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### ► To cite this version:

Morad Chadni, Nabil Grimi, Olivier Bals, Isabelle Ziegler-Devin, Stéphane Desobry, et al.. Elaboration of hemicellulose-based films: Impact of the extraction process from spruce wood on the film properties. Carbohydrate Research, 2020, 497, pp.108111. 10.1016/j.carres.2020.108111 . hal-02969583

**HAL Id: hal-02969583**

**<https://hal.univ-lorraine.fr/hal-02969583>**

Submitted on 30 Aug 2022

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1 **Elaboration of hemicellulose-based films: impact of the extraction process**  
2 **from spruce wood on the film properties**

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24 **Abstract**

25 In this work, steam explosion (STEX), microwave assisted extraction (MAE) and high  
26 voltage electrical discharges (HVED) pretreatments have been evaluated for their impact on  
27 the physicochemical characteristics of extracted hemicellulosic polymers and on the resulting  
28 hemicellulose-based films. Extraction was carried out on spruce sawdust pre-soaked in water  
29 (WPS) or 1 M NaOH solution (SPS). The results have shown that STEX pretreatment gave  
30 the highest hemicellulose yields (64 and 66 mg.g<sup>-1</sup> of dry wood from WPS and SPS  
31 respectively) followed by MAE and HVED whilst MAE pretreatment produced the highest  
32 molecular mass ( $M_w \sim 66$  kDa of arabinoglucoronoxylans from SPS and 56 kDa for  
33 galactoglucomannans from WPS). A relatively high acetylation degree was found for STEX  
34 WPS (acetylation degree  $\approx 0.35$ ) and a high lignin content for STEX SPS ( $\approx 12\%$ ). Films  
35 have been produced by casting using sorbitol as plasticizer. Low oxygen barrier and light  
36 transmittance properties were observed for the films obtained from hemicelluloses extracted  
37 from SPS due to their high molecular mass and to intermolecular bonding of hemicelluloses  
38 and lignin.

39 **Key words:** Hemicelluloses, spruce wood, film formation, pretreatment of biomass, steam  
40 explosion

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48 **Abbreviation**

AD	Acetylation degree
AcGGM	Acetyl-Galactoglucomannan
AD	Acetylation degree
AGX	Arabinoglucoronoxylan
ASL	Acid soluble lignin
ASTM	American Society for Testing and Materials
DW	Dry wood
kDa	Kilo Dalton
GGM	Galactoglucomannans
HPLC	High performance liquid chromatography
HVED	High voltage electrical discharges
M	Mole
MAE	Microwave assisted extraction
OTR	Oxygen transmission rate
PD	Polymerization Degree
RH	Relative humidity
SD	Standard Deviation
SF	Severity Factor
SPS	Sodium hydroxide Pre-soaked Sawdust
STEX	Steam explosion
W	Weight
WPS	Water pre-soaked sawdust

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## 50 **1. Introduction**

51 Hemicelluloses represent a very promising resource and are gaining an increasing interest in  
52 their recovery and transformation into functional products. Spruce hemicelluloses are  
53 composed principally of acetyl-galactoglucomannans (AcGGM) 20 % of wood and  
54 arbinoglucuronoxylans (ARX) 5 – 10 % (Timell, 1967). AcGGM has a backbone of  $\beta$ -D-  
55 (1 $\rightarrow$ 4) -glucopyranosyl and  $\beta$ -D-(1 $\rightarrow$ 4)-mannopyranosyl units in a linear or slightly branched  
56 chain. Single  $\alpha$ -D-galactopyranose units are attached to the main chain by (1 $\rightarrow$ 6)-bonds. The  
57 mannopyranosyl units are acetylated at C-2 or C-3 with a degree of acetylation  $\approx$  0.5 (Timell,  
58 1967) and for water-soluble AcGGM a galactose-to-glucose-to-mannose ratio  $\approx$  0.5–  
59 1.1:1:3.5–4.5 (Sjöström, 1993). ARX are composed of a backbone of (1 $\rightarrow$ 4)-linked  $\beta$ -D-  
60 xylopyranose units and side groups at C-2 of 4-O-methyl- $\alpha$ -D-glucuronic acid groups on the  
61 average of two residues per ten xylose units.

62 One of the most promising applications of polymeric hemicelluloses is the film production  
63 because of their film-forming properties, their biocompatibility and biodegradability. The  
64 films can be produced by solution-casting from water and a plasticizer such as sorbitol, xylitol  
65 or glycerol is usually employed in order to achieve a good film flexibility (Pomes 1971). In  
66 addition, like most polysaccharides, hemicelluloses-based films are known to exhibit gas  
67 barrier properties especially toward oxygen [2] which makes them interesting for bio-  
68 packaging since the oxygen permeability is critical for many food stabilization processes [3].  
69 Hartman et al. [4] have developed films with GGM obtained from thermomechanical pulping  
70 (TMP) with low oxygen permeability and good mechanical properties using polysaccharides  
71 and a plasticizer such as alginate and carboxymethylcellulose. Mikkonen et al. [5] have shown

72 that GGM recovered from TMP process and crosslinked with glyoxal exhibited high  
73 mechanical performance and low oxygen permeability and water vapor permeability.

74 The valorization methods of spruce hemicelluloses described in the literature generally rely  
75 on the recovery of solubilized hemicelluloses in TMP process by filtration or ethanolic  
76 precipitation [6–11]. Studies dedicated to the extraction from wood of high molecular weight  
77 hemicelluloses are scarce. The extraction of polymeric hemicelluloses from wood is limited  
78 by the structure of the plant cell walls. In fact, the inherent structure and the composition of  
79 native lignocellulosic materials make the access to hemicelluloses hindered [12]. Overcoming  
80 the recalcitrance of lignocellulosic biomass through physico-chemical pretreatments has been  
81 the subject of extensive literature in the context of 2G bioethanol [13,14]. These pretreatments  
82 act either by decomposing the structure of the lignin and carbohydrates of the vegetal matrix  
83 and/or by creating cracks in the fiber wall to make the cellulose more accessible to enzymes.  
84 Hemicelluloses extraction have been described by hydrothermal treatment at high  
85 temperatures ( $\geq 170$  °C) [10,15], by chemical extraction (alkaline) [16–19] and ionic liquids  
86 [20], by pressured hot water [21,22], and by microwave heat-fractionation ( $> 180$  °C) [23–  
87 25].

88 In previous papers, we described the optimization of hemicelluloses extraction from spruce  
89 wood using physical activations including steam explosion (STEX), microwave assisted  
90 extraction (MAE) and high voltage electrical discharges (HVED) [26–28]. In this work we  
91 assessed the effect of these pretreatment technologies on the extraction of high molecular  
92 weight hemicelluloses and thus the effect on the resulting films properties. Extracts have been  
93 fully characterized, hemicelluloses-based films have been produced by casting and the oxygen  
94 permeability, light transmittance and the mechanical properties have been examined. The  
95 impact of the pretreatment step on the properties of the hemicelluloses and the films produced  
96 is discussed.

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## 99 **2. Materiel and method**

### 100 **2.1 Raw material**

101 Spruce sawdust with a particle size of 1 to 5 mm was produced from a spruce tree from the  
102 Lorraine region in France and stored at room temperature in sealed polyethylene bags in the  
103 dark until extraction. The average moisture content of the raw material was 9.93% w/w. The  
104 hemicelluloses content of the sawdust (~30% w/w dry wood) was calculated by analyzing  
105 noncellulosic monosaccharides of spruce wood according to NREL/TP-510-42618 method  
106 [29].

### 107 **2.2 Impregnation**

108 For HVED and MAE a mass of 20 g of spruce sawdust was pre-soaked with a solution of 1M  
109 sodium hydroxide or water (ratio solid:liquid = 1:7). The sawdust was left for one night 15h  
110 before treatment at room temperature. The same procedure was followed for STEX  
111 pretreatment, but with 50 g of sawdust instead of 20 g. In next paragraphs, Water Pre-soaked  
112 Samples are named (WPS) and Sodium hydroxide Pre-soaked Samples are named (SPS).

### 113 **2.3 Extraction procedure**

#### 114 **2.3.1 HVED pretreatment**

##### 115 **A. Pretreatment**

116 HVED pretreatment was carried out using a high voltage pulsed power 40 kV-10 kA  
117 generator (Basis, Saint Quentin, France), coupled to a 1-liter cylindrical batch treatment  
118 chamber. The HVED treatment chamber was equipped with needle-plate geometry electrodes.  
119 The diameters of stainless-steel needle and the grounded disk electrodes were 10 and 35 mm,

120 respectively. The distance between the electrodes was 10 mm. The energy was stored in a set  
121 of low-inductance capacitors, which were charged by the high-voltage power supply. The  
122 electrical discharges were generated by electrical breakdown in the medium of extraction  
123 (liquid) at the peak pulse voltage of 40 kV.

124 In all experiments the liquid-to-solid ratio was fixed at 15 (w/w). The HVED generator  
125 (40 kV, 10 kA) provided pulses of a sine form with a pulse repetition rate of 0.5 Hz.

## 126 **B. Diffusion**

127 The diffusion step **was added** in order to facilitate the transfer of hemicelluloses chains from  
128 wood matrix to the extracellular medium. Temperature during HVED treatment was 50 °C. In  
129 order to maintain mild conditions of extraction (low temperature, low decrease of pH), the  
130 diffusion was carried out in an Erlenmeyer flask under reflux at 50°C during 3 h with  
131 agitation.

132 A pretreatment at 4 ms was chosen as a reference for extraction with HVED based on  
133 previous work [28].

## 134 **2.3.2 Microwave pretreatment**

### 135 **A. Pretreatment**

136 MAE experiments for the extraction of hemicelluloses from spruce sawdust were carried out  
137 using a microwave laboratory system (230V-50 Hz, NEOS-GR, Milestone, Italy). This mono-  
138 mode apparatus operates at 2.45 GHz with maximum delivered power of 900 W regulated in  
139 10-Watt increments with a temperature and power feedback/control. This instrument **was**  
140 equipped with time controller. The experiments were performed at atmospheric pressure.  
141 Time and power were controlled and followed by the software. The MAE experiments were  
142 conducted in a glass extraction vessel. The samples were treated for 1h using different



143 selected powers. Indeed, the effects of microwave irradiation, nature of solvent and consumed  
144 energy were studied. The liquid-to-solid ratio was fixed at 7 during microwave treatment.

145

## 146 **B. Diffusion**

147 After microwave treatment, supplementary diffusion step was done by a heating under reflux  
148 at low temperature to avoid degradation of polymeric chains (70 °C for 3 h). The liquid-to-  
149 solid ratio was fixed at 15 (w/w).

150 A treatment at 573 Watts was chosen as reference for MAE based on previous studies [26].

### 151 **2.3.3 Steam explosion**

152 Soaked sawdust was placed into a 2-liter reactor with heat jacket and automatic control for  
153 steam pressure and sampler residence time. The biomass was treated at different temperatures  
154 by injecting a saturated steam into a pressure resistance chamber. After a given reaction time,  
155 the steam saturated biomass was released into a discharge tank as well the biomass.

156 A treatment at 190 °C for 10 min was chosen as reference for steam explosion extraction  
157 based on previous work [27] .

158 The reference conditions chosen for HVED, MAE, and STEX are based on the previous  
159 studies. For each pretreatment, these conditions gave hemicelluloses with the highest  
160 molecular mass [26, 27,28].

## 161 **2.4 Hemicelluloses recovery**

162 After extraction, the obtained suspension was filtered on qualitative filter paper with  
163 retention particle size of 5–13 µm (VWR International, Fontenay-sous-Bois, France). The  
164 volume and final pH of the extract solutions were measured at room temperature shortly  
165 after the extraction. The liquid fraction from 1M NaOH impregnated sawdust was  
166 neutralized to a pH of 5.5-6 by a solution of 72 % H<sub>2</sub>SO<sub>4</sub>. 10 mL were taken from the

167 filtered extract for analyses. The extract solution was concentrated by vacuum evaporation  
168 using a water bath at 50 °C. To precipitate high-molecular weight hemicelluloses, four  
169 volumes of ethanol (95%) were added to the liquid extracts. The liquid phase was separated  
170 from the precipitated hemicelluloses by settling at room temperature and decantation.  
171 Hemicelluloses were further separated from the remaining liquid by centrifugation at 3724 g  
172 for 10 min at room temperature. The precipitated hemicelluloses were re-dissolved in  
173 distilled water and then dialyzed with a dialysis membrane with a cut-off of 3.4 kDa  
174 (Spectrum Laboratories, Inc., Rancho Dominguez, CA, USA). Finally, dialyzed  
175 hemicelluloses solutions were freeze-dried.  
176 Calculated yield represents the weight of recovered hemicelluloses powder related to dry  
177 wood weight.

## 178 **2.5 Measurement of monosaccharides and uronic acids using HAPE-PAD**

179 The monosaccharides content of the soluble fraction was analyzed by ionic chromatography  
180 according to NREL/TP-510-42618 procedure. After acid hydrolysis of samples, sugars and  
181 uronic acids were quantified by HAPE-PAD (ICS-3000 Dionex, Dionex Corp., Sunnyvale,  
182 USA) equipped with a Dionex CarboPac<sup>TM</sup> PA-20 (3 × 150 mm) analytical column. Filtered  
183 (0.20 μm) samples (20 μL) were eluted at 35°C and at 0.4 mL.min<sup>-1</sup> with the following  
184 composition: pure water 99.2 %/250 mM NaOH 0.8%: 0–20 min; pure water 75 %/250 mM  
185 NaOH 20%/ NaOCOCH<sub>3</sub> (1 M)- NaOH (20 mM) 5% 20–37 min; and pure water 40%/250  
186 mM NaOH 20%/NaOCOCH<sub>3</sub> (1 M)- NaOH (20 mM) 40 % 37–41 min. Each elution was  
187 followed by a wash and a subsequent equilibration step. External sugar and uronic acid  
188 standards were used for calibration (7 points per curve). The reagents and standards are  
189 provided by Sigma-Aldrich and Fisher Scientific.

## 190 **2.6 Acetyl content**

191 Acetyl content of extracted hemicelluloses was calculated by measuring the acetic acid  
192 concentration after a saponification reaction. Acetic acid was analyzed according to  
193 NREL/TP-510-42623 method using an Ultimate 3000 HPLC system.

194 Acetic acid was separated in 45 min on an Agilent Hi-Plex H column at 55 °C with an  
195 isocratic flow rate of 0.4 mL.min<sup>-1</sup> with sulfuric acid (5. 10<sup>-3</sup> M) as an eluant and detected by  
196 UV at 210 nm. An external calibration was performed with six calibration points per standard.  
197 Reagents and standards were provided by Sigma-Aldrich.

## 198 **2.7 Gel filtration chromatography**

199 A Shimadzu Prominence HPLC system was used to estimate the relative molecular weight  
200 distribution of hemicelluloses by gel permeation chromatography. The stationary phase was  
201 composed of two columns linked in series: Phenomenex Polysep GFC-P as a guard column  
202 (7.8×35 mm), Phenomenex Polysep GFC-P3000 and GFC-P2000 as analytical columns  
203 (7.8×300 mm). Sodium nitrate (0.25 M) was used as an eluent with a 0.5 mL.min<sup>-1</sup> flow rate.  
204 Samples were solubilized in sodium nitrate (0.25 M) solution and filtered (0.45 µm) and 20  
205 µL are injected. Samples were separated at 30 °C and detection was done with a Refractive  
206 Index Detector (Shimadzu RID-20A). Solutions (1 mg.ml<sup>-1</sup>) of dextran standards with  
207 molecular weights of 1; 5; 12; 24; 50 and 80 kDa were used to prepare the calibration curve.

## 208 **2.8 Soluble lignin**

209 The acid-soluble lignin (ASL) content of hemicelluloses was determined by solubilizing  
210 hemicelluloses and measuring the absorbance at 205 nm according to the laboratory analytical  
211 procedure (LAP) provided by the National Renewable Energy Laboratory [29]

$$212 \quad \% \text{ ASL} = \frac{(Abs_{205 \text{ nm}} \times V_t \times Dilution \times 100)}{\epsilon \times DM_i \times Pathlength} \quad Eq. (1)$$

213 where  $V_t$  is the total volume of sample (L);  $\epsilon$  is the absorptivity of biomass at specific  
214 wavelength and  $DM_i$  is the initial dry matter (g).

## 2.9 Preparation of films

Films were prepared from hemicelluloses extracted by pretreatments according to the proposed procedure of Mikkonen (2010). Hemicelluloses powder were dispersed in distilled water ( $10 \text{ g.L}^{-1}$ ) under magnetic stirring at  $90 \text{ }^\circ\text{C}$  for 10 min. Sorbitol was then added at 40 wt% of the weight of hemicelluloses. Sorbitol was used as plasticizer for all films, because was recently shown in hemicellulose films to result in more stable plasticization (less migration of plasticizer) [30]. The suspension was dispersed a second time under magnetic stirring at  $60 \text{ }^\circ\text{C}$  for 5 min, then degassed by ultrasonication, cast into Teflon Petri dishes, and dried at  $60 \text{ }^\circ\text{C}$ .

## 2.10 Characterization of films

### 2.10.1 Mechanical properties

The mechanical properties of the prepared films were determined at 46 % RH using a universal testing machine Lloyd instrument (AMETEK, United Kingdom) according to ASTM D882. These properties consisted of elongation at break (%), tensile strength (kPa) and Young's modulus (kPa). Sample films of  $2 \text{ cm} \times 6 \text{ cm}$  (analyzed area =  $3.5 \text{ cm} \times 2 \text{ cm}$ ) uniaxially stretched (with a constant speed of  $10 \text{ mm.min}^{-1}$ ). The stress–strain curves were recorded and analyzed with Nexygen software.

### 2.10.2 Oxygen permeability determination

#### A. Oxygen transmission rate

The oxygen transmission rate (OTR) was measured with an oxygen permeation analyzer (8001 Oxygen Permeation Analyzers, SYSTECH Illinois) at  $23 \text{ }^\circ\text{C}$  and 0 % RH. The apparatus allows a direct measurement of the oxygen without using complex extrapolations. The oxygen permeability (OP) ( $\text{cm}^3 \cdot \mu\text{m} \cdot \text{m}^{-2} \cdot \text{day}^{-1} \cdot \text{kPa}^{-1}$ ) was then calculated by the following equation:

239 
$$OP = OTR \times \frac{X}{\Delta p} \qquad \text{Eq. (2)}$$

240 where,  $X$  is the film thickness ( $\mu\text{m}$ ) and  $\Delta p$  is the partial pressure difference of  $\text{O}_2$  across the  
241 film (kPa).

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## 244 **B. Thickness measurement**

245 The thickness of the films was photographed by a scanning electron microscope (HITACHI,  
246 TM 3000). The thickness of the films was then measured by the software (Image Pro  
247 Premier). No preparation was made before the analysis, the films were cut in the form of  
248 small rectangles and placed directly on the microscope. The thickness was taken in 3 points  
249 on each film and then the average of three films was calculated ( $\mu\text{m}$ ).

### 250 **2.10.3 Light transmittance**

251 The light transmittances of the films were scanned from 190 to 900 nm wavelength using a  
252 Shimadzu UV-vis spectrophotometer (Libra S32, Biochrom, Lagny-sur- Marne, France).

### 253 **2.11 Statistical analysis**

254 All experiments were conducted at least in duplicates. The means and error bars were  
255 calculated and were represented in all figures.

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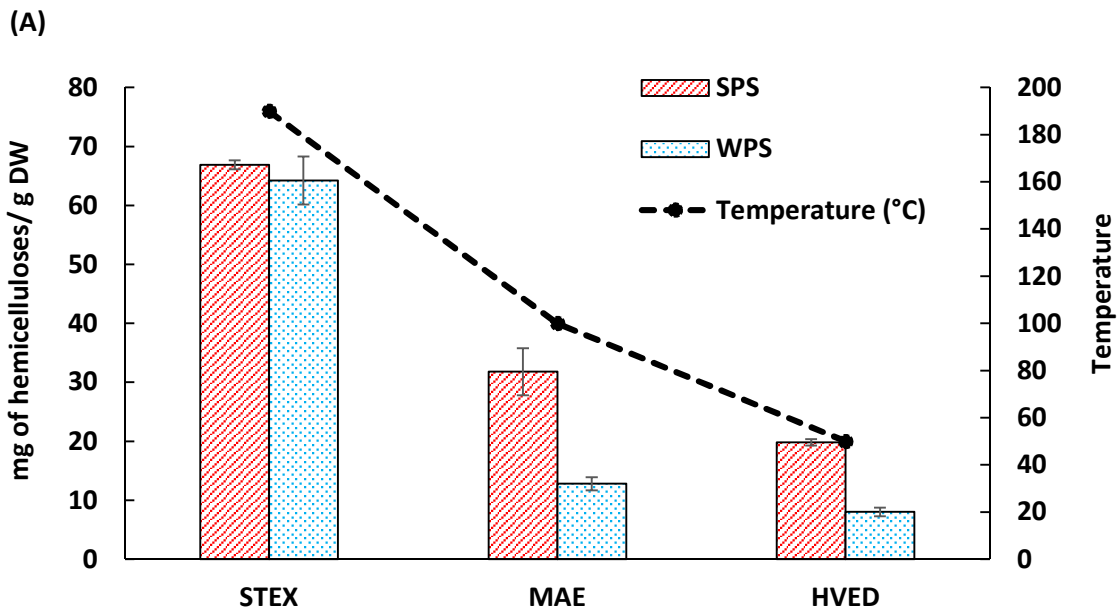
### 3. Results and discussion

#### 3.1 Hemicelluloses extraction yields and molecular weights

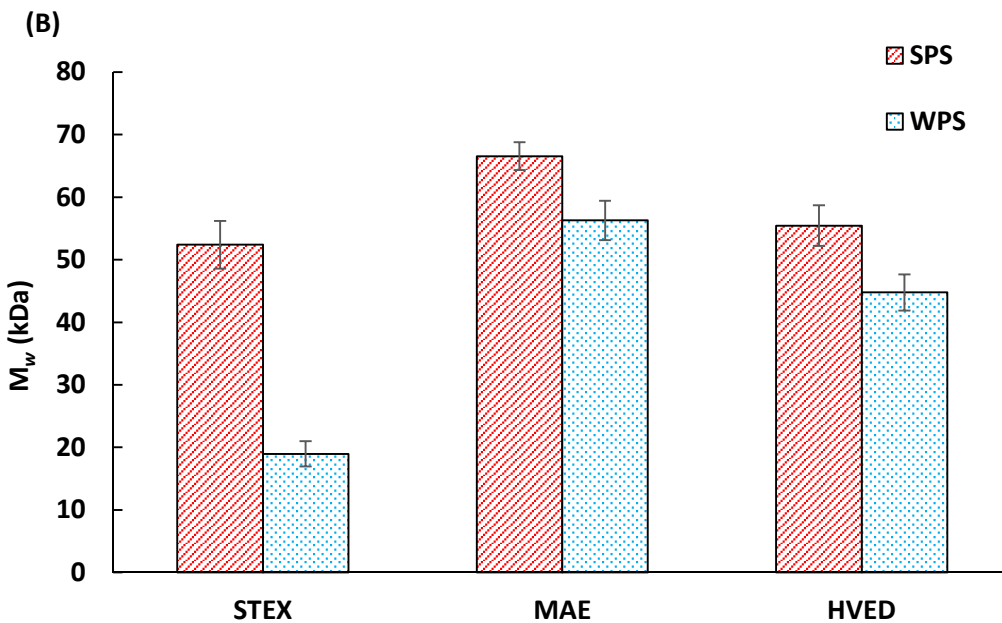
Fig. 1 shows the extraction yields and molecular weight of polymeric hemicelluloses recovered after neutral and basic pretreatment (WPS and SPS respectively). Three different pretreatment technologies have been compared: steam explosion (190 °C, 10 min), microwave at atmospheric pressure (100°C, 1 h) and high voltage electrical discharges (50 °C, 4 ms).

It appears from Fig. 1. A that STEX gave higher extraction yields (64 and 66 mg.g<sup>-1</sup> DW for WPS and SPS respectively) than MAE (12.8 and 31.8 mg.g<sup>-1</sup> DW for WPS and SPS respectively) and HVED (8 and 19.8 mg.g<sup>-1</sup> DW for WPS and SPS respectively). STEX relies on the extraction of hemicelluloses chains from wood matrix by autohydrolysis (due to an auto-catalyzed acid hydrolysis). During the steaming stage of STEX performed at 190 °C - 10 min after a water impregnation (WPS), hemicelluloses carboxylic acids generated acidic conditions which are responsible for the hydrolysis of glycosidic bonds. As a result, hemicellulosic chains with a relatively low molecular weight ( $M_w \sim 20$  kDa) (Fig. 1. B) and high amount of monomer sugars (2 mg. g<sup>-1</sup> DW) have been isolated. For basic impregnation (SPS), significantly higher molecular mass of hemicelluloses ( $M_w \sim 52.4$  kDa) have been recovered associated with a lower concentration of monosaccharides (less than 0.1 mg. g<sup>-1</sup> DW).

283 The molecular weight of hemicelluloses extracted by MAE (56.30 kDa and 66 kDa from WPS  
284 and SPS fraction respectively) were higher than those obtained by STEX and HVED. Based  
285 on literature data, microwave irradiations involve the disruption of wood fibers which is due  
286 to the selective interaction of microwaves with the inhomogeneous lignocellulosic materials  
287 [31]; The HVED pretreatment gave hemicelluloses with  $M_w \approx 44.7$  and 55.4 kDa from WPS  
288 and SPS fraction respectively. HVED pretreatment primarily relies only on the physical and  
289 mechanical effects caused by electrical discharges since the reached temperature during the  
290 pretreatment is relatively low (50 °C). The application of HVED-treatment results in  
291 generation of shockwaves. These shockwaves may play an important role in the raw material  
292 fragmentation, thus facilitating hemicelluloses extraction [32]. The formation of the shock  
293 waves in liquid medium is often followed by the formation of cavitation bubbles. The  
294 combined effect of shockwaves and cavitation bubbles may improve the disruption and the  
295 destabilization of cell walls [32–34].



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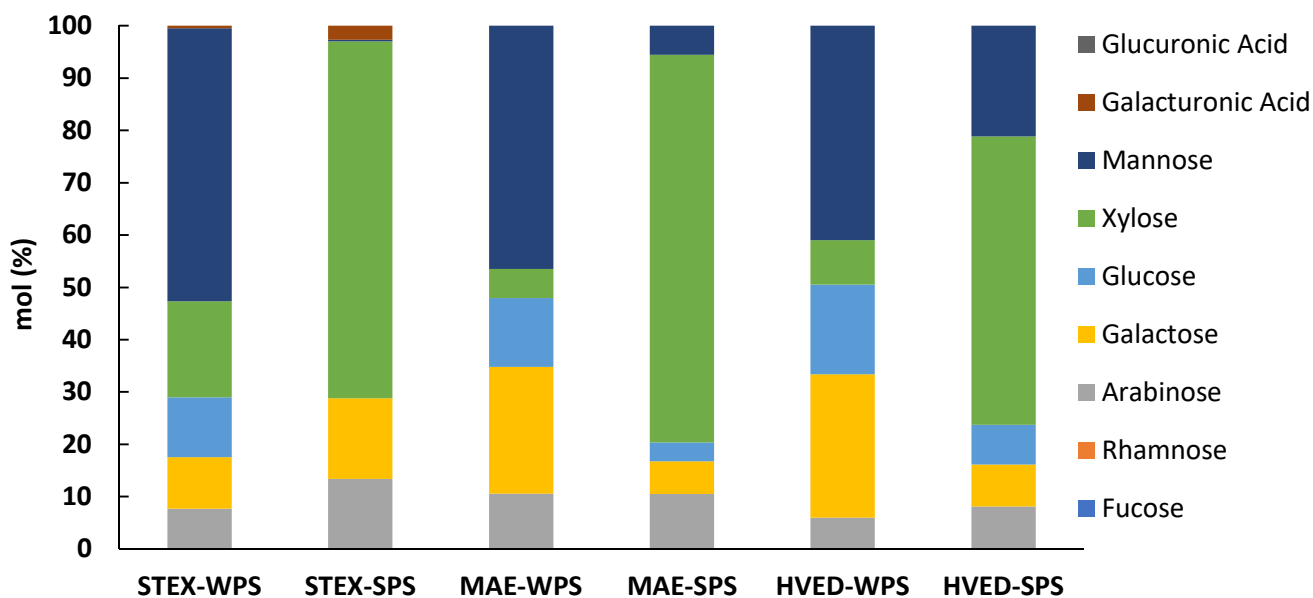
298 Fig. 1. Yield of extraction of hemicelluloses (A) and molecular mass analysis (B).

299 **3.2 Sugar composition, acetylation degree and phenolics content of extracted**  
 300 **hemicelluloses**

301 The monomeric sugar compositions of the hemicellulosic fractions have been established after  
 302 acid hydrolysis by ionic chromatography. From Fig. 2 it appears that the presoaking  
 303 conditions strongly influenced the selectivity of extraction. For WPS, mannose is the



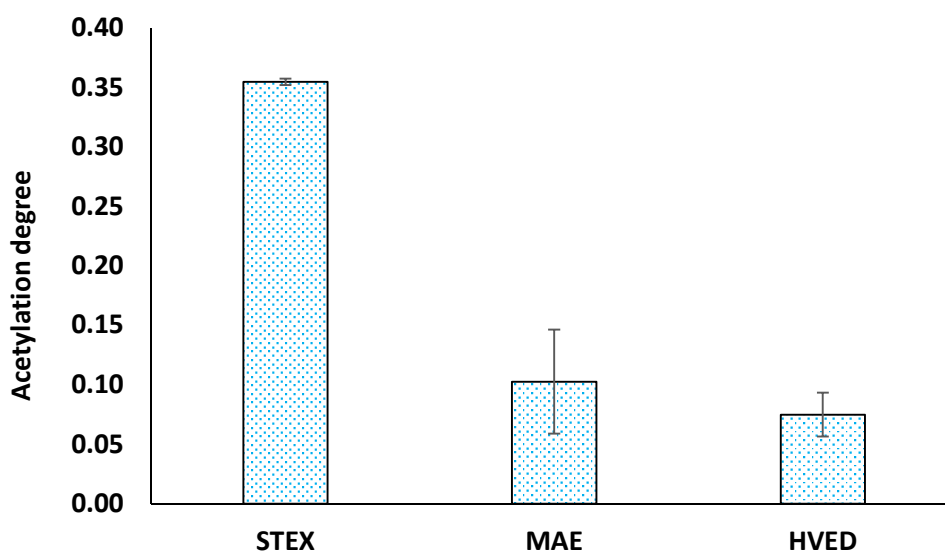
304 dominant sugar (41–52%), followed by galactose (10–28%), glucose (12–18%). Concerning  
 305 SPS, xylose and arabinose are the most abundant (55–69% and 8–13% respectively), and  
 306 mannose is present in low amounts. These observations are in agreement with those reported  
 307 by Perez et al. [35] who have found that spruce hemicelluloses extracted in acidic conditions  
 308 are primarily composed of galactoglucomannans with a high proportion of mannans (at least  
 309 45%, up to 57%), then glucans (16 to 25%) and galactans (13 to 19%). Some arabinoxylans  
 310 are also present (>15%), while, the hemicelluloses obtained in basic conditions are a mixture  
 311 of arabinoxylans and galactoglucomannans with a heavily contamination with lignin (> 18%).  
 312 According to Svard et al. [36], the sugar composition of hemicelluloses extracted from  
 313 lignocellulosic biomass is a function of the extraction pH because their solubility is affected  
 314 by the substituents on the polymeric chain [37]. As a result, neutral and acidic media could  
 315 promote the solubilization of water soluble AcGGM [25]. On the other hand, basic medium  
 316 yielded a xylose-rich extract because of the methyl glucuronic acid and arabinose substituents  
 317 of AGX [38,39]. It can also be observed that with STEX-WPS and HVED-SPS, higher  
 318 amounts of xylose and mannose were detected respectively.



3

320 Fig. 2. Sugar composition of extracted hemicelluloses from WPS (A) and SPS (B)

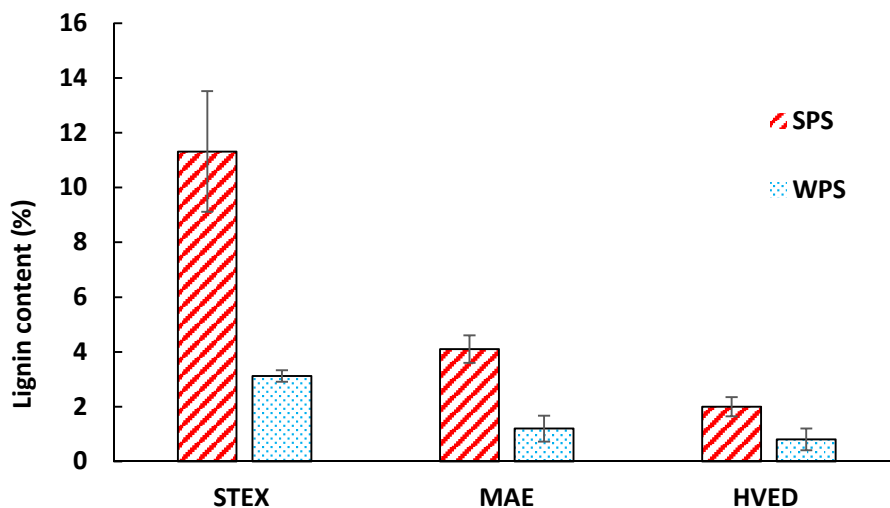
321 The acetylation degree of extracted hemicelluloses from WPS has been determined by HPLC  
322 after saponification and are given in Fig. 3. The molar Ac/Man ratios were used as a measure  
323 for the acetylation degree (AD). As expected, hemicelluloses recovered from SPS are totally  
324 deacetylated due to the saponification of acetyl moieties in basic conditions (results are not  
325 shown). After water presoaking, the AD for hemicelluloses extracted by STEX (AD = 0.36) is  
326 closed to the values reported for native AcGGM, determined by NMR and titration methods  
327 [8,40] and higher compared to those reported in previous studies for AcGGM recovered from  
328 TMP process and from spruce wood [41,42]. Hemicelluloses from MAE and HVED  
329 displayed a lower AD (0.1 and 0.07 respectively). From this result, it can be concluded that  
330 STEX pretreatment allows to extract slightly modified and highly acetylated AcGGM  
331 oligomers from spruce.



332  
333 Fig. 3. Acetylation degree of extracted hemicelluloses from WPS

334 The hemicellulosic fractions recovered after precipitation and dialysis contained minor  
335 amounts of lignin. As shown in Fig. 4, the lignin content is a function of the extraction  
336 conditions. Higher amounts of lignin were detected for hemicelluloses extracted from SPS.  
337 This can be explained by the well-known delignification reactions in basic media, producing  
338 small fragments of soda lignin recovered in the liquid stream with the polysaccharides. Higher

339 lignin contents were observed for STEX compared to MAE and HVED because of the higher  
340 temperature used during the steaming step. The presence of lignin fraction co-extracted with  
341 hemicelluloses in basic conditions (lignin-hemicellulose complexes), may restrict the  
342 dissolution of certain hemicellulose fractions especially for (STEX SPS) and could affect their  
343 molecular mass.



344

Fig. 4. Lignin content of extracted hemicelluloses

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### 3.3 Characterization of films

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347 The extracted hemicelluloses from each pretreatment and from both conditions (SPS and  
348 WPS) were used to prepare films by a casting procedure in the presence of 40% of sorbitol  
349 used as a plasticizer. The resulting films (Fig. 5) have been analyzed in terms of oxygen  
350 permeability, mechanical strength and light transmittance and then compared to starch film.

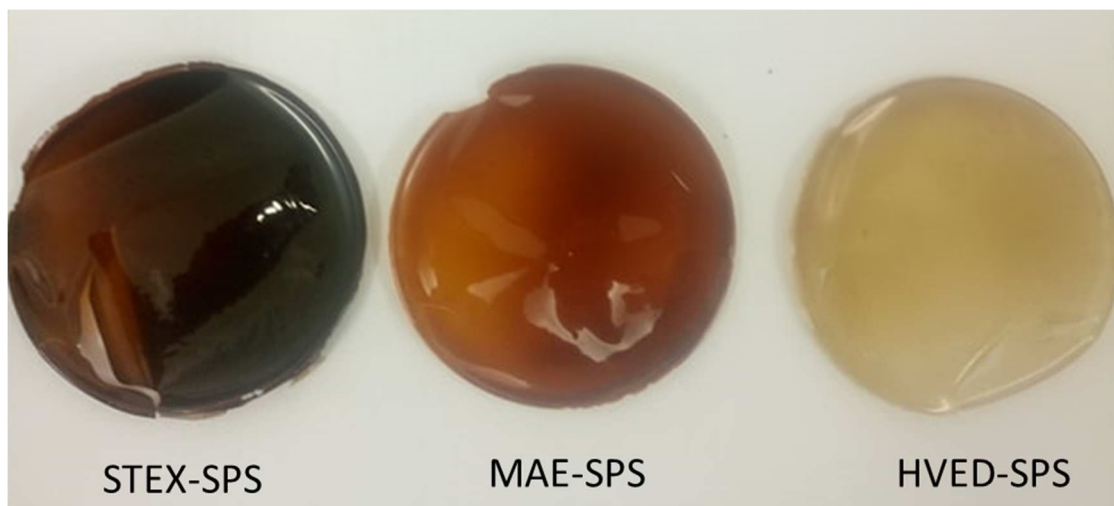


Fig. 5. Aspect of film made from hemicelluloses extracted from SPS.

### 3.3.1 Mechanical strength

Results of mechanical tests are given in Table 1. Elongation at break is the ratio between changed length and initial length after breakage of the film (elastic and plastic deformations). This factor indicates the ability of the film to resist to the changes of the shape without cracking. The highest elongation was found for MAE SPS (6.55%) followed by HVED SPS (6.3%), HVED WPS (5.65%) and MAE WPS (4.95%). The elongation of starch film was 8.45%. Films from STEX showed low elongation, especially for STEX WPS, which is due principally to the low molecular weight of hemicelluloses ( $M_w \sim 14$  kDa). Considering the films composition (cf. Fig. 4), the higher lignin content of films obtained after STEX SPS might be responsible for their lower mechanical properties. In accordance with Westbye et al. (2007), the relatively high lignin content in the hemicelluloses extract ( $\approx 11\%$  w/w, Fig. 4) could impact the film formation and decrease its mechanical performance because of lignin agglomeration and uniform dispersion that had a negative effect on the mechanical strength of films.

Tensile tests measure the force required to break the sample and the extent to which the specimen stretches or elongates to that breaking point. The tensile strength of films was

369 interestingly found to be independent on the type of pretreatment and the composition of  
370 hemicelluloses. In comparison, the tensile strength of films from hemicelluloses extracted  
371 from SPS was higher than those from WPS. Thus, the tensile strength of HVED SPS (16.48  
372 MPa) films was higher compared to STEX SPS and MAE SPS films (8.85 and 8.44 MPa  
373 respectively).

374 Mikkonen et al. [5] have found that the tensile strength and the elongation at break of films is  
375 dependent on the degree of polymerization (DP) of hemicellulose chains. The elongation at  
376 break of guar gum-based films reached a maximum at medium low polymerization, and the  
377 tensile strength reached a maximum at medium high and medium low polymerization. In our  
378 study a DP between 254 and 406 was found to be the optimum value for high elongation at  
379 break ( $> 4.95\%$ ) which match with HVED SPS, HVED WPS, MW WPS and MAE WPS  
380 films. The high amount of lignin in STEX SPS films reduces its elongation at break. The  
381 highest value of tensile strength was for HVED SPS films (16.48 MPa) which means that DP  
382 of 338 is the optimum value for high tensile strength.

383 Young's modulus (E) is a mechanical property that measures the stiffness of a solid material.  
384 The values of E was very close for all films made from hemicelluloses extracted in basic  
385 medium due to their high DP ( $>238$ ). For STEX WPS film, the Young's modulus is very low  
386 ( $E = 42.4$  MPa) due to the lowest DP of hemicelluloses (DP = 85).

387 The mechanical properties of pure spruce hemicellulose films can be improved by mixing  
388 them with other polysaccharides. For example, addition of microfibrillated cellulose (MFC) as  
389 reinforcement can enhance film performance. GGM from spruce reinforced with MFC gave  
390 films with a high Young's modulus (0.8–1 GPa) and elongation at break at 3–5% [43].  
391 Arabinoxylan from rye blended with MFC resulted in higher film characteristics (Young's  
392 modulus: 2–2.5 GPa and elongation at break: 5–10%) [44].

Table 1: Mechanical properties of hemicellulose films

	Young's Modulus (MPa)		Tensile Strength (MPa)		Elongation at break (%)	
	Average	SD	Average	SD	Average	SD
HVED WPS	149.5	19.1	3.0	0.2	5.7	0.3
HVED SPS	402.4	5.0	16.5	1.3	6.3	0.5
MAE WPS	255.1	20.1	5.2	0.0	5.0	0.3
MAE SPS	331.4	15.0	8.4	2.8	6.6	0.4
STEX WPS	42.4	2.3	0.9	0.1	3.3	0.0
STEX SPS	366.3	0.2	8.9	0.0	0.1	0.1
Starch	1279.1	46.1	23.1	2.2	8.5	0.0

### 3.3.2 Oxygen permeability

396 Polysaccharides are generally a good oxygen barrier. The hydrogen bonds of polysaccharides  
397 contribute to good packing of the material and thus a low permeability of gas. The oxygen  
398 permeability (OP) of prepared films is shown in Table 2. The results show that values of the  
399 OP of films from hemicelluloses are lower than  $10 \text{ cm}^3 \cdot \mu\text{m} \cdot \text{day}^{-1} \cdot \text{kPa}^{-1}$ , thus they can be  
400 considered as a good oxygen barrier for food packaging [45]. The oxygen permeability of  
401 films made from hemicelluloses extracted from SPS is slightly lower than those extracted  
402 from WPS. The high amount of lignin present in these films and the sugar composition of  
403 hemicelluloses can explain this difference. In fact, it was reported that the presence of lignin  
404 and native intermolecular and intramolecular hemicelluloses–lignin interactions in  
405 hemicellulose-based coatings applied on polyethylene terephthalate films decrease the OP up  
406 to more than 5-fold compared with the coatings obtained with purified spruce hemicelluloses

407 [46]. This property of lignin could provide a new application of spruce hemicelluloses without  
408 delignification of wood or high refining procedure. In this sense, the pretreatment with STEX  
409 of SPS might be thought to be more advantageous compared to other pretreatments since the  
410 lignin contents of these hemicelluloses was significantly higher and could lead to better  
411 oxygen barrier properties on the basis of our results and those reported by Zhu Ryberg et al.  
412 [46] and Bahcegul et al. [47].

413 The type of pretreatment (STEX, MAE, HVED) did not significantly affect the OP of the  
414 resulting films. The OP of spruce hemicellulose films in our study are near to films from  
415 AcGGM–alginate ( $0.6 \text{ cm}^3 \cdot \mu\text{m} \cdot \text{day}^{-1} \cdot \text{kPa}^{-1}$ ) [4], Rye bran arabinoxylan ( $0.87 \text{ cm}^3 \cdot \mu\text{m} \cdot \text{day}^{-1} \cdot \text{kPa}^{-1}$  at 50 % RH) [48] and lower than those from Konjac tuber glucomannan ( $6.1 \text{ cm}^3 \cdot \mu\text{m} \cdot \text{day}^{-1} \cdot \text{kPa}^{-1}$  at 50 % RH) [30], Locust bean galactomannan ( $18 \text{ cm}^3 \cdot \mu\text{m} \cdot \text{day}^{-1} \cdot \text{kPa}^{-1}$  at RH 50–75%) [30]. Furthermore the OP obtained for those films are lower than those of  
419 conventional petroleum-based barrier materials at (23 °C - 50 % RH), such as polyethylene  
420 terephthalate  $1,000\text{-}5,000 \text{ cm}^3 \cdot \mu\text{m} \cdot \text{m}^{-2} \cdot \text{day}^{-1} \cdot \text{atm}^{-1}$  which correspond to  $10\text{-}50 \text{ cm}^3 \cdot \mu\text{m} \cdot \text{m}^{-2} \cdot \text{day}^{-1} \cdot \text{kPa}^{-1}$ , and polypropylene  $50,000\text{-}10,000 \text{ cm}^3 \cdot \mu\text{m} \cdot \text{m}^{-2} \cdot \text{day}^{-1} \cdot \text{atm}^{-1}$  which correspond to  $500\text{-}100 \text{ cm}^3 \cdot \mu\text{m} \cdot \text{m}^{-2} \cdot \text{day}^{-1} \cdot \text{kPa}^{-1}$  [49].

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Table 2: Oxygen permeability of films

Film	OP (cm <sup>3</sup> .μm. m <sup>-2</sup> .day <sup>-1</sup> . kPa <sup>-1</sup> )	
	Average	SD
HVED SPS	0.75	2.25E-03
HVED WPS	0.83	2.25E-03
STEX SPS	0.73	4.50E-03
STEX WPS	0.80	2.25E-03
MAE SPS	0.67	0.00E+00
MAE WPS	0.81	2.25E-03
Starch	0.7	0.00E+00

431

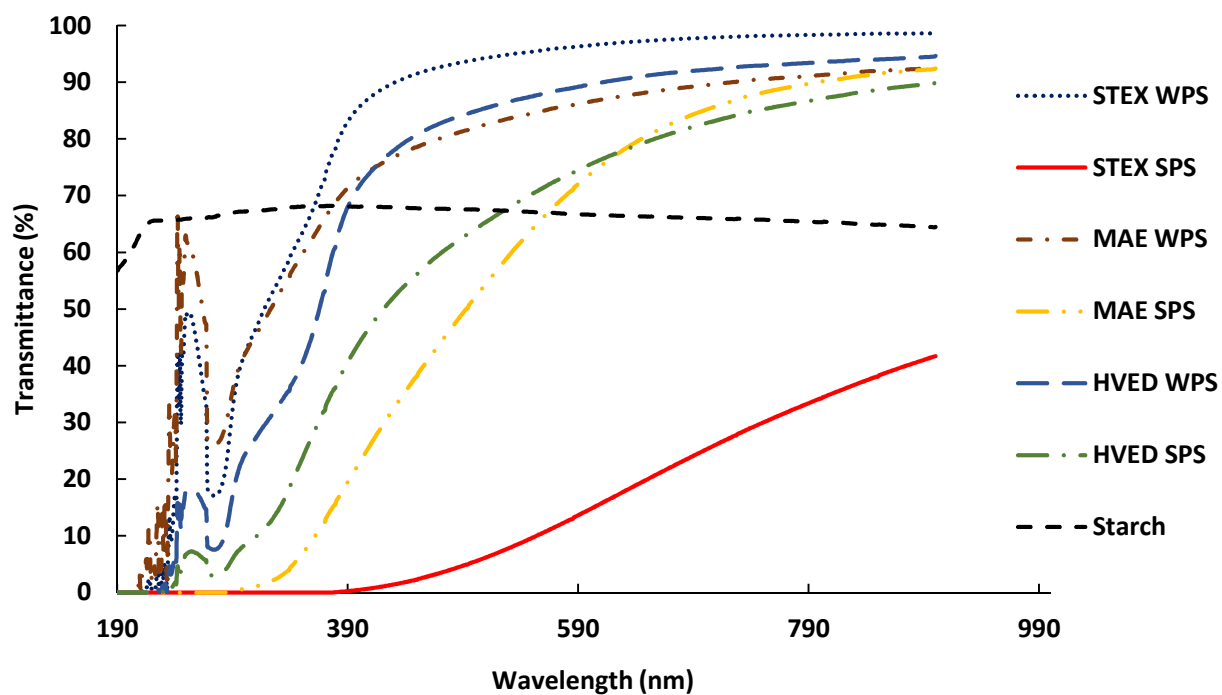
432

### 3.3.3 Light transmittance

433 Light exposure may lead to some adverse effects on foods. It is well known that the light  
434 exposure may catalyze some reactions which are considered to be complex in nature and the  
435 most-pronounced effects are observed with light in the lower wavelengths of the visible  
436 spectrum and in the UV spectrum [50]. The damage caused by light exposure on food may be  
437 summarized as the oxidation of fats and oils, the formation of unpleasant off-flavors, losses of  
438 vitamins A, B, C and the discoloration of pigments [50]. Fig. 6 shows that hemicellulose-  
439 based films block the light transmission mostly in UV region (190-400 nm). In accordance  
440 with the lignin contents and the colors of the films, WPS- films are almost transparent in the  
441 visible area of spectrum in contrast to films produced from hemicelluloses extracted in basic  
442 medium (11.3, 4.1 and 2 % for STEX-SPS, MAE-SPS and HVED-SPS hemicelluloses  
443 respectively). Film from starch did not affect the light transmittance significantly in the UV



444 region. All GGM containing films showed a drop in the UV region (278 nm). Films rich with  
445 ARX and lignin are opaque in the UV region of the spectra.



446

447 Fig. 6. Light transmittance of films

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## 459 **Conclusion**

460 The extraction of polymeric hemicelluloses by steam explosion, high voltage electrical  
461 discharges and microwave assisted extraction pretreatments of impregnated spruce sawdust  
462 was investigated. The study has shown that the impregnation in water have promoted the  
463 solubilization of GGM with low lignin content ( $\% \text{ ASL} < 3.12 \%$ ) while the impregnation in  
464 basic solution has promoted the solubilization of ARX with a higher lignin contamination ( $2 <$   
465  $\text{ASL} \% < 11.5$ ). The results have shown that the operating conditions of pretreatment  
466 especially temperature and pH, were the main reason behind the differences of yield and  
467 molar mass observed between pretreatments. STEX was found to be more efficient for the  
468 extraction of high amounts of low molecular mass hemicellulose chains followed by MAE  
469 and HVED. Films prepared from hemicelluloses with high content of lignin (STEX SPS)  
470 present a good barrier property and a very low light transmittance, but weaker mechanical  
471 strength. Films from HVED pretreatments also present a good barrier to oxygen and have a  
472 good mechanical characteristic compared to MAE and STEX films.

473

## 474 **Acknowledgment:**

475 This work was financially supported by SOFREN Company and ANRT “Agence National de  
476 la Recherche et de la Technologie”. The authors appreciate the financial support from  
477 SOFREN and ANRT. LERMAB is supported by the French National Research Agency  
478 through the Laboratory of Excellence ARBRE (ANR-12- LABXARBRE-01). LIBio is  
479 acknowledged for the assistance in films characterization.

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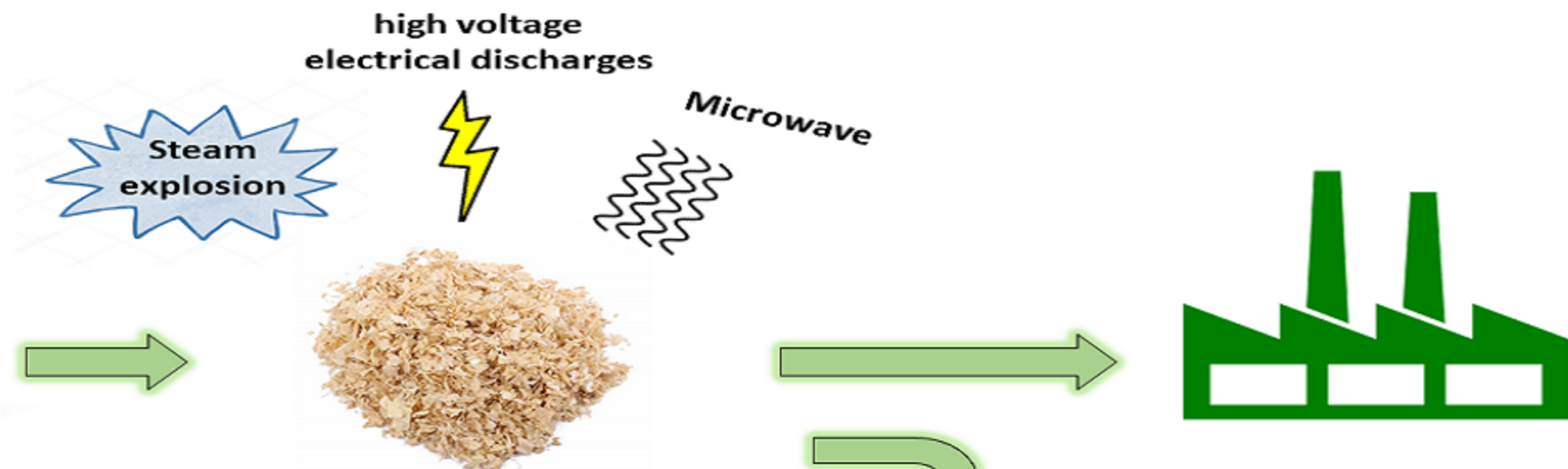
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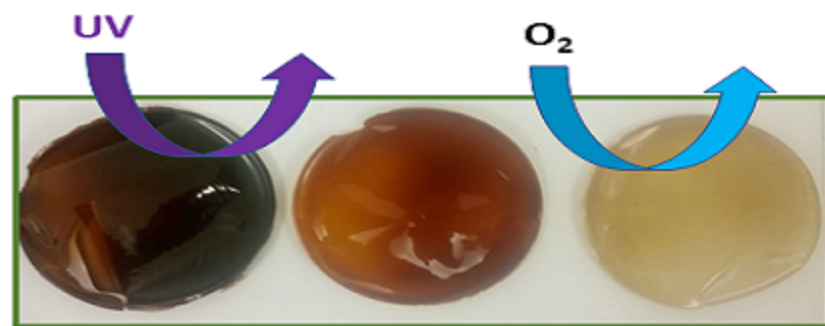
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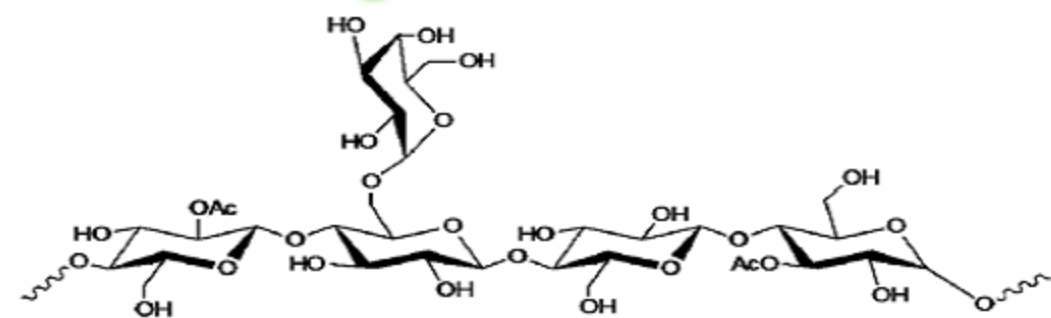
Spruce tree



Physical pretreatments



Hemicellulose-based films



Hemicellulose polymers