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## Potential of polysaccharides for food packaging applications. Part 1/2: An experimental review of the functional properties of polysaccharide coatings

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1                                   **Potential of polysaccharides for food packaging applications**  
2   **An experimental review of the functional properties of polysaccharide coatings: Part 1/2**  
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18   **Abstract**

19   Environmental issues related to the use of plastic packaging have sparked a growing interest  
20   in the development of more sustainable solutions. Biopolymers, used alone or in combination  
21   with other materials, have been considered a potential alternative to conventional fossil-based  
22   plastics. Hence, this study aimed at unraveling the potentiality offered by polysaccharides for  
23   food packaging applications. To that purpose, an extended characterization of the barrier (to  
24   oxygen and water vapor), mechanical and optical properties (transparency and UV-blocking  
25   ability) of nine different polysaccharide films (hydroxypropyl methylcellulose, methylcellu-  
26   lose, hydroxypropyl cellulose, low-methoxyl pectin, cationic starch, sodium alginate, kappa-  
27   carrageenan, chitosan, and pullulan) was performed to provide a broad overview of their  
28   main physicochemical properties under standardized conditions. In addition, the properties of  
29   the film-forming solutions, such as viscosity and surface tension, were also evaluated. All  
30   polysaccharides obviously presented low water vapor barrier performance due to their hydro-  
31   philic nature (water vapor permeance from  $10^{-6}$  to  $10^{-8}$  mol.m<sup>-2</sup>.s<sup>-1</sup>.Pa<sup>-1</sup>). Among all the pol-  
32   ysaccharides studied, chitosan, low-methoxyl pectic, kappa-carrageenan, pullulan, cationic  
33   starch and sodium alginate, displayed medium to very high oxygen barrier performance in  
34   semi-dry (50 % RH) and humid (80 % RH) conditions (oxygen permeance from  $10^{-14}$  to  $10^{-15}$   
35   mol.m<sup>-2</sup>.s<sup>-1</sup>.Pa<sup>-1</sup>), contrarily to cellulose derivatives which showed the poorest performance

36 (oxygen permeance  $> 10^{-12} \text{ mol.m}^{-2}.\text{s}^{-1}.\text{Pa}^{-1}$ ). This opens on interesting perspectives for the  
37 use of polysaccharides as coating materials for high oxygen barrier packaging.

38 **Keywords:** polysaccharides, biopolymer film, multilayer packaging, paper-based packaging,  
39 coatings.

## 40 **1. Introduction**

41 Conventional petroleum-based plastics, such as polyethylene terephthalate (PET), polyamide  
42 (PA), high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), polypro-  
43 pylene (PP), and ethylene vinyl alcohol (EVOH), still dominate the food packaging sector  
44 (Stoica, Antohi, Zlati & Stoica, 2020). Although they offer numerous advantages, they also  
45 represent a waste to manage and a potential pollution when the collection system fails. The  
46 main issue with their use for food packaging remains the post-consumer waste, where pack-  
47 aging is by far the most significant contributor of plastic waste worldwide. Packaging repre-  
48 sents 47 % of the total plastic waste, which corresponded to 141 million tons of plastic waste  
49 in 2015 (United Nations Environment Programme, 2018). According to Parker (2019), half of  
50 all plastics ever manufactured have been produced in the last 15 years. The production has  
51 increased from 2.3 million tons in 1950 to 448 million tons in 2015 and is expected to double  
52 by 2050. Only 14 % of all plastic waste ever produced has been recycled, 14 % has been in-  
53 cinerated, and the rest (72 %) has been accumulated in landfills and water bodies around the  
54 world (United Nations Environment Program, 2018).

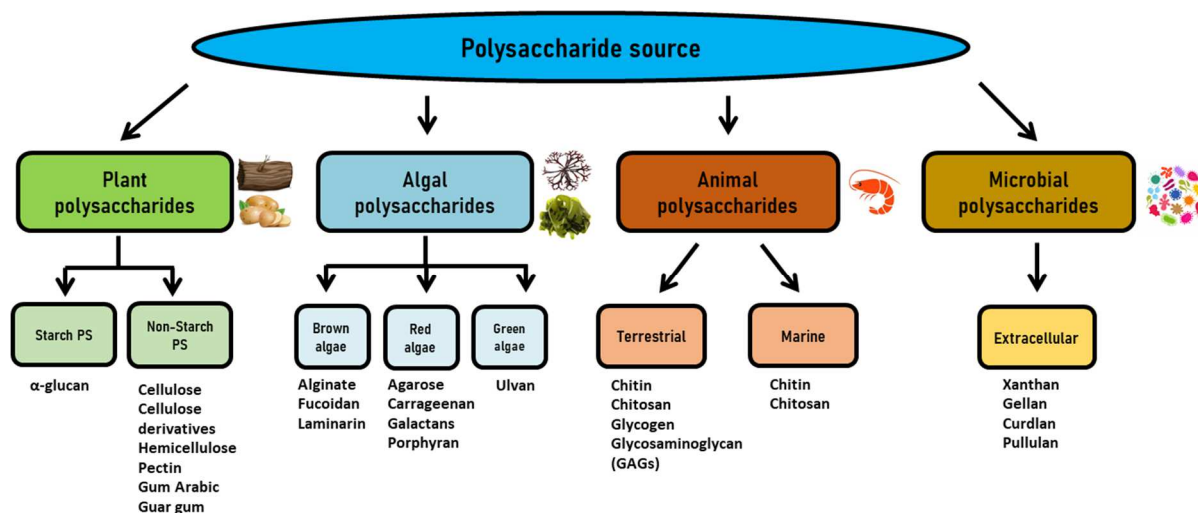
55 For this reason, different strategies have recently been implemented around the world. In Eu-  
56 rope, the "European Strategy for Plastics in a Circular Economy", aims at reducing the de-  
57 pendence on fuel-based raw materials, increasing the recyclability of plastics and reducing  
58 the leakage of plastics into the environment (European Parliament and Council, 2018). This  
59 strategy targeted the end of single-use plastics by 2040. As a consequence, one of the strate-  
60 gies consists in substituting conventional plastics by paper-based materials. Several food  
61 product brands worldwide are switching from traditional plastic to paper-based packaging in  
62 order to shift to recyclable materials and to decrease the impact of plastics on the environ-  
63 ment. However, even though paper is recyclable and even compostable under certain condi-  
64 tions (Venelampi, Weber, Rönkkö & Itävaara, 2003), it has significant drawbacks such as  
65 high porosity and, therefore, poor barrier properties towards water vapor and oxygen  
66 (Deshwal, Panjagari & Alam, 2019). Thus, to lessen these disadvantages, paper-based pack-  
67 aging is usually coated with conventional fossil-based polymers like polypropylene (PP) and  
68 polyethylene (PE). However, this practice compromises its recyclability and increases the  
69 carbon footprint of the packed food.

70 Biopolymers, especially those derived from renewable organic resources, such as polysaccha-  
71 rides and proteins, seem to be a promising solution to replace conventional polymers in spe-

72 cific applications (Tardy et al., 2022). Most films made from proteins and polysaccharides  
 73 generally exhibit excellent barriers to gases, aromas and lipids and have acceptable mechani-  
 74 cal strength (Nechita & Roman, 2020). However, these biopolymers show a very high sensi-  
 75 tivity to water due to their hydrophilic nature (Stoica et al., 2020), which is the main limita-  
 76 tion when considering their use for food packaging applications.

77 Many investigations were based on the exclusive use of proteins for packaging applications  
 78 (Kchaou, Jridi, Benbettaieb, Debeaufort & Nasri, 2020; Salem et al., 2021; Xu et al., 2022).  
 79 However, proteins generally find higher value-added applications as food or feed ingredients.  
 80 Conversely, polysaccharides are the most abundant natural polymers (Guo, Liu & Cui, 2021).  
 81 Their extraction and chemical modification are relatively easy-performing, thus making them  
 82 readily available on the market at a relatively lower price. Therefore, polysaccharides might  
 83 be considered the most suitable candidates for food packaging applications, such as coatings  
 84 or self-standing films, and for the design of new food packaging materials, such as paper-  
 85 based and multilayer packaging.

86 Polysaccharides can be classified according to their source, dividing them into four catego-  
 87 ries, namely plant, algal, animal, and microbial polysaccharides (Guo et al., 2021; Yadav &  
 88 Karthikeyan, 2019). Each category can be further divided into subcategories depending on  
 89 the environment from which the polysaccharides are extracted (Fig. 1).



90 Fig 1. Classification of polysaccharides according to their source. (Adapted from Guo et al., 2021 and Yadav & Karthikeyan,  
 91 2019).

92 The molecular structures of polysaccharides are quite complex due to many variables, includ-  
 93 ing the composition of the monosaccharides, the stereochemistry of glycosidic bonds, the

94 degree of branching, branch positions, the presence of functional groups and the molecular  
95 weight distribution, amongst others (Edens, 2005). Based on these premises, a study of sever-  
96 al polysaccharides with different molecular structures is strictly sought after to provide a mul-  
97 ti-criteria overview of their potential applicability in the food packaging sector.

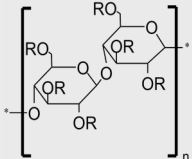
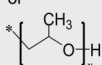
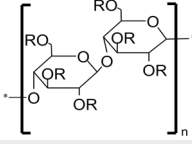
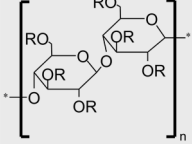
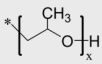
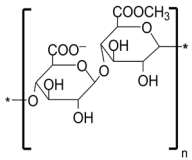
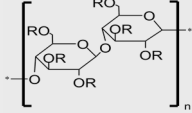
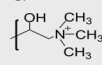
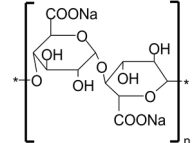
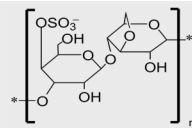
98 Although extensive information on the performance of different polysaccharide films for  
99 food packaging applications is already available, it remains challenging to compare results  
100 from the literature due to the lack of compatibility of results and standardization of methods.  
101 Accordingly, the objective of this study was to offer an extensive overview of the main phys-  
102 icochemical properties of nine different polysaccharides under standardized conditions. Their  
103 properties were evaluated as film-forming solutions for viscosity and surface tension and as  
104 self-standing films (produced by the solvent casting method) for the barrier, mechanical and  
105 optical properties.

## 106 **2. Materials and methods**

### 107 **2.1. Materials**

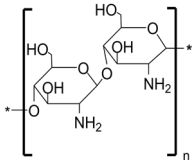
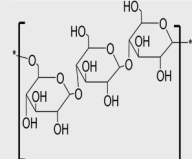
108 Nine different polysaccharides from different natural sources, highly studied for their poten-  
109 tial food packaging applications, were selected (**Table 1**). The plasticizer chosen for all the  
110 polysaccharides was glycerol ( $\geq 99.5\%$ , Fisher Scientific, Strasbourg, France). Lactic acid  
111 (90 %, ProLABO, Paris, France) was additionally used only for the solubilization of chitosan  
112 as reported in the next section.

113 Table 1. Main physicochemical characteristics of the polysaccharides selected in this work as film-forming materials.

| Organ | Polysaccharide                 | Abbreviation | Structure  | Specification   | Moisture content (%) <sup>a</sup> | Ash content (%) <sup>b</sup> | Source                              | Supplier n° CAS   | Purity (%) | E <sub>coh</sub> <sup>c</sup> (kJ/mol) | δ <sub>c</sub> <sup>d</sup> (MPa <sup>1/2</sup> ) |
|-------|--------------------------------|--------------|--|---|-----------------------------------|------------------------------|-------------------------------------|---|------------|--|---|
| Plant | Hydroxypropyl Methyl Cellulose | HPMC         |  R = H or CH <sub>3</sub><br>or  | Uncharged, soluble in water at T < 45 °C, methyl = 28-30 % and hydroxypropyl = 7-12 % | 5.92 (±0.14)                      | 0.18 (±0.01)                 | Semi-synthetic cellulose derivative | Sigma Aldrich, (Saint-Quentin-Fallavier, France) CAS: 9004-65-3 | ≥ 93.5     | 85.2                                   | 50.2  |
| Plant | Methyl Cellulose               | MC           |  R = H or CH <sub>3</sub>   | Uncharged, soluble in water at T < 40-55 °C   | 6.46 (±0.21)                      | 0.47 (±0.01)                 | Semi-synthetic cellulose derivative | (Louis François, Croissy-Beaubourg, France) CAS: 9004-67-5      | ≥ 88.5     | 54.1 - 71.4                            | 23.9 - 38.7                                       |
| Plant | Hydroxypropyl Cellulose        | HPC          |  R = H<br>or                     | Uncharged, soluble in water at T < 45 °C  | 16.26 (±0.14)                     | 0.17 (±0.02)                 | Semi-synthetic cellulose derivative | Sigma Aldrich CAS: 9004-64-2                                    | ≥ 95       | 106.1 - 163.6                          | 32.8 - 40.3                                       |
| Plant | Low-Methoxyl Pectin            | LMP          |   | Anionic Galacturonic acid ≥ 74 %, pKa = 3.5   | 11.15 (±0.18)                     | 8.86 (±0.68)                 | Pectin from citrus peels            | Sigma Aldrich CAS: 9000-69-5                                    | ≥ 90       | 92.6                                   | 49.2  |
| Plant | Cationic Starch                | CS           |  R = H<br>or                  | Cationic degree of substitution: 1.4-1.6 %  | 13.94 (±0.10)                     | 3.36 (±0.13)                 | Potato starch                       | Cargill (Hau-bourdin, France) CAS: 56780-58-6                   | N.S        | N.S                                    | N.S   |
| Algae | Sodium Alginate                | SA           |   | Anionic pKa = 3.2   | 14.51 (±0.24)                     | 31.34 (±1.63)                | Brown seaweed <i>Phaeophyceae</i>   | Sigma Aldrich CAS: 9005-38-3                                    | ≥ 84.5     | 95.1                                   | 46.1  |
| Algae | Kappa-Carrageenan              | KC           |   | Anionic pKa = 4.9, solubility = 5 g/L in water at T > 80 °C                           | 11.03 (±0.27)                     | 20.93 (±0.07)                | Red seaweed                         | Sigma Aldrich CAS: 11114-20-8                                   | ≥ 88       | N.S                                    | N.S   |

114

115 Table 1 (continued)

| Origin    | Polysaccharide | Abbreviation | Structure   | Specification                                     | Moisture content (%) <sup>a</sup> | Ash content (%) <sup>b</sup> | Source  | Supplier n° CAS  | Purity (%) | E <sub>coh</sub> <sup>c</sup> (kJ/mol) | δ <sub>t</sub> <sup>d</sup> (MPa <sup>1/2</sup> ) |
|-----------|----------------|--------------|---|---|-----------------------------------|------------------------------|---|--|------------|--|---|
| Animal    | Chitosan       | CHI          |  | Cationic<br>75-85 %<br>deacetylated,<br>pKa = 6.5 | 8.71<br>(±0.02)                   | 0.58<br>(±0.07)              | Deacetylated<br>product of<br>chitin  | Sigma<br>Aldrich<br>CAS:<br>9012-76-4                      | N.S        | 96.8 - 113.2                           | 42.8 - 45.6                                       |
| Microbial | Pullulan       | PL           |  | Uncharged   | 11.25<br>(±0.13)                  | 0.27<br>(±0.01)              | Polymer of<br>maltotriose<br>produced from<br>starch by the<br>fungus<br><i>Aureobasidium<br/>pullulans</i> | ATP Chemical,<br>(Shanghai,<br>China)<br>CAS:<br>9057-02-7 | ≥ 95.9     | 102.2                                  | 53.1  |

116 <sup>a</sup>Moisture content was determined by heating the samples at 103 °C until constant mass for samples previously stored at 25 °C and 50 % relative humidity (RH). <sup>b</sup>Ash content was determined by  
 117 furnacing the samples at 500 °C for 10 h. Values are reported as mean ± standard deviation. Number of replicates (n) = 3. Other data were provided by suppliers. **N.S:** Not Specified. <sup>c</sup>Cohesive  
 118 energy density (E<sub>coh</sub>) of the polysaccharides was calculated according to the group contribution method based on Fedors (Krevelen & Nijenhuis, 2009). <sup>d</sup>Overall solubility parameter (δ<sub>t</sub>) of the  
 119 polysaccharides was calculated according to the group contribution method based on Van Krevelen (Hansen, 2007).



## 120           **2.2. Preparation of film-forming solutions**

121 All the film-forming solutions were prepared following the same procedure. Only slight mod-  
122 ifications related to mixing time, temperature and air bubbles removal method were applied  
123 depending on the properties of each polysaccharide, as described below. For the preparation  
124 of the film-forming solutions, 2 % (w/w) of each polysaccharide was slowly dispersed in 1  
125 liter of distilled water together with glycerol at different percentages (0, 10, 20, or 30 %  
126 (w/w) based on a dry basis). For the cellulose derivatives (HPMC, MC, and HPC), SA and PL  
127 solutions, the polysaccharides were dispersed in distilled water at 25 °C and stirred at 500  
128 rpm until complete dissolution (around 1 hour). The solutions were then treated using an ul-  
129 trasonic bath (Branson 3510; Milford, Connecticut, USA) with a frequency of 40 Hz and a  
130 power of 130 W for 1 hour to remove air bubbles. CHI was dispersed in distilled water con-  
131 taining 1 % (v/v) lactic acid at 25 °C and stirred at 500 rpm until complete dissolution  
132 (around 1 hour). No treatment was required for the removal of air bubbles in that case. KC,  
133 CS and LMP were dissolved in distilled water at 90 °C for the first two and 70 °C for the last  
134 one and stirred at 500 rpm until complete dissolution (around 1 hour). The solutions were  
135 then treated under vacuum to remove air bubbles.

## 136           **2.3. Films formation**

137 The solutions previously prepared (according to the protocol described in section 2.2.1) were  
138 casted in square polystyrene (PS) Petri dishes (12 x 12 cm<sup>2</sup>) to form the films. Then, they  
139 were dried at 25 °C and 50 % RH for 48 h. Calibration curves were previously established for  
140 each film-forming solution to determine the exact amount of solution required to be poured  
141 into the Petri dish in order to achieve 50±5 µm thick film in all cases (data not shown). The  
142 thickness was controlled in at least five different positions using a micrometer Thickness  
143 Gauge FD-100 with a resolution of 0.001mm (Hans Schmidt & Co GmbH; D-84478,  
144 Waldkraiburg, Germany).

## 145           **2.4. Film-forming solutions characterization**

### 146           **2.4.1. Rheological properties**

147 The rheological properties of the solutions (shear stress  $\tau$  and apparent viscosity  $\mu_{ap}$ ) were  
148 determined using a rotational rheometer (HAAKE™ RotoVisco™ 1; Thermo Fisher Scien-  
149 tific, Boston, USA) at 25±1 °C for all polysaccharide solutions, except for Kappa-  
150 Carrageenan (KC), which was measured at 70±1 °C. A Z34DIN sensor with a rotor No 222-  
151 1499 (radius = 17.00 mm, length 51 mm, clearance to bottom 7.2 mm) and a cup No 222-

1498 (radius = 18.44 mm), were used for the analysis. Measurements were done in triplicate  
153 for the polysaccharide solutions without glycerol. The rheological properties were recorded at  
154 shear rates from  $0.5 \text{ s}^{-1}$  to  $200 \text{ s}^{-1}$ .

#### 155 **2.4.1.1. Shear stress**

156 The experimental data of the polysaccharide flow curves (shear stress  $\tau$  according to shear  
157 rate  $\dot{\gamma}$ ) were analyzed using the Ostwald de Waele model fitting (**Eq. 1**):

$$158 \quad \tau = \kappa \dot{\gamma}^n \quad (1)$$

159 where  $\tau$  is the shear stress ( $Pa$ ),  $\dot{\gamma}$  is the shear rate ( $s^{-1}$ ),  $\kappa$  is the consistency index ( $Pa \cdot s^n$ )  
160 and  $n$  is the flow behavior index (dimensionless).

#### 161 **2.4.1.2. Apparent viscosity**

162 The apparent viscosity ( $\mu_{ap}$ ) of the polysaccharide solutions was extrapolated using  $\kappa$  and  $n$   
163 constants previously calculated to predict the apparent viscosity of the solutions at  $1000 \text{ s}^{-1}$ .  
164 The values of apparent viscosity at  $10 \text{ s}^{-1}$  and  $1000 \text{ s}^{-1}$  were chosen as targeted values to  
165 compare the different polysaccharide solutions and their application as coatings.

#### 166 **2.4.2. Surface tension**

167 The total surface tension ( $\sigma_L$ ) of the solutions and their polar ( $\sigma_L^p$ ) and dispersive ( $\sigma_L^d$ ) com-  
168 ponents were determined at  $25 \pm 1 \text{ }^\circ\text{C}$  using a Krüss K100 tensiometer (Krüss GmbH, Ham-  
169 burg, Germany). At least 5 repetitions were made for the polysaccharide solution without  
170 glycerol. The total surface tension ( $\sigma_L$ ) was measured using the Wilhelmy method with a plat-  
171 inum plate and was furtherly calculated according to **Eq. 3**:

$$172 \quad \sigma_L = \frac{F}{L \cdot \cos\theta} \quad (3)$$

173 where  $\sigma_L$  is the total surface tension ( $mN \cdot m^{-1}$ ),  $F$  is the force measured ( $mN$ ),  $L$  is the wetted  
174 length ( $m$ ), and  $\theta$  is the angle formed between the plate and the liquid, which corresponds to  
175  $0^\circ$  in the case of the platinum plate.

#### 176 **2.4.2.1. Dispersive and polar components**

177 The dispersive component of the surface tension was determined by the contact angle meas-  
178 urement using a polytetrafluoroethylene (PTFE) plate and it was calculated using the Owens  
179 and Wendt equation (**Eq. 4**):

$$180 \quad \frac{\sigma_L (\cos\theta + 1)}{2\sqrt{\sigma_L^d}} = \frac{\sqrt{\sigma_S^p} \cdot \sqrt{\sigma_L^p}}{\sqrt{\sigma_L^d}} + \sqrt{\sigma_S^d} \quad (4)$$

181 where  $\sigma_L$  is the total surface tension of the liquid ( $\text{mN}\cdot\text{m}^{-1}$ ) determined by the Wilhelmy  
 182 method,  $\theta$  is the contact angle between the solid (PTFE plate) and the liquid.  $\sigma_L^d$  is the disper-  
 183 sive part of the liquid ( $\text{mN}\cdot\text{m}^{-1}$ ),  $\sigma_L^p$  is the polar part of the liquid ( $\text{mN}\cdot\text{m}^{-1}$ ).  $\sigma_S^d$  is the disper-  
 184 sive part of the solid and  $\sigma_S^p$  is the polar part of the solid ( $\sigma_S^d = 18$  ( $\text{mN}\cdot\text{m}^{-1}$ ) and  $\sigma_S^p = 0$   
 185 ( $\text{mN}\cdot\text{m}^{-1}$ ) in the case of PTFE plate).

186 By rearranging the above equation (4), the dispersive part of the solutions was then calculated  
 187 as shown in **Eq. 5**:

$$188 \quad \sigma_L^d = \frac{\sigma_L^2 (\cos\theta + 1)^2}{4 \cdot \sigma_S^d} \quad (5)$$

189 Ultimately, the polar part of the solutions was then calculated according to **Eq. 6**:

$$190 \quad \sigma_L^p = \sigma_L - \sigma_L^d \quad (6)$$

#### 191 2.4.2.2. Wetting envelope

192 The wetting envelope analysis was performed to predict the contact angle of polysaccharide  
 193 solutions on a solid surface. Kraft paper was chosen in the present case. The polar and disper-  
 194 sive components of the polysaccharide solutions were entered into a coordinate system.  
 195 Hence, the wetting parameter  $R$  was obtained from a geometrical transformation using **Eq. 7**,  
 196 with  $\sigma_L^p = R \cdot \sin\varphi$  the polar component and  $\sigma_L^d = R \cdot \cos\varphi$  the dispersive component.  $R$  and  $\varphi$   
 197 are the auxiliary polar coordinates to calculate the wetting envelope.

$$198 \quad R = \sqrt{(\sigma_L^d)^2 + (\sigma_L^p)^2} \quad (7)$$

199  $R$  is also related to the dispersive and polar components of the surface tension of the solid by  
 200 the relation (**Eq. 8**):

$$201 \quad R(\varphi) = \left( \frac{2}{1 + \cos\theta} \frac{\sqrt{\cos\varphi \cdot \sigma_S^d + \sin\varphi \cdot \sigma_S^p}}{\cos\varphi + \sin\varphi} \right)^2, \text{ for } 0^\circ \leq \varphi \leq 90^\circ \quad (8)$$

202 In this equation,  $R$  can be calculated for different angles  $\varphi$  between  $0^\circ$  and  $90^\circ$ , to form a wet-  
 203 ting envelope that describes the polar and dispersive surface tension for theoretical wetting of  
 204 the surface with different contact angles  $\theta$ . The wetting envelopes corresponding to a contact  
 205 angle of  $0^\circ$ ,  $20^\circ$ ,  $40^\circ$ ,  $60^\circ$ ,  $80^\circ$  and  $100^\circ$  were plotted.

206 **2.5. Films characterization**

207 **2.5.1. Moisture sorption isotherms**

208 Rectangular specimens of the films (dimensions 2 x 1 cm<sup>2</sup>) without and with 30 % glycerol  
209 were equilibrated in triplicate under various relative humidity environments in air-tight con-  
210 tainers. To that purpose, P<sub>2</sub>O<sub>5</sub>, or various saturated salt solutions (LiCl, KC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, MgCl<sub>2</sub>,  
211 K<sub>2</sub>CO<sub>3</sub>, NaBr, SrCl<sub>2</sub>, KCl) were used at 25 °C, in order to set 0 %, 11.1 %, 23.1 %, 33 %, 46  
212 %, 58.7 %, 72.5 % and 85.1 % RH, respectively. Equilibrium was considered to be achieved  
213 when the weight change did not exceed 0.05 % (wet basis) over one week. After equilibra-  
214 tion, the samples were weighed using an analytical balance with an accuracy of 0.1 mg (Sar-  
215 torius Analytical balance - Sartorius Lab Instruments GmbH & Co. KG – Goettingen, Ger-  
216 many). Then, the dry weight was determined using an oven at 103 °C for 24 h. The moisture  
217 content of the films was calculated according to **Eq. 9**.

218 
$$MC (\%) = \frac{m_w - m_d}{m_d} \times 100 \quad (9)$$

219 Where *MC* is the moisture content (*dry basis*), *mw* is the wet weight (*g*), and *md* is the  
220 weight after drying (*g*).

221 **2.5.2. Mechanical properties**

222 The mechanical behavior of the polysaccharide films was assessed by uniaxial tensile tests  
223 under ambient conditions (T ≈ 25 °C, RH ≈ 50 %) using a texture analyzer (TA.HD plus; Sta-  
224 ble Micro Systems Company, Godalming Surrey GU7 1YL, United Kingdom). The tests were  
225 carried out following the standard method ISO 527-3:2018 with some modifications (Interna-  
226 tional Organization for Standardization, 2018). A 30 kg load cell was used, and tests were  
227 performed with a constant crosshead speed of 50 mm.min<sup>-1</sup>. Six to nine rectangular speci-  
228 mens for each polysaccharide film condition (dimensions 7 x 2.5 cm<sup>2</sup>), previously equilibrat-  
229 ed at 50 % RH and 25 °C in a climatic chamber model KBF 240 (Binder GmbH, Tuttlingen,  
230 Germany), were prepared with a precision cutter (JDC; Thwing Albert Instrument Company,  
231 West Berlin, NJ, USA). Young's modulus (*GPa*), tensile strength (*MPa*) and elongation at  
232 break (%) were determined from the corresponding stress-strain curves.

233 **2.5.3. Barrier properties to oxygen**

234 The permeance of the polysaccharide films to oxygen (*P<sub>O<sub>2</sub></sub>*) was determined by the manomet-  
235 ric method using a GTT permeameter (Brugger Feinmechanik GmbH, Munich, Germany) at  
236 25 °C under three different relative humidity conditions (10 %, 50 % and 80 % RH). The sys-  
237 tem was outgassed under primary vacuum before testing. At time zero, one side of the film

238 was flushed with the gas (flow  $\approx 27 \text{ cm}^3 \cdot \text{min}^{-1}$ ) and the increase in pressure on the other side  
239 was recorded over time. The partial pressure differential was 1000 hPa. The experiments  
240 were performed in triplicate

241 The permeance (expressed in  $\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ ) was determined from the steady-state of the  
242 transfer according to **Eq. 10**:

$$243 \quad P = \frac{\Delta n}{A \cdot \Delta t \cdot \Delta p} \quad (10)$$

244 where  $P$  is permeance,  $\Delta n$  is the average molar quantity associated with the gas transfer  
245 ( $\text{mol}$ ),  $A$  is the surface area of the film ( $\text{m}^2$ ),  $\Delta t$  is the time ( $\text{s}$ ),  $\Delta p$  is the pressure difference  
246 between the two sides of the film ( $\text{Pa}$ ).

#### 247 **2.5.4. Barrier properties to water vapor**

248 The permeance of the polysaccharide films to water vapor ( $P_{H_2O}$ ) was determined using the  
249 gravimetric method at 25 °C, according to the standard method ISO 2528:2017 with some  
250 modifications (International Organization for Standardization, 2017). Two different relative  
251 humidity conditions were used. These two conditions are referred to, in the present work, as  
252 "semi-dry" condition (0 %-50 % RH) and "humid" condition (50 %-100 % RH). For the  
253 semi-dry condition, silica gel was used inside the permeability cell (3.4 cm inner diameter) to  
254 maintain the relative humidity close to 0 %. For the humid condition, distilled water was used  
255 inside the permeability cell to maintain a relative humidity close to 100 %. For both condi-  
256 tions, the permeability cells containing silica gel or distilled water with the polysaccharide  
257 film fixed between two silicon O-rings at the top were placed in a climatic chamber at 50 %  
258 RH and 25 °C. The cell weight was measured once a day using an analytical balance with an  
259 accuracy of 0.1 mg model A200 FS1 (Sartorius Analytical balance; Sartorius Lab Instruments  
260 GmbH & Co. KG – Goettingen, Germany). The permeance to water vapor was determined  
261 from the steady-state of the transfer according to **Equation 10**. The partial pressure differen-  
262 tial was 1584 Pa for both "semi-dry" and "humid" conditions. The analyses were performed  
263 in quadruplicate.

#### 264 **2.5.6. Barrier properties to light**

265 The UV/Visible transmission spectra of the polysaccharide films without glycerol were  
266 measured using a UV-Visible spectrophotometer (SAFAS UVmc, Monaco). The rectangular  
267 specimens (dimensions  $5 \times 2.5 \text{ cm}^2$ ) were fixed so that the light beam could pass through the  
268 film. Air was used as the blank. Transmittance spectra were recorded at wavelengths between

269 200 and 800 nm. UV screening ability of the films was given as the percentage of transmit-  
270 tance at 280 nm and transparency as the percentage of transmittance at 550 nm. The values  
271 obtained were divided by the exact thickness of the measured sample and multiplied by 50  
272  $\mu\text{m}$  for normalization purpose. Three specimens were analyzed for each film.

### 273 **2.6. Statistical analysis**

274 Data were expressed as the mean  $\pm$  standard deviation of at least three replicates. A signifi-  
275 cant difference in the mean was tested using one-way ANOVA Tukey's test at the 95 % confi-  
276 dence level ( $p < 0.05$ ). Data were processed using MATLAB 2014, Orange Data Mining  
277 3.28.0 and IBM SPSS Statistic 20.

278 **3. Results and Discussion**

279 **3.1. Properties of polysaccharide film-forming solutions for their use as coatings**

280 **3.1.1. Rheological properties of film-forming solutions**

281 The rheological properties of the polysaccharide solutions were measured at different shear  
 282 rates, from 0 to 200 s<sup>-1</sup> at 25±1 °C (except for KC, which was measured at 70±1 °C due to  
 283 the gelation of KC at ambient temperature). Shear stress as a function of the shear rate is dis-  
 284 played in **Fig. 2A**. The experimental shear data were fitted by the Ostwald de Waele model,  
 285 which generally applies to flow curves for hydrocolloids (Ma, Lin, Chen, Zhao & Zhang,  
 286 2014). The model parameters for the different polysaccharide solutions are reported in **Table**  
 287 **2**. All the solutions displayed a pseudo-plastic fluid's non-Newtonian behavior, characterized  
 288 by a flow behavior index (*n*) lower than 1. Nevertheless, LMP, SA and PL solutions presented  
 289 a flow behavior index (*n*) approaching a unitary value, indicating to be relatively close to  
 290 Newtonian fluids, and thus showing a lower influence of shear rate on viscosity. The Ostwald  
 291 de Waele model fitted well the flow curves experimental data (with R<sup>2</sup> > 0.99), except for PL  
 292 (with R<sup>2</sup> < 0.72), indicating that in this case the model was not suitable.

293 **Table 2.** Ostwald de Waele model fitting parameters and apparent viscosity values determined at a shear rate of 10 s<sup>-1</sup> and  
 294 extrapolated by modeling at 1000 s<sup>-1</sup> for the different polysaccharide solutions at 25 °C.

| Polysaccharide | $\mu_{ap}$ (Pa.s)<br>at 10 S <sup>-1</sup> | $\mu_{ap}$ (Pa.s)<br>at 1000 S <sup>-1</sup> (*) | Ostwald de Waele model fitting parameters |          |                       |           |
|----------------|--|--|---|----------|-----------------------|-----------|
|                |  |  | <i>K</i>                                  | <i>n</i> | <i>R</i> <sup>2</sup> | <i>SD</i> |
| <b>HPMC</b>    | 1.991±0.176                                | 0.469±0.045                                      | 4.845                                     | 0.662    | 0.997                 | 6.080     |
| <b>MC</b>      | 2.341±0.273                                | 0.441±0.038                                      | 6.177                                     | 0.619    | 0.996                 | 7.720     |
| <b>HPC</b>     | 0.224±0.019                                | 0.102±0.003                                      | 0.392                                     | 0.806    | 0.998                 | 0.780     |
| <b>LMP</b>     | 0.097±0.032                                | 0.082±0.002                                      | 0.114                                     | 0.953    | 0.999                 | 0.400     |
| <b>CS</b>      | 0.275±0.021                                | 0.030±0.001                                      | 0.818                                     | 0.522    | 0.996                 | 0.350     |
| <b>SA</b>      | 0.095±0.005                                | 0.091±0.006                                      | 0.149                                     | 0.929    | 0.999                 | 0.190     |
| <b>+KC</b>     | 0.235±0.065                                | 0.109±0.002                                      | 0.490                                     | 0.784    | 0.998                 | 4.410     |
| <b>CHI</b>     | 2.110±0.119                                | 0.400±0.012                                      | 5.285                                     | 0.627    | 0.997                 | 5.520     |
| <b>PL</b>      | 0.004±0.002                                | 0.003±0.001                                      | 0.005                                     | 0.948    | 0.720                 | 0.040     |

295 **HPMC:** Hydroxypropyl Methylcellulose. **MC:** Methyl Cellulose. **HPC:** Hydroxypropyl Cellulose. **LMP:** Low Methoxyl  
 296 Pectin. **CS:** Cationic Starch. **SA:** Sodium Alginate. **KC:** Kappa-Carrageenan (+: Temperature of measurement 70(±1) °C).  
 297 **CHI:** Chitosan. **PL:** Pullulan. Values of apparent viscosity at 10 s<sup>-1</sup> are reported as mean ± standard deviation (n = 3). \*  
 298 Values of viscosity at 1000 s<sup>-1</sup> were calculated by extrapolation of the data.

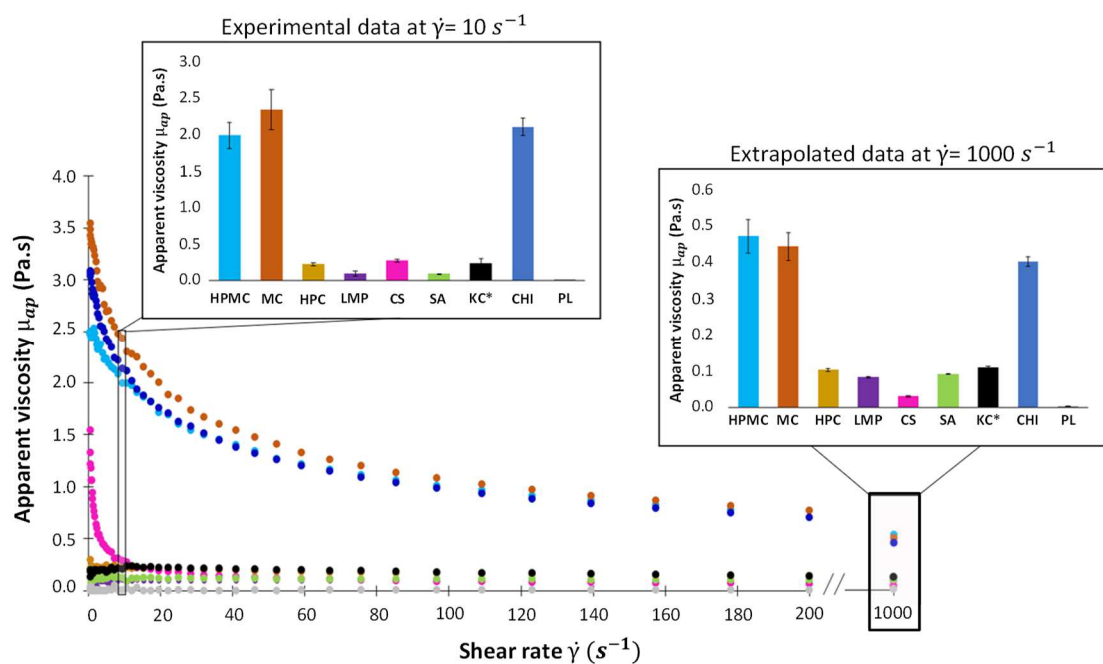
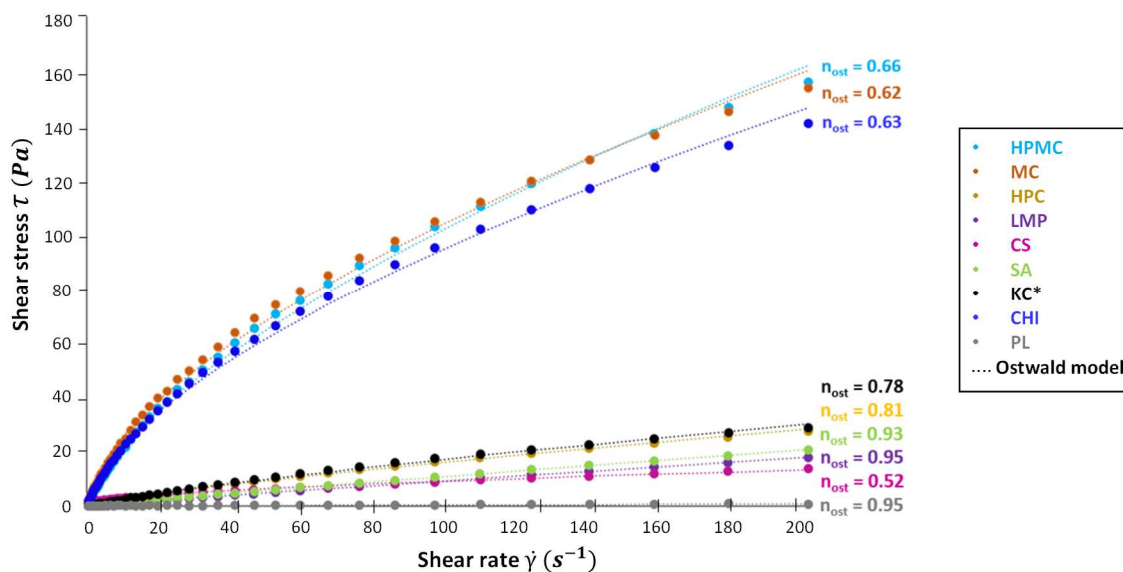
299 The correlation between apparent viscosity and shear rate of the polysaccharide solutions is  
 300 reported in **Fig. 2B**. A shear-thinning behavior was observed for all polysaccharide solutions,  
 301 indicating that the apparent viscosity decreased as the shear rate increased. According to Hos-  
 302 seini, Ghaderi & Gómez-Guillén, (2020); Pamies, Schmidt, Martínez & Garcia De la Torre,  
 303 (2010) and Sharmin, Sone, Walsh, Sivertsvik & Fernández, (2021), the decrease in viscosity

304 as shear rate increases can be explained by the theory of disentanglement. The breakdown of  
305 the polysaccharide molecular structure due to shear stress leads to a reduction of the interac-  
306 tions between adjacent chains. At a shear rate of  $10 \text{ s}^{-1}$ , MC, CHI and HPMC presented the  
307 higher apparent viscosity ( $\geq 2 \text{ Pa}\cdot\text{s}$ ) among all the polysaccharides evaluated, while the other  
308 polysaccharide solutions exhibited at the same shear rate an apparent viscosity lower than  $0.3$   
309  $\text{Pa}\cdot\text{s}$ . The values of apparent viscosity were also extrapolated to predict the apparent viscosity  
310 of the solutions at a shear rate of  $1000 \text{ s}^{-1}$ . This allows comparison to be made when high  
311 shear rates are applied to coatings during different unit operations at industrial scale. Based  
312 on these extrapolated data, it can be estimated that, at a shear rate of  $1000 \text{ s}^{-1}$ , polysaccharide  
313 solutions will present in all cases an apparent viscosity lower than  $0.5 \text{ Pa}\cdot\text{s}$ .

314 In the preparation of self-standing films using polysaccharide solutions by the solvent casting  
315 method, viscosity was not a critical parameter to consider since at relatively low polymer  
316 concentrations, the solutions efficiently spread over the surface area of a petri dish to produce  
317 films at the lab scale (data not shown). However, polysaccharide film-forming solutions can  
318 also be used to coat different materials, such as paper or plastics. For coating, the rheological  
319 behavior of the solution is an important parameter to be considered, especially for further  
320 industrial applications since it determines the design of the different unit operations and pro-  
321 cesses involved in the coating process as well as the performance of the coating. The targeted  
322 apparent viscosity of a biopolymer solution for coating applications at industrial scale de-  
323 pends on different factors and, particularly, the method used for the coating operation. Meth-  
324 ods such as dip-coating require high viscosity values ( $> 10 \text{ Pa}\cdot\text{s}$ ) since low shear rate values  
325 are applied ( $< 10 \text{ s}^{-1}$ ), whereas techniques such as brushing or rolling may require lower vis-  
326 cosity values ( $< 0.5 \text{ Pa}\cdot\text{s}$ ) since high shear rate values are applied to the solutions ( $> 1000 \text{ s}^{-1}$ )  
327 (Fluidan, 2018). Therefore, the polysaccharide solutions, with the concentration used in this  
328 study could not be suitable for applications like dip-coating since their viscosity at low shear  
329 rates was lower than  $3 \text{ Pa}\cdot\text{s}$ . However, they could preferably be used for applications such as  
330 brushing and rolling as their viscosity was estimated to be less than  $0.5 \text{ Pa}\cdot\text{s}$  at a shear rate of  
331  $1000 \text{ s}^{-1}$ .



332 **A.**



333 **B.**

334 **Fig. 2.** Rheological properties of polysaccharide solutions at a concentration of 2 % (w/w). **A.** Shear stress ( $\tau$ ) as a function  
 335 of shear rate ( $\dot{\gamma}$ ) of polysaccharide solutions measured at  $25(\pm 1)$  °C. Dotted lines represent the fitted curves based on the  
 336 Ostwald de Waele model.  $n_{ost}$  indicates the  $n$  value given by the model for each curve. **B.** Apparent viscosity ( $\mu_{app}$ ) as a func-  
 337 tion of shear rate of polysaccharide solutions, measured at  $25(\pm 1)$  °C. Values of the apparent viscosity at  $1000\text{ s}^{-1}$  were  
 338 calculated by extrapolation of the data. **HPMC:** Hydroxypropyl Methylcellulose. **MC:** Methyl Cellulose. **HPC:** Hydroxy-  
 339 propyl Cellulose. **LMP:** Low Methoxyl Pectin. **CS:** Cationic Starch. **SA:** Sodium Alginate. **KC:** Kappa-Carrageenan (\*:  
 340 Temperature of measurement  $70(\pm 1)$  °C). **CHI:** Chitosan. **PL:** Pullulan. Values are reported as mean  $\pm$  standard deviation ( $n$   
 341 = 3).

342 **3.1.2. Surface properties of film-forming solutions**

343 The surface tension of the polysaccharide solutions, including their polar and dispersive  
 344 components, were measured at 25 °C. Results are displayed in **Table 3**. Among all polysac-  
 345 charides analyzed, CS showed the highest surface tension (63 mN.m<sup>-1</sup>), while HPC showed  
 346 the lowest one (39 mN.m<sup>-1</sup>). It is also noteworthy that the cellulose derivatives HPMC, MC  
 347 and HPC ranged among the lowest values (lower than 45 mN.m<sup>-1</sup>). For the other polysaccha-  
 348 ride solutions, the surface tension was always higher than 50 mN.m<sup>-1</sup>. In all polysaccharide  
 349 solutions, the polar component represented more than 48 % of the total surface tension. This  
 350 high level of polar interactions was expected due to the hydrophilic nature of polysaccha-  
 351 rides.

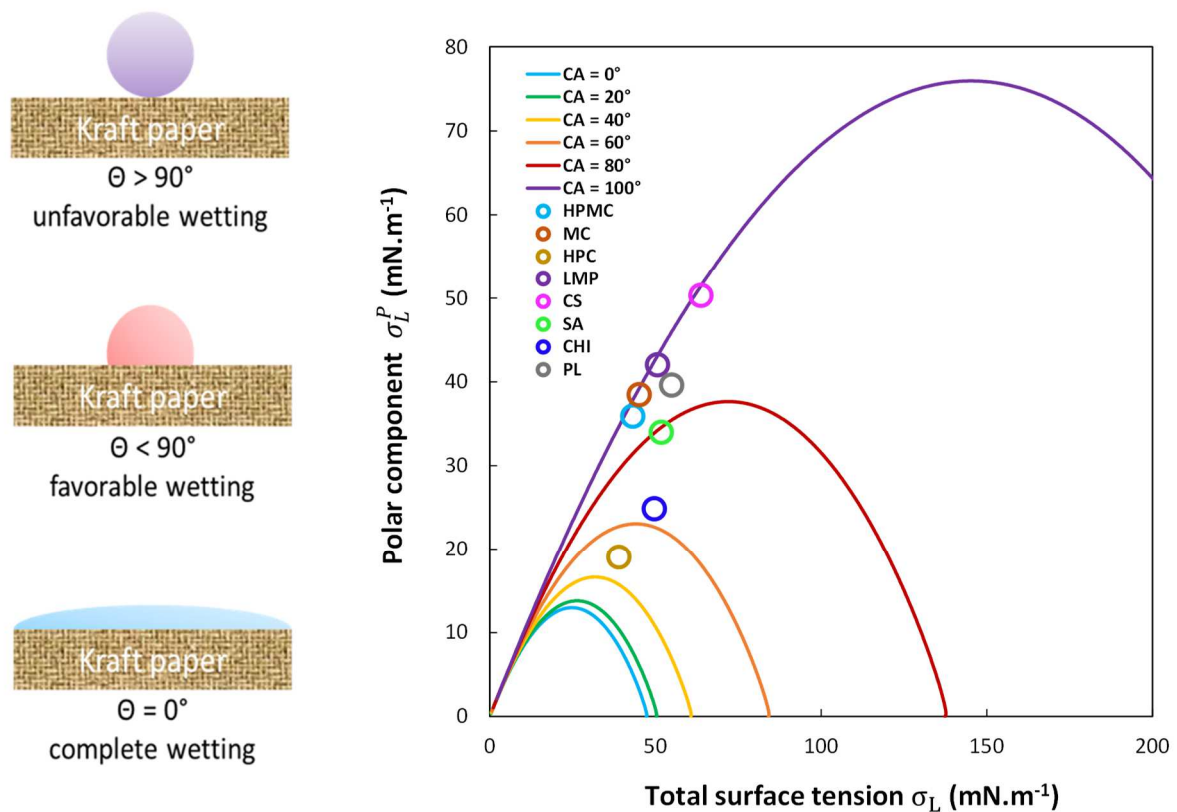
352 **Table 3.** Surface tension, with polar and dispersive components, of polysaccharide solutions at 25 °C.

| Polysaccharide | Total surface tension               | Dispersive component                  | Polar component                       | Polar % |
|----------------|-------------------------------------|---------------------------------------|---------------------------------------|---------|
|                | $\sigma_L$<br>(mN.m <sup>-1</sup> ) | $\sigma_L^d$<br>(mN.m <sup>-1</sup> ) | $\sigma_L^P$<br>(mN.m <sup>-1</sup> ) |         |
| <b>HPMC</b>    | 43.2±0.5                            | 7.3±0.7                               | 35.9±0.7                              | 83.1    |
| <b>MC</b>      | 45.1±0.5                            | 6.6±0.8                               | 38.5±0.8                              | 85.2    |
| <b>HPC</b>     | 38.9±0.8                            | 19.9±0.8                              | 19.0±0.8                              | 48.8    |
| <b>LMP</b>     | 50.6±1.1                            | 8.6±0.6                               | 42.0±0.6                              | 83.1    |
| <b>CS</b>      | 63.7±2.4                            | 13.4±1.5                              | 50.3±1.5                              | 70.9    |
| <b>SA</b>      | 51.8±0.2                            | 17.8±1.4                              | 34.0±1.4                              | 65.6    |
| <b>*KC</b>     | N/A                                 | N/A                                   | N/A                                   | N/A     |
| <b>CHI</b>     | 49.7±0.6                            | 24.8±0.8                              | 24.9±0.8                              | 50.0    |
| <b>PL</b>      | 54.9±0.2                            | 15.3±2.4                              | 39.6±2.4                              | 72.1    |

353 **HPMC:** Hydroxypropyl Methylcellulose. **MC:** Methyl Cellulose. **HPC:** Hydroxypropyl Cellulose. **LMP:** Low Methoxyl  
 354 Pectin. **CS:** Cationic Starch. **SA:** Sodium Alginate. **\*KC:** Kappa-Carrageenan (N/A: not applicable due to gelation at 25 °C).  
 355 **CHI:** Chitosan. **PL:** Pullulan. Values are reported as mean ± standard deviation (n = 3).

356 The interactions between a liquid and a solid are of great importance since they determine the  
 357 wetting properties of the liquid on the surface. As an example, industrial processes like coat-  
 358 ing and printing of paper and board are complex procedures involving spreading and absorb-  
 359 ing a liquid into the fiber network. Predicting the wettability and adhesion of a liquid on a  
 360 specific surface requires information about the polar and dispersive interactions of both the  
 361 liquid and the solid. Indeed, they will determine the contact angle formed between the two  
 362 components. As shown in **Fig. 3A**, liquids giving a contact angle equal to 0° are classified as  
 363 having "complete wettability" of the solid surface, while those whose contact angle lie be-  
 364 tween 0° and 90° are classified as having "favorable wetting". Those which present a contact  
 365 angle above 90° are classified as having "unfavorable wetting" (Fathi Azarbayjani, Jouyban  
 366 & Chan, 2009).

367 The determination of the so-called "wetting envelope" provides the wettability for current or  
 368 future coatings, as any liquids whose polar and dispersed components lie within the contour  
 369 for a particular contact angle will wet the corresponding solid surface with the contact angle  
 370 of this contour (Chen, Cheng & Lee, 2021). For this study, the wetting envelope of a Kraft  
 371 paper, reported by Saraiva et al. (2010) as having a total surface tension of  $47.4 \text{ mN}\cdot\text{m}^{-1}$ , with  
 372 a polar component of  $0.1 \text{ mN}\cdot\text{m}^{-1}$  and a dispersive component of  $47.3 \text{ mN}\cdot\text{m}^{-1}$ , was plotted to  
 373 compare the wettability of the different polysaccharide solutions on that specific surface.  
 374 Kraft paper was selected as a support due to its common applications for the packaging of  
 375 flour, sugar, dried fruits and vegetables (Deshwal et al., 2019). The wetting envelope of Kraft  
 376 paper and the wettability of polysaccharide solutions on this surface are displayed in **Fig. 3B**.



377 **A.**

**B.**

378 **Fig. 3.** A. Schematic diagram of contact angle and wettability behavior. B. Wetting envelope with 0°, 20°, 40°, 60°, 80° and  
 379 100° contours of an uncoated paper (80 g/m<sup>2</sup>) produced with a Eucalyptus globulus Kraft pulp and wettability of the poly-  
 380 saccharide solutions on the surface of Kraft paper at 25 °C. Values of the surface tension of Kraft paper were taken from  
 381 Saraiva et al. (2010).  $\theta$ : contact angle. **HPMC**: Hydroxypropyl Methylcellulose. **MC**: Methyl Cellulose. **HPC**: Hydroxy-  
 382 propyl Cellulose. **LMP**: Low Methoxyl Pectin. **CS**: Cationic Starch. **SA**: Sodium Alginate. **CHI**: Chitosan. **PL**: Pullulan.

383 According to this wetting envelope, HPC is the polysaccharide solution that would have the  
 384 lowest contact angle ( $< 60^\circ$ ) once deposited onto Kraft paper, followed by CHI and SA ( $<$

385 80°), then by HPMC, MC, LMP, PL and CS with a contact angle higher than 90°. This means  
386 that polysaccharide solutions such as HPC, CHI, and SA would spread well and wet the sur-  
387 face of Kraft paper since they are in the range of liquids with favorable wetting ( $\theta < 90^\circ$ ). In  
388 contrast, solutions such as HPMC, MC, LMP, PL and CS would only establish a few interac-  
389 tions with the surface of Kraft paper. They would have an unfavorable wetting ( $\theta > 90^\circ$ ) that  
390 may lead to heterogeneous thickness, holes or crack formation.

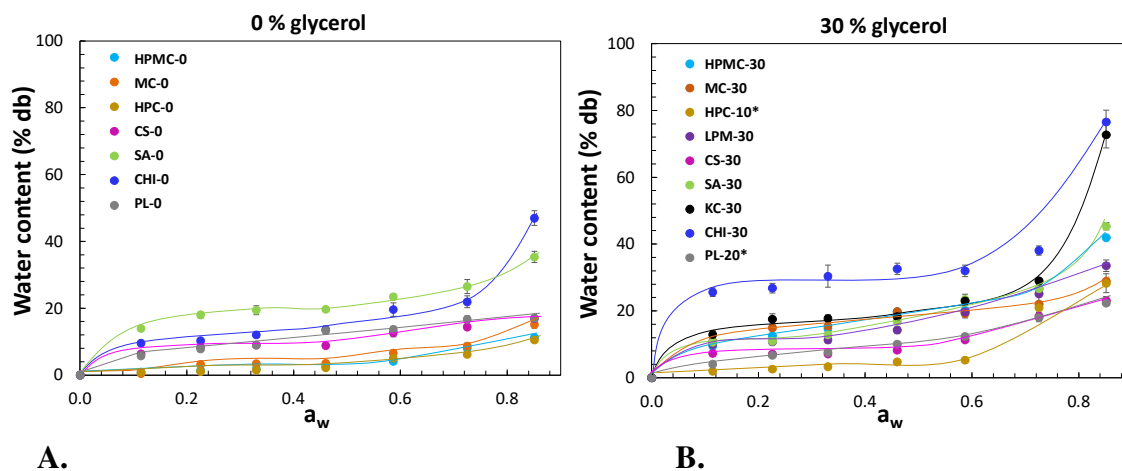
391 Liquids with similar total surface tension  $\sigma_L$  can thus have a different contact angle with the  
392 solid, as observed for the different polysaccharide solutions studied. HPC and HPMC solu-  
393 tions displayed a similar total surface tension, 38.9 and 43.2 mN.m<sup>-1</sup>, respectively. However,  
394 the wetting envelope of Kraft paper showed that HPC would form a contact angle just below  
395 60°, whereas HPMC would give a contact angle of more than 90°. This can be explained by  
396 the fact that the ratio between the dispersive and polar components of the HPC solution is  
397 different from that of the HPMC solution. Polar components accounted for 49 % of the sur-  
398 face tension of HPC, while they represented 83 % for HPMC. Therefore, Kraft paper would  
399 form more interactions with a low-polar solution since its structure is mostly dispersive.

## 400 **3.2. Functional properties of polysaccharide films as self-standing materials**

### 401 **3.2.1. Water sorption isotherm of films**

402 Water sorption isotherms of polysaccharide films without glycerol and with 30 % of glycerol  
403 at 25 ° C are displayed in **Fig. 4**. First, polysaccharides films without addition of glycerol  
404 (**Fig. 4A**) started to significantly sorb water at a relative humidity of 60 %. CHI and SA  
405 demonstrated the highest sensitivity to moisture, even at low relative humidity. The moisture  
406 sorption of these films increased by a factor two from 60 % to 85 % relative humidity. The  
407 water content of these two polysaccharides increased from 19.6 and 23.4 % to 46.9 and 35.3  
408 %, respectively. This is in agreement with the values previously reported by Monte, Moreno,  
409 Senna, Arrieche & Pinto, (2018) for CHI and Xiao & Tong, (2013) for SA films. These au-  
410 thors also evidenced a slow increase in the moisture content of CHI and SA films up to a rela-  
411 tive humidity of 60 %. Above this threshold value, a slight increase in the relative humidity  
412 led to a significant increase in the moisture content of the films. Such phenomenon occurs  
413 because the first water molecules that enter the polymer loosen the structure and make it easi-  
414 er for subsequent molecules to enter the polymer network (Su et al., 2010). The presence of  
415 functional groups such as hydroxyl (-OH), glycosidic linkage (C-O-C) as well as amino  
416 (NH<sub>2</sub>, in the form of NH<sub>3</sub><sup>+</sup>) in the case of CHI films (Crouvisier-Urien et al., 2016; Made-  
417 leine-Perdrillat et al., 2016) and carboxylic groups (-COOH) in SA films, confers to these

418 polysaccharides. a high affinity for water molecules. In contrast, the cellulose derivatives  
 419 (HPMC, MC and HPC) showed to be the polysaccharides with the lowest sensitivity to mois-  
 420 ture sorption. At a relative humidity of 11 %, they presented a moisture content 7 to 17 times  
 421 lower than the other polysaccharides. They also showed to be less affected by an increase in  
 422 the relative humidity. This lower affinity to water presented by the cellulose derivatives may  
 423 be due to the presence of methyl groups (-CH<sub>3</sub>) that have replaced part of the hydroxyls (-  
 424 OH) (Nasatto et al., 2015), thus decreasing their hydrophilicity.



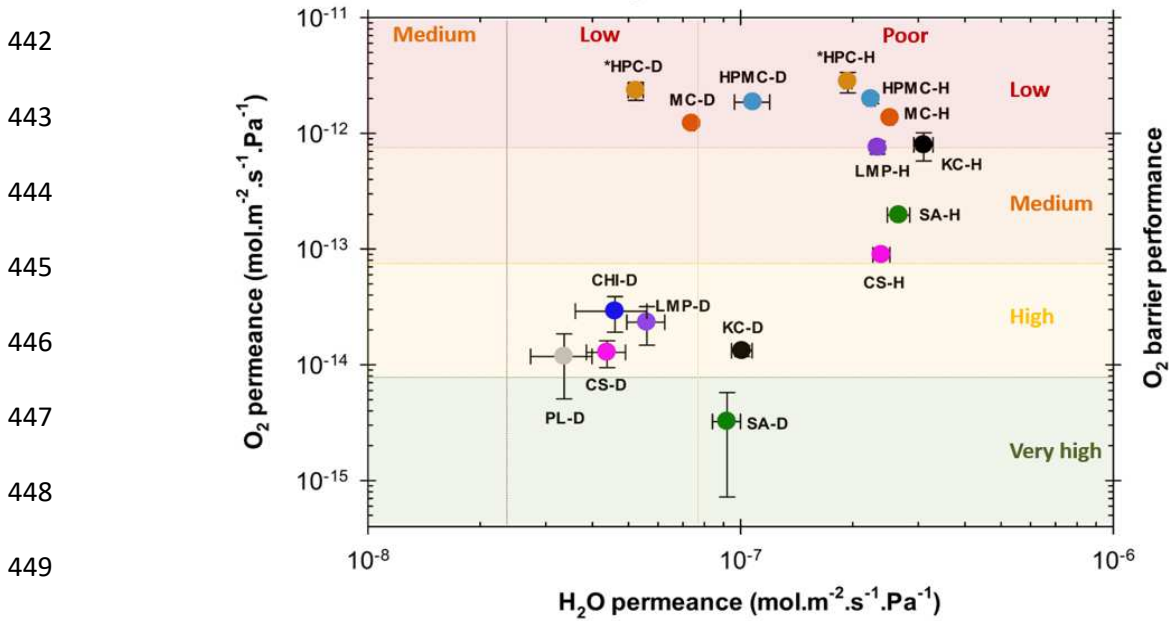
425 **A.** **B.**  
 426 **Fig. 4.** Moisture sorption isotherms of polysaccharide films displaying the water content of the films (expressed as percent-  
 427 age of the dry basis) according to the water activity ( $a_w$ ). **A.** Films without glycerol. LMP-0 and KC-0 were not measured  
 428 due to brittleness of the films. **B.** Films containing 30 % glycerol (\*except HPC with 10 % and PL with 20 %). Dotted lines  
 429 are a guide for the eyes. **HPMC:** Hydroxypropyl Methylcellulose. **MC:** Methyl Cellulose. **HPC:** Hydroxypropyl Cellulose.  
 430 **LMP:** Low Methoxyl Pectin. **CS:** Cationic Starch. **SA:** Sodium Alginate. **KC:** Kappa-Carrageenan. **CHI:** Chitosan. **PL:**  
 431 Pullulan. Values are reported as mean  $\pm$  standard deviation ( $n = 3$ ).

432 The addition of 30 % of glycerol to the films (**Fig. 4B**) increased the moisture content by a  
 433 factor of two for polysaccharides such as CHI, MC and HPMC. Such phenomenon has al-  
 434 ready been highly reported in the literature (Choi, Kim, Hanna, Weller & Kerr, 2008; Su et  
 435 al., 2010). This occurs because glycerol not only loosens the microstructure of the films, but  
 436 also increases their hydrophilicity (Choi et al., 2008). For the other polysaccharides, such as  
 437 HPC, SA, CS and PL, the effect was less pronounced.

### 438 3.2.2. Barrier properties of films

439 The oxygen permeance as a function of the water vapor permeance of the polysaccharide  
 440 films under two different relative humidity differentials is displayed in **Fig. 5**.

441 A.



449 B.

| Barrier performance | Oxygen permeance                                       | Water vapor permeance                                  |
|---------------------|--|--|
|                     | mol.m <sup>-2</sup> .s <sup>-1</sup> .Pa <sup>-1</sup> | mol.m <sup>-2</sup> .s <sup>-1</sup> .Pa <sup>-1</sup> |
| Very high           | < 7.6x10 <sup>-15</sup>                                | < 7.6x10 <sup>-12</sup>                                |
| High                | 7.6x10 <sup>-15</sup> - 7.6x10 <sup>-14</sup>          | 1.0x10 <sup>-09</sup> - 1.0x10 <sup>-08</sup>          |
| Medium              | 7.6x10 <sup>-14</sup> - 7.6x10 <sup>-13</sup>          | 1.0x10 <sup>-08</sup> - 2.6x10 <sup>-08</sup>          |
| Low                 | 7.6x10 <sup>-13</sup> - 7.6x10 <sup>-12</sup>          | 2.6x10 <sup>-08</sup> - 7.8x10 <sup>-08</sup>          |
| Poor                | > 7.6x10 <sup>-12</sup>                                | > 7.8x10 <sup>-08</sup>                                |

451 **Fig. 5.** Barrier properties of polysaccharide films to water vapor and oxygen. **A.** Oxygen permeance ( $P_{O_2}$ ) as a function of  
 452 the water vapor permeance ( $P_{H_2O}$ ) of polysaccharide films with 20 % of glycerol (\*Except HPC films with 10 % of glycerol)  
 453 under two different relative humidity conditions at 25 °C. Semi-dry condition (indicated with a D) corresponds to:  $P_{H_2O}$  (0  
 454 %-50 % RH differential),  $P_{O_2}$  (50 % RH). Humid condition (indicated with an H) corresponds to:  $P_{H_2O}$  (50 %-100 % RH),  
 455  $P_{O_2}$  (80 % RH). **HPMC:** Hydroxypropyl Methylcellulose. **MC:** Methyl Cellulose. **HPC:** Hydroxypropyl Cellulose. **LMP:**  
 456 Low Methoxyl Pectin. **CS:** Cationic Starch. **SA:** Sodium Alginate. **CHI:** Chitosan. **PL:** Pullulan. Values are reported as  
 457 mean  $\pm$  standard deviation. (n = 3 for  $P_{O_2}$ , n = 4 for  $P_{H_2O}$ ). Detailed values are provided in **Appendix A.** **B.** Classification of  
 458 the  $O_2$  and  $H_2O$  barrier performance of polysaccharide films. The classification of the  $O_2$  and  $H_2O$  barrier performance,  
 459 referred to as poor, low, medium, high and very high, was adapted from Wu et al. (2021). For practical purpose, the oxygen  
 460 permeance value (mol.m<sup>-2</sup>.s<sup>-1</sup>.Pa<sup>-1</sup>) can be simply converted into OTR (cm<sup>3</sup>.m<sup>-2</sup>.day<sup>-1</sup>) by multiplying the value by  
 461 2.09x10<sup>14</sup>. For conversion of the water vapor permeance (mol.m<sup>-2</sup>.s<sup>-1</sup>.Pa<sup>-1</sup>) into WVTR (g.m<sup>-2</sup>.day<sup>-1</sup>) the value can be multi-  
 462 plied by 2.46x10<sup>9</sup>. The partial pressure differential used for the permeance measurement was 1000 hPa for oxygen and 1584  
 463 Pa for water vapor.

464 Regarding the permeance to oxygen, the cellulose derivatives HPMC, MC and HPC appeared  
 465 to be the most permeable polysaccharides under both humid and semi-dry conditions (>  
 466  $1.1 \times 10^{-12}$  mol.m<sup>-2</sup>.s<sup>-1</sup>.Pa<sup>-1</sup>). A decrease of less than 17 % was observed in the permeance to

467 oxygen for the three cellulose derivatives from humid to semi-dry condition. They also  
468 showed to be the least affected by changes in the relative humidity conditions, as previously  
469 evidenced by the moisture sorption isotherms presented in **Fig. 4**. This higher oxygen perme-  
470 ance of the films from the three cellulose derivatives (HPMC, MC and HPC) compared with  
471 other polysaccharide films could be a consequence of the presence of bulky side groups that  
472 generate a larger fractional free volume (Lagaron, Catalá & Gavara, 2004). In addition, the  
473 presence of methyl groups (-CH<sub>3</sub>), which are non-polar functional groups, could also contrib-  
474 ute to a greater affinity of the films with oxygen molecules, which are also non-polar, thus  
475 facilitating their transfer through the films. Furthermore, in the case of HPC, the hydroxypro-  
476 pyl pendant groups may generate more steric hindrance than the methyl groups of MC and, to  
477 a lesser extent, HPMC, leading to a less compact polymer network and higher oxygen perme-  
478 ance.

479 For all the other polysaccharides, a significant decrease in the oxygen permeance (> 85 %)   
480 was observed when going from humid to semi-dry condition. In particular, the oxygen per-  
481 meance of SA, KC and LMP, decreased by more than 97 %. Under humid condition, CS pre-  
482 sented the lowest permeance to oxygen ( $8.9 \times 10^{-14}$  mol.m<sup>-2</sup>.s<sup>-1</sup>.Pa<sup>-1</sup>), followed by SA  
483 ( $2.0 \times 10^{-13}$  mol.m<sup>-2</sup>.s<sup>-1</sup>.Pa<sup>-1</sup>), LMP ( $7.6 \times 10^{-13}$  mol.m<sup>-2</sup>.s<sup>-1</sup>.Pa<sup>-1</sup>), and KC ( $8.0 \times 10^{-13}$   
484 mol.m<sup>-2</sup>.s<sup>-1</sup>.Pa<sup>-1</sup>), respectively. The order changed under semi-dry condition, with SA pre-  
485 senting the lowest permeance to oxygen ( $3.2 \times 10^{-15}$  mol.m<sup>-2</sup>.s<sup>-1</sup>.Pa<sup>-1</sup>), followed by PL  
486 ( $1.2 \times 10^{-14}$  mol.m<sup>-2</sup>.s<sup>-1</sup>.Pa<sup>-1</sup>), CS and KC ( $1.3 \times 10^{-14}$  mol.m<sup>-2</sup>.s<sup>-1</sup>.Pa<sup>-1</sup> for both of them), LMP  
487 ( $2.3 \times 10^{-14}$  mol.m<sup>-2</sup>.s<sup>-1</sup>.Pa<sup>-1</sup>) and CHI ( $2.9 \times 10^{-14}$  mol.m<sup>-2</sup>.s<sup>-1</sup>.Pa<sup>-1</sup>), respectively. Concerning  
488 the water vapor permeance, a significant decrease (> 50 %) was observed for all polysaccha-  
489 rides from humid to semi-dry condition. In humid condition, the values ranged from 1.9 to  
490  $3.1 \times 10^{-7}$  mol.m<sup>-2</sup>.s<sup>-1</sup>.Pa<sup>-1</sup>, while in semi-dry condition, their permeance values were widely  
491 spread, with PL having the lowest water vapor permeance ( $3.4 \times 10^{-8}$  mol.m<sup>-2</sup>.s<sup>-1</sup>.Pa<sup>-1</sup>) and  
492 KC having the highest one ( $1.8 \times 10^{-7}$  mol.m<sup>-2</sup>.s<sup>-1</sup>.Pa<sup>-1</sup>).

493 As expected, the permeance to oxygen and water vapor of the polysaccharides was always  
494 significantly higher when the films were exposed to high relative humidity. This is because  
495 water induces a plasticizing or swelling effect on polymers that increases the molecular free  
496 volume and, therefore the gas permeability (Wang et al., 2018). However, this plasticizing  
497 effect brought by water molecules is not the same for all polymers since they do not sorb wa-  
498 ter at the same level, as evidenced by the moisture sorption isotherms displayed in **Fig. 4**. The  
499 variations in oxygen and water vapor permeance between the different polysaccharide films

500 result from different cohesive energy densities, free volume, and degree of crystallinity in the  
501 matrix (Khalil et al., 2019). Materials with good resistance to oxygen often have high number  
502 of polar interactions and hydrogen bonding, which usually results in high hydrophilicity and,  
503 thus, poor water vapor barrier (Wang et al., 2018).

504 In order to evaluate the performance of the polysaccharide films, the classification proposed  
505 by Wu, Misra & Mohanty, (2021) for biodegradable polymers according to their barrier prop-  
506 erties was used and it is displayed in **Fig. 5A**. Detailed values of this classification are pre-  
507 sented in **Fig. 5B**. According to this classification, SA in semi-dry condition showed a "very  
508 high" barrier against oxygen ( $P_{O_2} < 7.6 \times 10^{-15} \text{ mol.m}^{-2}.\text{s}^{-1}.\text{Pa}^{-1}$ ). This lie within the same range  
509 as certain conventional plastics with very good oxygen barrier such as EVOH ( $\sim 2.3 \times 10^{-15}$   
510  $\text{mol.m}^{-2}.\text{s}^{-1}.\text{Pa}^{-1}$ ) and PVDC ( $\sim 4.7 \times 10^{-15} \text{ mol.m}^{-2}.\text{s}^{-1}.\text{Pa}^{-1}$ ) and to that of biodegradable plas-  
511 tics like polyglycolic acid (PGA) ( $\sim 4.7 \times 10^{-15} \text{ mol.m}^{-2}.\text{s}^{-1}.\text{Pa}^{-1}$ ), which has been considered  
512 as one of the highest barrier polymers that can be biodegraded (Wu et al., 2021). However, as  
513 previously noted, the relative humidity plays an important role in the oxygen and water vapor  
514 barrier properties of the polysaccharide films. SA shifted from a "very high" barrier against  
515 oxygen in semi-dry condition to a "medium" barrier ( $P_{O_2}$  between  $7.6 \times 10^{-14}$  and  $7.6 \times 10^{-13}$   
516  $\text{mol.m}^{-2}.\text{s}^{-1}.\text{Pa}^{-1}$ ) in humid condition. The other polysaccharides also moved from "high" ( $P_{O_2}$   
517 between  $7.6 \times 10^{-15}$  and  $7.6 \times 10^{-14} \text{ mol.m}^{-2}.\text{s}^{-1}.\text{Pa}^{-1}$ ) barrier in semi-dry condition to a "medi-  
518 um" barrier in humid condition, except for the cellulose derivatives (HPMC, MC and HPC),  
519 which showed a "low" ( $P_{O_2}$  between  $7.6 \times 10^{-13}$  and  $7.6 \times 10^{-12} \text{ mol.m}^{-2}.\text{s}^{-1}.\text{Pa}^{-1}$ ) barrier against  
520 oxygen at both humid and semi-dry conditions and KC which moved from "high" to "low"  
521 barrier. Regarding the barrier property against water vapor, all polysaccharides showed a  
522 "poor" barrier ( $P_{H_2O} > 7.8 \times 10^{-8} \text{ mol.m}^{-2}.\text{s}^{-1}.\text{Pa}^{-1}$ ) in humid condition and a "low" barrier  
523 ( $P_{H_2O}$  between  $2.6 \times 10^{-8}$  and  $7.8 \times 10^{-8} \text{ mol.m}^{-2}.\text{s}^{-1}.\text{Pa}^{-1}$ ) in semi-dry condition, except for  
524 HPMC, SA and KC which also exhibited a "poor" barrier in semi-dry condition.

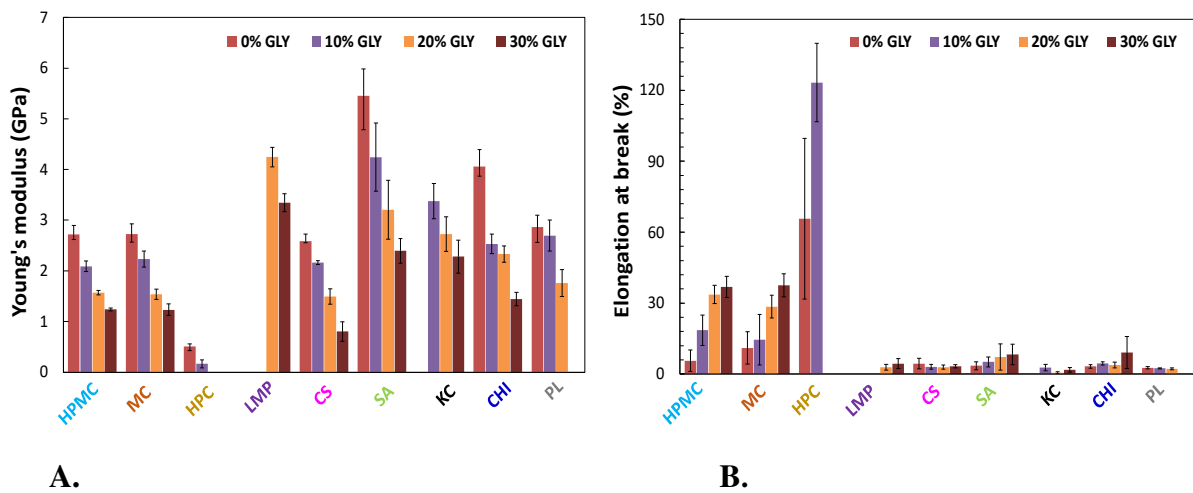
525 Although the plasticizing effect of glycerol is not discussed in detail in this part of the work,  
526 the oxygen and water vapor permeance of the polysaccharide films containing different glyc-  
527 erol concentrations are provided in **Appendix A**.

### 528 **3.2.3. Mechanical properties of films**

529 Young's modulus and the elongation at break of the polysaccharide films with different per-  
530 centages of glycerol were measured and are displayed in **Fig. 6**.



531 Regarding the Young's modulus of the films (**Fig. 6A**) without addition of glycerol, values  
 532 ranged from 0.5 to 5.5 GPa. HPC was the polysaccharide that presented the lowest Young's  
 533 modulus of all polysaccharides (0.5 GPa). It was followed by CS (2.6 GPa), HPMC (2.7  
 534 GPa), MC (2.7 GPa), PL (2.9 GPa), CHI (4.1 GPa) and finally SA, which exhibited the high-  
 535 est Young's modulus value (> 5 GPa). Polysaccharides such as LMP and KC could not be  
 536 measured when no plasticizer was added due to their brittleness. When glycerol was added to  
 537 the films, Young's modulus decreased in all cases due to the plasticization effect. This de-  
 538 crease was greater than 54 % for HPMC, MC, CHI, CS and SA when the glycerol concentra-  
 539 tion increased from 0 % to 30 %.



540 **A.** **B.**  
 541 **Fig. 6.** Mechanical properties of polysaccharide films at 25 °C and 50 % RH with different glycerol percentages (0, 10, 20  
 542 and 30 %). **(A).** Young's modulus (GPa). **(B).** Elongation at break (%). **HPMC:** Hydroxypropyl Methylcellulose. **MC:** Me-  
 543 thyl Cellulose. **HPC:** Hydroxypropyl Cellulose. **LMP:** Low Methoxyl Pectin. **CS:** Cationic Starch. **SA:** Sodium Alginate.  
 544 **KC:** Kappa-Carrageenan. **CHI:** Chitosan **PL:** Pullulan. Values are reported as mean ± standard deviation (n = 6). Detailed  
 545 values are provided in **Appendix B.**

546 The elongation at break of the films is presented in **Fig. 6B**. Without glycerol, HPC films  
 547 showed the highest elongation at break (65 %), with the longest plastic deformation com-  
 548 pared with the other polysaccharides. It was followed by the other cellulose derivatives MC  
 549 and HPMC, with more than 5 % of elongation. The other polysaccharides displayed an elon-  
 550 gation of less than 5 %, thus being less stretchable and more brittle than the cellulose deriva-  
 551 tives. When glycerol was added to the films, a strong increase in the elongation at break was  
 552 observed for most of the films. The cellulose derivatives HPMC, MC and HPC presented an  
 553 increase of 555 %, 239 % and 87 %, respectively, when glycerol was added (from 0 % to 30  
 554 % for HPMC and MC and from 0 % to 10 % for HPC). Both SA and CHI showed an in-

555 crease, higher than 138 % when glycerol was added from 0 % to 30 %. For the other polysac-  
556 charides, LMP, CS, KC and PL, the plasticizing effect was found not to be significant. In the  
557 case of HPC and PL, the addition of glycerol was even limited to 10 % and 20 % (w/w), re-  
558 spectively, as above this concentration, phase separation occurred in the films.

559 The use of a plasticizer is required in most of the cases, to improve the mechanical properties  
560 of biopolymer films. Their brittleness and stiffness are due to extensive interactions between  
561 polymer chains such as intermolecular bonds that lead to high mechanical cohesion between  
562 chains (Jantrawut, Chaiwarit, Jantanasakulwong, Brachais & Chambin, 2017; Jarray, Gerbaud  
563 & Hemati, 2016). The higher this mechanical cohesion, the stiffer the polymer network. Plas-  
564 ticizers, such as glycerol, decrease the cohesion within the polymer network by reducing  
565 these intermolecular forces between adjacent polymer chains and substituting them with hy-  
566 drogen bonds formed between the plasticizer and the polymer chains (Immergut & Mark,  
567 1965). However, plasticizers do not follow the same behavior in all biopolymer matrices. The  
568 efficiency of a plasticizer depends on the polymer properties, such as the molecular weight,  
569 the chemical composition (Avella et al., 2007), the rate of plasticizer diffusion into the poly-  
570 mer matrix (Sothornvit & Krochta, 2005), and the type of interaction (intramolecu-  
571 lar/intermolecular) between the polymer and the plasticizer (Smith, Escobar, Andris, Board-  
572 man & Peters, 2021). These parameters generally vary between polymers, leading to a com-  
573 pletely different compatibility and, therefore, a different plasticizing effect. It is also worth  
574 noting that even though the use of glycerol as plasticizer improves the mechanical properties  
575 of the polysaccharide films, these changes remain in a rather limited range and are not even  
576 significant enough in some cases to drastically improve the performance of the films. There-  
577 fore, it can be concluded that the mechanical behavior of the films is predominantly governed  
578 by the polymer molecular structure, rather than by the effect of the plasticizer. Furthermore,  
579 although the different mechanical behaviors observed for polysaccharide films are related to  
580 structural factors (such as degree of substitution, crystallinity, free volume, thermal history,  
581 molecular orientation, etc.), it is very difficult to establish a link with a single parameter.  
582 Even considering only cellulose derivatives, as also reported by Espinoza-Herrera, Pedroza-  
583 Islas, San Martín-Martínez, Cruz-Orea & Tomás, (2011), the differences between polysaccha-  
584 rides cannot be explained merely by the degree of substitution or the percentage of crystal-  
585 linity, but would require extensive multiparametric analysis.

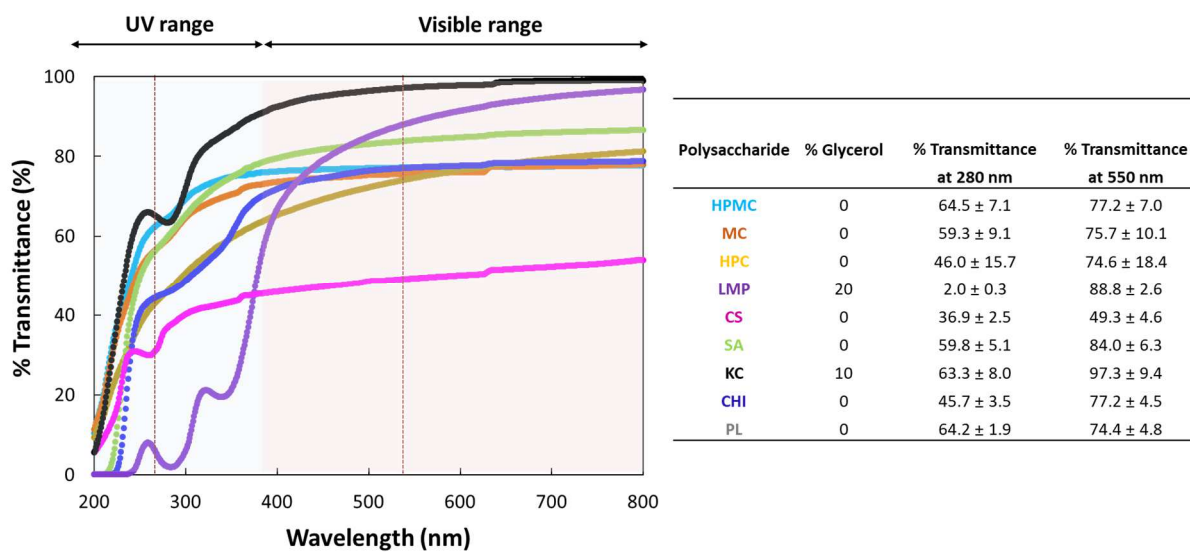
586 Moreover, it should be noticed that, for coating applications, the mechanical properties of  
587 polysaccharides are less critical because the mechanical support is mostly provided by the

588 material on which the polysaccharide is coated (for example, paper). However, the mechani-  
 589 cal properties remain important parameters for the selection of the polysaccharide coating  
 590 since the material must preserve its structure during any further manipulation in order to en-  
 591 sure the efficiency of the coating and the preservation of the properties over time.

### 592 3.2.4. Transparency and UV-blocking ability of films

593 The transparency and UV blocking ability of the polysaccharide films were measured by the  
 594 percentage of transmittance in the 200-800 nm wavelength range. Although the UV light  
 595 ranges between 200-380 nm, for convenience purpose, the transmittance at 280 nm was se-  
 596 lected to compare the UV blocking ability of the films. Similarly, at a wavelength of 550 nm,  
 597 the transmittance was chosen for comparing the quantity of visible light that can pass through  
 598 the films (transparency). Transmittance values at the different wavelengths obtained for the  
 599 polysaccharide films are displayed in Fig. 7.

600 All the polysaccharide films showed good transparency since the transmittance at 550 nm  
 601 was higher than 74 %, except for CS, whose transmittance was less than 50 %. Of all poly-  
 602 saccharides, KC showed the highest transparency (97 %), followed by LPM (89 %), SA (84  
 603 %), CHI (77 %), HPMC, MC, HPC, and PL (from 77 to 75 % respectively) and, lastly, CS  
 604 with 50 %. Regarding the UV screening capacity, polysaccharide films showed a transmit-  
 605 tance lower than 65 % in all cases. LMP was the polysaccharide with the lowest transmit-  
 606 tance (2 %). It was followed by CS (37 %), CHI and HPC (46 % for both), MC and SA (59 %



607 for both) and lastly KC, PL and HPMC (from 63 to 65 % respectively).

608 **Fig. 7.** UV-Visible transmission spectra of polysaccharide films and values of transmittance at 280 nm (UV range) and 550  
609 nm (Visible range) at 25 °C. **HPMC:** Hydroxypropyl Methylcellulose. **MC:** Methyl Cellulose. **HPC:** Hydroxypropyl Cellu-  
610 lose. **LMP:** Low Methoxyl Pectin. **CS:** Cationic Starch. **SA:** Sodium Alginate. **KC:** Kappa-Carrageenan. **CHI:** Chitosan.  
611 **PL:** Pullulan. Values are reported as mean  $\pm$  standard deviation (n = 3).

612 Of particular interest is pectin which has also previously been reported by Shankar, Tanom-  
613 rod, Rawdkuen & Rhim, (2016) and Younis, Abdellatif, Ye & Zhao, (2020) as a good UV  
614 barrier polysaccharide, avoiding more than 70 % of incident UV light. The origin of this UV  
615 protection arising in pectin is not well known in the literature. However, such behavior of  
616 pectin against UV light might be related to their functional role in the cell wall of fruits and  
617 vegetables, these products being constantly exposed to ultraviolet radiation and requiring  
618 protection to avoid photo-oxidation.

619 The level of transparency of packaging materials influences the perception and acceptability  
620 of consumers. The level required for a material depends mostly on its application. On the  
621 contrary, the UV screening capacity of food packaging materials is a critical parameter since  
622 UV radiation (200-400 nm) can promote lipid photo-oxidation mechanisms in many food  
623 products. It can also damage photosensitive substances such as pigments and vitamins (Sun  
624 Lee, L.Yam & PierGiovanni, 2008). Moreover, UV radiation can cause photooxidative degra-  
625 dation leading to a break in the polymer chain that reduces molecular weight, causing deterio-  
626 ration of mechanical properties, and resulting in inefficient materials after an unpredictable  
627 period (Yousif & Haddad, 2013).

### 628 **3.2.5. Correlations between functional properties**

629 The functional properties of polymers depend on many factors related to the polymer struc-  
630 ture, including cohesive energy density, free volume, degree of crystallinity, orientation and  
631 degree of cross-linking (Abdan et al., 2020). Although some obvious correlations can be ob-  
632 served when considering the change in functional properties as a function of plasticizer con-  
633 centration for a given polymer, there is no direct correlation when it comes to the different  
634 polysaccharides studied in this work. Taking into account all polysaccharides together at the  
635 same glycerol concentration and the same water activity, there are no further correlations be-  
636 tween the measured properties. For example, the barrier properties (to oxygen and water va-  
637 por) correlate neither with the mechanical properties (Young's modulus, elongation at break  
638 and tensile strength) nor with the polar/dispersive ratio of the surface tension, as expected.  
639 Even when considering the cohesive energy density and the solubility parameter of the poly-  
640 mers, calculated by the group contribution method (Table 1), these are not explanatory pa-

641 rameters of the measured macroscopic properties as no clear correlation can be found. There-  
642 fore, when dealing with polysaccharides having different chemical structures and thus various  
643 film-forming mechanisms, the relationships between molecular-scale parameters and macro-  
644 scopic functional properties are likely multiparametric and remain a critical issue to be fur-  
645 ther addressed. Although some studies have already identified tentative correlations for the  
646 same polymer as a function of the degree of substitution (Elidrissi, 2012) or the degree of  
647 crystallinity (Udayakumar et al., 2020), for the time being there is no ubiquitous model that  
648 can be applied to all polymers.

#### 649 **4. Conclusions**

650 This study provides an extensive experimental review of the main functional properties of the  
651 most promising polysaccharides for potential application in the field of food packaging. Their  
652 permeability to water vapor and to oxygen, as well as their mechanical and optical properties  
653 were measured under standardized conditions for polysaccharide films with different percent-  
654 ages of glycerol used as a plasticizer. Film-forming solutions were also characterized for their  
655 viscosity and surface tension properties. Regarding water vapor barrier property, all polysac-  
656 charide films showed rather low performance, due to their hydrophilicity. Considering the  
657 oxygen barrier property, CHI, LMP, KC, SA, CS and PL films displayed good oxygen barrier  
658 properties in semi-dry (50 % RH) and humid (80 % RH) conditions. Among all polysaccha-  
659 rides, SA even presented the highest oxygen barrier, with permeance values comparable to  
660 those of conventional high oxygen barrier plastics, such as EVOH and PVDC. On the contra-  
661 ry, cellulose derivatives (HPMC, MC and HPC) showed low oxygen barrier performance  
662 both in semi-dry and humid conditions. The implementation of polysaccharides for packaging  
663 applications represents an opportunity for waste valorization, contributing to the concept of a  
664 circular economy. The most promising application of polysaccharides could be their use as  
665 coating materials on paper-based packaging, offering a good protective barrier against oxy-  
666 gen for oxidation-sensitive food products. They might also help in the strategies to replace  
667 conventional coating materials, which are based on synthetic polymers, leading to recyclabil-  
668 ity issues for such multilayer materials.

#### 669 **Declaration of competing interest**

670 The authors have declared no conflict of interest.

671 **Credit authorship contribution statement**

672 **María Ureña:** Conceptualization, Methodology, Formal analysis, Investigation, Writing –  
673 original draft. **Thị- Thanh-Trúc Phùng:** Conceptualization, Methodology, Writing – review  
674 & editing. **Massimiliano Gerometta:** Methodology, Writing – review & editing. **Luciana de**  
675 **Siqueira Oliveira:** Methodology, Writing – review & editing. **Julie Chanut:** Methodology,  
676 Writing – review & editing. **Sandra Domenek:** Methodology, Writing – review & editing.  
677 **Patrice Dole:** Methodology, Writing – review & editing. **Gaelle Roudaut:** Methodology,  
678 Writing – review & editing. **Aurélié Lagorce:** Conceptualization, Methodology, Writing –  
679 review & editing. **Thomas Karbowskiak:** Conceptualization, Methodology, Formal analysis,  
680 Investigation, Writing – original draft.

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842 APPENDIX A. Barrier properties of polysaccharide films to water vapor and oxygen. **HPMC**: Hydroxypropyl Methylcellulose. **MC**: Methyl Cellulose. **HPC**: Hydroxypropyl  
843 Cellulose. **LMP**: Low Methoxyl Pectin. **CS**: Cationic Starch. **SA**: Sodium Alginate. **KC**: Kappa-Carrageenan. **CHI**: Chitosan. **PL**: Pullulan. **RH**: relative humidity. **N/A**: not

| Polysaccharide | % glycerol | Water vapor permeance<br>(mol.m <sup>-2</sup> .s <sup>-1</sup> .Pa <sup>-1</sup> ) |  | Oxygen permeance<br>(mol.m <sup>-2</sup> .s <sup>-1</sup> .Pa <sup>-1</sup> ) |  |  |
|----------------|------------|--|--|---|--|--|
|                |            | 0-50 % RH  | 50-100 % RH  | 10 % RH   | 50 % RH  | 80 % RH  |
| HPMC           | 0          | 6.96x10 <sup>-8</sup> ±6.78x10 <sup>-9</sup> <sup>α</sup>                          | 1.66x10 <sup>-7</sup> ±6.85x10 <sup>-9</sup> <sup>αβ</sup> | 5.43x10 <sup>-12</sup> ±7.06x10 <sup>-13</sup> <sup>α</sup>                   | 2.85x10 <sup>-12</sup> ±5.19x10 <sup>-13</sup> <sup>α</sup>  | 2.77x10 <sup>-12</sup> ±2.99x10 <sup>-13</sup> <sup>α</sup>  |
|                | 10         | 8.28x10 <sup>-8</sup> ±6.39x10 <sup>-9</sup> <sup>αβ</sup>                         | 1.94x10 <sup>-7</sup> ±4.88x10 <sup>-9</sup> <sup>α</sup>  | 1.84x10 <sup>-12</sup> ±1.11x10 <sup>-13</sup> <sup>β</sup>                   | 1.94x10 <sup>-12</sup> ±3.95x10 <sup>-13</sup> <sup>β</sup>  | 2.20x10 <sup>-12</sup> ±4.61x10 <sup>-13</sup> <sup>αβ</sup> |
|                | 20         | 1.08x10 <sup>-7</sup> ±1.17x10 <sup>-8</sup> <sup>βδ</sup>                         | 2.24x10 <sup>-7</sup> ±5.67x10 <sup>-9</sup> <sup>αβ</sup> | 1.38x10 <sup>-12</sup> ±5.50x10 <sup>-14</sup> <sup>δ</sup>                   | 1.86x10 <sup>-12</sup> ±4.35x10 <sup>-14</sup> <sup>β</sup>  | 1.98x10 <sup>-12</sup> ±1.72x10 <sup>-13</sup> <sup>β</sup>  |
|                | 30         | 1.08x10 <sup>-7</sup> ±1.07x10 <sup>-8</sup> <sup>δ</sup>                          | 2.68x10 <sup>-7</sup> ±3.33x10 <sup>-9</sup> <sup>β</sup>  | 1.31x10 <sup>-12</sup> ±9.53x10 <sup>-14</sup> <sup>δ</sup>                   | 2.35x10 <sup>-12</sup> ±1.74x10 <sup>-13</sup> <sup>αβ</sup> | 2.47x10 <sup>-12</sup> ±1.60x10 <sup>-13</sup> <sup>αβ</sup> |
| MC             | 0          | 9.10x10 <sup>-8</sup> ±2.87x10 <sup>-8</sup> <sup>α</sup>                          | 1.86x10 <sup>-7</sup> ±4.14x10 <sup>-9</sup> <sup>α</sup>  | 2.74x10 <sup>-12</sup> ±8.09x10 <sup>-13</sup> <sup>α</sup>                   | 1.40x10 <sup>-12</sup> ±1.11x10 <sup>-13</sup> <sup>α</sup>  | 1.63x10 <sup>-12</sup> ±2.38x10 <sup>-13</sup> <sup>α</sup>  |
|                | 10         | 1.05x10 <sup>-7</sup> ±1.27x10 <sup>-8</sup> <sup>α</sup>                          | 2.21x10 <sup>-7</sup> ±1.03x10 <sup>-9</sup> <sup>β</sup>  | 8.61x10 <sup>-13</sup> ±3.66x10 <sup>-14</sup> <sup>β</sup>                   | 1.14x10 <sup>-12</sup> ±1.15x10 <sup>-13</sup> <sup>β</sup>  | 1.45x10 <sup>-12</sup> ±3.16x10 <sup>-13</sup> <sup>α</sup>  |
|                | 20         | 7.39x10 <sup>-8</sup> ±2.27x10 <sup>-9</sup> <sup>α</sup>                          | 2.52x10 <sup>-7</sup> ±4.81x10 <sup>-9</sup> <sup>δ</sup>  | 6.62x10 <sup>-13</sup> ±2.43x10 <sup>-14</sup> <sup>β</sup>                   | 1.22x10 <sup>-12</sup> ±6.55x10 <sup>-14</sup> <sup>αβ</sup> | 1.36x10 <sup>-12</sup> ±2.08x10 <sup>-14</sup> <sup>α</sup>  |
|                | 30         | 1.26x10 <sup>-7</sup> ±9.03x10 <sup>-9</sup> <sup>α</sup>                          | 2.75x10 <sup>-7</sup> ±6.61x10 <sup>-9</sup> <sup>ψ</sup>  | 5.75x10 <sup>-13</sup> ±2.90x10 <sup>-14</sup> <sup>β</sup>                   | 1.09x10 <sup>-12</sup> ±7.09x10 <sup>-14</sup> <sup>β</sup>  | 1.30x10 <sup>-12</sup> ±1.05x10 <sup>-13</sup> <sup>α</sup>  |
| HPC            | 0          | 4.84x10 <sup>-8</sup> ±9.84x10 <sup>-10</sup>                                      | 1.27x10 <sup>-7</sup> ±4.16x10 <sup>-9</sup>               | 1.49x10 <sup>-12</sup> ±8.50x10 <sup>-14</sup>                                | 1.83x10 <sup>-12</sup> ±2.10x10 <sup>-13</sup>               | 2.11x10 <sup>-12</sup> ±1.21x10 <sup>-13</sup>               |
|                | 10         | 5.23x10 <sup>-8</sup> ±2.42x10 <sup>-9</sup>                                       | 1.94x10 <sup>-7</sup> ±4.82x10 <sup>-9</sup>               | 1.71x10 <sup>-12</sup> ±3.61x10 <sup>-13</sup>                                | 2.34x10 <sup>-12</sup> ±4.12x10 <sup>-13</sup>               | 2.80x10 <sup>-12</sup> ±5.60x10 <sup>-13</sup>               |
| LMP            | 20         | 5.60x10 <sup>-8</sup> ±6.56x10 <sup>-9</sup>                                       | 2.33x10 <sup>-7</sup> ±7.87x10 <sup>-9</sup>               | N/A   | 2.33x10 <sup>-14</sup> ±8.53x10 <sup>-15</sup>               | 7.57x10 <sup>-13</sup> ±9.60x10 <sup>-14</sup>               |
|                | 30         | 7.56x10 <sup>-8</sup> ±2.72x10 <sup>-9</sup>                                       | 2.60x10 <sup>-7</sup> ±8.08x10 <sup>-9</sup>               | N/A   | 3.76x10 <sup>-14</sup> ±2.00x10 <sup>-15</sup>               | 1.10x10 <sup>-12</sup> ±2.84x10 <sup>-13</sup>               |
| CS             | 0          | 5.38x10 <sup>-8</sup> ±8.80x10 <sup>-9</sup> <sup>α</sup>                          | 2.27x10 <sup>-7</sup> ±9.29x10 <sup>-9</sup> <sup>β</sup>  | N/A   | N/A  | N/A  |
|                | 10         | 3.85x10 <sup>-8</sup> ±3.19x10 <sup>-9</sup> <sup>β</sup>                          | 1.87x10 <sup>-7</sup> ±1.48x10 <sup>-8</sup> <sup>α</sup>  | N/A   | 3.12x10 <sup>-14</sup> ±4.08x10 <sup>-14</sup> <sup>α</sup>  | 7.78x10 <sup>-14</sup> ±4.03x10 <sup>-14</sup>               |
|                | 20         | 4.38x10 <sup>-8</sup> ±5.27x10 <sup>-9</sup> <sup>β</sup>                          | 2.39x10 <sup>-7</sup> ±1.26x10 <sup>-8</sup> <sup>β</sup>  | N/A   | 1.28x10 <sup>-14</sup> ±3.33x10 <sup>-15</sup> <sup>α</sup>  | 8.91x10 <sup>-14</sup> ±3.65x10 <sup>-15</sup>               |
|                | 30         | 5.39x10 <sup>-8</sup> ±1.67x10 <sup>-9</sup> <sup>β</sup>                          | 2.87x10 <sup>-7</sup> ±1.47x10 <sup>-8</sup> <sup>δ</sup>  | N/A   | 3.61x10 <sup>-14</sup> ±1.72x10 <sup>-14</sup> <sup>α</sup>  | N/A  |
| SA             | 0          | 9.22x10 <sup>-8</sup> ±4.37x10 <sup>-9</sup> <sup>α</sup>                          | 3.53x10 <sup>-7</sup> ±1.79x10 <sup>-8</sup> <sup>α</sup>  | N/A   | 5.40x10 <sup>-15</sup> ±3.40x10 <sup>-15</sup> <sup>α</sup>  | 6.88x10 <sup>-14</sup> ±1.51x10 <sup>-14</sup> <sup>α</sup>  |
|                | 10         | 6.52x10 <sup>-8</sup> ±4.84x10 <sup>-9</sup> <sup>α</sup>                          | 2.67x10 <sup>-7</sup> ±1.28x10 <sup>-8</sup> <sup>β</sup>  | N/A   | 2.63x10 <sup>-15</sup> ±1.39x10 <sup>-15</sup> <sup>α</sup>  | 1.73x10 <sup>-13</sup> ±1.93x10 <sup>-13</sup> <sup>β</sup>  |
|                | 20         | 9.20x10 <sup>-8</sup> ±7.97x10 <sup>-9</sup> <sup>α</sup>                          | 2.66x10 <sup>-7</sup> ±1.84x10 <sup>-8</sup> <sup>β</sup>  | N/A   | 3.24x10 <sup>-15</sup> ±2.52x10 <sup>-15</sup> <sup>β</sup>  | 1.97x10 <sup>-13</sup> ±8.71x10 <sup>-15</sup> <sup>αβ</sup> |
|                | 30         | 7.32x10 <sup>-8</sup> ±1.01x10 <sup>-8</sup> <sup>α</sup>                          | 2.77x10 <sup>-7</sup> ±1.34x10 <sup>-8</sup> <sup>β</sup>  | N/A   | 8.19x10 <sup>-15</sup> ±3.51x10 <sup>-15</sup> <sup>α</sup>  | 5.33x10 <sup>-13</sup> ±2.23x10 <sup>-13</sup> <sup>αβ</sup> |
| KC             | 10         | 1.00x10 <sup>-7</sup> ±8.91x10 <sup>-10</sup> <sup>α</sup>                         | 3.00x10 <sup>-7</sup> ±8.82x10 <sup>-9</sup> <sup>α</sup>  | N/A   | 9.41x10 <sup>-15</sup> ±5.43x10 <sup>-15</sup> <sup>α</sup>  | 7.26x10 <sup>-13</sup> ±3.28x10 <sup>-13</sup> <sup>α</sup>  |
|                | 20         | 1.01x10 <sup>-7</sup> ±6.44x10 <sup>-9</sup> <sup>β</sup>                          | 3.10x10 <sup>-7</sup> ±1.82x10 <sup>-8</sup> <sup>α</sup>  | N/A   | 1.32x10 <sup>-14</sup> ±1.44x10 <sup>-15</sup> <sup>α</sup>  | 7.95x10 <sup>-13</sup> ±2.18x10 <sup>-13</sup> <sup>α</sup>  |
|                | 30         | 1.06x10 <sup>-7</sup> ±3.80x10 <sup>-9</sup> <sup>δ</sup>                          | 3.37x10 <sup>-7</sup> ±5.47x10 <sup>-9</sup> <sup>β</sup>  | N/A   | 4.53x10 <sup>-14</sup> ±2.04x10 <sup>-15</sup> <sup>α</sup>  | 1.38x10 <sup>-12</sup> ±6.35x10 <sup>-14</sup> <sup>β</sup>  |
| CHI            | 0          | 1.68x10 <sup>-8</sup> ±1.09x10 <sup>-9</sup> <sup>α</sup>                          | 1.72x10 <sup>-7</sup> ±2.14x10 <sup>-8</sup> <sup>α</sup>  | N/A   | 9.49x10 <sup>-15</sup> ±2.27x10 <sup>-15</sup> <sup>α</sup>  | N/A  |
|                | 10         | 2.16x10 <sup>-8</sup> ±6.11x10 <sup>-10</sup> <sup>α</sup>                         | 2.06x10 <sup>-7</sup> ±6.06x10 <sup>-9</sup> <sup>αβ</sup> | N/A   | 3.20x10 <sup>-14</sup> ±1.33x10 <sup>-14</sup> <sup>αβ</sup> | N/A  |
|                | 20         | 4.60x10 <sup>-8</sup> ±1.00x10 <sup>-8</sup> <sup>β</sup>                          | 2.18x10 <sup>-7</sup> ±1.35x10 <sup>-8</sup> <sup>αβ</sup> | N/A   | 2.90x10 <sup>-14</sup> ±9.89x10 <sup>-15</sup> <sup>αβ</sup> | N/A  |
|                | 30         | 6.93x10 <sup>-8</sup> ±6.64x10 <sup>-9</sup> <sup>δ</sup>                          | 2.52x10 <sup>-7</sup> ±9.32x10 <sup>-9</sup> <sup>β</sup>  | N/A   | 3.73x10 <sup>-14</sup> ±4.26x10 <sup>-15</sup> <sup>β</sup>  | N/A  |
| PL             | 0          | 5.12x10 <sup>-8</sup> ±5.95x10 <sup>-9</sup> <sup>α</sup>                          | 2.47x10 <sup>-7</sup> ±2.28x10 <sup>-8</sup> <sup>α</sup>  | N/A   | 2.32x10 <sup>-14</sup> ±5.5x10 <sup>-16</sup> <sup>α</sup>   | N/A  |
|                | 10         | 2.58x10 <sup>-8</sup> ±2.04x10 <sup>-9</sup> <sup>β</sup>                          | 1.61x10 <sup>-7</sup> ±1.05x10 <sup>-8</sup> <sup>β</sup>  | N/A   | 2.46x10 <sup>-14</sup> ±1.39x10 <sup>-16</sup> <sup>α</sup>  | N/A  |
|                | 20         | 3.36x10 <sup>-8</sup> ±6.29x10 <sup>-9</sup> <sup>β</sup>                          | 2.16x10 <sup>-7</sup> ±1.47x10 <sup>-9</sup> <sup>α</sup>  | N/A   | 1.18x10 <sup>-14</sup> ±6.74x10 <sup>-15</sup> <sup>α</sup>  | N/A  |

844 applicable.

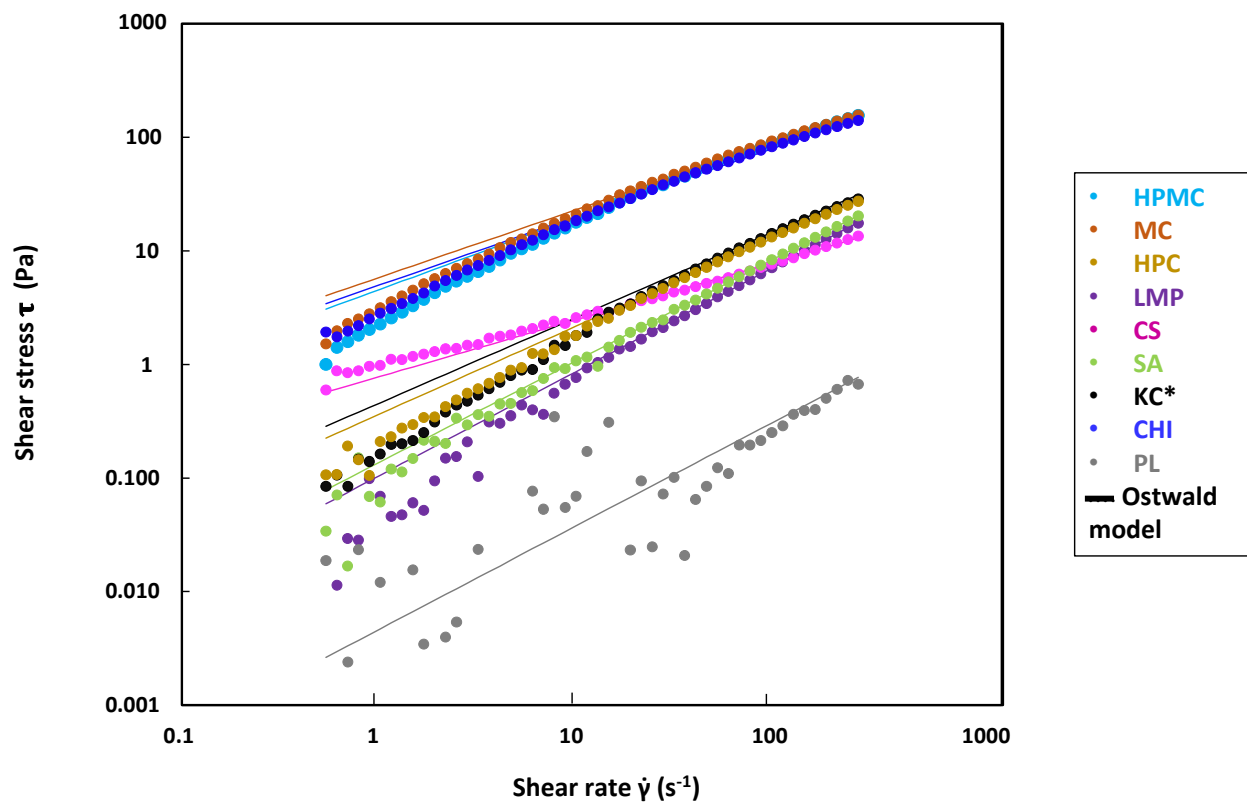
845 Values are reported as mean  $\pm$  standard deviation. Significant differences with a p-value  $< 0.05$  are provided. The characters  $\alpha$ ,  $\beta$ ,  $\delta$ ,  $\psi$  are used to identify the difference of a parameter for the same polymer with different  
846 glycerol ratios.

847 **APPENDIX B.** Mechanical properties of polysaccharide films. **HPMC:** Hydroxypropyl Methylcellulose. **MC:** Methyl Cellulose. **HPC:** Hydroxypropyl Cellulose. **LMP:** Low  
848 Methoxyl Pectin. **CS:** Cationic Starch. **SA:** Sodium Alginate. **KC:** Kappa-Carrageenan. **CHI:** Chitosan. **PL:** Pullulan.







| Polysaccharide | % glycerol | Young's modulus (GPa)       | Tensile strength (MPa)             | Elongation at break (%)       |
|----------------|------------|-----------------------------|------------------------------------|-------------------------------|
| HPMC           | 0          | 2.72 $\pm$ 0.18 $^{\alpha}$ | 60.11 $\pm$ 29.16 $^{\alpha}$      | 5.62 $\pm$ 4.51 $^{\alpha}$   |
|                | 10         | 2.09 $\pm$ 0.10 $^{\beta}$  | 68.48 $\pm$ 11.63 $^{\alpha}$      | 18.55 $\pm$ 6.43 $^{\beta}$   |
|                | 20         | 1.57 $\pm$ 0.04 $^{\delta}$ | 69.48 $\pm$ 7.25 $^{\alpha}$       | 33.62 $\pm$ 3.86 $^{\delta}$  |
|                | 30         | 1.24 $\pm$ 0.03 $^{\psi}$   | 52.36 $\pm$ 4.58 $^{\alpha}$       | 36.85 $\pm$ 4.53 $^{\delta}$  |
| MC             | 0          | 2.72 $\pm$ 0.20 $^{\alpha}$ | 79.35 $\pm$ 16.41 $^{\alpha}$      | 11.04 $\pm$ 6.84 $^{\alpha}$  |
|                | 10         | 2.23 $\pm$ 0.16 $^{\beta}$  | 59.63 $\pm$ 15.66 $^{\beta}$       | 14.50 $\pm$ 10.69 $^{\alpha}$ |
|                | 20         | 1.54 $\pm$ 0.10 $^{\delta}$ | 51.14 $\pm$ 4.60 $^{\beta}$        | 28.50 $\pm$ 4.82 $^{\beta}$   |
|                | 30         | 1.23 $\pm$ 0.11 $^{\psi}$   | 50.30 $\pm$ 6.84 $^{\beta}$        | 37.50 $\pm$ 4.90 $^{\beta}$   |
| HPC            | 0          | 0.51 $\pm$ 0.05             | 14.14 $\pm$ 2.86                   | 65.64 $\pm$ 33.78             |
|                | 10         | 0.17 $\pm$ 0.08             | 11.69 $\pm$ 3.00                   | 123.28 $\pm$ 16.56            |
| LMP            | 20         | 4.28 $\pm$ 0.19             | 92.37 $\pm$ 10.95                  | 3.08 $\pm$ 1.12               |
|                | 30         | 3.35 $\pm$ 0.17             | 74.99 $\pm$ 9.45                   | 4.41 $\pm$ 2.10               |
| CS             | 0          | 2.59 $\pm$ 0.13 $^{\alpha}$ | 49.19 $\pm$ 5.19 $^{\alpha}$       | 4.38 $\pm$ 2.24 $^{\alpha}$   |
|                | 10         | 2.16 $\pm$ 0.04 $^{\beta}$  | 45.53 $\pm$ 5.95 $^{\alpha}$       | 3.06 $\pm$ 1.00 $^{\alpha}$   |
|                | 20         | 1.50 $\pm$ 0.15 $^{\delta}$ | 30.55 $\pm$ 6.84 $^{\beta}$        | 2.93 $\pm$ 0.85 $^{\alpha}$   |
|                | 30         | 0.80 $\pm$ 0.19 $^{\psi}$   | 16.25 $\pm$ 3.54 $^{\delta}$       | 3.33 $\pm$ 0.69 $^{\alpha}$   |
| SA             | 0          | 5.46 $\pm$ 0.53 $^{\alpha}$ | 86.37 $\pm$ 11.66 $^{\alpha}$      | 3.49 $\pm$ 1.65 $^{\alpha}$   |
|                | 10         | 4.24 $\pm$ 0.67 $^{\beta}$  | 84.66 $\pm$ 9.58 $^{\alpha\beta}$  | 5.12 $\pm$ 2.05 $^{\alpha}$   |
|                | 20         | 3.21 $\pm$ 0.58 $^{\delta}$ | 65.13 $\pm$ 22.46 $^{\beta\delta}$ | 7.19 $\pm$ 5.55 $^{\alpha}$   |
|                | 30         | 2.40 $\pm$ 0.24 $^{\psi}$   | 52.74 $\pm$ 7.36 $^{\delta}$       | 8.30 $\pm$ 4.37 $^{\alpha}$   |
| KC             | 10         | 3.38 $\pm$ 0.35 $^{\alpha}$ | 68.10 $\pm$ 28.47 $^{\alpha}$      | 2.75 $\pm$ 1.30 $^{\alpha}$   |
|                | 20         | 2.72 $\pm$ 0.34 $^{\beta}$  | 15.61 $\pm$ 8.16 $^{\beta}$        | 0.55 $\pm$ 0.41 $^{\beta}$    |
|                | 30         | 2.28 $\pm$ 0.33 $^{\beta}$  | 36.36 $\pm$ 16.04 $^{\beta}$       | 1.77 $\pm$ 0.96 $^{\beta}$    |
| CHI            | 0          | 4.06 $\pm$ 0.34 $^{\alpha}$ | 104.18 $\pm$ 9.62 $^{\alpha}$      | 3.22 $\pm$ 0.79 $^{\alpha}$   |
|                | 10         | 2.53 $\pm$ 0.19 $^{\beta}$  | 74.17 $\pm$ 4.61 $^{\beta}$        | 4.51 $\pm$ 0.73 $^{\beta}$    |
|                | 20         | 2.33 $\pm$ 0.16 $^{\beta}$  | 59.8 $\pm$ 11.49 $^{\delta}$       | 3.83 $\pm$ 1.25 $^{\beta}$    |
|                | 30         | 1.44 $\pm$ 0.13 $^{\delta}$ | 38.21 $\pm$ 3.58 $^{\psi}$         | 9.08 $\pm$ 6.73 $^{\delta}$   |
| PL             | 0          | 2.87 $\pm$ 0.24 $^{\alpha}$ | 50.77 $\pm$ 7.25 $^{\alpha}$       | 2.64 $\pm$ 0.48 $^{\alpha}$   |
|                | 10         | 2.70 $\pm$ 0.28 $^{\alpha}$ | 49.77 $\pm$ 5.97 $^{\alpha}$       | 2.37 $\pm$ 0.30 $^{\alpha}$   |
|                | 20         | 1.76 $\pm$ 0.27 $^{\beta}$  | 30.01 $\pm$ 2.99 $^{\beta}$        | 2.18 $\pm$ 0.37 $^{\alpha}$   |

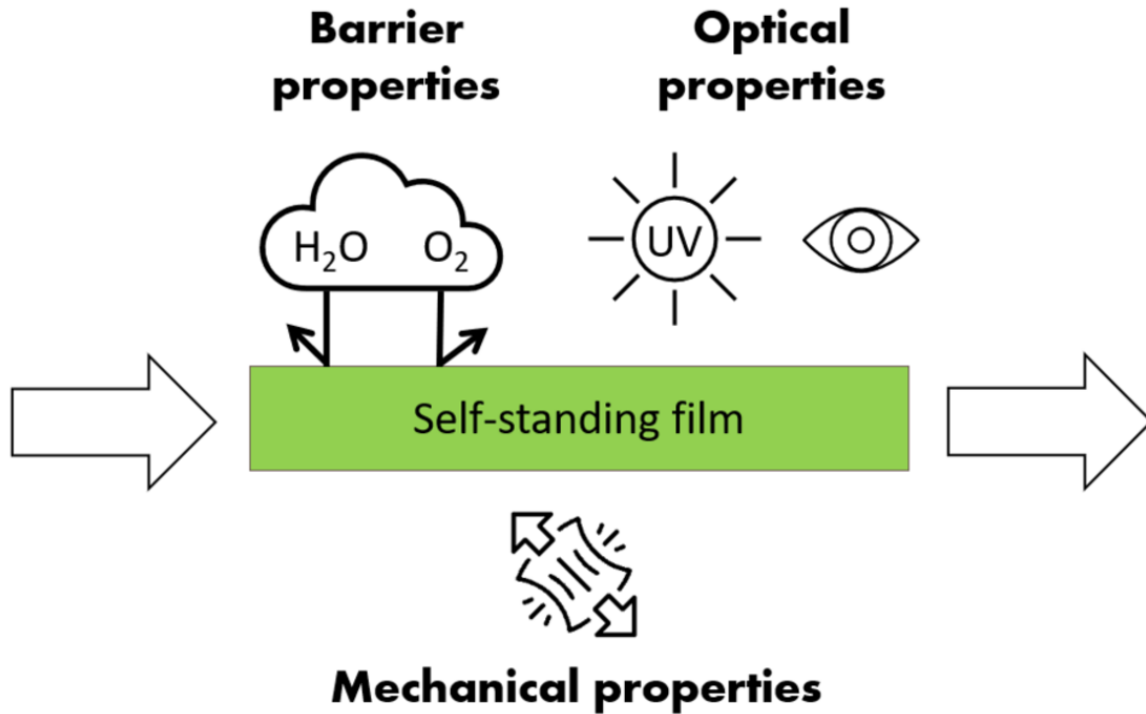
849 Values are reported as mean  $\pm$  standard deviation. Significant differences with a p-value  $< 0.05$  are provided. The characters  $\alpha$ ,  $\beta$ ,  $\delta$ ,  $\psi$  are used to identify the difference of a parameter for the same polymer with differ-  
850 ent glycerol ratio.

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**Appendix C.** Shear stress ( $\tau$ ) as a function of shear rate ( $\dot{\gamma}$ ) of polysaccharide solutions measured at  $25(\pm 1)$  °C. Continuous lines represent the fitted curves based on the Ostwald de Waele model. **HPMC:** Hydroxypropyl Methylcellulose. **MC:** Methyl Cellulose. **HPC:** Hydroxypropyl Cellulose. **LMP:** Low Methoxyl Pectin. **CS:** Cationic Starch. **SA:** Sodium Alginate. **KC:** Kappa-Carrageenan (\*: Temperature of measurement  $70(\pm 1)$  °C). **CHI:** Chitosan. **PL:** Pullulan.

| Polysaccharides       |   |
|-----------------------|---|
| Cellulose derivatives |  |
| Pectin                |  |
| Starch                |  |
| Alginate              |  |
| Carrageenan           |  |
| Chitosan              |  |



**Food packaging applications**

