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Impact of bio-based binders on rheological properties of aqueous alumina slurries for tape casting

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Abstract

This work describes the preparation of concentrated alumina suspensions based on bio-sourced additives with a low environmental impact and with the rheological properties adapted to the tape casting process. Natural polysaccharides extracted from plants and fruits (pectin, psyllium...) were characterized (molar weight) and identified as promising binders for substituting the classical organic binders from petrochemical industry. The rheological behavior of the additives and of the suspensions containing these bio-sourced additives was studied in flow and in oscillations. The mechanical properties of the green tapes obtained with the different bio-sourced binders were determined from tensile experiment. This paper studies the relations between the nature of the binder, the rheological behavior of the suspension, the ability to tape cast the suspensions and the final properties of the green and sintered tapes.

1 Introduction

Tape-casting is widely employed in the ceramic industry for the shaping of thin and flat ceramic tapes, for example, for the production of alumina substrates or multi-layer capacitors in the microelectronic industry [1] or for the manufacturing of solid oxide fuel cell devices (SOFC) [1][2]. The cast suspension generally consists in the ceramic powder dispersed in a solvent thanks to a dispersing agent, and the addition of a binder and a plasticizer. Traditionally, tape casting implies the use of organic solvent and solvent-based binders [3] [4]. For several years, water-based systems have been developed to reduce the health and environmental risks. Other advantages of water-based systems are lower costs linked to the better working conditions for the operators.

Different types of binder have been reported in the literature for aqueous systems. A lot of them come from the petrochemical industry, like latex binders, which are defined as a stable colloidal dispersion of a polymeric substance in an aqueous medium [5]. Latex binders used for tape casting are generally synthesized from acrylic polymers (such as poly (acrylic acid), poly(vinyl acetate), poly(methylacrylate) ...). For example, Baquero *et al.* [2] added a styrene acrylic copolymer as a binder to manufacture SOFC electrolytes through water-based tape casting. Polyvinyl alcohol (PVA) has also been used as a binder, for instance, by Albano *et al.* [5] for the aqueous tape casting of yttrium stabilized zirconia or by Zhou *et al.* [6] to

41 produce translucent Al₂O₃ ceramics. Other binders, more recent, are water-soluble binders
42 derived from bio-sourced polymer, such as methylcellulose (a cellulosic ether), mentioned by
43 Kristoffersson et al. [7] and Chartier and Bruneau [8], or gelatin based systems as reported
44 by Snijkers et al [9]. However, from the life cycle analysis of organic additives, their
45 environmental impact could still be improved with the substitution by more ecologically
46 friendly biopolymers.

47 The aim of the present work is then (i) to substitute synthetic additives coming from
48 petrochemical industry by eco-friendly products, in particular bio-sourced polysaccharides, in
49 alumina suspensions and (ii), to determine if such suspensions can be adapted for tape
50 casting. In this respect, citrus pectin is a promising binder candidate [10]. This recent study
51 shows that the incorporation order of the biosourced additives plays a strong role on the final
52 rheological properties of the alumina slurries. Pectins belongs to a large family of
53 polysaccharides, also named carbohydrates polymers, with molar weights typically between
54 50 and 150 kg.mol⁻¹, found as apple pomace, citrus peel and pulp, or sugar beet pulp, among
55 other sources. They are largely used in the food industry as stabilizing agent in jams, jellies,
56 preserves, confections and beverages. Pectin chains consists in a few hundreds to
57 thousands galacturonic acid monomer units linked via α -(1→4)-glycosidic [11]. The main
58 chain can be substituted with α -(1→2) rhamnopyranose units from which side chains of
59 galactose, mannose, glucose, and xylose may occur. Pectins are water-soluble polymers,
60 which become gels by mixing with water thanks to a combination of hydrogen bonds and
61 hydrophobic interactions forming a three-dimensional network.

62 The study focused on a commercial pectin from citrus. It has been selected as a promising
63 binder for alumina systems because of its highly anionic character and also because it is the
64 most commonly marketed pectin thus ensuring a good reproducibility of the product.

65 In this work, two other polysaccharides bio-sourced binders have been tested in addition to
66 citrus pectin: microcrystalline cellulose and psyllium. Microcrystalline cellulose (MCC) with
67 size about few micrometers are widely used in cosmetics (as a thickener or binder), food (as
68 a stabilizer, fat substitute or emulsifier), defense and medical industries (as a binder or
69 adsorbent). MCC is currently produced from different cellulosic sources, such as wood and
70 mainly cotton [12] and is generally obtained after the hydrolysis of pure cellulose. The
71 hydrolysis treatment is usually followed by neutralization, washing and drying processes.
72 Currently, the common manufacturing process is performed by spray-drying a neutralized
73 aqueous slurry obtained from the hydrolysis of cellulose [13]. By using low shear energy
74 (dissolver, kneader) it is possible to convert MCC into a stable gel, which can (i) increase the
75 yield stress and/or the viscosity of water-based systems and (ii) bring cohesion to a green
76 ceramic part after drying. Indeed, the gelation of microcrystalline cellulose is achieved by the
77 association of particles using hydrophobic interactions leading to a colloidal suspension [14].

78 Psyllium is, in this work, the most eco-friendly additive because it has not undergone any
79 industrial or chemical transformation, which is not the case for MCC. It is a poorly water
80 soluble polysaccharide extracted from the husks of the seeds of *Plantago ovata* [15,16]. The
81 polymer backbone consists in a α -(1→3) - α -(1→4) xylan with substitution on C-2 or C-3 by
82 L-arabinose, D-xylose, and α -D-galactouronyl-(1→2)-L-rhamnose. Chemically, the
83 polysaccharide is arabinosyl (galacturonic acid) rhamnosylxylan [17]. Psyllium seed mucilage
84 contains 22.6 % arabinose, 74.7 % xylose and traces of other sugars. This polymer is an

85 excellent water absorber, widely used in pharmaceuticals as a therapeutic agent to prevent
86 diabetes, cholesterol, colon cancer, constipation or as drug delivery agent [18], [19,20].
87 Psyllium aqueous solutions are known to show pseudo gel like behavior at low polymer
88 concentration with weakly temperature dependent rheological behavior [18]. It appears as a
89 good potential candidate as binder.

90 To go more deeply in this approach, ammonium lignosulfonate was chosen as bio-
91 sourced dispersing agent. The rheological behavior of the suspensions formulated with these
92 bio-additives has to be adapted to the tape casting process. Then this paper focuses to
93 establish the relation between the nature of the binder, the rheological behavior of the
94 suspensions, the ability to tape cast the suspensions and the final properties of the green
95 and sintered tapes. Indeed, the green tapes must be easily handled without cracks or
96 bubbles, and the sintered tapes must be dense.

97 2 Materials and methods

98 2.1 Starting materials

99 2.1.1 Alumina powder

100 Alumina powder was supplied by Alteo (grade P172SB, France). According to the technical
101 data given by the supplier, the median particle size is 0.4 μm , the specific area is 7.5 $\text{m}^2 \text{g}^{-1}$
102 and the chemical purity is 99.7%.

103 2.1.2 Binders

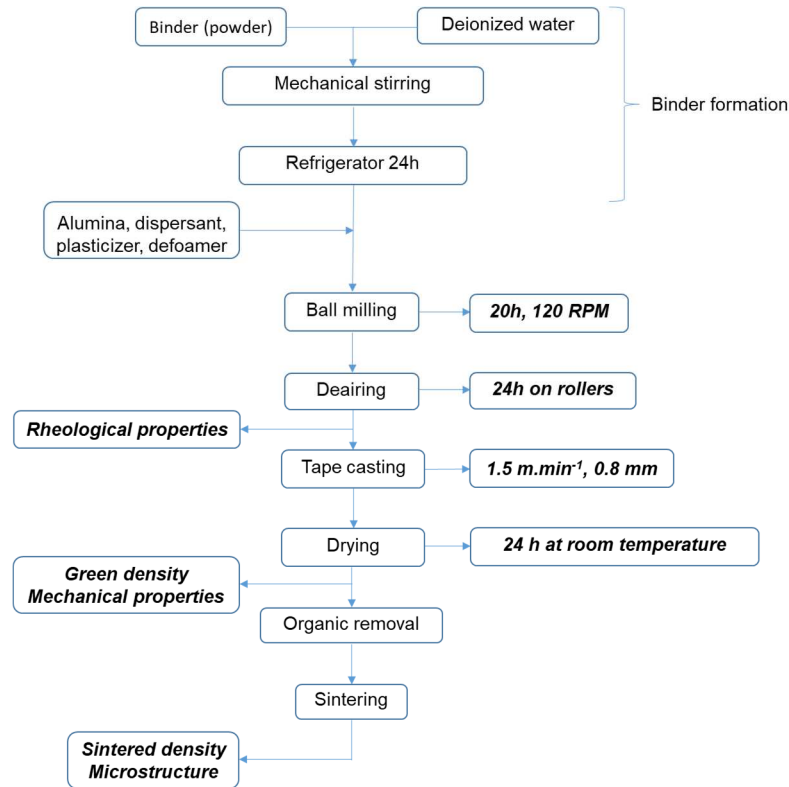
104 Three natural polysaccharides were identified as potential binders for the tape casting
105 process: (i) citrus pectin (Alfa Aesar), (ii) microcrystalline cellulose (Arbocel P4000,
106 Rettenmaier & Söhne, Germany) and (iii) psyllium extracted from plantago (Psyllium P99,
107 Rettenmaier & Söhne, Germany). These polysaccharides have been selected in relation with
108 their availability to form a gel by mixing them with deionized water, which can act as a binder
109 and ensure the cohesion of the ceramic particles in the green part. Moreover, these three
110 polysaccharides have been chosen according to their different organization in water. Pectin
111 is expected to give rise to classical polyelectrolyte polymer entangled in water. Psyllium is
112 expected to give rise to associated aggregated systems in water. Finally, MCC is known to
113 give structured suspensions in water as MCC is not water soluble.

114 2.1.3 Dispersant, plasticizer and defoamer

115 The bio-based ammonium lignosulfonate dispersant (Arbo T11 N5, 6 600 g/mol, Tembec
116 Avebene, France) extracted from maritime pines of the Landes region (France) has been
117 selected to stabilize the alumina suspensions. Marie *et al.* [10] have already highlighted the
118 stabilizing properties of the ammonium lignosulfonate for aqueous alumina suspensions.
119 Glycerol (ProLabo, France) was used as a plasticizer and Byk LPC 22787 (Byk Chemie,
120 Germany) was used as a defoamer.

121 2.2 Production and consolidation of the tapes

122 Previous works [10] have described the protocol for preparing tape casting suspensions
123 containing these bio-sourced binders (Figure 1).



124

125 *Figure 1. Protocol of the ceramic slurry preparation with the use of bio-sourced binders for tape casting process*

126 The first step corresponds to the preparation of the binder suspension. The binder powder
 127 was mixed by mechanical stirring in deionized water. The amount of the corresponding
 128 polymer is adjusted from the rheological properties of the gel with respect to the used shear
 129 rate domain (see Table 2).

130 The alumina powder, the dispersant, the plasticizer and the defoamer were then added to the
 131 binder suspension, and mixed by ball milling during 20 h at 120 rpm for homogenization and
 132 de- agglomeration. Finally, the resulting suspension was de-aired on rollers during 24 h.
 133 Tapes were cast with a blade at a speed of $1.5 \text{ m}\cdot\text{min}^{-1}$. The thickness of the deposited film
 134 was 0.8 mm. This corresponds to a shear rate of around 31 s^{-1} . Tapes were finally dried at
 135 room temperature in a saturated humidity atmosphere.

136 Green tapes were cut in 30 mm diameter disks. Some of them were laminated at 75°C under
 137 uniaxial pressure according to the following cycle: 10 MPa during 10 min and 50 MPa during
 138 5 min. Differential thermal (DTA) and thermogravimetric (TGA) analysis (SETERAM, France)
 139 showed that all the organic compounds were removed from green tapes below 600°C in air.
 140 Thus, the debinding was performed between 100°C and 600°C at a slow heating rate
 141 ($1^\circ\text{C}\cdot\text{min}^{-1}$). Finally, a thermal treatment in two steps was performed: a first treatment at
 142 1200°C for 1 h ($5^\circ\text{C}\cdot\text{min}^{-1}$) for debinding and a first consolidation necessary to be able to
 143 handle the product, followed by a treatment at 1600°C during 1 h ($10^\circ\text{C}\cdot\text{min}^{-1}$).

144 2.3 Characterizations

145 In order to better understand the behavior of these biopolymers in solution or in suspension,
 146 it is necessary to characterize their properties such as molecular weight and rheological
 147 behavior in water.

148 2.3.1 Molecular weights measurements of binders and dispersant

149 Average number and weight molar masses (respectively M_n and M_w), distributions, molar
150 masses dispersity, intrinsic viscosity $[\eta]$ and hydrodynamic radii (R_h) of citrus pectin, psyllium
151 and ammonium lignosulfonate were determined by Size Exclusion Chromatography (SEC)
152 coupled on-line with triple detection: multi-angle light scattering (MALS) (HELEOS II, Wyatt
153 Technology, Ca, USA), a viscometer detector (VD) (Viscostar II, Wyatt Technology, Ca,
154 USA) and a differential refractive index (DRI) (RID 10 A Shimadzu, Japan). This method
155 cannot be applied to microcrystalline cellulose because of its non-solubility in water.

156 SEC line comprises a degazer, a pump (LC10 Ai Shimadzu, Japan), a guard column and 2
157 columns OHPAK SB 804 and 806 HQ (Shodex, Japan). The eluent LiNO_3 (0.1 mol.l^{-1}) is
158 filtered on $0.1 \mu\text{m}$ and the flow rate is 0.5 ml.min^{-1} . Polymers samples were solubilized in
159 eluent by stirring at room temperature (excepted for Psyllium at 80°C) during 24 hours.
160 Polymer concentrations were 1.35 , 0.5 and 5.2 g.l^{-1} for citrus pectins, psyllium and
161 ammonium sulfonate respectively. $100 \mu\text{L}$ were injected with an automatic injector (SIL-20A,
162 Shimadzu, Japan) after filtration on $0.45 \mu\text{m}$. dn/dc value of 0.15 ml.g^{-1} usually used for
163 polysaccharides (citrus pectin [21] and psyllium) and 0.18 ml.g^{-1} as average value for
164 ammonium lignosulfonate [22] were used. The analysis was performed via data processing
165 with Astra® 6.1.7 soft from Wyatt using Zimm order 1 mode with angles from 44.8° to 140°

166 Equation 1 gives the dispersity of the molar masses (\mathfrak{D}).

$$167 \quad \mathfrak{D} = \frac{\overline{M_w}}{M_n} \quad \text{Equation 1}$$

168 The critical concentration at which chains overlap (C^*) can be calculated from $[\eta]$, according
169 Equation 2 [23].

$$170 \quad C^* = \frac{1}{[\eta]} \quad \text{Equation 2}$$

171 2.3.2 Rheological measurements of the binder suspensions and the alumina slurriess

172 Viscosity measurements were performed using an ARG2 equipment, a controlled stress
173 rotating rheometer from TA Instrument (USA). A cone/plate geometry ($R = 30 \text{ mm}$, tip angle
174 2°) or a coaxial geometry with double wall concentric cylinders ($R_{bob} =$
175 20 & 22.38 mm , $R_{cup} = 20.38$ & 21.96 mm , immersed height $H = 20.5 \text{ mm}$) were used, at
176 room temperature.

177 Flow measurements have been conducted with up and down stress or shear rate ramps in
178 order to evidence thixotropy.

179 For the dynamic mode, the linear viscoelastic domain (LVED) for the different systems was
180 checked at 1 Hz leading to the determination of the suitable stress or strain for frequency
181 sweep chosen on the plateau. The LVED and all critical values collected (elastic and viscous
182 moduli G'_c and G''_c , critical stress and strain σ_c and γ_c) were taken as the range where stress
183 and strain display a linear relationship. Then mechanical spectra were obtained thanks to a
184 frequency sweep at fixed stress or a fixed strain in the LVED.

185 2.3.3 Tensile tests on the green tapes

186 Tensile tests were performed using an Easy test EZ20 equipment (Lloyd Instruments, UK)
187 with a sensor of 100 N in order to compare the mechanical resistance of green tapes with
188 different formulations. The tensile test specimens (dog-bone shape, 15 mm tensile width and
189 40 mm gauge length) were cut in the dried green tapes by a laser-cutting machine. The
190 traverse speed was set to 0.5 mm.min⁻¹. Specimens were cut transversally and parallel to the
191 tape casting direction in order to evaluate its influence on the mechanical properties.

192 2.3.4 Microstructures of the tapes

193 Microstructure of the alumina green and sintered tapes were observed by an environmental
194 Scanning Electron Microscope (Quanta 450 FEG, FEI, USA). The porosity and the particle
195 size in the sintered tapes have been analyzed using Image J software.

196 3 Results

197 3.1 Molecular weight and intrinsic viscosity measurements

198

199 Table 1 shows the results of the molecular weight and intrinsic viscosity measurements.

200 *Table 1. Characterization of the bio-based additives*

| | | M _n (g.mol ⁻¹) | M _w (g.mol ⁻¹) | Đ (± 0.5%) | [η] (mL.g ⁻¹) | R _{hw} (nm) | % recovery | C* (g/L) |
|---------------------|----------------------------|---------------------------------------|---------------------------------------|---------------|------------------------------|-------------------------|---------------|----------|
| Binder | Psyllium | 190 000 (± 6%) | 995 000 (± 1%) | 5.1 | - | 26 (± 4%) | 11 | - |
| | Citrus Pectin | 77 000 (± 1%) | 165 000 (± 0.5%) | 2.1 | 330 (± 0.4%) | 18 (± 0.1%) | 100 | 3 |
| Dispersing agent | Ammonium lignosulfonate | 38 000 (± 1%) | 113 000 (± 0.5%) | 3.0 | 5.2 (± 8%) | 4 (± 2%) | 75 | |

201

202 Details about these measurements are given in Appendices.

203 3.2. Composition and rheological behavior of the binder systems

204 Three aqueous solutions or suspensions called “binder systems” were prepared by mixing a
205 binder (powder) with water. According the nature of the added binder, they are respectively
206 named B_Pectin, B_MCC and B_Psyllium. The mass concentration of the binders with
207 respect to water are respectively 2, 3 and 1.2 %wt. for B_Pectin, B_MCC and B_Psyllium.
208 These concentrations of pectin in water is slightly above the C* value. They were adjusted
209 according to the suitable viscosity of the final formulations (between 0.5 and 1 Pa.s at the
210 expected shear rate of 31 s⁻¹) (see Figure 5). The compositions (%wt) of these formulations
211 are reported in Table 2.

212 The flow rheological properties of the binder systems are shown in Figure 2.

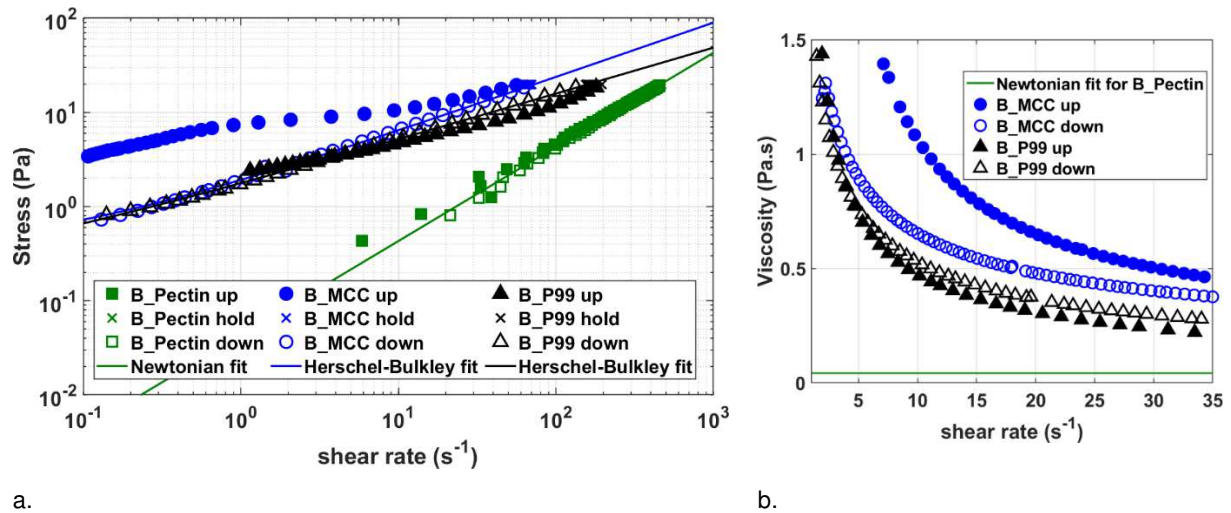


Figure 2. Rheological behavior of the three binder systems at 22°C. The stress was raised from 0.01 to 20 Pa for 60 s, followed by a peak hold at 20 Pa during 60 s, and finally a decrease from 20 to 0.01 Pa in 60 s. The relevant fits for each decreasing ramp are also shown. a. Stress as a function of shear rate. b. viscosity as a function of shear rate, zoom below 31 s⁻¹.

213 Pectin aqueous solution (B_Pectin) (2 %_{w/w}) shows a Newtonian behavior, which is normal
 214 considering the concentration which is just above the C*.

215 B_Psyllium (1.2 %) and B_MCC (3 %) are largely more viscous, between 2 and 3 orders of
 216 magnitude above water viscosity at 31 s⁻¹. Psyllium and MCC systems are strongly shear
 217 thinning with a low anti-thixotropic behavior for B_Psyllium and clear and expected
 218 thixotropic one for B_MCC dispersion (respectively -330 and 216 Pa.s⁻¹ as indicated by
 219 TRIOS software thixotropy analysis) (Table 3). For the case of psyllium, the anti-thixotropy
 220 could be associated with the role of shear rate on aggregated structures. Psyllium
 221 aggregates in polysaccharide entanglement due to associated properties (hydrogens bonds,
 222 hydrophobic interactions and so on) has been evidenced thanks to light scattering analysis.
 223 Such aggregates could be disrupted under high shear leading to more associated structures
 224 when back to low shear rates.

225 The decreasing ramps for B_MCC and B_Psyllium (completely unstructured state) are best
 226 fitted by Herschel-Bulkley model $\sigma = \sigma_c^{HB} + \dot{\gamma}^n$, where K is the consistency (Pa.sⁿ) and n the
 227 rate exponent with a very low yield stress σ_c^{HB} . These behaviors are consistent with psyllium
 228 systems corresponding to a large pseudogel lumps stacked together. All fits results are
 229 reported in Table 3. Except for pectin, binder suspensions also display yield stresses
 230 subsequently called σ_0 for increasing ramps, larger than for the decreasing one for B_MCC
 231 and lower for B_Psyllium. Due to thixotropic or antithixotropic effects, no time independent
 232 model can be fitted on increasing ramps, so these yield stresses could only be estimated
 233 from close scrutiny of the flow curves, and are reported in Table 4.

234 In order to assess the viscoelastic properties of the binder systems, oscillatory
 235 measurements have been conducted on B_Pectin, B_MCC (Figure 3) and B_Psyllium
 236 (Figure 4) systems. Dynamic critical stress σ_c and critical strain γ_c correspond respectively to
 237 the values of stress and strain from which the stress-strain relationship is no longer linear.
 238 The linear viscoelasticity domain has been checked at 1 Hz, for all binder suspensions. A
 239 frequency sweep was performed for B_MCC and B_Psyllium systems only (see figures
 240 Figure 3b and Figure 4 b).

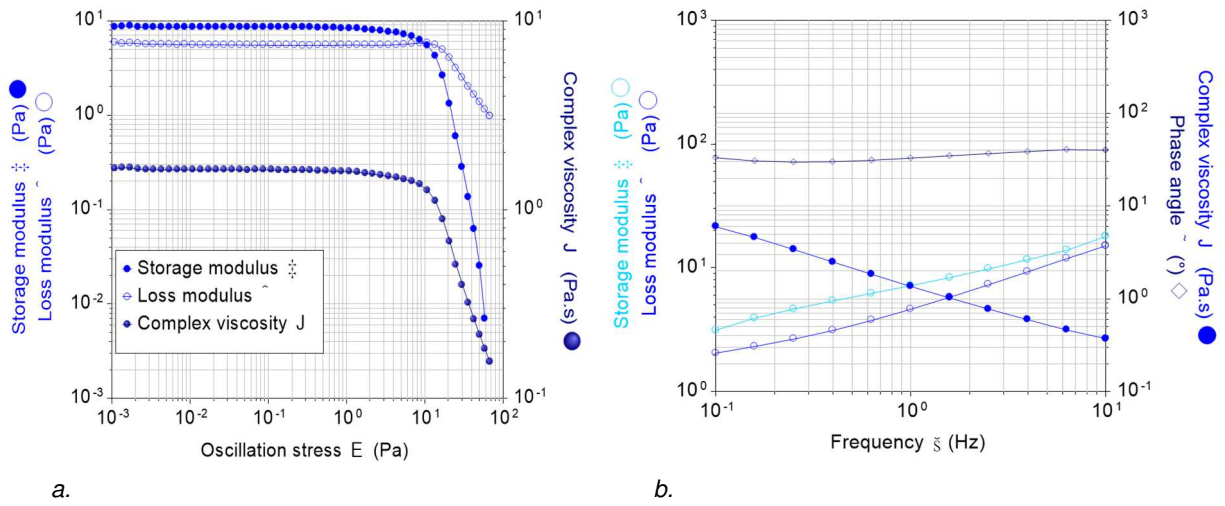


Figure 3: MCC rheological oscillatory behavior (a: evolution of the storage modulus and of the viscosity as a function of the stress, $f = 1$ Hz; b: evolution of the storage and the loss modulus and of the viscosity and the phase angle as a function of the frequency as a function of frequency, $\sigma = 10^{-2}$ Pa)

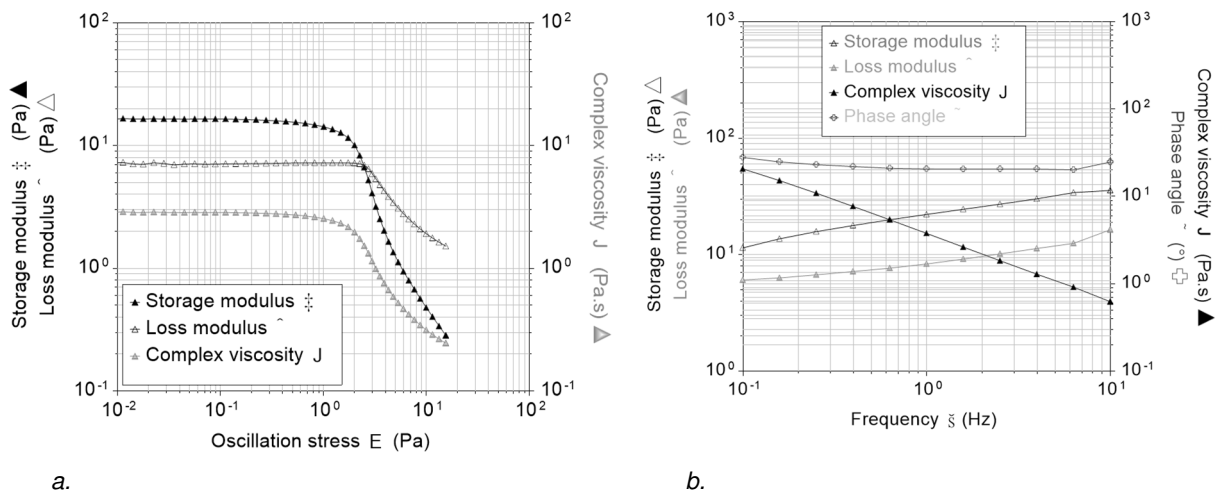


Figure 4: B_Psyllium oscillatory rheological behavior (a: evolution of the storage modulus and of the viscosity as a function of the stress, $f = 1$ Hz; b: evolution of the storage and the loss modulus and of the viscosity and the phase angle as a function of the frequency, $\sigma = 10^{-2}$ Pa)

241

242 According to the Newtonian behavior of pectin system, the LVED could not be determined (γ_c
 243 and σ_c). Only a few correct values at extremely low oscillation stress amplitude ($<10^{-2}$ Pa)
 244 were obtained on the plateau. The value of G_c' is around 10^{-2} Pa and G_c'' around $5 \cdot 10^{-2}$ Pa.
 245 These values are too low for the working range of the rheometer. The loss modulus is larger
 246 than the storage modulus, indicating a liquid-like behavior. Thus, no frequency sweep could
 247 be performed on this sample.

248 Both B_Psyllium and B_MCC systems display a linear domain and a larger storage modulus,
 249 indicating a solid-like behavior coherent with the presence of yield stress estimated at the
 250 end of the linear domain. Dynamic critical stresses σ_c give a good estimate of the stress
 251 above which the system begins to flow and are reasonably well correlated with yield stresses
 252 σ_0 obtained from increasing ramp of the flow curves (0.5 and 3.5 Pa for B_Psyllium and
 253 B_MCC for flow and 0.9 and 1.3 Pa for oscillation, see Table 4). There can be small
 254 variations between the yield stresses measured in flow and in oscillations. MCC polymers

255 can be thought of as an assembly of sticks, stuck together. It is then conceivable that from a
 256 certain volume fraction, if a shear stress is applied to the system, the polymers will orient
 257 themselves in the same direction and cause the flow.

258 Concerning the B_Psyllium system, the pseudo-gel consists of polymeric chains and
 259 aggregates bonded together, a typical structure of a soft material. As usual, dynamic critical
 260 stress values are slightly different, but similar to the ones obtained from flow curves. The
 261 critical strain is almost four times larger for B_MCC, which can be interesting for other
 262 shaping techniques like micro-extrusion.

263 Frequency sweeps measured at 10^{-2} Pa (*i.e.* in the linear domain) show a storage modulus
 264 always higher than the loss modulus on the whole range of studied frequencies indicating a
 265 solid like behavior. B_MCC may reach a modulus crossover at a frequency slightly outside
 266 the available measurement range. Such structures with large excess of water (98.5 here),
 267 with yield stresses and elastic rheological behaviors (a very slight frequency dependence of
 268 the modulus) are fully consistent with a pseudogel behavior. This behavior appears less
 269 pronounced for B_MCC compared to B_Psyllium since the ratio between loss and storage
 270 moduli (*i.e.* loss tangent) is noticeably higher.

271 Both B_Psyllium and B_MCC systems alone can be considered as pseudogels, but as a
 272 confirmation of the conclusion of appendices (*i.e.* very aggregative behavior), B_Psyllium
 273 seems more structured than B_MCC. On the other hand, B_Pectin corresponds only to a
 274 modest viscosifying agent.

275 3.2 Composition and rheological behavior of the alumina suspensions

276 Three suspensions were elaborated from the three binder systems previously studied. They
 277 are respectively called S_Pectin, S_MCC and S_Psyllium. For tape casting, the viscosities of
 278 the suspensions should be ideally between 0.5 and 1.0 Pa.s at the shear rate of 31 s^{-1} which
 279 is applied during casting. Amounts of binder systems in the formulation have been adjusted
 280 according to the suitable viscosity at the expected shear rate (Figure 5.a). The compositions
 281 (wt %) of these formulations are reported in Table 2.

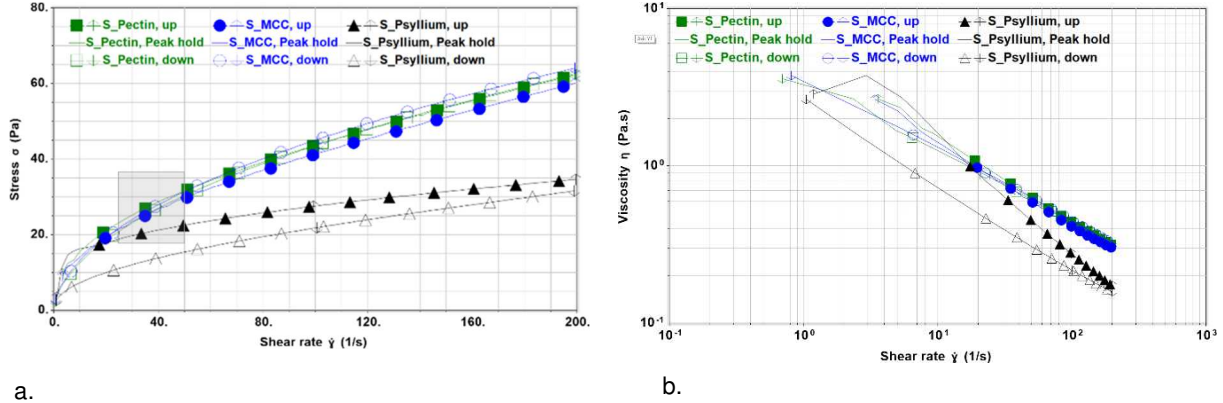
282 *Table 2. % weight composition of the S_Pectin, S_MCC and S_Psyllium respectively containing citrus pectin,*
 283 *microcrystalline cellulose and psyllium as binders*

| Function | | S_Pectin | S_MCC | S_Psyllium |
|--------------------------------|----------------------------------|----------|-------|------------|
| Mineral powder | Alumina | 40 | 40 | 40 |
| Dispersing agent | Ammonium Lignosulfonate | 0.4 | 0.4 | 0.4 |
| Plastizicer | Glycerol | 3.3 | 4.8 | 4.0 |
| Defoamer agent | Byk LP-C 22787 | 0.1 | 0.1 | 0.1 |
| Binder | Citrus Pectin | 1.1 | / | / |
| | Microcrystalline cellulose (MMC) | / | 1.6 | / |
| | Psyllium | / | / | 0.7 |
| Solvent | Water | 55.1 | 53.1 | 54.8 |
| Total | | 100 | 100 | 100 |
| Binder/ (binder system) (% wt) | | 2 | 3 | 1.3 |

284

285 The rheological results summarized in Table 3 indicate that by the addition of alumina and
 286 other additives, the rheological behavior of S_Pectin, S_MCC or S_Psyllium is not the same
 287 as for each binder system alone. The three suspensions evidence strong shear thinning
 288 (Figure 5 and Table 3). This behavior is beneficial for the tape casting process [1]. No clear

289 yield stress was observed in the range of the measurements on the decreasing ramps. A
 290 modeling of the stress evolutions according to the shear rate was carried out on the
 291 decreasing ramp using the Ostwald power law model $\sigma = K\dot{\gamma}^n$ where K is the consistency
 292 (Pa.sⁿ) and n the rate exponent, which is quite similar for all the suspensions (Table 3). This
 293 can be attributed to the interaction of alumina particles through the gel. This idea will also be
 294 developed in the following using dynamic rheological measurements.



a.
 b.
 Figure 5. Rheological flow behavior of the S_Pectin, S_MCC and S_Psyllium suspensions. The shear rate was raised from 0.01 to 200 s⁻¹ in 100 s, followed by a dwell at 200 s⁻¹ during 180 s, and finally a decrease from 200 to 0.01 s⁻¹ in 100 s. The grey area corresponds to the optimal conditions for tape casting process [1]. a. Shear stress (Pa) as function of shear rate (s⁻¹) for the S_Pectin, S_MCC and S_Psyllium suspensions; b. Viscosity (Pa.s) as function of shear rate (s⁻¹) for the S_Pectin, S_MCC and S_Psyllium suspensions

295 At the shear rate of 31 s⁻¹ for the tape casting conditions, the three alumina suspensions
 296 have a viscosity of respectively 0.5, 0.7 and 0.4 Pa.s for S_Pectin, S_MCC and S_Psyllium.
 297 Among the three suspensions, S_Psyllium has the lowest viscosity.

298 It should be noted that the thixotropy is reversed between the formulation S_Psyllium and
 299 S_MCC and the gel alone. A possible explanation for the case of Psyllium could be the
 300 following. During the shear involved in the slip preparation process, the Psyllium gel reaches
 301 an equilibrium swelled state, which was evidenced by anti-thixotropy on the hysteresis loop
 302 of the binder alone. With the addition of alumina, a network is formed, which can be
 303 destroyed by shear and take a long time to form again, thus leading to thixotropic behavior of
 304 the complete suspension. The fact that this does not occur for pectin-based systems may be
 305 related to its low concentration in water. As for MCC systems, the origin of the observed
 306 reversal is still unclear. Similarly to binder gels analysis, yield stresses σ_0 observed on the
 307 increasing ramps were estimated and reported in Table 4, to be compared with oscillatory
 308 results.

309 Table 3. Fit results for gels alone and for complete formulations on the decreasing ramp or steady state when
 310 available. B_Pectin: Newtonian fit, other gels: Herschel-Bulkley, formulations: power law. Thixotropy was
 311 calculated using TRIOS software.

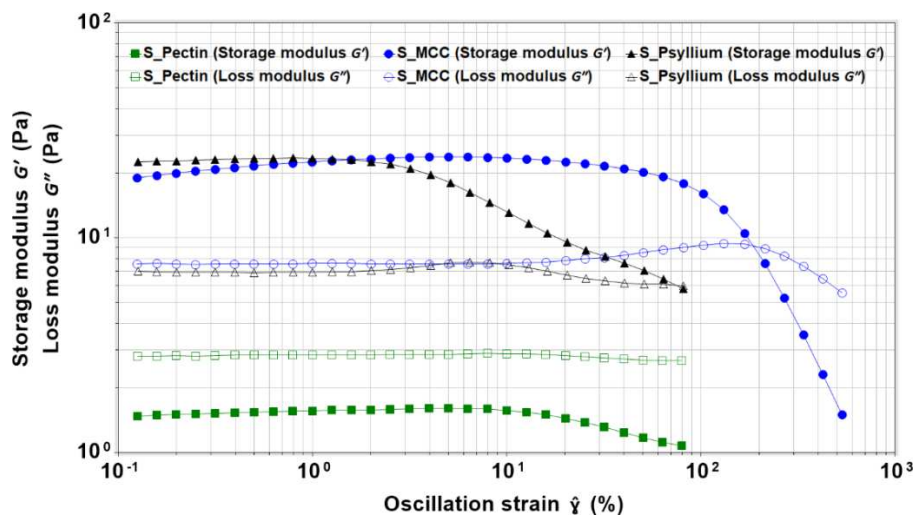
| | σ_c^{HB} (Pa) | K (Pa.s ⁿ) | n (-) | Thixotropy (Pa/s) |
|------------|----------------------|------------------------|-------|-------------------|
| B_Pectin* | - | 0.043 | 1 | none |
| S_Pectin | - | 4.0 | 0.52 | 0 |
| B_MCC | 0.3 | 1.618 | 0.58 | 216 |
| S_MCC | - | 3.6 | 0.53 | -280 |
| B_Psyllium | 0.1 | 1.644 | 0.49 | -330 |
| S_Psyllium | - | 2.2 | 0.51 | 1161 |

312

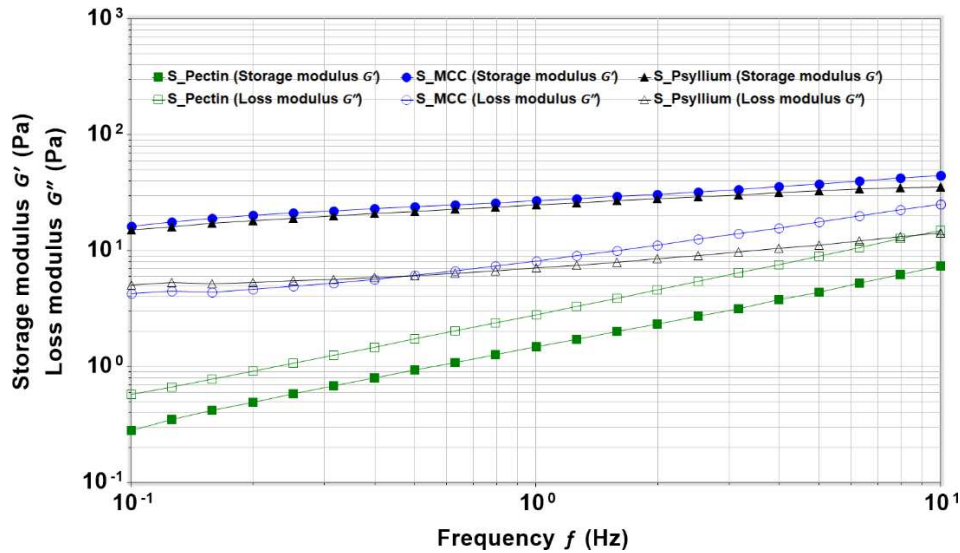
313 Figure 6 shows evolutions of the storage (G'), the loss modulus (G'') as a function of the
 314 stress for the three suspensions, obtained by oscillation measurements. For the suspensions
 315 S_MCC and S_Psyllium, G' is larger than G'' , which is characteristic of a solid like behavior
 316 with a structural stability under small deformations. Conversely, the suspension S_Pectin
 317 displays a liquid-like behavior with $G'' > G'$.

318 Table 4 shows a summary of all the oscillatory results for both binders and slips. Binders and
 319 suspensions have very close LVED, especially γ_c , suspensions having slightly larger values
 320 for the moduli. This indicates that the binder gel dictates the overall behavior, and that
 321 alumina adds some rigidity to the systems. As for the frequency dependence, measurements
 322 in the LVED for MCC and psyllium systems show a gel-like behavior with no moduli
 323 crossover on the investigated frequency range and almost no dependence on frequency.

324 Interestingly, the suspension S_Pectin shows a liquid behavior where $G'' > G'$. Therefore, this
 325 suspension appears more suitable for tape casting because it has a pseudo-liquid behavior.
 326 With a pseudo-solid behavior, suspensions S_MCC and S_Psyllium appear more suitable for
 327 extrusion. Indeed, such formulations of alumina pastes containing psyllium have been
 328 developed for the micro-extrusion process [24] Moreover, the frequency dependence is more
 329 pronounced.



a.



b.

330 Figure 6. Stress sweep and frequency sweep measurements for *S_Pectin*, *S_MCC* and *S_Psyllium* suspension.
 331 a. Stress sweep (at 1Hz); b. Frequency sweep for strain= 1 % corresponding to a strain in the LVER

332 Table 4. Summary of LVER detection for all systems, with the average results of binder systems alone and of
 333 complete formulations associated with their respective standard deviation.

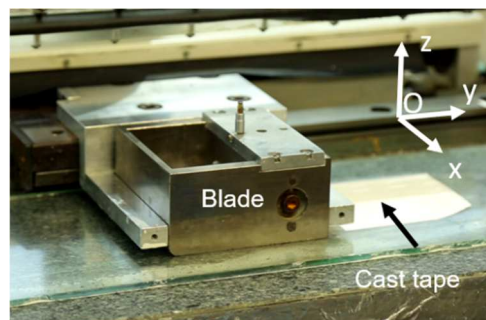
| System | Flow | | Oscillations | | |
|------------|---------------------------------|-----------------|----------------|-----------------------|-----------------------|
| | σ_0 (Pa) from flow ramps | σ_c (Pa) | γ_c (%) | G'_c (Pa) | G''_c (Pa) |
| B_Pectin | - | - | - | $8.0E-03 \pm 3.0E-03$ | $4.2E-02 \pm 0.3E-02$ |
| S_Pectin | - | 0.3 ± 0.0 | 7.5 ± 0.7 | 1.5 ± 0.1 | 2.9 ± 0.0 |
| B_MCC | 3.5 | 1.3 ± 0.1 | 19.0 ± 1.6 | 6.0 ± 0.3 | 3.9 ± 0.1 |
| S_MCC | 1.7 | 3.5 ± 0.3 | 14.8 ± 1.6 | 22.5 ± 0.7 | 7.7 ± 0.1 |
| B_Psyllium | 0.5 | 0.9 ± 0.3 | 5.5 ± 1.5 | 15.5 ± 0.8 | 6.3 ± 0.2 |
| S_Psyllium | 3.8 | 0.3 ± 0.0 | 1.3 ± 0.0 | 23.0 ± 0.1 | 6.8 ± 0.1 |

334

335 3.4 Mechanical resistances of the green tapes

336 Tensile tests have been performed on the dried green tapes obtained from the three
 337 suspensions *S_Pectin*, *S_MCC* and *S_Psyllium*. A preloading of about 400 kPa or 60 kPa
 338 has been applied before carrying out experiments. Figure 8 shows the stress-strain curves
 339 for the green tapes in the directions perpendicular and parallel to the casting direction
 340 (respectively (Ox) and (Oy), see Figure 7). The mechanical properties of green tapes are
 341 anisotropic, and the maximum stress before rupture is higher in the casting direction than
 342 perpendicular to the casting direction.

343

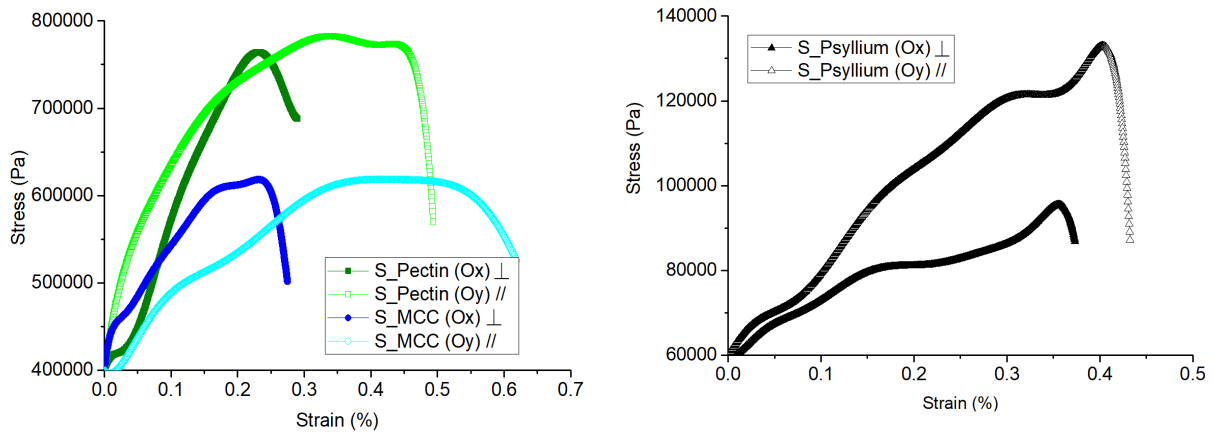


344 Figure 7. Photograph of the casting of a tape. Indications of the considered directions.
 345

346
 347
 348
 349
 350

According to Figure 8, the curves can be separated in two main domains:

- The first one, which is the linear part, is related to the elastic deformation,
- The second one is related to the plastic deformation, until the rupture.



a.

b.

351 *Figure 8. Stress - strain curves for the green tapes in perpendicular (Ox) and parallel (Oy) to the casting direction.*
 352 *a. Stress - strain curves for green tapes obtained with the suspensions S_Pectin and S_MCC; b. Stress - strain*
 353 *curves for green tapes obtained with the suspension S_Psyllium in perpendicular (Ox) and parallel (Oy) to the*
 354 *casting direction*

355 The plastic deformation domain of the green tapes is fairly large, (for example, from 0.2 to
 356 0.6% for the tape based on pectin) especially parallel to the casting direction. The main
 357 mechanical properties of green tapes obtained with the three suspensions are reported in
 358 Table 5. The nature of binder has a large impact on the maximum stress of the green tapes.
 359 The green tape obtained with S_Psyllium shows a lower maximum tensile strength at
 360 fracture (σ_m) in comparison to the values obtained with S_Pectin or S_MCC suspensions
 361 (Table 5). Besides, these values are close to those found in the literature [25] (no data found
 362 for systems based on psyllium) which are of the order of a few MPa for tapes obtained from
 363 aqueous and non-aqueous suspension and additives from petrochemicals.

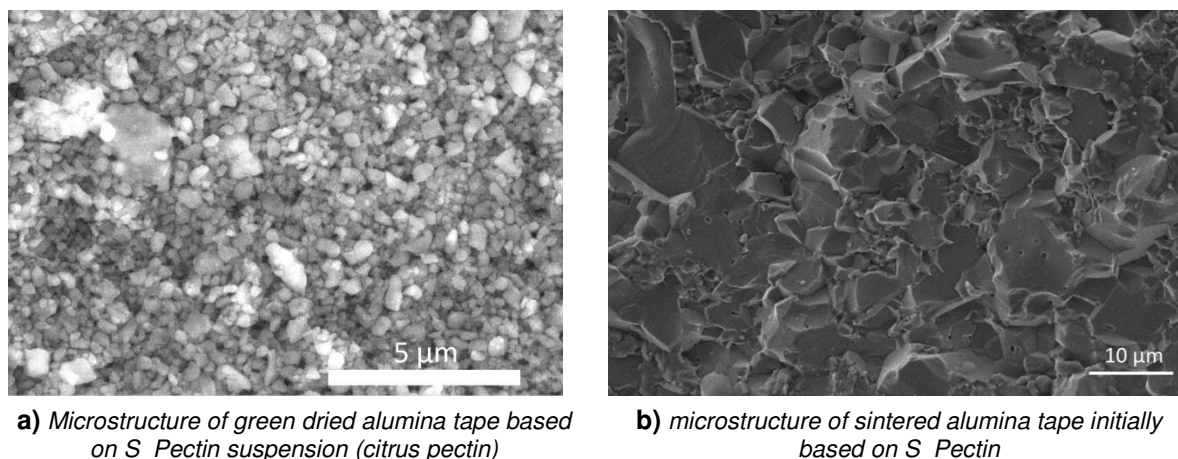
364 The green tapes obtained from citrus pectin binder show the highest maximum stress with a
 365 lower relative density of green tape (Table 5). This suggests that the citrus binder leads the
 366 formation of cohesive polymeric bridge between alumina particles, which are favorable to
 367 higher mechanical properties of the green tapes.

368 *Table 5. Mechanical properties of the green tapes obtained with the suspension S_Pectin, S_MCC and*
 369 *S_Psyllium*

| | Relative density of green tape (after drying) | Parallel to the casting direction | | Perpendicular to the casting direction | |
|----------|---|-----------------------------------|---------------------------------|--|----------------------|
| | | Strain at break (%) | Maximum stress σ_m (MPa) | Strain at break (%) | Maximum stress (MPa) |
| S_Pectin | 60 ± 1,0 % | 0.44 ± 0.02 | 0.78 ± 0.06 | 0.32 ± 0.02 | 0.74 ± 0.06 |
| S_MCC | 64 ± 1,0 % | 0.40 ± 0.02 | 0.63 ± 0.05 | 0.27 ± 0.02 | 0.61 ± 0.05 |

370

371 Moreover, for each suspension, the samples cut perpendicularly to the direction of casting do
 372 not show a plastic domain but instead exhibit a sudden rupture. The specimens cut parallel
 373 to the casting direction have a more or less large plastic domain with slightly larger
 374 elongations. Besides, the green tapes obtained with psyllium binder have maximum stress
 375 values larger in parallel direction than in perpendicular direction. The bio-sourced polymers
 376 are likely oriented preferentially by the shear imposed between the substrate and the blade
 377 during the casting. This phenomenon has already been put forward by Doreau et al [26].



378

Figure 9. Microstructure of green or sintered alumina tape initially based on S_Pectin

379 The relative densities of the sintered tapes obtained with the three suspensions (S_Pectin,
 380 S_MCC and S_Psyllium) are reported in Table 6. The relative densities of sintered tapes
 381 obtained from suspension S_Pectin and S_Psyllium show similar values, close to 93-94%,
 382 and the sintered density of tapes obtained using MCC is lower, close to 90% (Table 6).
 383 According to the formulations (Table 2), the tape containing MCC has the higher amount of
 384 additives after water removal (drying). This could explain that after sintering, the MCC_tape
 385 is less dense.

386 *Table 6. Relative densities of sintered tapes manufactured with the suspensions S_Pectin, S_MCC and*
 387 *S_Psyllium*

| | Relative density of sintered tapes |
|-------------------------------|---------------------------------------|
| Tape obtained from S_Pectin | $93 \pm 1.0 \%$ |
| Tape obtained from S_MCC | $90 \pm 1.0 \%$ |
| Tape obtained from S_Psyllium | $94 \pm 1.0 \%$ |

388

389 Finally, the use of citrus pectin as a binder (suspension S_Pectin) corresponds to the best
 390 compromise between the mechanical resistance of the green tapes and the density of the
 391 sintered tapes.

392 As an indication, Figure 9 shows the microstructure of a typical S_Pectin alumina tape, after
 393 drying (a) and after sintering (b). No apparent defects are observed. Small alumina particles
 394 of average sizes between 0.2 and 0.5 μm, cohesive with each other, are observed for the

395 green tape while the average grain size (5-10 μm) is larger in the sintered tape indicating an
396 important grain growth during sintering.

397 4 Conclusion

398 The aim of this work was to formulate aqueous suspensions of alumina from bio-based
399 additives for the tape casting process. These suspensions required a rheological behavior
400 adapted for tape casting and led to green and sintered tapes, with characteristics similar to
401 those obtained from traditional suspensions. The first step was to identify eco-friendly
402 molecules (binder, dispersant and plasticizer) in order to replace the additives from
403 petrochemicals usually used in such suspensions.

404 Thus, three aqueous solution, hydrogels and suspension have been chosen as binders in
405 order to maintain the cohesion of the granular compact after drying. Citrus pectin,
406 microcrystalline cellulose and psyllium were selected respectively. Among these three
407 polysaccharides, psyllium has the advantage of being mechanically extracted without any
408 chemical treatment. In addition, the ammonium lignosulphonate extracted from the Landes
409 maritime pine was selected as a dispersant because its dispersing ability has already been
410 demonstrated in the literature. Finally, glycerol, a residue from the production of biodiesel
411 and soap, already widely used in casting suspensions, has been used as a plasticizer. A bio-
412 sourced anti-bubble agent from the company Byk, LP-C 22787, was also used.

413 The second step of this work was to characterize the selected bio-sourced additives. Thus,
414 the molar masses of ammonium lignosulfonate and then those of the polysaccharides used
415 as binder were determined. Very diverse molar weight M_w are obtained: approximately
416 1,000,000 $\text{g}\cdot\text{mol}^{-1}$ for psyllium, 165,000 $\text{g}\cdot\text{mol}^{-1}$ for pectin, MCC corresponds to nano-object in
417 suspension.

418 Subsequently, the rheological behavior and the binding ability of citrus pectin,
419 microcrystalline cellulose and psyllium were evaluated. First, the rheological properties of the
420 formed systems from these polysaccharides were studied in flow and in oscillations. Citrus
421 pectin mixed with water presents a slightly shear thinning almost Newtonian and non-
422 thixotropic behavior. This corresponds to slightly entangled polymer solution just above the
423 entangled critical concentration (C^*). Psyllium and microcrystalline cellulose systems can be
424 considered as pseudo gels: associated aggregates structure bonded in polymer
425 entanglement and structured suspension, respectively. They appear largely more
426 viscosifying. They are respectively shear thinning with an anti-thixotropy and a thixotropy and
427 display yield stress. This point suggests that they can also been used as a binder in pastes
428 for micro-extrusion [24].

429 Finally, using an optimized protocol, suspensions were prepared from citrus pectin,
430 microcrystalline cellulose and psyllium. The composition of these suspensions has been
431 optimized in order to have rheological characteristics adapted for the tape casting process.
432 The rheological behavior of suspension based on citrus pectin seems to be the most suitable
433 for this process. However, all three suspensions lead to easily handled green tapes with no
434 apparent surface defects.

435 In addition, the green tapes obtained from citrus pectin showed higher tensile strength and
436 the relative densities of the sintered tapes are about 93 %, knowing that the sintering thermal
437 cycle has not be optimized.

438 Finally, the objective of this study, which was to develop aqueous alumina suspensions
439 composed of eco-friendly additives and adapted for the tape casting process, is achieved.

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442 Appendices

443 Molar masses M_n and M_w of the citrus pectin together with dispersity (\mathcal{D}), intrinsic viscosity
444 and size appear classical of pectins [27]. About 100% of the pectin is recovered after
445 analysis, that means this polysaccharide is completely water soluble as expected for a low
446 methylated pectin.

447 Psyllium binder has higher molar masses and much larger dispersity than citrus pectin
448 binder. Nevertheless, the analysis evidences only about 10 % of recovered polymer,
449 determined by the difference between known injected mass and integrated analyzed mass
450 from DRI signal under the peak. This result means firstly that the given results concern only a
451 few part of the sample and is not characteristic of the polymer. Secondly about 90 % of the
452 psyllium is retained on the 0.45 μm filter indicating that large aggregates probably
453 predominate in aqueous solution. Thus, psyllium binder appears likely as large aggregated
454 structure with large sizes even when solution is mixed at 80°C (LiNO_3 0.1M, $\text{pH} \cong 6$). It has
455 been reported that psyllium gives rise to pseudogels in aqueous solvent [18] [28], that seems
456 coherent with the aggregation tendency observed.

457 Finally, the analysis of ammonium lignosulfonate is considered as representative of the
458 sample with a recovering of 75 % and classical values.

459 These results are consistent with the expected binder role of the used polysaccharide
460 notably for citrus pectin, which evidences large intrinsic viscosity and hydrodynamic radii
461 compared to the molar masses. This shows that the conformation of pectin appears as
462 expanded coils, due to both semi-rigid backbone and polyelectrolyte character. Large
463 aggregates evidenced for psyllium permit also to envisage that it could be used to increase
464 the viscosity with probably gelling properties. MCC dispersions in water at a chosen volume
465 fraction are also expected to give rise to pseudogel like behavior.

466 Ammonium lignosulfonate appears logically more flexible and compact than polysaccharides
467 as evidenced by the very low values of the intrinsic viscosity and hydrodynamic radii
468 compared to the molar masses. These characteristics, added with the anionic character of
469 lignosulfonate, are consistent with the expected role of dispersant in alumina suspension.

470

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