

1 **PHYSICOCHEMICAL PROPERTIES OF GELS OBTAINED FROM CORN**  
2 **POROUS STARCHES WITH DIFFERENT LEVELS OF POROSITY**

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15 **Running title: Gels from porous starches**

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17 **List of abbreviations:**

18 AMG Amyloglucosidase

19  
20 **Keywords:** gel matrix, microstructure, porous starch, viscoelastic behavior

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22 **Authors declare that they do not have any conflict of interest in this submission.**

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25 **Novelty:** Up to authors knowledge, this study shows for the first time the characteristics  
26 of gels produced from porous starches and their interesting properties for different  
27 applications.

28 **Abstract**

29

30 Porous starches are attracting much attention owing to their adsorption ability of different  
31 compounds. However, only their granular structure has been exploited. The objective of  
32 the present research was to analyze the structure and properties of the gels obtained from  
33 porous starches having diverse degree of porosity (0-15%). Gels were obtained from corn  
34 starches with different degree of porosity and their microstructure, gel rheology, hardness  
35 and syneresis during storage was determined. SEM micrographs revealed honeycomb  
36 structures with diverse size and number of holes depending on the porosity of the initial  
37 porous starches. In addition, when increasing porosity, gels showed lower viscoelasticity,  
38 decreasing  $G'$  and  $G''$  and leading to low elastic gels, with also soft texture. Syneresis of  
39 starches was accelerated during the storage of the samples during the first week.  
40 However, no significant differences were observed during the second week. Therefore,  
41 porous starches with diverse porosity offer an attractive alternative to obtain hydrogels  
42 with diverse network matrix.

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46 **1. Introduction**

47 Starch is an important ingredient widely used in the food industry due to its biodegradable  
48 nature, competitive cost, accessibility, and feasibility to modify its properties. Prior to its  
49 use, starch can be structurally modified to increase its applicability as an ingredient by  
50 decreasing retrogradation and improving paste properties and gel texture during  
51 processing [1]. Among the various starch modification methods, enzymatic modification  
52 is applied to alter starch granular and molecular structure. Research carried out on  
53 enzymatic treatments of starches has been accomplished using diverse enzymes and  
54 experimental conditions [2, 3], most of them focused on applying glucoamylase (AMG)  
55 [4]. Lately, many studies have been focused on assessing the effects of AMG treatment  
56 on starch granules, including functional properties, biochemical features, thermal and  
57 structural analyses [5-9], as well as digestibility behavior [10, 11].

58 Numerous researchers have conducted their studies selecting corn starch as substrate to  
59 produce porous starch by AMG treatment, since it is easier to be hydrolyzed and has more  
60 inerratic matrices as compared to other starches [12]. It is well known that glucoamylase  
61 is an exo-acting enzyme that catalyzes the hydrolysis of both  $\alpha$ -D-(1  $\rightarrow$  4) and  $\alpha$ -D-(1  $\rightarrow$   
62 6)-linkages from the non-reducing ends of the starch chain. As a result of AMG action,  
63 the molecular chains were shortened by hydrolysis [12]. Studies carried out on granular  
64 starch after AMG treatment suggested that AMG action affected amorphous and  
65 crystalline regions following a cooperative process [10], hydrolyzing preferentially the  
66 amylopectin chains [9]. The general behavior of corn starch under AMG treatment is  
67 characterized by pores developed from the surface to the center of the starch granule [13],  
68 resulting in greatly perforated granules. These structural characteristics can be modulated  
69 by varying the enzyme dosages, so that the resulting starches have different functional  
70 properties [9]. The expandable space within the granule significantly increases the  
71 specific surface area [8], because of that those porous structures are used as carriers or  
72 vehicles of diverse compounds [12]. Because of that all studies carried out on porous  
73 starches have been focused on their granular structure, despite in industrial settings,  
74 gelatinization is a crucial stage. For many processing applications involving starch, starch  
75 granules are heated in excess of water. This process (gelatinization) results in the loss of  
76 granular integrity and gives rise to the formation of a network, which turns the solution  
77 into a gel. Therefore, the properties of starch gel determine the exploitation of starch in  
78 an increasing number of applications. Nevertheless, little information has been provided

79 about how granule porosity present on porous starches affects gelatinization behavior and  
80 gel properties, as well as the resulting microstructure.

81 In the present work, a selection of porous corn starches with varied structural changes [9],  
82 have been used to determine the impact of pores intensity on the gel properties. Porous  
83 starches were obtained from a previous study using increasing levels of AMG to modulate  
84 the severity of the surface perforation. To achieve this goal, resulting starch gels were  
85 characterized based on their microstructure and physical behavior. This work will provide  
86 a greater understanding of the use of porous starches as a main component or additive in  
87 food applications, where the texture and stability of the gels, as well as the properties of  
88 the paste are fundamental.

## 89 **2. Materials and methods**

### 90 *2.1. Materials*

91 Native corn starch (Miwon, Seoul, Korea) without being subjected to the action of the  
92 enzyme were used as reference. The development and preparation of enzymatically  
93 modified porous starches were described in detail in a previous publication by Benavent-  
94 Gil and Rosell [9]. The AMG modified starches were used for the study since they  
95 produced the largest difference in microstructure characteristics, which are summarized  
96 in Table 1. The notation used for the samples was C to denote corn starch and a number  
97 that specified the porosity of the porous starches.

98 All the other chemicals were analytical reagent grade and used without further  
99 purification. All solutions and standards were prepared by using deionized water.

### 100 *2.2. Flow behavior of corn starch slurries (granular state)*

101 Corn starch slurries were prepared by dispersing 20 mg of starch in 40 mL of distilled  
102 water in aluminum canisters and vigorously mixing the content with a wire rod until  
103 complete starch suspension. Shear stress versus shear rate data was recorded using a  
104 rheometer (Haake RheoStress 1, Thermo Fischer Scientific, Scheverte, Germany) with a  
105 Z34 DIN Ti concentric cylinder system (1 mm gap) at a temperature of 30°C. Shear rate  
106 was logarithmically increased from 1 to 500 s<sup>-1</sup> in step mode (30 seconds per point) and  
107 data were fitted to the Ostwald-de Waele model (R equal to or higher than 0.99):

$$108 \quad \sigma = K \cdot \dot{\gamma}^n$$

109 where  $\sigma$  is the shear stress (Pa),  $\dot{\gamma}$  s the shear rate (s<sup>-1</sup>),  $K$  is the consistency coefficient  
110 (Pa.s<sup>n</sup>), and  $n$  is the flow behavior index (dimensionless). In this model, the apparent  
111 viscosity ( $\eta$ ) can be calculated as ( $\eta = K \cdot \dot{\gamma}^{n-1}$ ). All measurements were made in  
112 duplicate.

### 113 *2.3. Porous starch gel preparation*

114 Corn starch was gelatinized by running the standard method 61-02.01 for pasting  
115 properties (AACC, 2015) with modifications according to Martínez, Pico and Gómez [14]  
116 using a Rapid Visco Analyser (RVA-4) (Perten Instruments, Macquarie Park, Australia).  
117 Briefly, the starch-water mixture, prepared by adding 3.5 g of starch to 25 mL of distilled  
118 water, was held at 50 °C for 1 min, then heated from 50 to 95°C, and held at this  
119 temperature for 2 min 30 s. Subsequently, the sample was cooled down to 30°C, and held  
120 at 30 °C for 4 min. Gel/paste preparation was made in duplicate.

### 121 *2.4. Scanning electron microscopy (SEM)*

122 Morphology of the gelatinized starch samples was observed with a scanning electron  
123 microscope (SEM) (S-4800, Hitachi, Ibaraki, Japan). The freeze-dried gelatinized  
124 samples were split, and then the sections were mounted on specimen holders followed by  
125 coating with gold in a vacuum evaporator (JEE 400, JEOL, Tokyo, Japan). All  
126 micrographs were recorded at an accelerating voltage of 10 kV and at 300 x  
127 magnification.

128 The microstructure analysis was carried out using the image analysis program (ImageJ,  
129 UTHSCSA Image Tool software). The SEM images were saved as 8-bit tiff format. Scale  
130 was initially set using the relationship between pixels and known distance. Threshold was  
131 assessed applying the Otsu's algorithm according to [15] and then particle analysis was  
132 carried out. The following parameters were measured: void size and void frequency.

### 133 *2.5. Viscoelastic behavior of porous gels/pastes*

134 To assess the linear viscoelastic behavior of corn starch gels, the gels were loaded in a  
135 Haake RheoStress1 rheometer (Thermo Fischer Scientific, Schevete, Germany)  
136 immediately after RVA cycle. Rheological tests were conducted with a titanium parallel  
137 plate geometry sensor PP60 Ti (60 mm diameter, and 1 mm gap). After gap adjustment,  
138 sample surface between plates was covered with Panreac vaseline oil (Panreac Quimica  
139 S.A., Castellar del Valles, Spain) to avoid drying. Before conducting any rheological test,  
140 the pastes were allowed to rest for 500 s in the measurement position. Dynamic linear  
141 viscoelastic range at 30°C was estimated by performing a stress sweep from 0.1 to 100  
142 Pa at 1 Hz frequency. Frequency dependence experiments were conducted from 10 to  
143 0.01 Hz at 30°C. The applied stress in the frequency sweep was always selected to  
144 guarantee the existence of linear viscoelastic response. The storage ( $G'$ ) and loss ( $G''$ )  
145 modulus as a function of frequency ( $\omega$ ) were obtained. All measurements were performed  
146 in duplicated.

147        *2.6. Gel hardness*

148        Gel hardness was evaluated using a TA.XT-Plus Texture Analyses (Stable Micro Systems  
149        Ltd., Godalming, UK) equipped with a 5 kg load cell and a 2-mm aluminum cylindrical  
150        probe. Briefly, the paste obtained from RVA was transferred in 13 g portions into  
151        disposable sample cups with a height of 15 mm. These were allowed to cool to room  
152        temperature and then stored at 4°C for 24 h. Gel penetration measurement was performed  
153        by placing perpendicularly each gel in the equipment and compressed at a speed of 1  
154        mm/s.

155        *2.7. Syneresis*

156        Syneresis was measured by a centrifugation test [16] using a Eppendorf 5415 R  
157        centrifuge, (Eppendorf, Germany). Starch gels were stored 10 days at 4°C. After storage,  
158        the gels were tempered at 25°C for 2 h and centrifuged at 3000 x g for 10 min at 25°C.  
159        After centrifugation the free water was separated, weighed, and expressed as percentage  
160        of amount of water released from gels. Measurements were the mean of three repetitions  
161        for each duplicated gel.

162        *2.8. Statistical analysis*

163        All experiments were repeated at least in duplicate. Experimental data were statistically  
164        analyzed using an analysis of variance (ANOVA) and values were expressed as a mean  
165        ± standard deviation. Fisher's least significant differences test was used for assessment  
166        of significant differences among experimental mean values with 95% confidence.  
167        Pearson correlation coefficient (*r*) and *P*-value were used to indicate correlations and their  
168        significance using Statgraphics Centurion XV software (Bitstream, Cambridge, N).  
169        Differences of *P* < 0.05 were considered significant.

170        **3. Results and discussion**

171        *3.1. Flow behavior index of non-gelatinized starch dispersions*

172        The flow behavior of starch slurries prepared in the absence of heating are reported in  
173        Table 2. The consistency index (*K*) of the non-gelatinized pastes augmented with  
174        increasing starch porosity, although no significant differences were visible up to a  
175        porosity of 13% (starch C-13). Likewise, the values for the flow behavior index (*n*)  
176        decreased progressively as the porosity increased, but in this case, differences were  
177        significant even with the smallest porosity. These results are in agreement with those  
178        found in  $\alpha$ -amylase hydrolyzed corn starches in which the overall resistance of the sample  
179        to flow decreases [17]. Regarding the flow behavior of the starch dispersions, it was  
180        visible that the native corn starch dispersion corresponded to the model for shear-

181 thickening fluids (also incorrectly known as dilatant), i.e. an increase in apparent viscosity  
182 is observed at higher shear rates ( $n > 1$ ), while this behavior was steadily lost with  
183 increasing the severity of the porosity. A decrease in the severity of shear-thickening can  
184 be attributed to a number of factors including polydispersity in granule size, granule  
185 volume fraction, and deformability of the dispersed granules [18]. It is noteworthy that  
186 with the maximum porosity the flow behavior became shear-thinning ( $n < 1$ ), close to  
187 Newtonian, meaning that the apparent viscosity decreases at higher shear rates. This  
188 behavior may be due to better alignment properties of more deformable starch granules  
189 with porous on its surface or to a reduction in the granule volume fraction as Rao,  
190 Okechukwu, Da Silva and Oliveira [18] suggested. Likewise, Kwon, Auh, Choi, Kang,  
191 Kim and Park [19] reported an almost Newtonian behavior of liquefied corn starches  
192 treated by maltogenic amylases, probably due to the increase of the molecular mobility.  
193 Shear-thickening is a typical behavior of suspensions of smooth spheres in Newtonian  
194 suspending fluids [20]. Thus, it is known that severe starch treatments can destroy the  
195 starch ability to form shear-thickened fluids [21, 22]. It has been shown that shear-  
196 thickening behavior of starch pastes shifts to a more shear thinning one when starch  
197 granules are disrupted by gelatinization process [18]. Similarly, the change to shear-  
198 thinning behavior could steadily occur as the starch surface is modified by the action of  
199 the AMG hydrolytic enzyme. The presence of more surface porous may account for a  
200 greater water uptake (as the higher consistency index indicates), turning the insoluble  
201 starch granule into a more soluble one, facilitating interaction among granules, and,  
202 making water more difficult to be squeezed out from the granules at higher shear rates.  
203 In fact, a more hydrophilic nature (higher water absorption capacity) of these  
204 enzymatically treated corn starches was found in a previous study [9]. The more swollen  
205 starch granules would be better aligned along the flow direction; reducing in this form  
206 the drag experimented by the microstructure [23].

### 207 *3.2. Gel matrix structure*

208 Native and AMG treated corn starch granules had an irregular and mostly polygonal  
209 shape. Nevertheless, enzymatic treatments modify the surface of starch granules by  
210 producing pores in a random way [9]. In addition, no significant change in relative  
211 crystallinity has been reported among native corn starch and AMG treated starch [24],  
212 neither in the amylose content (Table 1) [9]. SEM characterization of the sample gel  
213 matrices was carried out to investigate any possible structural changes induced by the  
214 sample porosity (Fig. 1). In line with previous reports [25], SEM micrographs revealed a

215 dense structure, similar to a honeycomb construction, due to the loss of granular structure.  
216 It has been described that heating starch in the presence of sufficient water leads to the  
217 mobilized amylose molecules being dispersed from the interior of the granule to the  
218 surrounding aqueous medium [26]. As a consequence of this process, an amorphous  
219 structure is generated, which is composed of spherical or oval holes and surrounded by a  
220 gel matrix [27].

221 From SEM micrographs, it was clear the effect of porosity on starch gel microstructure.  
222 The network obtained from the different porous starches was significantly different  
223 regarding the hole size distribution within the matrix and the number of voids (Fig. 2).  
224 Overall, the starch porosity caused a reduction in the hole size distribution compared with  
225 non-porous sample, except in the case of the lowest porosity (carried out with 5.5 %  
226 porosity). The smallest hole size was observed in the sample with a porosity of 8 % (Fig.  
227 2A). Meanwhile the larger hole size was displayed by the sample with the porosity of 5.5  
228 %. The other samples studied in this study did not show significant differences in terms  
229 of hole size among them. As a consequence, the number of voids significantly varied  
230 among samples (Fig. 2B). Nevertheless, no correlation was observed between both  
231 parameters. The lowest porosity did not differ in the number of holes respect to non-  
232 porous gel matrix. The largest number of holes was obtained with the porous starch with  
233 8 % of porosity, which led to the smallest pores, followed by the gels with 13 % and 15  
234 % of porosity. Therefore, although enzymatic treatment is initially carried out to obtain  
235 porous starches, results revealed that enzymatic treatment allowed obtaining gels with  
236 significant different microstructures.

### 237 *3.3. Viscoelastic behavior of gelatinized starch pastes*

238 The mechanical spectra of gelatinized corn starch pastes (starch in non-granular form) in  
239 Fig. 3 showed the existence of solid-like starch gels, with values of  $G'$  greater than  $G''$  for  
240 all the studied starches and with increasing values for increasing frequencies. This  
241 behavior has already been described for other starch gels [23]. It is known that any  
242 damage of the starch prior to gelatinization decreases the values of the moduli as indicated  
243 by Kochkina and Khokhlova [28] when modifying the starches by means of solid state  
244 milling. In this sense, it was observed that both moduli, elastic and viscous modulus,  
245 decreased as the porosity increased. The lower value of the viscous and elastic moduli is  
246 expected for porous starches according to their higher starch damage produced due to the  
247 AMG hydrolytic action on the granule surface [5], which may lead to a granular

248 weakening that increases the cooking loss and reduces the water uptake during and after  
249 gelatinization [29].

250 However, no significant changes on the moduli values with respect to the non-porous  
251 material (C-0) were observed until the porosity of 8 %, values (C-8), which seems to  
252 reach a plateau from 13 % porosity (Table 3). Therefore, a minimum enzymatic treatment  
253 seems to be necessary to modify the rheology of the cooked starch pastes, this is, to affect  
254 the changes of the starch after the gelatinization and retrogradation processes, reducing  
255 the values of  $G'$  and  $G''$ , but these changes did not continue from a certain treatment.

256 Regarding the value of  $\tan \delta$ , the smaller porosities (mildest treatments) reduced the  
257 values of this parameter, but as soon as the porosity is increased, the  $\tan \delta$  value increased  
258 progressively, exceeding the value of the non-porous starch in the highest porosities,  
259 which indicates a decrease in the elastic character. These results agree again with those  
260 found by Kochkina and Khokhlova [28], with changes only being observed when they  
261 damaged the starch for a certain time of treatment. They associated these results to the  
262 more destructed starch molecules, which would form a weaker network with a low  
263 entanglement density.

#### 264 *3.4. Texture profile analysis (TPA)*

265 The hardness of non-porous and porous gel matrices after storage at 4 °C for 24 h is  
266 shown in Fig. 4. The statistical analysis indicated that gels from diverse porous starches  
267 had significant different hardness. The trend observed was the same as the one described  
268 for the microstructure and the viscoelastic behavior, observing different tendencies  
269 between the lowest and the highest porosities compared with non-porous starch.  
270 Specifically, it was observed that porous starches with lower porosity resulted in gels with  
271 a significant increase in hardness (from  $33.43 \pm 2.89$  g in C-0 to  $49.28 \pm 3.28$  and  $43.68$   
272  $\pm 2.52$  g for C-5.5 and C-7.8, respectively). But after certain porosity (8 %), a steady  
273 decrease of gels hardness was obtained; consequently, more intensive porosity of the  
274 granular starches led to softer gels. These results suggested that enzyme dosage in the  
275 enzymatic treatment with AMG could potentially be used to increase or reduce the  
276 hardness of corn starch gels.

#### 277 *3.5. Effect of enzymatic treatment on syneresis*

278 After cooling, the release of the bulk phase water from the polymer network occurs, which  
279 is the so-called syneresis [30], and has been directly related to the starch ability to hold  
280 water and its tendency to retrograde [31, 32]. The syneresis of the gels was measured over  
281 a period of up to 240 h at 4 °C (Fig. 5). The syneresis was virtually zero for all samples

282 at the onset. In line with previous reports [30-34], the syneresis of all samples increased  
283 significantly with storage time. Previous reports observed an increase in syneresis during  
284 the first two weeks of storage, but then did not change for up to 8 weeks [35]. The gels  
285 obtained from porous starches had higher syneresis values than the non-porous corn  
286 starch after 144 h, with no significant differences regarding the porosity observed in  
287 porous starches. In spite of the lower initial ability of the gels obtained from porous  
288 starches to retain the water molecules, they exhibited better performance after longer  
289 storage periods. Especially, those gels that had closed microstructure with small voids  
290 (C-8), which might help to retain the water molecules.

#### 291 **4. Conclusions**

292 Gels obtained from porous starches exhibited a network microstructure similar to the one  
293 displayed by native starch. However, the size and number of holes within the gel structure  
294 was significantly dependent on the initial porosity of the porous starches. Starch with 8%  
295 porosity produced gels with closed microstructure, which were softer than the gel  
296 obtained from native starch but were able to retain better the water molecules at longer  
297 storage. In addition, higher surface porosity resulted in less viscoelastic starch gels.  
298 Therefore, porous starches not only have different granular structure, surface pores also  
299 induced the production of diverse gels matrixes, and their structure will be dependent on  
300 the porosity of the original porous starch.

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398

399 **Figure 1:** Scanning electron micrograph of starch gels obtained from native corn (A)  
400 and porous starches with increasing level of porosity (5.5, 7.8, 8.0, 13, 15) (B–F).  
401 Magnification 300×.

402 **Figure 2:** Analysis of the microstructure of the gels obtained from porous starches with  
403 different porosity. A) Hole size and B) number of holes by boxplot. Numbers following  
404 the abbreviation are referred to the porosity of the starches (5.5, 7.8, 8.0, 13, 15).

405 **Figure 3:** Variation of storage ( $G'$ ) and loss ( $G''$ ) moduli with frequency of corn starch  
406 gels.

407 **Figure 4:** Hardness (g) of the gels produced from different porous starches. Numbers  
408 following the abbreviation are referred to the porosity of the starches (5.5, 7.8, 8.0, 13,  
409 15).

410 **Figure 5.** Syneresis (%) of the starch gels obtained from porous starches after 144, 196  
411 and 240 hours of storage. Numbers following the abbreviation are referred to the  
412 porosity of the starches (5.5, 7.8, 8.0, 13, 15). Letters, showing significant differences  
413 ( $P < 0.05$ ) within gels samples at each specific storage time, are included in those  
414 samples with significant different behavior.

415 **Table 1:** Structural characteristics of native and modified starches used as supporting  
416 materials (data from [9]).

417

Name	Enzyme (U/g starch)	Porosity (%)	Apparent amylose (%)
C-0	0	0.00	25.76
C-5.5	5.5	5.49	23.47
C-7.8	11	7.76	27.36
C-8	16.5	8.32	26.97
C-13	33	12.53	28.01
C-15	55	14.67	26.91

418

419 **Table 2: Flow behavior of corn starch slurries**

420

	Flow behavior	
	$K$ (Pa·s <sup>n</sup> )	n
C-0	0.0003a	1.52e
C-5.5	0.0008a	1.36d
C-7.8	0.0010a	1.32cd
C-8	0.0013a	1.28c
C-13	0.0043b	1.09b
C-15	0.0081c	0.98a
St. error	0.0006	0.02

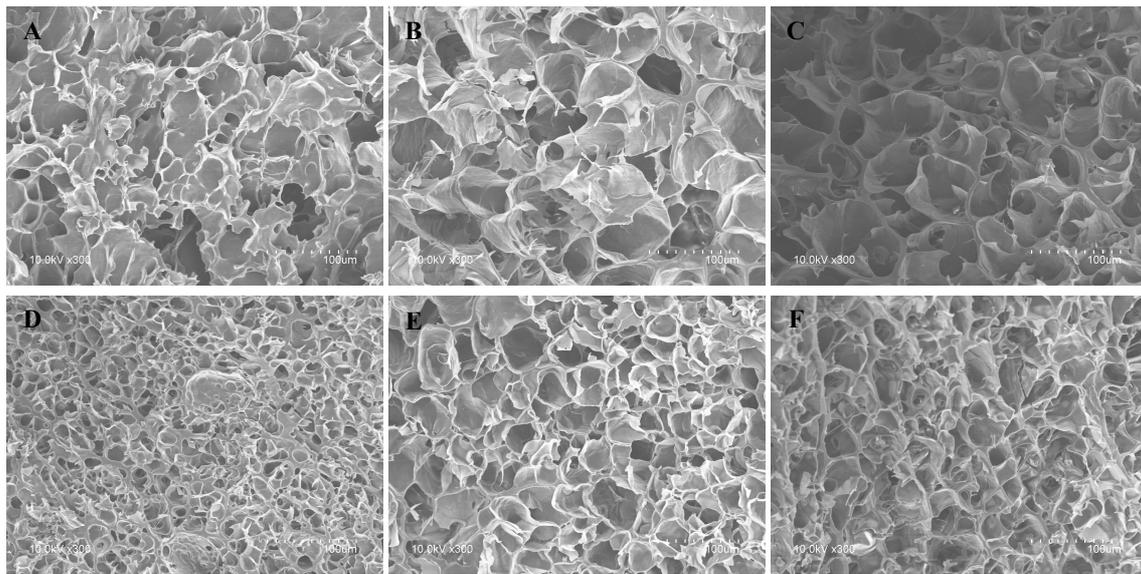
421

422 **Table 3: Viscoelastic behavior of gelatinized starch pastes**

	Viscoelastic behavior		
	$G'$ (Pa)	$G''$ (Pa)	$\tan \delta$
C-0	1300c	48.75b	0.041c
C-5.5	1637d	44.83b	0.027a
C-7.8	1300c	43.73b	0.034b
C-8	911b	31.90a	0.035bc
C-13	451a	25.15a	0.056d
C-15	485a	28.80a	0.059d
St. error	92	2.65	0.002

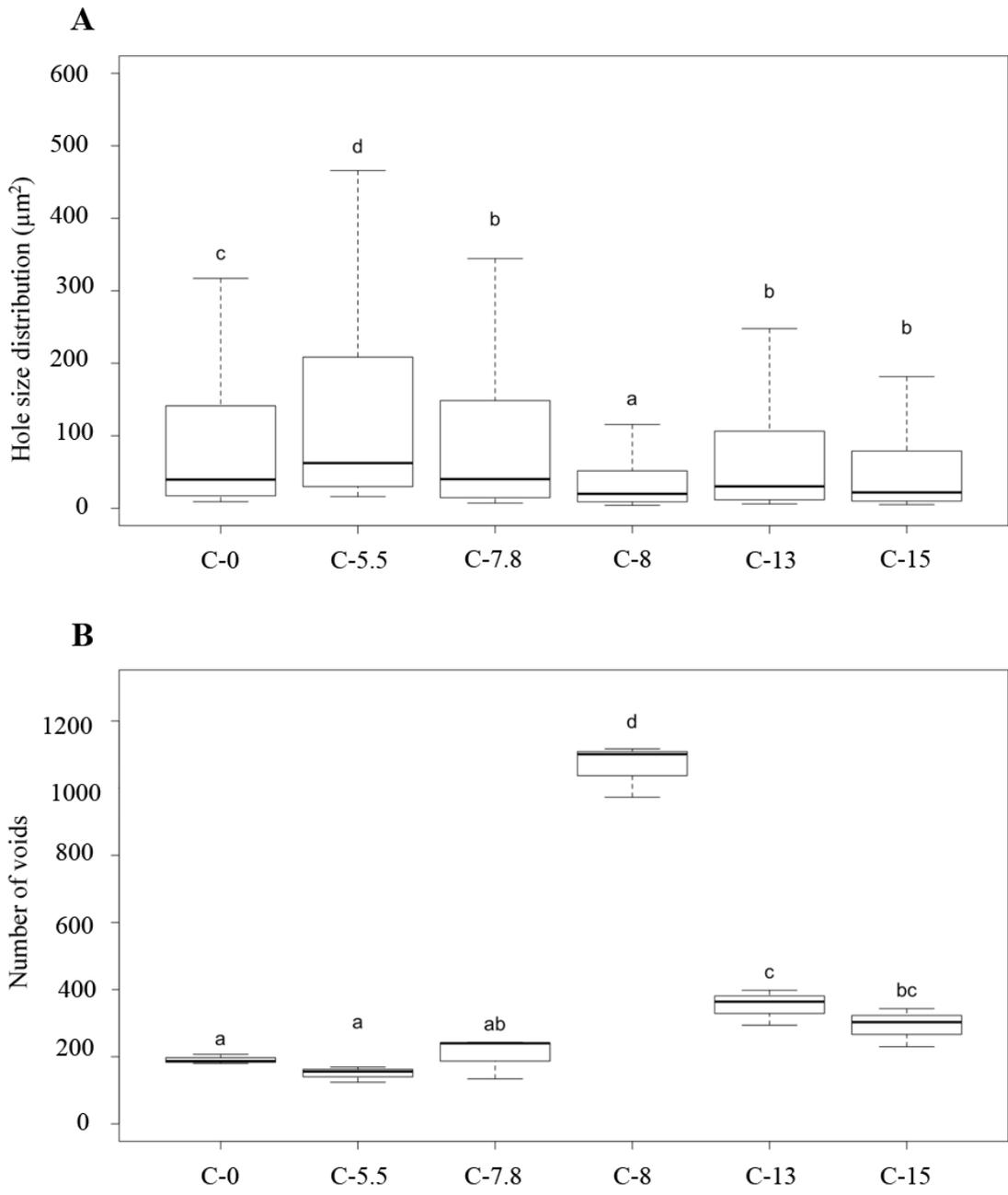
423

424 **Figure 1.**



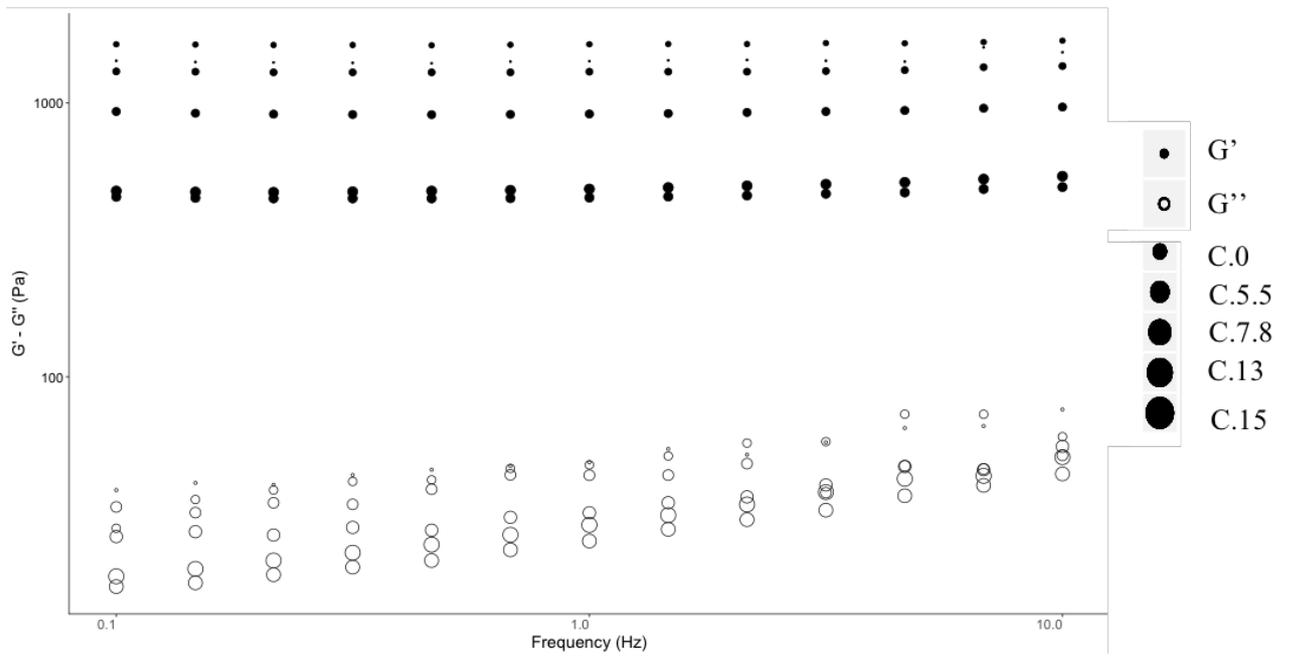
425

426 **Figure 2.**

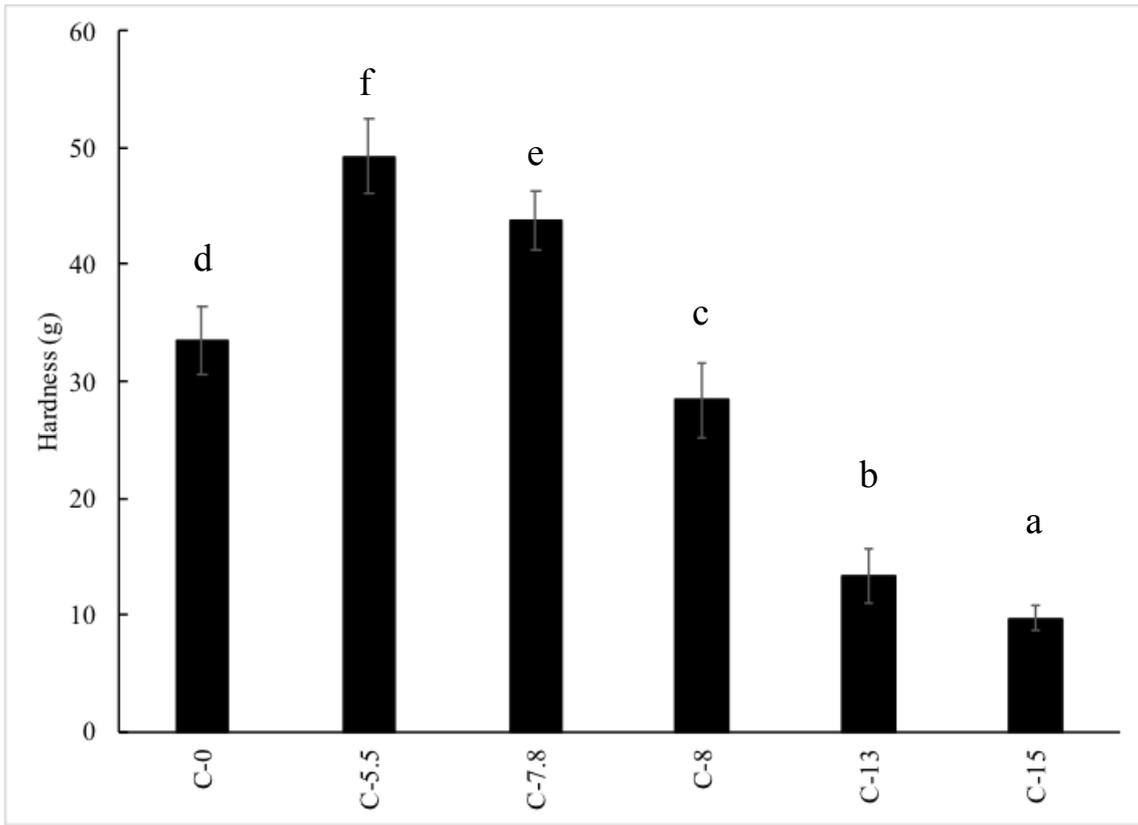


427

428 **Figure 3.**



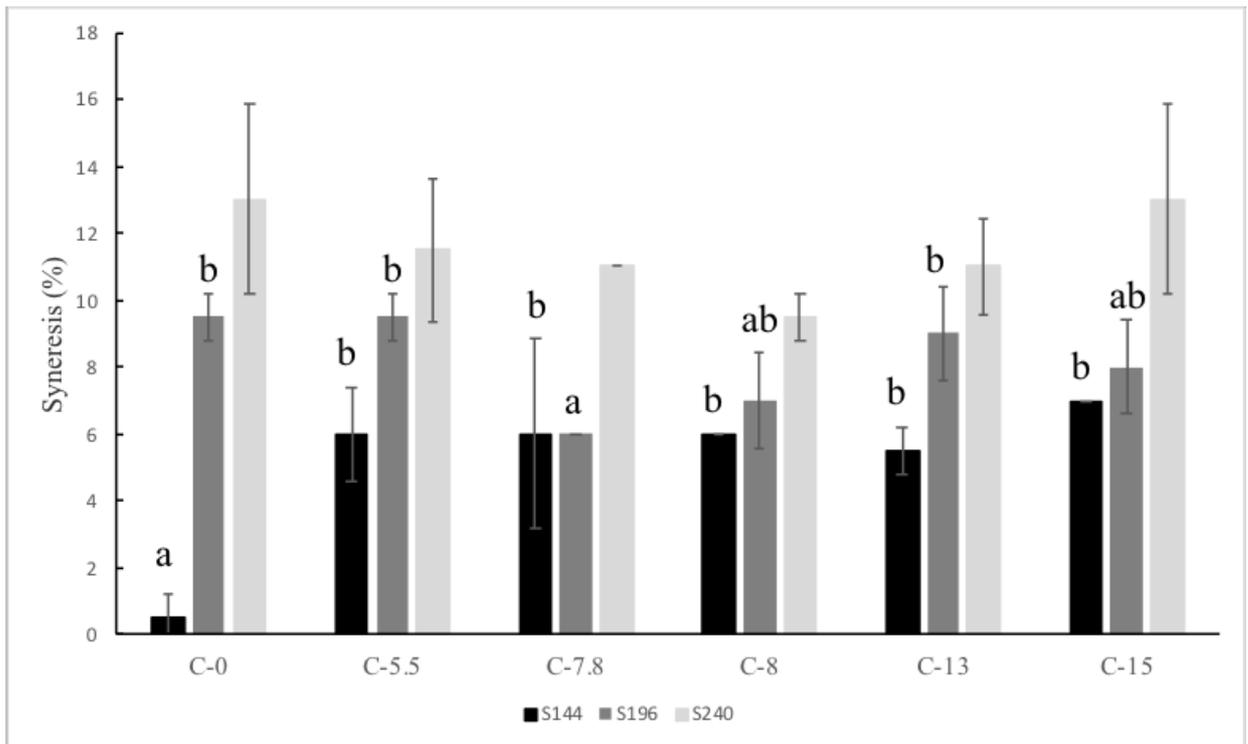
431 **Figure 4.**



432

433

434 **Figure 5.**



435