

1 **Assessing the microstructural and rheological changes induced by food additives on potato puree**

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10

11 **Abstract**

12 The effects of agar, alginate, lecithin and glycerol on the rheological properties of commercial potato  
13 puree were investigated and interpreted in terms of starch microstructural changes, and the applicability  
14 of the Cox-Merz rule was evaluated. Each additive was applied separately at two concentrations (0.5  
15 and 1%). Microscopic observations revealed more swollen starch aggregations in lecithin and glycerol  
16 compared with those of potato puree and agar, consequently affecting the rheological properties of  
17 potato puree. All samples exhibited shear thinning non-Newtonian behaviour. Rheological  
18 measurements were strongly concentration dependent. At 0.5% concentration, additives exerted  
19 decreases in all the rheological properties of potato puree in the order of  
20 glycerol>alginate>lecithin>agar, while at 1% concentration, the order changed to  
21 glycerol>lecithin>alginate, whereas 1% agar behaved differently, increasing all rheological values.  
22 This study also showed that agar and alginate in addition to potato puree could be valuable and  
23 advantageous for further technological processes, such as 3D printing.

24 **Keywords:** Dynamic rheological test, Starch microstructure, Steady rotational test, Potato starch.

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26

27 **1. Introduction**

28 There is a movement towards potato vegetable purees as high-quality products and part of the  
29 rapidly growing ready-to-eat (convenience) food market. Recently, potato purees have been used as a  
30 potential substrate for the innovative technique of 3D food printing due to the malleable textural  
31 properties of starch, its capability of water retention and its capacity as an excellent colloidal stabilizer  
32 and bulking agent (Eliasson A.C. 2004). Potato starch is a natural-versatile biopolymer composed of  
33 linear amylose chains and highly branched amylopectin. It can be easily obtained and modified using  
34 different chemical, enzymatic and physical methods to improve its functional characteristics, making  
35 potato starch one of the preferred polymers used in many technological manipulations in the food  
36 industry, such as in thickening, coating, and gelling and as an encapsulating agent (Singh et al. 2007).

37 In addition to the technological complexity of producing, processing and handling potato starches  
38 and potato purees, accepting these perishable food materials requires a wide knowledge of their  
39 physical properties, emphasizing the importance of studying their rheological properties. Monitoring  
40 the rheological behaviour of a product can aid in the development of a new successful product with the  
41 specific desired textural characteristics and quality attributes, enhancing the acceptability of the food.  
42 Additionally, this knowledge is important in food processing and handling for predicting the analysis of  
43 process design and flow conditions, such as in 3D printing (pump sizing, syringe size and length, total  
44 time of printing, extrusion, layer and conformation stabilization, etc.). Above all, investigating the  
45 rheological properties of a food, specifically potato puree, can serve as vital basic research into the  
46 different ingredient interactions (Tabilo-Munizaga and Barbosa-Cánovas 2005; Maceiras et al. 2007) .

47 Structurally, potato puree prepared from commercial potato flakes consists of single starch cells  
48 and cell aggregates embedded inside a matrix of starch gel released from damaged cells during the  
49 cooking, mashing and drying processes of preparation (Alvarez and Canet 1999). Thus, the rheological  
50 behaviour of commercial potato is governed by the starch structure, amylose content, granule size  
51 distribution, granule shape, granule volume fraction and interactions among different starch granules  
52 (Kaur et al. 2004), in which the maximum viscosity at a given concentration depends on the capacity of  
53 granules to swell freely prior to their physical breakdown (Adebowale and Lawal 2003). This swelling  
54 is attended by consequent leaching of granules constituents and the formation of a three-dimensional  
55 network responsible for rheological modifications upon heating and shearing starch (Li and Yeh 2001).

56 Potato starch and its derivatives, such as potato puree, are generally used in food industrial  
57 applications after being mixed with different hydrocolloids and food additives since native starches  
58 generally do not possess ideal properties for the preparation of food products. This mixing improves  
59 the functionality, stability, and texture of the product and facilitates its performance during processing  
60 and at the same time adjusts its rheological properties to compatible values (Chaisawang and  
61 Supphantharika 2005). However, it is very difficult to identify optimal combinations and rheological  
62 characterizations in a complex food system such as potato puree with different additives. BeMiller  
63 expressed the difficulty of finding a unique mechanism to explain the effects that several hydrocolloids  
64 have on starch structure. Because of the complexity and variety of those systems, their properties  
65 depend on both the starch-hydrocolloid ratio and the particular starch-hydrocolloid combination  
66 (BeMiller 2011). In the same sense, it was found that the addition of sodium alginate and carrageenan  
67 to starch could preserve the granular structure of amylose-rich, swollen rigid granules, consequently  
68 attributing to an increase in the rate of viscosity (Hongprabhas et al. 2007). The addition of other types  
69 of hydrocolloids revealed different methods of interaction, such as xanthan and guar gum, which  
70 inhibit the swelling of granules by preventing water penetration; they promote granular association by  
71 bridging and stabilizing the granular shape, forming a stronger three-dimensional network due to an  
72 amylose and amylose-gum system and allowing the starch paste to exhibit a more solid-like behaviour  
73 (Chaisawang and Supphantharika 2005).

74 Therefore, four food additives, agar-agar gum, alginate, lecithin and glycerol, with different known  
75 modes of behaviour, were used in this study at two different concentrations. Gum (Agar-Agar) was  
76 used based on its known capacity to interact with other polysaccharides, leading to a synergistic  
77 increase in viscosity, as in whipped cream and starch-based mixtures (Zhao et al. 2009). Alginate is a  
78 polysaccharide made up of 2 polymers,  $\beta$ -D-mannuronic acid (M) and  $\alpha$ -L-guluronic acid (G), which  
79 provide thickening, stabilizing, film-forming and gel-producing properties to the food agent (Koushki  
80 and Azizi 2015). Lecithin has been used to modify the properties of waxy maize starch because of its  
81 emulsifying property, colour and taste; it has been used also as a lubricant in food industrial  
82 applications, such as extrusion, resulting in less nozzle wear and tear. Lecithin is also used as an  
83 emulsifying agent in many confectionary and chocolate products (Lončarević et al. 2013), while  
84 glycerol is used more as a plasticizing agent with edible starch films to reduce their tensile strength,  
85 thus reducing their viscosity (Bonilla et al. 2015). Although glycerol is not widely used for food

86 processing, we included it in the study because of its chemical and physical characteristics in  
87 comparison with the other additives used. Therefore, the present work aims to contribute to the  
88 knowledge of the effects that these additives can exert on commercial potato starch microstructure and  
89 rheology and to provide proper explanations for such effects and mechanisms to improve the usage of  
90 potato puree in advanced food technologies. To this end, two types of rheological tests were conducted:  
91 dynamic oscillatory and steady rotational tests. Additionally, the Cox Merz rule, which is used to  
92 characterize material properties by examining the relationship between dynamic viscosity and steady  
93 shear viscosity, was applied and evaluated.

94

## 95 **2. Materials and Methods**

### 96 *2.1. Sample Preparation*

97 Dehydrated potato puree (Maggi, origin) and whole milk were purchased from the local  
98 supermarket. Agar-agar, soybean lecithin, sodium alginate and glycerol (food grade) were  
99 procured from Sigma–Aldrich Co. Potato puree samples were prepared according to the following  
100 ratio (90 mL milk and 10 mL water heated previously to 40°C, to which 23 g of potato powder was  
101 added). The mixture was then homogenized for 3 minutes using an electrical hand blender (Braun,  
102 Germany). The same procedure was followed for preparing the puree samples with the four  
103 different additives at two different concentrations (0.5 and 1%). Additives at their corresponding  
104 percentages were added and dissolved in the warmed solution (milk and water) prior to the  
105 incorporation of the potato powder. However, for agar, the solution was boiled to 100°C, after  
106 which the dehydrated potato powder was added. Subsequently, all samples were placed in an  
107 incubator, and the temperature was maintained at 20 °C prior to the microscopic observations and  
108 rheological measurements.

### 109 *2.2. Microscopic Observations*

110 To compare the structure and the alignment of the starch particles between the different  
111 preparations, a thin film from each of the potato puree samples was spread on a glass slide and  
112 stained with diluted Lugo’s Solution; the stained films were then examined under a compound  
113 light microscope (better images were taken at 10x magnification).

### 114 *2.3. Rheological Measurements*

115 The rheological measurements were performed in a rheometer (Rheostress RS1, version 127,  
116 Barcelona, Spain) controlled with commercial computer software (HAAKE RheoWin 3 Job and  
117 Data Manager Software). Samples were analysed for their flow properties using 35-mm plate-plate  
118 geometry (PP60 sensor) with a 2.5-mm gap between the plates. The upper plate was lowered, and  
119 the excess sample was trimmed off. After loading, samples were rested for 3 minutes prior to  
120 testing. Two types of rheological tests were conducted: a dynamic oscillatory test and a steady  
121 rotational test. The temperature of the rheological tests was kept constant at  $20.0 \pm 0.1$  °C. The  
122 results were reported as the average of three replicates (a new sample was loaded for each  
123 repetition).

#### 124 *2.3.1. Dynamic Rheological Measurement, Frequency Sweep Test:*

125 The strain sweep test was performed to identify the linear viscoelastic region.  
126 Thereafter, a shear rate of  $0.0025 \text{ s}^{-1}$  was selected and deformation within the elastic  
127 property was detected. Moreover, oscillatory tests were performed from 0.1 to 10 Hz to  
128 determine the strength and stability of the material and to clarify the behaviour of the  
129 sample, whether viscous or elastically dominated. Storage modulus  $G'$  (indicator of the  
130 elastic behaviour), loss modulus  $G''$  (indicator of the viscosity behaviour) and complex  
131 viscosity  $n^*$  (related to the global viscoelastic response) were recorded.

132 Results were reported as the average of three replicates (a new sample was loaded for  
133 each repetition).

134

#### 135 *2.3.2. Steady Rotational Rheological Measurements, Thixotropy and Yield stress:*

136 A hysteresis loop test was performed to provide an indication of whether the sample  
137 was thixotropic and to determine the degree of thixotropy. The shear rate was increased  
138 logarithmically from 0.1 to  $10 \text{ s}^{-1}$  during the first 30 secs, was then maintained at  $10 \text{ s}^{-1}$   
139 for 30 secs, and finally was decreased logarithmically again to  $0.1 \text{ s}^{-1}$  over 30 secs.  
140 Consequently, the viscosity ( $\eta$ ) and the shear stress ( $\tau$ ) were recorded, along with the  
141 yield stress for each sample. Accordingly, a rapid drop in viscosity as a response to  
142 increased shear stress and shear rate was registered. Two methods were used to quantify  
143 the yield stress. The first one involved attempting to fit the experimental data to the best  
144 mathematical equation or model (Hershel Bulkey, Casson Model, Power Law,

145 Bingham). Bingham was determined to be the best model to fit the flow characteristics  
146 of the samples, with a high coefficient of determination ( $R>0.957$ ). The Bingham  
147 equation is ( $\tau = \tau_0 + \eta_p\dot{\gamma}$ ), where  $\tau$  (Pa) is the shear stress,  $\tau_0$  (Pa) is the yield stress,  $\eta_p$   
148 (Pa s) is the viscosity and  $\dot{\gamma}$  ( $s^{-1}$ ) is the shear rate. Nevertheless, this model was not  
149 suitable for 1% agar (w/v). Therefore, an alternative method was used to estimate the  
150 yield stress, considering the point at which viscosity as a function of the shear stress ( $\eta=f(\tau)$ )  
151 changes abruptly (Tabilo-Munizaga & Barbosa-Cánovas, 2005).

152

### 153 3. Results and Discussion

#### 154 3.1. Microscopic Observations

155 Optical microscopic images of commercial starch puree (with and without additives) are  
156 shown in Figure 1. Observations for all samples showed swollen single cells and cell aggregates in  
157 which starch was encapsulated inside the cell wall; at the same time, these aggregates are  
158 embedded in a starch gel that is released from damaged cells due to preparation processes such as  
159 cooking, mashing and drying stages (Alvarez M.D. et al. 2004) or due to additives added to potato  
160 starch that may enhance or decrease starch rupture and swelling. Furthermore, swelling in the  
161 granule starch and cell separation were observed with this cell separation (cells push against each  
162 other due to the steric hindering effect of the added groups), accompanied by a rounding off of the  
163 cells as a result of the swelling of gelatinized starch (Damodaran and Parkin, 2017). Furthermore,  
164 minor cell rupture with large-sized swelling cells were detected with lecithin and glycerol.  
165 Conversely, 1% agar showed obvious changes in size and shape (more rupture and reduced  
166 swollen cell size), which could be explained by the fact that the bonding forces within the granules  
167 of starch were affected by these additives, consequently affecting the swelling power (Adebowale  
168 et al. 2002).

169

#### 170 3.2. Steady Rheological Characteristics

##### 171 3.2.1. Viscosity

172 The rheological starch properties with the different additives were studied using the  
173 behaviours of viscosity curves. Flow curves (Fig. 2) of puree samples exhibited an  
174 exponential decay of the shear viscosity, indicating a non-Newtonian, strong shear-

175 thinning behaviour, in agreement with several authors (Maceiras et al. 2007; Yousefi  
176 and Razavi 2015). Figure 2 shows that glycerol and lecithin decreased the viscosity of  
177 the potato puree from 80% to 90% and from 60% to 85%, respectively, as their  
178 concentrations increased (from 0.5 to 1%, respectively); hence, their effects on  
179 decreasing the viscosity of potato puree were enhanced at a higher concentration.  
180 Alginate also had a decreasing effect on the viscosity of potato puree, though this effect  
181 was more moderate compared with glycerol and lecithin and was inversely proportional  
182 to the alginate concentration; alginate produced a higher decrease in the viscosity of the  
183 puree at a lower rather than at a higher concentration (Fig. 2). Furthermore, agar exerted  
184 different effects on the shear viscosity of the commercial potato puree depending on the  
185 amount of agar added: at a low concentration (0.5%), an approximate 32% decrease in  
186 the viscosity of the commercial potato puree was observed, whereas at a higher  
187 concentration (1%), the agar increased the concentration of the potato puree by  
188 approximately 20%, completely eliminating the elastic behaviour of the commercial  
189 potato puree and allowing it to behave more as a rigid solid-like material. This effect is  
190 clearly elaborated as an abrupt stop, as observed in the viscosity curve versus the shear  
191 rate of puree with 1% agar (Fig. 2b).

192 The rheological behaviour of starch is governed by granule size distribution, granule  
193 shape and granule-granule interaction, among other factors (Sing et al. 2003; Kaur et al.  
194 2004). In this sense, viscosity reflects the capacity of the granules to swell freely prior  
195 to their physical breakdown. As mentioned previously, agar has a distinct effect on the  
196 viscosity of the commercial potato puree, depending on the concentration. It has been  
197 postulated (Achayuthakan and Supphantharika 2008) that some hydrocolloids decrease  
198 the viscosity of starch by retarding the water accessibility to the starch granule,  
199 inhibiting swelling. Another effect also has been reported (Liu et al. 2006) in which  
200 interactions between hydrocolloids and starch granules can create a network that  
201 increase starch's viscosity. In agreement with these findings, 0.5% agar can inhibit  
202 swelling, limiting water accessibility inside the starch granules and consequently  
203 reducing the viscosity, whereas at a high concentration (1%), the increase in viscosity  
204 can be explained by an agar gel formation and/or a network formation through the

205 interactions among agar chains and starch granules, thus bridging between granules and  
206 promoting their association, confirming previous microscopic observations regarding  
207 1% agar (Fig. 1).

208 Regarding the other additives, alginate (an anionic hydrocolloid), glycerol and  
209 lecithin, the response was always a decrease in the viscosity of the commercial potato  
210 puree at both concentrations studied (0.5 and 1%). Glycerol and lecithin act in similar  
211 ways, in both cases reducing the viscosity in proportion to their added concentration  
212 (Fig. 2). This action could be explained by the fact that the molecular weights of  
213 glycerol and lecithin are much smaller compared to those of agar and alginate, which  
214 would facilitate their entry inside the starch granule, consequently altering the  
215 microstructure by disrupting the intermolecular hydrogen bonds and/or crystalline and  
216 amorphous regions. It has been reported that surfactants and emulsifiers such as  
217 glycerol and lecithin have the capacity to penetrate starch granules and form weaker  
218 complexes (Hasenhuettl and Hartel 2008). Likewise, decreasing associations within the  
219 starch granules would increase their capacity to swell (Adebowale et al. 2002), in  
220 agreement with the microscopic observations on the effects of lecithin and glycerol  
221 (Fig. 1). At the same time, applying shear rate or force to starch with large swelled  
222 granules would cause their instant rupture and cause a dramatic decrease in viscosity  
223 (Achayuthakan and Suphantharika 2008) (Fig. 2). Alginate also decreases the viscosity  
224 of the commercial potato puree (Fig. 2), in agreement with other authors, which has  
225 been explained by the repulsion forces between the phosphate groups in potato starch  
226 granules and the negative charge on the alginate molecule when this hydrocolloid  
227 interacts with the starch granule surface (Shi and BeMiller 2002). The inversely  
228 proportional relationship between alginate concentration and viscosity can be explained  
229 by the domination of either of one effects of alginate: at low concentration (0.5%), the  
230 effect of repulsion among the starch granules due to alginate's negative charge  
231 dominates, leading to a decrease in viscosity, whereas at high concentration (1%), the  
232 capacity of alginate to interact among several starch granules predominates due to its  
233 high molecular weight, leading to a consequent increase in viscosity.

234 *3.2.2. Yield stress*



235           Several methods have been applied for the determination of the yield stress of food  
236 systems (Tabilo- Munizaga and Barbosa-Cánovas 2005, Sun and Gunasekaran 2009). In  
237 Figure 3a, a stress ramp was used to estimate the yield stress (see 2.3.2 section), which  
238 is one of the most frequently used techniques. This critical stress level is an important  
239 parameter, below which the material is fully elastic, and above which the structure  
240 breaks and flows (Sun and Gunasekaran 2009). At first, flow curves showed a slight  
241 increase in viscosity and then reached a plateau as shear stress increased to ~ 100, ~  
242 300, ~ 250, ~ 30, and ~ 30 (in Pa) for potato, agar, alginate lecithin and glycerol,  
243 respectively, at a concentration of 1% (Fig. 3a). This region corresponds to the shear  
244 stress in which the sample was fully elastic and was still able to absorb the stress energy  
245 without changing its internal microstructure (Sun and Gunasekaran 2009). When the  
246 critical stress level (in Pa) was reached (~1000 for agar, ~ 500 for alginate, ~ 400 for  
247 potato, ~ 200 for lecithin and ~ 200 for glycerol), the viscosity rapidly decreased for all  
248 samples. This abrupt decrease indicated a change in the starch microstructure because  
249 starch molecules were unable to absorb more energy without being deformed (Tabilo-  
250 Munizaga and Barbosa-Cánovas 2005). Therefore, a steep decrease in viscosity  
251 occurred as a result of the breakdown in the microstructure of starch molecules. The  
252 yield stress results corresponding to both concentrations are shown in Table 1.

253           All additives at 1% concentration exhibited different yield stress for potato puree  
254 compared with puree free of additives (~ 400 Pa). Indeed, agar presented the highest  
255 yield stress and had the effect of increasing the puree yield stress up to ~ 1000 Pa.  
256 Likewise, alginate increased this yield stress up to ~ 500 Pa, despite its capacity to  
257 decrease the viscosity of the puree in an inversely proportional manner. This  
258 lengthening in stress yield could be explained by the fact that the starch internal  
259 microstructure was affected by both agar and alginate, which contributed to the  
260 elasticity of the network of the potato starch puree, consequently generating a starch  
261 internal microstructure that was more resistant to deformation in the shear stress region,  
262 where the sample is fully elastic. BeMiller (2011) and Visakh (2015) reported that  
263 starch mixed with hydrocolloids usually had a better texture and appearance in starchy  
264 food since starch and hydrocolloids have certain degrees of similarity (both are

265 polysaccharide molecules). Conversely, lecithin and glycerol had decreasing effects that  
266 reduced potato puree yield stress (in the region of full elasticity) to ~200 Pa in both  
267 cases, indicating less resistance of the starch internal microstructure to deformation in  
268 the shear stress region preceding the yield stress.

269 As the concentration changed from 0.5% to 1% (Table 1), the yield stress increased  
270 for agar and alginate, while it decreased for glycerol and lecithin. Thereby, glycerol and  
271 lecithin had decreasing effects on the stability of potato puree, whereas agar and  
272 alginate had increasing effects.

273 Table 1 shows the values of the yield stress obtained using the two different approaches  
274 cited above. Good agreement with viscosity results can be observed for all of the  
275 samples studied.

### 276 3.2.3. *Thixotropy*

277 In the hysteresis loop test (Fig. 3b), all potato samples with and without additives  
278 were subjected to increasing shear rate (forward measurements 0 to 12 s<sup>-1</sup>), maintained  
279 shear rate and then decreasing shear rate (backward measurements 12 to 0 s<sup>-1</sup>). Flow  
280 curves obtained with a controlled shear stress for puree and puree-containing additives  
281 at 1% concentration are presented in Figure 3b; the values of thixotropic areas for puree  
282 with additives at 0.5% concentration are represented in Table 1. The results showed  
283 hysteresis loops, indicating that all samples of puree alone and with 0.5 and 1%  
284 additives exhibited thixotropic behaviours, except for 1% agar (see Table 1). Similar  
285 results have been reported by Hoover and Vasanthan (1994), who found that among oat,  
286 wheat, lentil and potato starches, a thixotropic loop was evident only in oat and potato  
287 starches. Others reported thixotropic behaviour of potato starches only under low shear  
288 rates below 10 Pa and at high shear rates above 150 Pa, whereas at intermediate shear  
289 rates between 10 and 150 Pa, potato starch possessed rheopectic behaviour (Zhang et al.  
290 2011), findings that are in good agreement with our results since the thixotropic test  
291 performed in our study was conducted at low shear rates, from 0.1 to 10 s<sup>-1</sup>.

292 Puree without additives exhibited the highest degree of thixotropy, with the largest  
293 area (the greater the hysteresis area, the stronger the thixotropic properties (Ma et al.

294 2014)) compared with those of the agar, alginate lecithin and glycerol samples.  
295 Moreover, it is assumed that the hysteresis loop area is a key indication of the energy  
296 required to destroy the internal structure of the material responsible for the flow time  
297 dependence (Tarrega 2004); thus, puree alone required the highest energy to breakdown  
298 the internal structure, indicating a high resistance to time-dependent flow and high  
299 levels of internal viscosity and stability. Among the other additives at 0.5%, agar  
300 represented the highest degree of thixotropic behaviour, followed (in decreasing order)  
301 by lecithin, alginate and glycerol. Whereas at 1% additive concentration, agar showed a  
302 high increasing effect until the elimination of the thixotropic loop; alginate also  
303 triggered an increase in the thixotropic loop, possessing a higher hysteresis area at this  
304 concentration than those of lecithin and glycerol but still lower than that of potato puree  
305 alone (Table 1). Additionally, for 1% lecithin and glycerol, smaller loops with nearly  
306 identical weak thixotropic behaviours were observed, which is an indication of poor  
307 tolerance of the sample under shear, as expressed by structure changes and collapses,  
308 reduced product resistance and a more disrupted internal network (Costa et al. 2016).  
309 Upon decreasing the shear rate, all puree samples showed the capacity to reform the  
310 damaged internal network and to recover their viscosities; only agar at 1% did not  
311 recover its viscosity after the shear rate decreased. This finding could be related to the  
312 increase in agar concentration and the formation of a harder gel that was unable to  
313 recover its viscosity (due to the loss of elastic and viscous characteristics). Thus, at 1%  
314 and in terms of thixotropic behaviour, with a highly stabilized internal network and a  
315 high product resistance to collapse and disruption, potato purees with the different  
316 additives can be classified in the following decreasing order: puree with agar, potato  
317 alone, alginate, lecithin and glycerol. Again, these thixotropy results are in good  
318 agreement with those obtained for yield stress and viscosity in this work.

### 319 3.3. *Viscoelastic behaviour*

320 Viscoelastic properties are determined by the level and nature of the leached material and the  
321 molecular interactions upon starch granule disintegration in a three-dimensional network structure  
322 (Alcázar-Alay and Meireles 2015). The mechanical spectra of all studied puree samples are

323 illustrated in Figure 4. Figure 4 a, b, c and d showed that the storage or elastic modulus  $G'$  (which  
324 measures the recovered or accumulated energy in each deformation cycle and determines the  
325 elastic behaviour of the sample) of commercial potato puree remained higher than the loss or  
326 viscous modulus  $G''$  (the loss of energy or dissipated energy in each deformation cycle, which  
327 describes the viscosity behaviour of the material), indicating an elastic (gel) property with an  
328 internal network structure of the potato puree sample being analysed (Tabilo-Munizaga and  
329 Barbosa-Cánovas, 2005). Similar observations were reported by several authors, such as Svegmak  
330 and Hermansson, (1993) and recently Chaisawang and Suphantharika, (2005) and Ahmed and  
331 Ramaswamy, (2006), who found that for potato starch and purees and cationic tapioca starch,  $G'$   
332 was always higher than  $G''$ , indicating the presence of a network arrangement and a gel-like  
333 structure. Among all the additives used, and at 0.5%, only agar had the capacity to increase the  
334 elastic and viscous modulus of potato puree up to peaks of 8500 and 5000 Pa, respectively,  
335 whereas the other additives decreased both moduli of potato puree in the following increasing  
336 order: lecithin, alginate, and glycerol, indicating a stretchy gel-like formation (Fig. 4 a, c). At a 1%  
337 concentration, the effects of agar on increasing the elastic and viscous moduli of potato puree were  
338 further enhanced, reaching peaks of 10,000 and 6500 Pa, respectively, indicating a firmer gel  
339 formation. In contrast, the other additives kept decreasing both moduli of potato puree, shifting  
340 their order of decreasing effect. When compared with potato puree, it was observed that alginate  
341 1% decreased the  $G'$  modulus slightly to 3600 Pa while maintaining the same value as that of  $G''$ :  
342 3200 Pa at ~100 Hz. The decreasing effect of glycerol 1% was more pronounced, decreasing the  
343 optima of the elastic and viscous moduli of potato puree to 1800 and 1200 Pa, respectively (Fig. 4  
344 b, d). Concerning the sample of lecithin at 1% concentration, it was not possible to calculate both  
345  $G$  moduli due to the strong effect of lecithin as an emulsifier in decreasing viscosity and reducing  
346 stickiness since it inhibits molecular interactions (Johansson and Bergenståhl 1992a, 1992b;  
347 Servais et al. 2003). In that case, lecithin acted by decreasing the viscosity approximately 90%,  
348 with the result that the viscoelastic behaviour practically disappeared (Fig. 2b).

349 Additionally, at a concentration of 0.5% additives, puree samples exhibited values of  $G'$  and  
350  $G''$  ranging between 1000-9000 Pa and 500-5000 Pa, respectively (Fig. 4a, c). Similarly, for the  
351 1% concentration, the values of  $G'$  and  $G''$  ranged between 900-10000 Pa and 600 to 6500 Pa,  
352 respectively (Fig. 4b, d). Therefore, in absolute value, all the samples exhibited greater changes in

353  $G'$  modulus compared with  $G''$  ( $|\Delta G'| > |\Delta G''|$ ), indicating that both elastic and viscous moduli  
354 were modified, but with all additives having a predominant effect on the elastic (solid) behaviour  
355 of the puree, thus possessing a higher capacity to recover energy from deformation. In other words,  
356 additives enhanced the capacity for reformation rather than deformation of the initial molecular  
357 structure after the cessation of stress.

358 A different effect on the  $G'$  dynamic modulus of the commercial potato puree was revealed by  
359 agar depending on its concentration. For the less concentrated agar sample (0.5%), at low  
360 frequencies, the  $G'$  was found under the curve corresponding to the potato puree, whereas at high  
361 frequencies, the  $G'$  rose slightly above it (Fig. 4a). This finding can be explained by the fact that at  
362 low concentration, the agar is not plentiful enough to form a gel network, but there is enough to  
363 connect different starch granules via hydrogen bonds with agar OH groups, making it harder to  
364 recover quickly upon deformation (less elastic) behaviour. Additionally, at low frequencies, these  
365 interactions build up in the presence of agar 0.5% have enough time to break and make up again,  
366 maintaining a less-elastic property when compared with puree alone, in which the molecules are  
367 free (not connected or entangled with other additives via hydrogen bonds), and thus this facilitates  
368 its faster recovery from the deformation (more elastic). At high frequencies, and due to the short  
369 period of oscillation, the network (agar-starch interactions) is broken and cannot recover after it is  
370 disentangled, resulting in an increase in the elasticity of the puree with 0.5% agar, which is  
371 explicated by the fact that its  $G'$  curve rises slightly above that of commercial potato puree. At the  
372 1% concentration, the  $G'$  modulus of agar is higher than that corresponding to the pure alone over  
373 all the range of frequencies studied and can be clarified by the formation of a strong interconnected  
374 network due to the effect of having both interactions, where the major part of the granules are  
375 strongly connected to each other by the high molecular weight and length of the agar molecule  
376 (agar-starch) interactions and the formation of (agar-agar) gel-like interactions. These interactions  
377 would result in a more elastic, structured and gel-like microstructure than in the case of the  
378 commercial puree.

379 *3.4. Applicability of the Cox-Merz rule.*

380 The empirical Cox-Merz rule (Cox and Merz 1958) states that values of the complex viscosity ( $\eta^*$ )  
381 and the steady shear viscosity ( $\eta$ ) must have equal magnitudes at equal values of frequency and  
382 shear rate (Eq. 1).

$$383 \quad \eta(\dot{\gamma}) = \eta^*(\omega)|_{\dot{\gamma}=\omega} \quad \text{Eq. 1}$$

384 The relationship between dynamic complex viscosity ( $\eta^*$ ) and the shear viscosity data ( $\eta$ ) in the  
385 frequency range 0.1-to 10  $\text{sec}^{-1}$  was studied for all of the potato puree samples. Parallel  
386 dependencies of  $\eta^*(\omega)$  and  $\eta(\dot{\gamma})$  were obtained for all of the samples, and some of them are  
387 illustrated in Fig. 5. As detected in most food systems, the complex viscosity was greater than the  
388 apparent viscosity, indicating that these purees did not obey the Cox-Merz rule.

389 A generalized Cox-Merz equation introducing a multiplicative horizontal shift factor ( $\alpha$ ) (see Eq.  
390 (2)) fitted well for the different potato purees; the two sets of data were superimposed on each  
391 other, following a single line, with  $R^2$  factors always higher than 0.99.

$$392 \quad \eta(\dot{\gamma}) = \eta^*(\alpha \cdot \omega)|_{\dot{\gamma}=\omega} \quad \text{Eq. 2}$$

393 Table 1 represents the multiplicative constant ( $\alpha$ ) and  $R^2$  factors found for all of the different puree  
394 samples studied. Variances among  $\alpha$  value can be spotted between the different potato puree  
395 samples, signifying differences within their structural organizations. For instance, the shift factor  $\alpha$   
396 was observed to increase with an increase in all of the additive concentrations in potato puree,  
397 (from 0.45 to 0.61 for agar, from 0.35 to 0.43 for alginate and from 0.30 to 0.38 for glycerol; it  
398 was not possible to record the oscillatory values for lecithin 1% (see section 3.3)). This increase in  
399 the  $\alpha$  shift factor implied the enhanced effect exerted by the additives on modifying the internal  
400 structure of the potato puree at their respective higher concentration, regardless of whether this  
401 modification would lead to a more stable and elastic material, as in the case of agar and alginate, or  
402 to an un-stable and viscous material, as in the case of glycerol.

403 In fact, potato puree alone or combined with different additives make up a complex system with  
404 many entanglements, intermolecular aggregations and dispersions, which in turn make the purees  
405 more susceptible to considerable structural breakdown and decay upon the application of an

406 extensive strain, which can explain the non-fitting of the potato puree samples to the Cox-Merz  
407 rule (Ahmed and Ramaswamy 2006).

408 The modified Cox-Merz rule obtained in this work is potentially useful for the determination of the  
409 rheological properties of commercial potato puree combined with different additives by predicting  
410 either of the materials' dynamic or steady-state data due to the linear relationship that was found  
411 between  $\eta$  and  $\eta^*$  among all of the puree samples, permitting for direct predictions of texture  
412 perceived in the mouth, in contrast to the results obtained by (Alvarez M. D et al. 2004), who  
413 found a non-linear relationship between steady and dynamic measurements for commercial potato  
414 puree but a linear one for purees made from natural potatoes.

415 However, dynamic experiments are not always preferably applicable (due to the low strain at  
416 which the test is done), especially when considering material characterization under various food  
417 processing techniques (such as pumping, mixing, and extrusion) that require large and strong  
418 deformation rates. In these cases, steady-state shear measurement must be proposed.

419

#### 420 **4. Conclusions**

421 The impacts of agar, lecithin, glycerol and alginate were studied to define the rheological and  
422 structural properties of commercial potato starch puree. Microscopic observations revealed large  
423 aggregations of starch granules in potato puree. These granules appeared more swollen in purees  
424 containing glycerol and lecithin, while more ruptured and reduced-size swollen granules were  
425 detected in puree with agar. These observations were correlated to and confirmed with the  
426 rheological findings.

427 Additionally, all samples possessed non-Newtonian, shear-thinning behaviour. Furthermore, the  
428 effects of all additives were concentration-dependent. At low concentration, agar and alginate  
429 decreased the viscosity of the puree, while at higher levels, they increased it. In contrast, glycerol  
430 and lecithin decreased the viscosity of the puree at both concentrations, with this decrease being  
431 more enhanced at the 1% concentration. Apparently, the sharp decreases in viscosity, yield stress  
432 and thixotropic behaviour observed when glycerol and lecithin (at 0.5% and 1%) were added were  
433 correlated with the abrupt starch granule disintegration under shearing, while the effects of agar

434 and alginate were governed by their high molecular weights, retarding their entry inside the starch  
435 granules and triggering a (hydrocolloid-starch) network formation.

436 Agar increased both G moduli, whereas all the other additives studied decreased them.  
437 Additionally, the steady shear and complex viscosities of all puree samples did not follow the Cox-  
438 Merz rule. However, a linear relationship between these data was obtained that fits well upon  
439 modifying the rule and introducing a frequency shift factor.

440 Generally, agar and alginate demonstrated their capacity to moderately affect and stabilize  
441 more potato puree, while having an exclusive effect of acting either as an increasing or decreasing  
442 agent on viscosity according to the concentration. Conversely, glycerol and lecithin showed strong  
443 and destabilizing effects on potato puree even at very small concentrations. These findings suggest  
444 that alginate and agar are good and helpful options to be used in food technology processes such as  
445 3D food printing.

446

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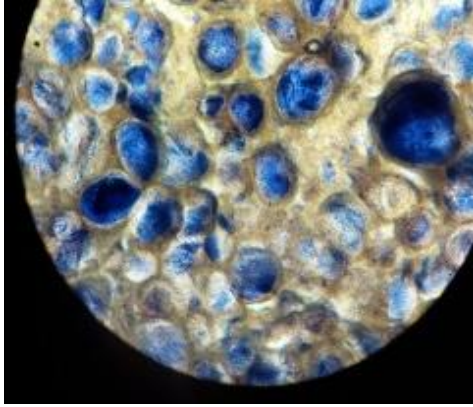
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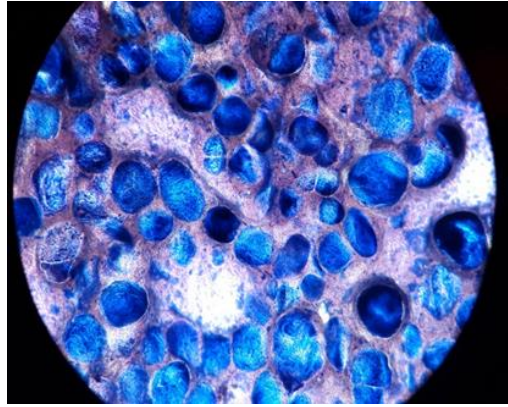
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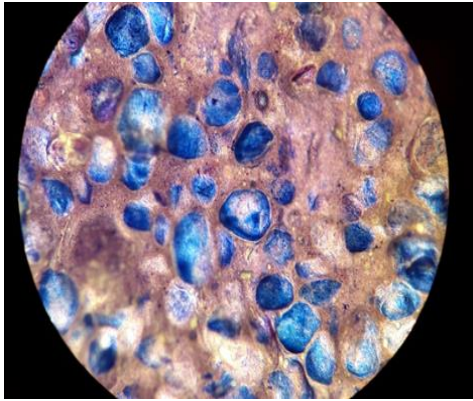
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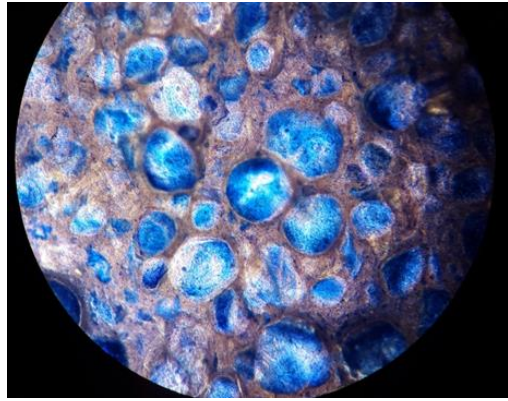
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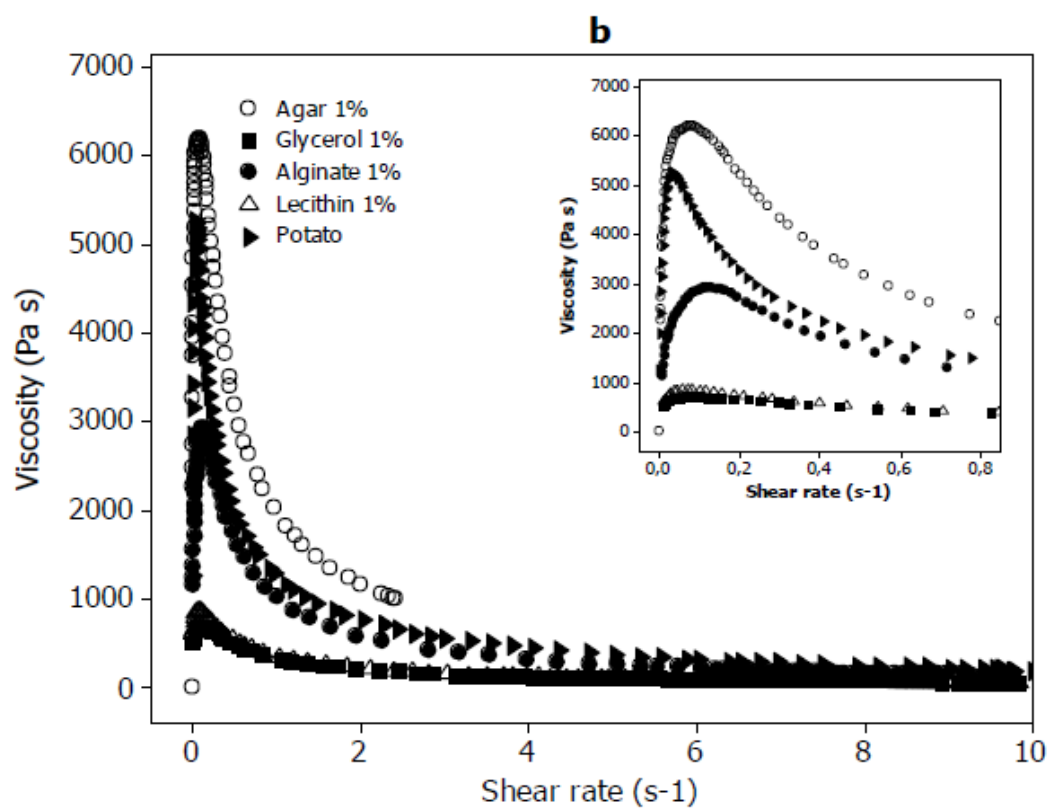
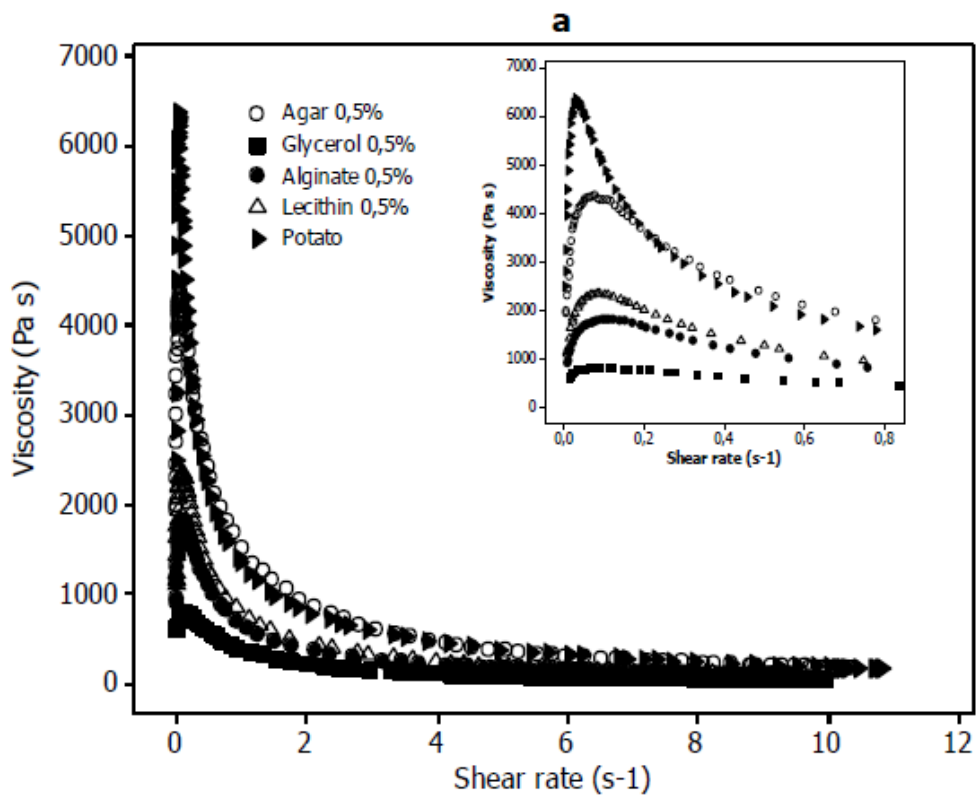
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573 **Fig. 1**

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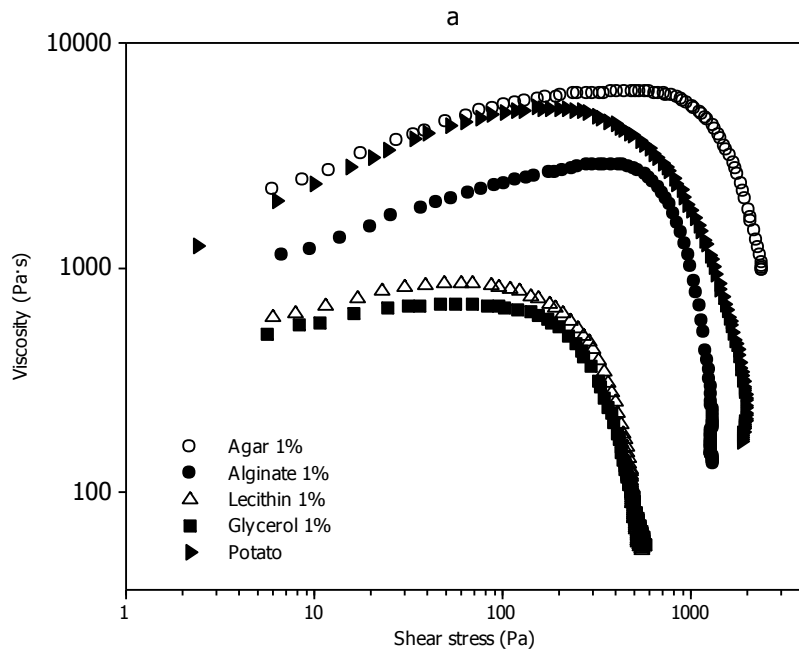
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577 Fig. 2

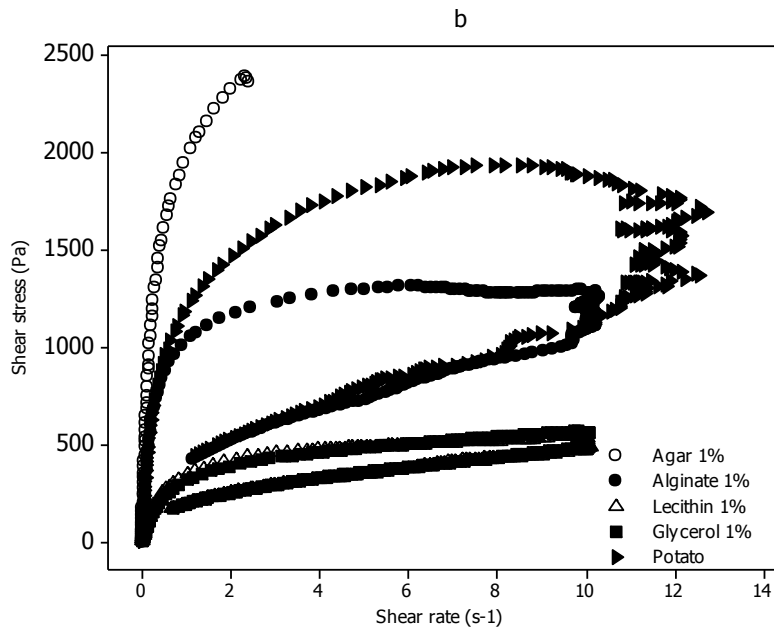
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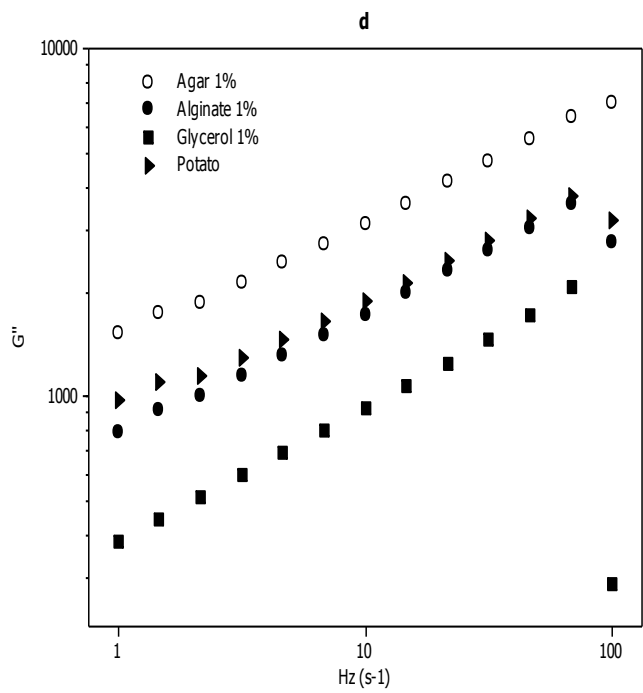
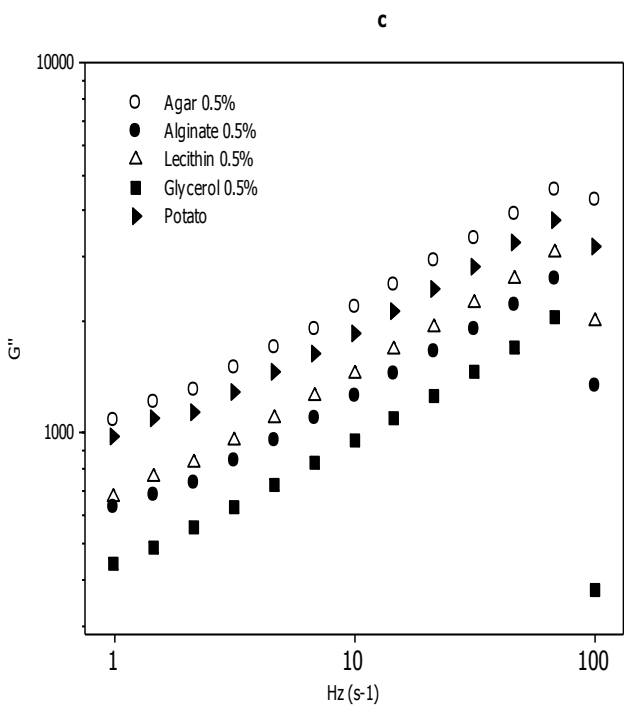
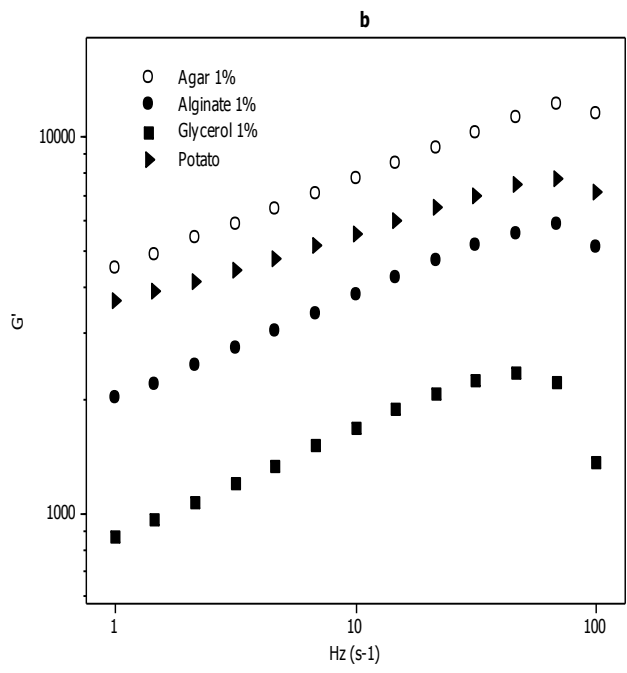
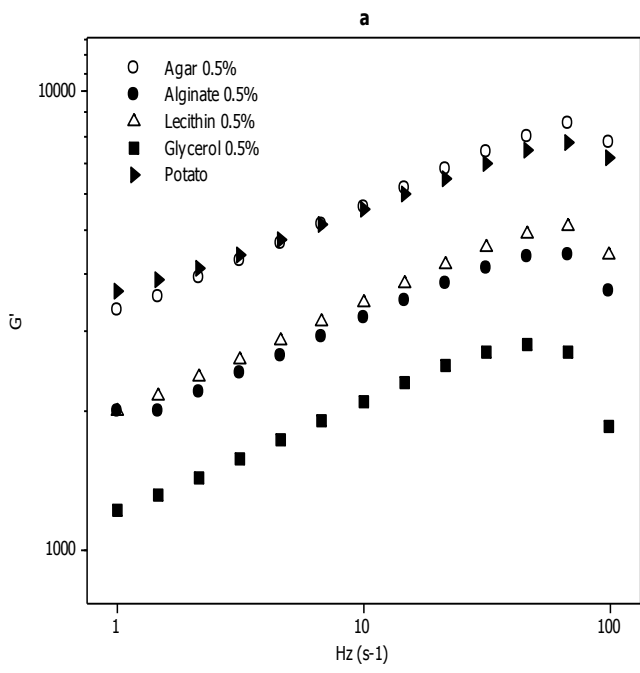
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582 **Fig. 3**

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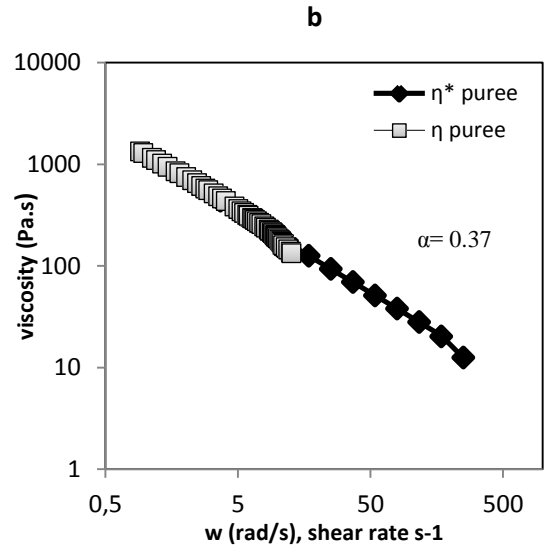
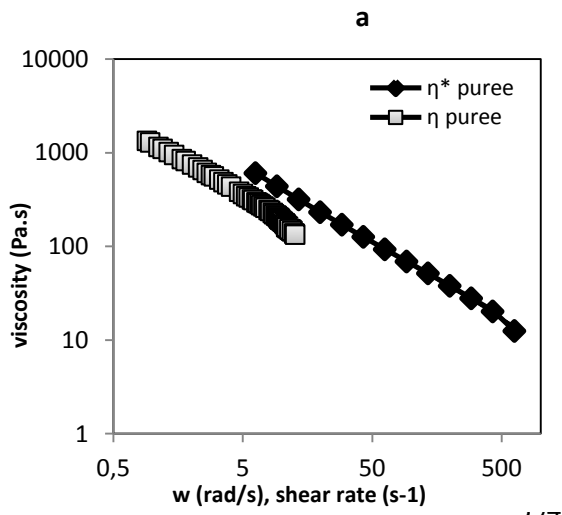


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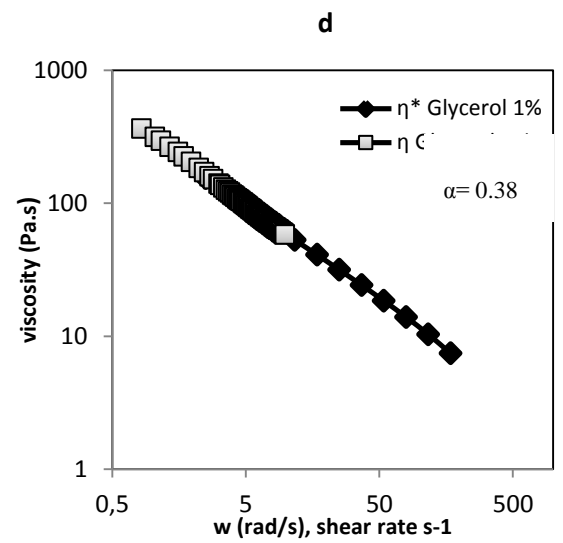
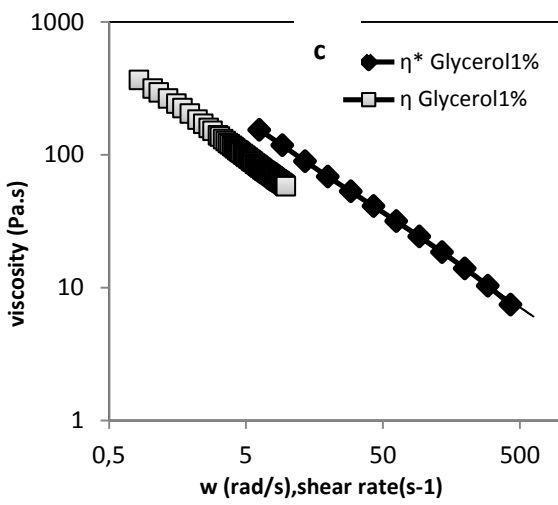
586 **Fig. 4**

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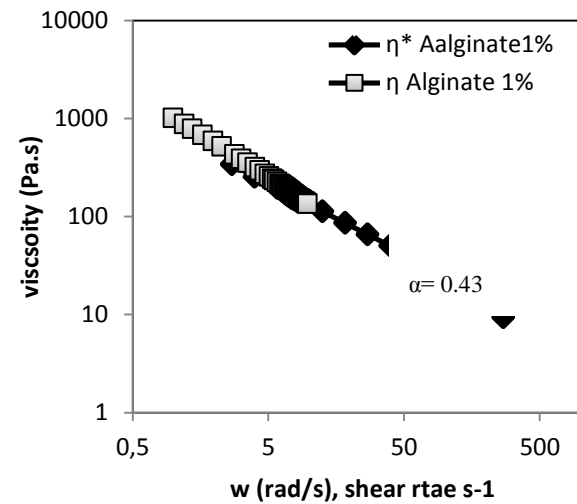
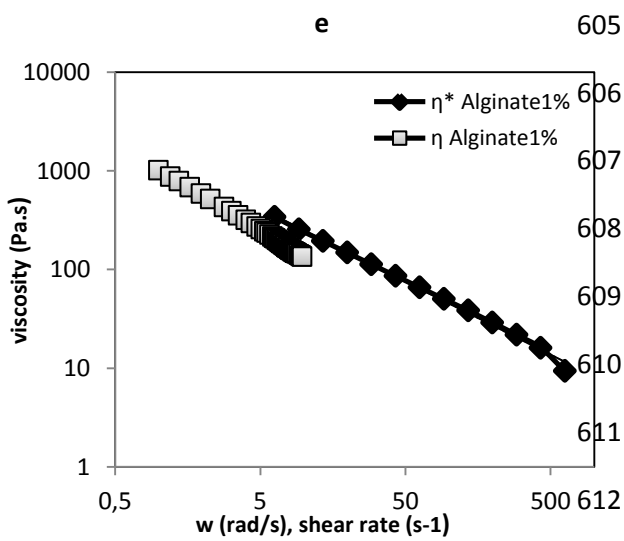




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613

614 **Fig. 5**

615 Figure caption

616

617 **Figure 1.** Microscopic observations (10x) of (a) commercial potato puree, (b) with lecithin 0.5%, (c)  
618 with agar 1%, and (d) with glycerol 1%, stained with Lugol's iodine solution. \*arrows refer to starch  
619 leached out due to cell rupture.

620

621 **Figure 2.** Typical flow curve of potato pure alone and with different additives at 0.5% concentration  
622 (a) and at 1% concentration (b). Inset: flow curves at a shear rate below  $1 \text{ s}^{-1}$ .

623

624 **Figure 3.** Measurement of the commercial potato puree and puree samples with additives (1% w/v,  
625  $20^\circ\text{C}$ ), for (a) Yield stress based on the stress ramp method. (b) Thixotropic hysteresis loop- Stress  
626 ramps at  $20^\circ\text{C}$ .

627 **Figure 4.** Dynamic mechanical spectra of potato pure alone and with different additives for storage  
628 modulus ( $G'$ ) at 0.5% concentration (a) and at 1% concentration (b) and Loss modulus ( $G''$ ) at 0.5%  
629 concentration (c) and at 1% concentration (d).

630 **Figure 5.** Plots of  $\log(\dot{\gamma})$  against  $\log(\eta)$  and  $\log(\omega)$  against  $\log(\eta^*)$  for (a) commercial potato puree, (c)  
631 with glycerol, (e) with alginate. Modified Cox-Merx rule for (b) commercial potato puree, (d) with  
632 glycerol and (f) with alginate.  $\alpha$  is the shift factor for  $\omega$ .

633

634 **Table 1** Experimental characterization of the yield stress  $\tau_0$  (Pa) using both Bingham model and the  
 635 intersection point of  $\gamma=f(\tau)$  as well as representing the values of the Thixotropy Hysteresis Loop area (in  
 636  $\text{Pa}\cdot\text{s}^{-1}$ ), and the Cox Merz parameters: shift factor ( $\alpha$ ), and  $R^2$  coefficient for the different potato puree  
 637 samples

638

		Potato puree	Agar		Alginate		Lecithin		Glycerol	
			0.50%	1%	0.50%	1%	0.50%	1%	0.50%	1%
yield stress $\tau_0$ (Pa)	Bingham model	1508 R=0.992	1309 R=0.998	-----	773 R=0.983	1150 R=0.958	867 R=0.991	429 R=0.992	418 R=0.966	393 R=0.997
	* Abrupt change in $\eta=f(\tau)$	400	600	1000	400	500	450	200	250	200
Thixotropy ( $\text{Pa}\cdot\text{s}^{-1}$ )	Hysteresis loop area	$3.9\cdot 10^4$	$2.64\cdot 10^4$	-----	4660	$1.27\cdot 10^4$	$1.26\cdot 10^4$	3469	2605	1449
Cox Merz Rule	( $\alpha$ ) Shift factor	0.37	0.45	0.61	0.35	0.43	0.34	-----	0.30	0.38
	Determination coefficient $R^2$	0.9943	0.9909	0.9998	0.9978	0.9913	0.9914	-----	0.9967	0.9984