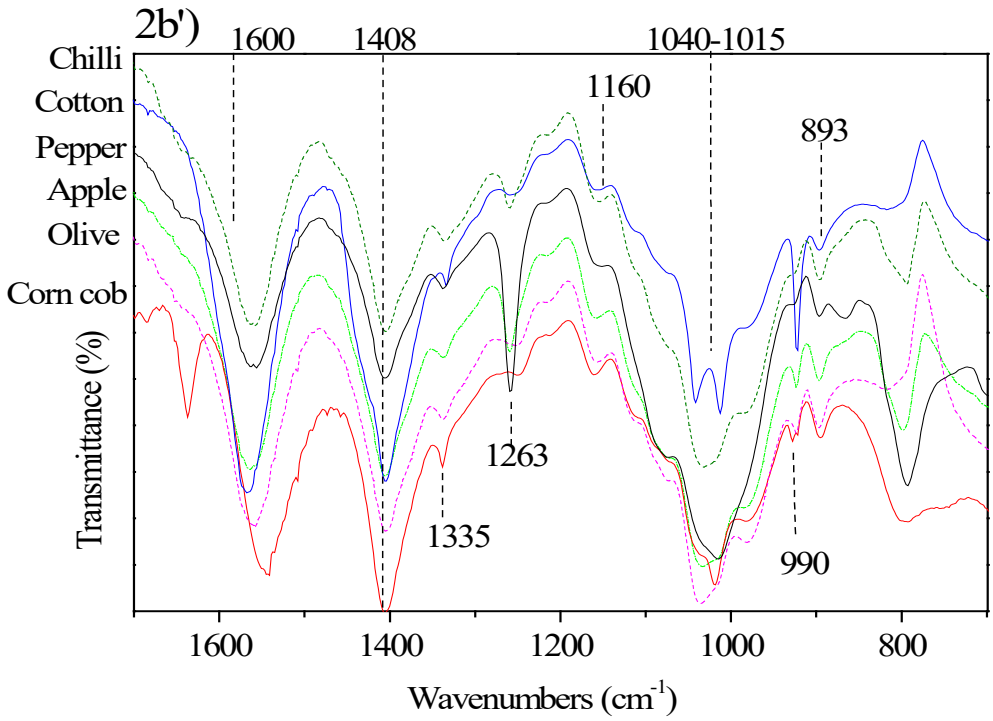

2b')
1600
1408
1040-1015
Chilli
Cotton
Pepper
Apple
Olive
Corn cob
1160
893
1263
1335
990
Transmittance (%)
1600
1400
1200
1000
800
Wavenumbers (cm-1)

Fig. 3

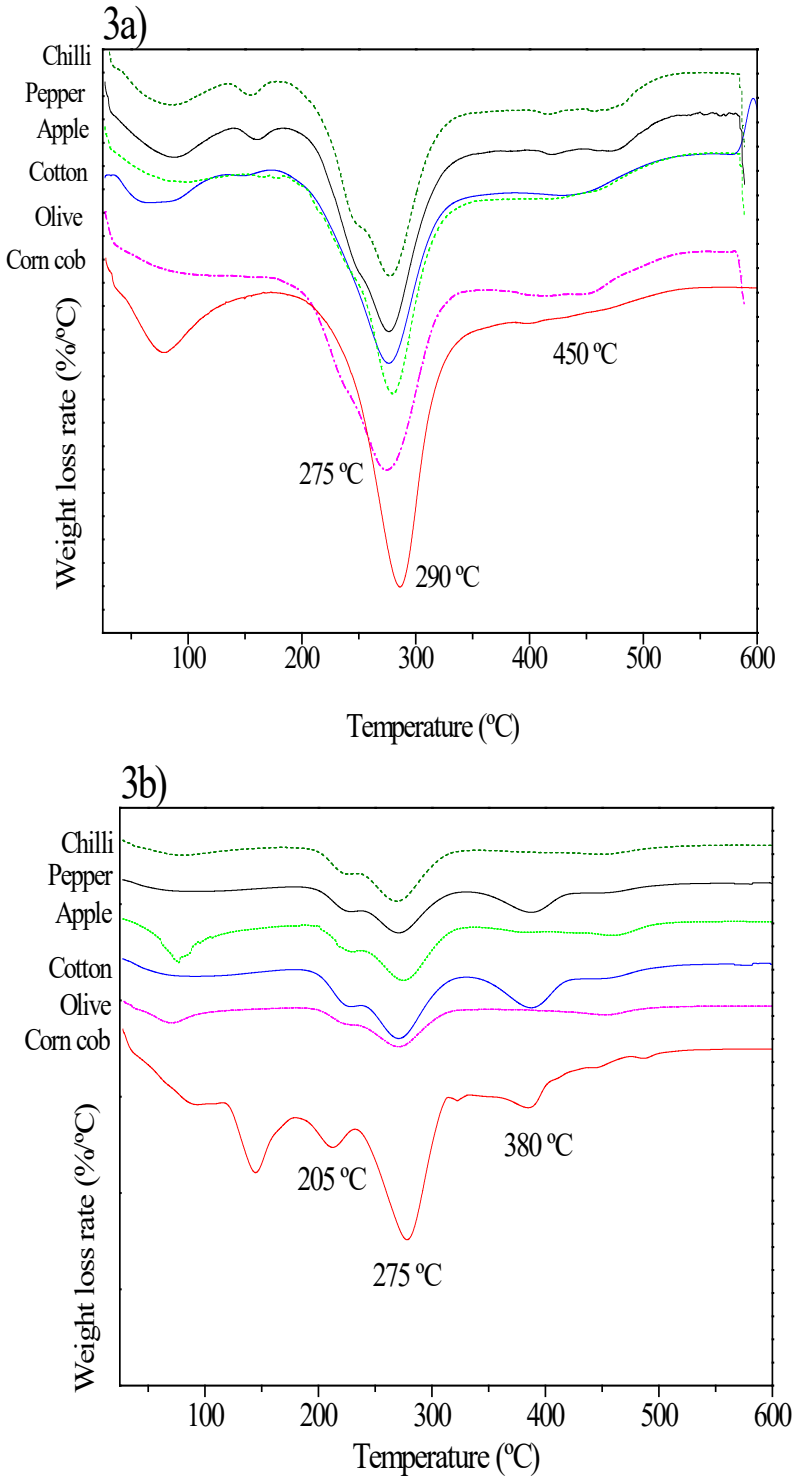
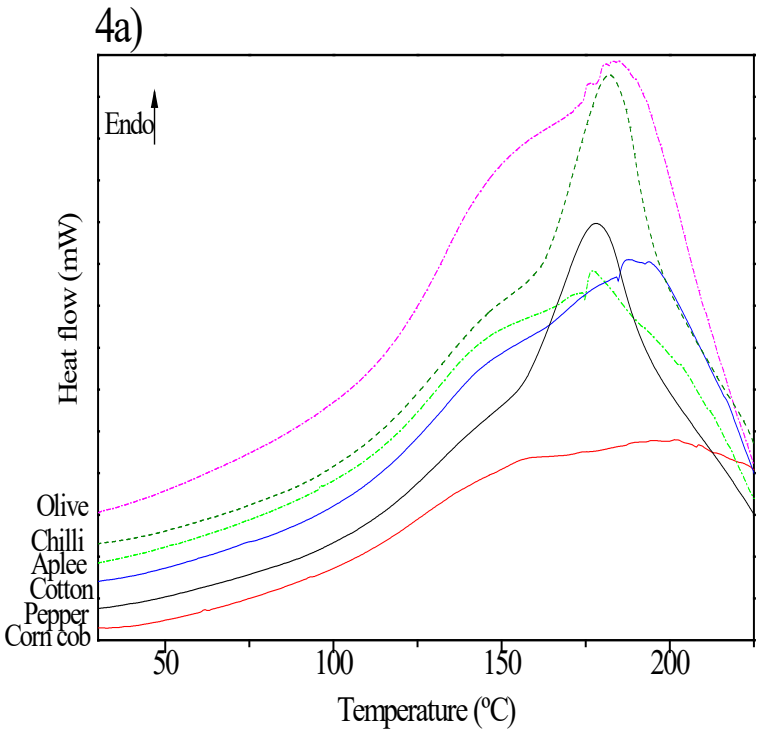

3a)
Chilli
Pepper
Apple
Cotton
Olive
Corn cob
Weight loss rate (%/°C)
450 °C
275 °C
290 °C
100
200
300
400
500
600
Temperature (°C)
3b)
Chilli
Pepper
Apple
Cotton
Olive
Corn cob
Weight loss rate (%/°C)
380 °C
205 °C
275 °C
100
200
300
400
500
600
Temperature (°C)

Fig. 4


4a)
Endo
Heat flow (mW)
Olive
Chilli
Aplee
Cotton
Pepper
Corn cob
50
100
150
200
Temperature (°C)

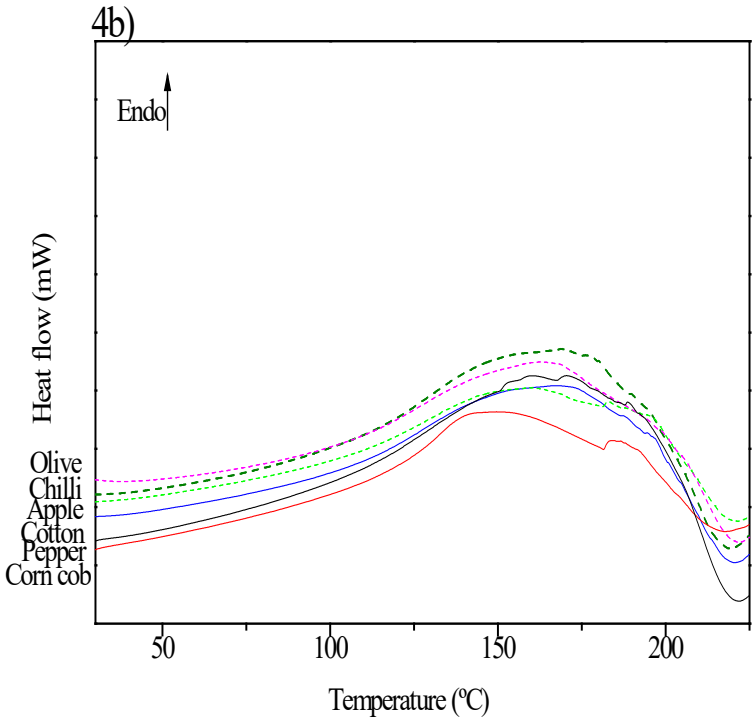
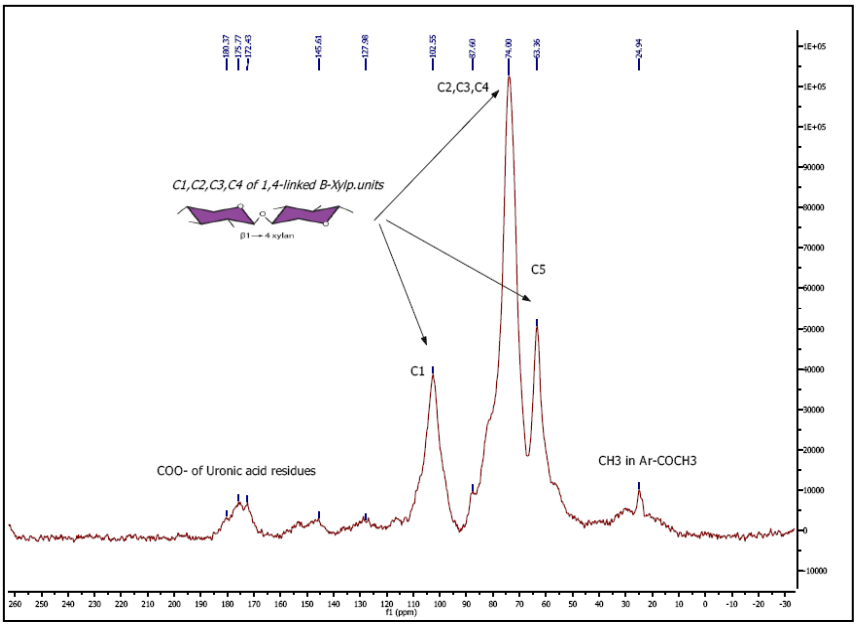

4b)
Endo
Heat flow (mW)
Olive
Chilli
Apple
Cotton
Pepper
Corn cob
50
100
150
200
Temperature (°C)

Fig. 5

a)


C2,C3,C4
C1,C2,C3,C4 of 1,4-linked B-Xylp.units
β1→4 xylan
C5
C1
COO- of Uronic acid residues
CH3 in Ar-COCH3
f1 (ppm)

b)

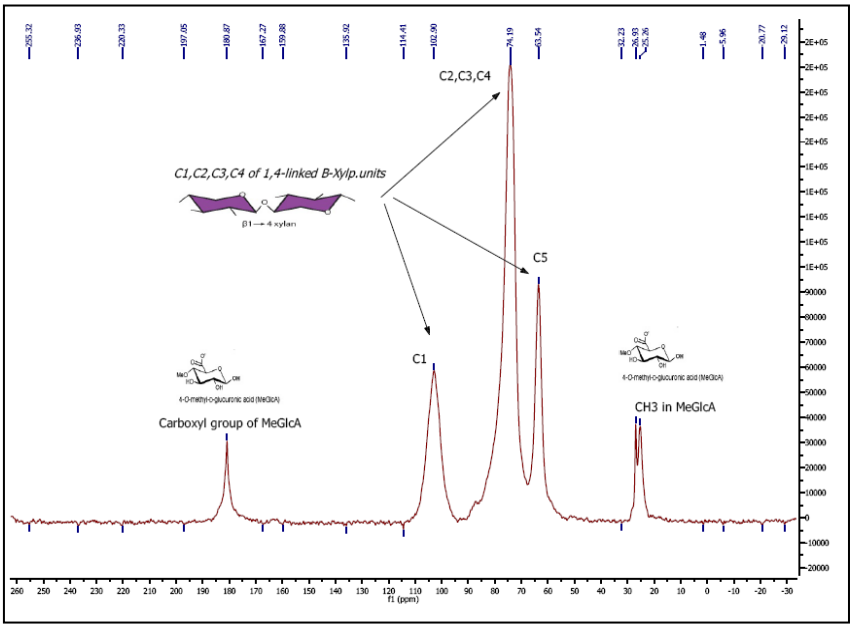
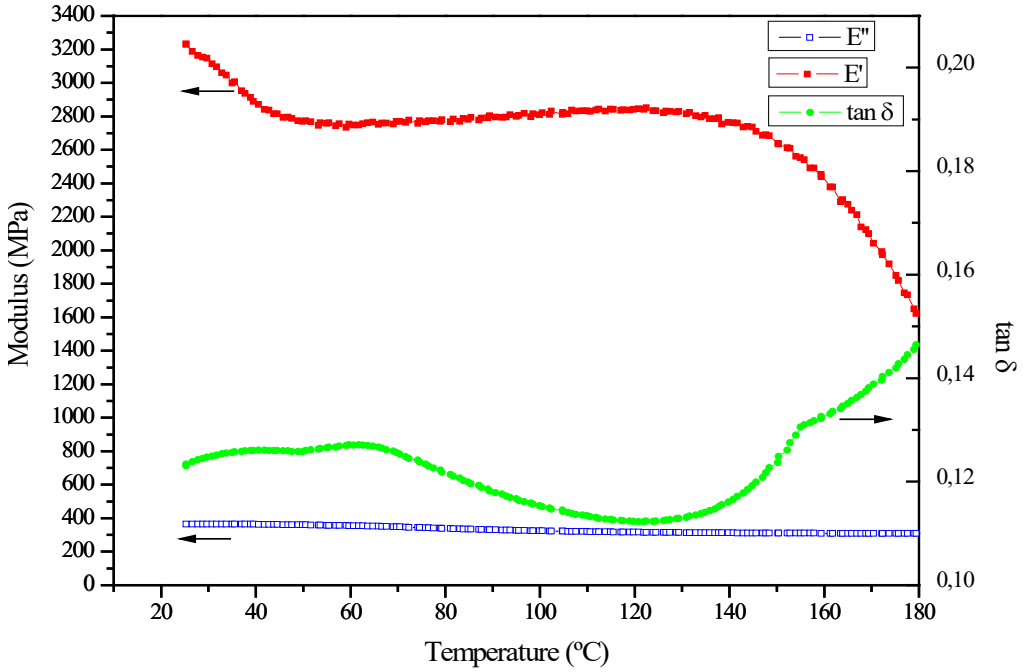

C2,C3,C4
C1,C2,C3,C4 of 1,4-linked B-Xylp.units
β1→4 xylan
C5
C1
4-O-methyl-α-glucuronic acid (MeGlcA)
Carboxyl group of MeGlcA
CH3 in MeGlcA
f1 (ppm)

Fig. 6


E''
E'
tan δ
Modulus (MPa)
tan δ
Temperature (ºC)
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
0,20
0,18
0,16
0,14
0,12
0,10
20
40
60
80
100
120
140
160
180