Bioplastics based on wheat gluten processed by extrusion

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30   **ABSTRACT**

31   Recently, bioplastic have generated an increasing interest as an alternative to

32   conventional plastics. For this reason, their manufacture using the traditional techniques

33   used for the production of plastics, such as extrusion, would help transferring

34   bioplastics production to an industrial scale. In this way, the preparation of wheat gluten

35   bioplastics by extrusion was the main objective of this research, modifying their

36   structure by varying the pH value or by incorporating additives (glyoxal or xanthan

37   gum). These bioplastics were characterized by the measurement of their mechanical

38   properties and their water uptake capacity, proving that the modification of bioplastics

39   cause variations in their properties. Thus, extrusion resulted in a greater gluten-

40   plasticizer compatibility compared to compression, as denoted the temperature ramp

41   tests, especially in the presence of additives (ie. Xanthan gum, glyoxal). Moreover,

42   tensile strength was enhanced at pH 9, probably due to bonding promotion at alkaline

43   conditions. These results demonstrate the great potential of these materials for the

44   replacement of conventional plastics.

45

46   *Keywords:* **rheology; additives; wheat gluten; extrusion; bioplastics**

1. Introduction

Bioplastics, such as protein-based bioplastics, are a potential alternative to replace conventional plastics. So they would help minimizing the environmental issues associated with the predominant use of plastics derived from petrochemicals (Derraik, 2002; Sheavly and Register, 2007). Moreover, it should be highlighted that the Food and Agriculture Organization (FAO) has reported that around 1.3 billion tons of food are lost or wasted every year in the world. In addition, the fact that the land area used to grow biomass for the production of bioplastics in 2018 corresponded to less than 0.02 percent of the global agricultural area (European Bioplastics, 2018), supports the idea that there is no competition between the use of biomass to produce bioplastics and the use of biomass for food and feed. In this context, the use of wheat gluten, which is obtained as a by-product from the bio-ethanol industry, to make protein-based bioplastics is a potential option (Ye et al., 2006). Thus, Guillaume et al. (2010) showed that wheat gluten-coated paper was very effective at improving the shelf life of mushrooms compared to PVC films; Tunc et al. (2007) studied its properties as nanocomposite and Gennadios et al. (1994) found that it is a very effective oxygen barrier at low relative humidity. Moreover, it is used mainly as animal feed, thereby its use as raw material for bioplastics could increase its value (Ye et al., 2006). Therefore, its use in the development of bioplastics would result in a revalorization of an abundant by-product of the food industry (Patni et al., 2014). In this way, as wheat gluten is profusely available and relatively inexpensive, a growing interest on its potential application as packaging for the food industry has arisen due to its interesting biodegradation, film formation, gas barrier, and mechanical properties (Olabarrieta et al., 2006).

71 One of the most used techniques for the production of plastics is extrusion, due to its

72 high mixing and molding efficiency for thermoplastic materials (Pommet et al., 2003).

73 Most of the commercial synthetic plastic films (i.e. polyethylene) are produced in

74 extruders (Hernandez-Izquierdo and Krochta, 2008). The use of this widespread

75 technology with an agricultural renewable raw material, such as wheat gluten,

76 represents an interesting opportunity for the industrial production of bioplastics (Gug et

77 al., 2018; Herniou-Julien et al., 2019; Mathiot et al., 2019; Pommet et al., 2003),

78 helping their industrial scale-up (Ferrar et al., 2018). Unlike thermoplastic polymers,

79 wheat gluten protein may undergo some crosslinking reactions upon heating, which

80 would eventually result in an increase in the viscoelastic properties of plasticized

81 gluten-based materials. These structural changes occur at lower temperatures compared

82 to synthetic polymers (Balaguer et al., 2014; Lagrain et al., 2010). In this way, the

83 extrusion of wheat gluten is only possible under certain operating conditions, ranging

84 from the point at which protein chains begin to flow to the point where they start to

85 aggregate.

86 In the extrusion of wheat gluten proteins, certain key parameters must be considered in

87 order to have optimal operating conditions, such as plasticizer content, mechanical

88 energy input, applied shear, as well as operating time, temperature and pressure.

89 Therefore, the degree of aggregation, molecular conformational changes and chemical

90 crosslinking that occur along the extrusion process can be determined by these

91 parameters. In this respect, it is important not only to select an adequate temperature

92 window to obtain a moderate viscosity, which facilitates the processing of the

93 protein/plasticizer blend, but also to ensure a proper aggregation of protein molecules

94 that allows the formation of a homogeneous material, without exceeding thermal

95 conditions leading to degradation. On the one hand, the lowest temperature is defined

96 by the glass transition temperature of the protein, which is required to allow the material

97 to achieve its final shape (Ullsten et al., 2009). On the other hand, the upper temperature

98 limit is defined by either an extensive aggregation or the thermal degradation of the

99 protein. Thus, wheat gluten materials are generally processed between 80 and 130 ℃,

100 with their properties depending on those operating conditions (Redl et al., 2003).

101 Another parameter to be considered when replacing conventional plastics with any

102 alternative bioplastic is their final properties, such as their mechanical characteristics

103 and water uptake capacity. Within this scope, several techniques have been investigated

104 to reinforce bioplastics and improve their characteristics (Rasheed et al., 2018;

105 Thammahiwes et al., 2018, 2017). In this manner, studies can be found where the pH of

106 the bioplastics has been modified (Cortes-Trivino and Martinez, 2018), altering the net

107 charge of the protein system as it moves further away from the isoelectric point. Thus, a

108 pH shift may enhance certain bioplastic properties, such as Young's modulus or

109 absorption capacity, as it strongly influences the nature of intermolecular interactions.

110 Another procedure investigated to improve the quality of bioplastics is the inclusion of

111 different additives in the system (Cieśla et al., 2006; Erdohan and Turhan, 2005;

112 Gounga et al., 2007; Parris et al., 1995; Siracusa et al., 2008; Turkoz et al., 2018). The

113 addition of polysaccharides into a protein matrix, with both of them being complex

114 heteropolymers, may promote the formation of non-covalent interactions and

115 intermolecular linkages between them (Turgeon et al., 2003). For this reason, protein-

116 polysaccharide mixtures may present a wide range of structures with different

117 rheological and physical-chemical properties that may allow the tailoring of the final

118 properties of the bioplastic material (Coughlan et al., 2004; Gómez-Martínez et al.,

119 2009; López-Castejón et al., 2016; Schmitt et al., 2009, 1998; Turgeon and Beaulieu,

120 2001; Zaleska et al., 2000). Although some gums, such as xanthan gum, have proved to

121 be stable over a wide pH and temperature range, as well as to enzymatic degradation or

122 in the presence of salts (Sworn, 2009; Vega et al., 2015), all these factors may alter the

123 protein-polysaccharide interactions. Since xanthan gum is an anionic polymer,

124 depending on whether the pH is below or above the protein isoelectric point (IEP),

125 attractive or repulsive electrostatic interactions between the protein and the

126 polysaccharide are expected (Gosh and Bandyopadhyay, 2012). On the other hand, the

127 incorporation of crosslinking additives, such as aldehydes (e.g. glyoxal), to wheat gluten

128 protein-based bioplastics has proved to promote covalent crosslinking both intra- and

129 intermolecularly in wheat gluten protein (Zárate-Ramírez et al., 2014b). However,

130 Bruyninckx et al. (2016) have recently shown that an increase in crosslink density does

131 not always lead to enhanced mechanical properties of gluten-based bioplastics. These

132 authors postulated that crosslinks between protein segments may lead to a positive

133 reinforcement of the protein network, although but they may also force some kind of

134 unfavorable configurations that could prevent the formation of further physical

135 entanglements, thus compromising the overall network quality.

136 Taking into account all these parameters, the overall aim of this research was to process

137 biodegradable protein-based bioplastics with wheat gluten by extrusion, comparing this

138 with the compression molding method and determining the influence of the pH

139 modification and the addition of xanthan gum (polysaccharide) and glyoxal (aldehyde)

140 to them. In this way, their rheological properties and water uptake capacity were

141 studied.

2. Experimental

2.1. Materials

The protein-based biopolymer used was wheat gluten (WG) from Productos Riba S.A. (Spain). This material, according to its technical data sheet, contains a minimum of 83 wt.% protein, 10 wt.% starch, 3 wt.% lipids and 1 wt.% ashes and the rest is moisture. Glycerol (GL), provided by Panreac Química S.A.U. (Spain), and distilled water (W) were used as protein plasticizers. Xanthan gum (*Xanthomonas Campestris,* XG), from Sigma Aldrich (USA) and glyoxal (GXAL) from Panreac Química S.A.U. (Spain), were used as additives. Finally, NaOH 2 M solution was used to modify the pH of the systems from 6 to 9.

2.2. Processing of gluten/plasticizer samples

2.2.1. Batch Mixing of gluten/plasticizer samples

Prior to extruding, gluten/glycerol/water blends were obtained by a mixing stage using a mixer torque rheometer fitted with two delta-shaped counter-rotating rollers which turn at an angular velocity ratio of 3:2 (Brabender Plastograph, PL 3s model). In the literature on rheometry, a detailed description of this equipment, which can record the evolution of torque over mixing time, may be found (Dealy, 1982). These dough-like blends, which were referred to as reference, had a pH of 6 and were composed of 50 wt.% WG, 18 wt.% GL, 32 wt.% W, following the relation used previously (Zárate-Ramírez et al., 2014a, 2014b, 2011).

Some modifications were made to this reference sample: (i) by adding the necessary amount of NaOH 2M solution to reach a pH of 9; (ii) by adding 3 wt.% GXAL with respect to the wheat gluten protein percentage or (iii) by adding 1.5 wt.% XG dispersed in the water fraction. The percentage of XG or GXAL was counteracted with the

166 percentage of water required to maintain the initial ratio WG:GL (25:9). These

167 modifications were carried out following the same procedure used in previous papers

168 (Zárate-Ramírez et al., 2014b) (Zárate-Ramírez et al., 2014a)

169 The mixing process was carried out under adiabatic conditions at 50 rpm for 10 min

170 approximately. Other authors have also used this mixing step (Ottenhof and Farhat,

171 2004; Türe et al., 2012; Ullsten et al., 2009) in order to facilitate the thermomechanical

172 processing through extrusion (Chantapet et al., 2013; Ottenhof and Farhat, 2004),

173 thermo or compression molding (Jerez et al., 2007; Sun et al., 2008) and injection

174 molding (John et al., 1998). All of them, traditional polymer processing techniques that

175 can improve the industrial escalation of this bioplastic. However, the properties of the

176 final dough-like material blends may affect their subsequent processing. Thus, it is very

177 convenient to monitor parameter such as, torque and temperature throughout the mixing

178 time.

179   2.2.2. Extrusion of gluten/plasticizer bioplastics

180 The dough-like materials after the mixing step were introduced into a Rheomex 302p

181 screw extruder (Thermo-Haake, Germany) coupled to the mixer. This extruder has a

182 spindle barrel diameter of 19 mm with a total length of 830 mm. In addition, it has an

183 electric heating system at four zones (feed, nozzle and two in the mixing zone) from

184 where the temperature profile indicated in Table 1 was established for the different

185 blends (based on previous studies). The nozzle used was of laminar geometry, and the

186 spindle speed applied was 30 rpm.

187 **Table 1:** Temperature profile used during the extrusion of the dough-like materials of wheat gluten (WG), glycerol

188 (GL), water (W) and different percentages of xanthan gum (XG, 0 and 1.5 wt.%).

Systems	Feed (ºC)	Mixing zone 1(ºC)	Mixing zone 2(ºC)	Nozzle
WG/GL/W pH6	55	65	80	100
WG/GL/W pH9	55	65	80	100
WG/GL/GXAL-W	80	110	120	100
WG/GL/XG-W	80	120	110	100

189

190 2.2.3. Die cutting

191 The material obtained after the extrusion step was subjected to punching to obtain

192 bioplastic specimens with different dimensions: rectangular probes (50x10x3 mm) and

193 type IV probes ("ASTM D638-14: Standard Test Method for Tensile Properties of

194 Plastics," 2014).

195 2.2.4 Compression molding of gluten/plasticizer blends

196 Different bioplastic specimens (rectangular and type IV) of the reference formulation

197 (WG/GL/W at pH 6) were also processed by compression molding in order to make a

198 comparison with those specimens prepared by extrusion (and die-cutting). In this case,

199 the blends were subjected to compressing molding at 130 ºC and 9 MPa for 10 min,

200 following a procedure previously described (Zárate-Ramírez et al., 2014a, 2014b,

201 2011).

202 2.2.5 Conditioning of moisture content of gluten/plasticizer specimens

203   All the probes obtained by extrusion and die cutting or by compression molding were

204   subjected to a conditioning step for 2 weeks before testing into recipients at 53%

205   relative humidity (RH) to reach moisture equilibrium at room temperature. After this

206   conditioning period, the actual moisture content was determined maintaining each

207   sample for 24 h at 105 ºC ((AOAC), 2003).

208   ### *2.3. Characterization of gluten/plasticizer bioplastic specimens*

209   ### 2.3.1. Dynamic Mechanical Temperature Analysis (DMTA)

210   DMTA tests were carried out with a dynamic-mechanical strain analyser RSA3 (TA

211   Instruments, USA) with a dual cantilever bending geometry. The tests were performed

212   on rectangular probes from -30 to 130 ºC at a heating rate of 3 ºC·min^{-1}. The frequency

213   was kept constant at 1 Hz and a strain between 0.01 and 0.3 was used (i.e, well within

214   the linear viscoelastic region). Results were obtained for the elastic (E') and viscous

215   (E'') moduli and loss tangent (tan δ).

216   ### 2.3.2. Uniaxial tension tests

217   The Insight 10 kN Electromechanical Testing System (MTS, USA) was used to perform

218   the tensile measurements, according to ASTM D638 ("ASTM D638-14: Standard Test

219   Method for Tensile Properties of Plastics," 2014). So, type IV probes were subjected to

220   an extensional rate of 22 mm·min^{-1} at room temperature, recording the strain at break

221   (ε_{max}), maximum tensile stress (σ_{max}) and Young's modulus (E).

222   ### 2.3.3. Water absorption tests

223   Water absorption tests was carried out following the ASTM D570-98 norm ("ASTM

224   D570-98: Standard Test Method for Water Absorption Of Plastics," 2005), where

225   rectangular probes were immersed in 300 mL of distilled water for 24 h at room
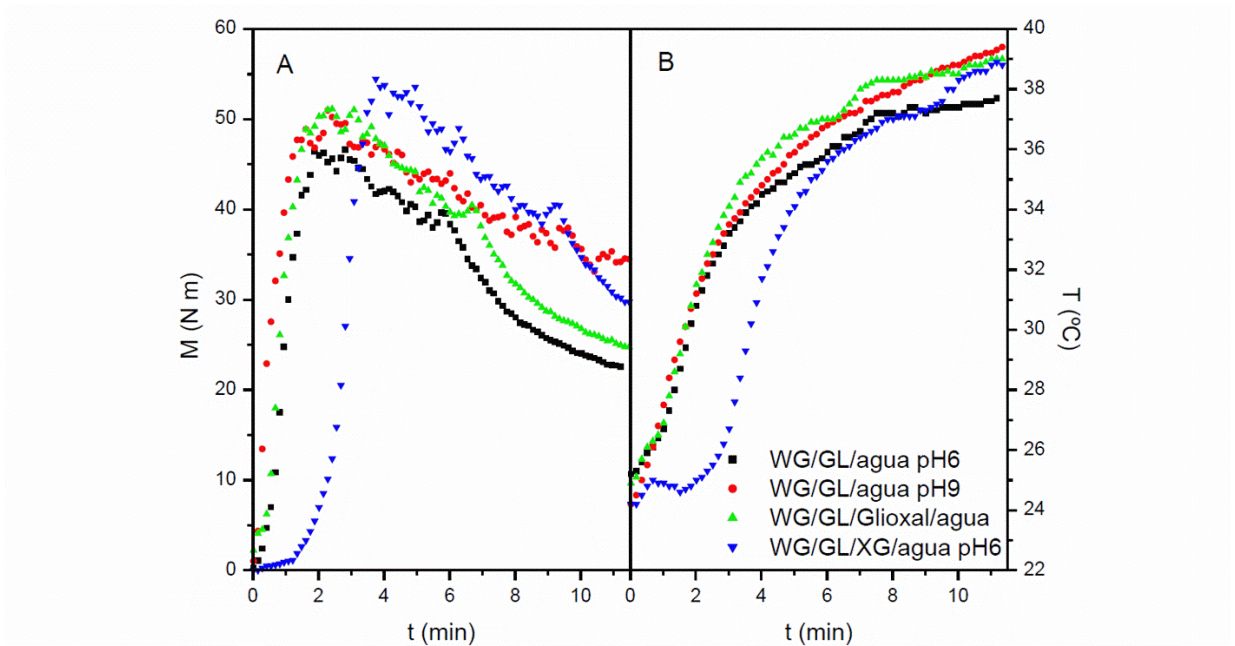
226   temperature.

227 *2.4. Statistical analysis*

228 The data were presented as mean ± standard deviation (SD) of at least three (water

229 uptake capacity and DMTA tests) or six (tensile tests) determinations. A probability

230 value of $p < 0.05$ was considered significant.

231 **3. Results and discussion**

232 *3.1. Batch Mixing of gluten/plasticizer samples*

233 Figure 1 shows the torque (M) and temperature (T) profiles obtained by the systems

234 WG/GL/W with different modifications during the mixing step. As may observed in

235 Figure 1A, all systems show an increase in the mixing torque up to a maximum value,

236 followed by an asymptotic decrease. The torque profile for the blend prepared with XG

237 shows a delay time in its evolution over the other blends, as well as a displacement

238 towards higher values. Both effects can be also observed in the thermal profile (Figure

239 1B). These results might be caused by the higher mobility induced by the presence of

240 water, which exhibits a higher plasticising efficiency than the XG dispersion. The

241 plasticizing efficiency is generally based on the ability of an ingredient to decrease the

242 glass transition temperature, T_g, resulting in a softening of the structure (Verbeek and

243 van den Berg, 2010). Water is an efficient plasticizer for proteins as it enters easily the

244 protein network, preventing protein-protein interaction and thereby promoting chains

245 mobility. It must be considered that when a hydrophilic compound like XG is present,

246 the large number of hydroxyl groups present within its structure show a great affinity to

247 bind water. The high-water binding capacity of XG reduces the amount of free water

248 available, which retards the movement of particles along mixing (Noorlaila et al., 2017).

249 Moreover, the energy dissipation is higher for modified blends as the change (pH or

250 additives) contributes a higher viscosity to the medium. This behaviour is also found in

251 data reported in the literature (Redl et al., 2003). Thus, in absence of water, torque and

252 temperature profiles typically show an induction stage (Jerez et al., 2005; Redl et al.,

253 2003), whereas the induction period vanishes when water is used in combination with

254 other plasticizer (Zárate-Ramírez et al., 2011). It seems that water plays the same role as

255 temperature as reported by Pommet et al. (2003) who did not find such induction stage

256 at temperatures above 40 ºC.

257

258 **Figure 1:** Torque (A) and temperature (B) profiles along mixing. WG: Wheat gluten. GL: Glycerol. GXAL: Glyoxal.

259 XG: Xanthan gum.

260 In view of the results from the mixing-rheometry test the selected mixing time for the

261 preparation of the different blends was 10 min. This mixing time seems to be long

262 enough to ensure a proper homogenization degree since it is much longer than the time

263 at which the torque peak is located and temperature remains moderate, indicating that

264 crosslinking reactions still play a minor role.

265 ### 3.2. Extrusion of gluten/plasticizer bioplastics

266 The dough-like blends, once mixed, were introduced in an extruder as mentioned in

267 section 2.2.2. Figure 2 shows the appearance of the bioplastic sheets after passing

268 through the extrusion or compression molding. As can be seen, the modification of

269 compression molding to extrusion (Figures 2A' and 2A) made a smooth change in the

270 colour of the bioplastic. In addition, the change of pH to that of the extruder reference

271 matrix WG/GL/W (Figures 2B and 2A, respectively) made its appearance more

272 homogeneous, with no surface roughness. This same behaviour was observed with the

273 incorporation of XG to the sample (Figure 2D). When GXAL was incorporated (Figure

274 2C), apart from the homogenization of its surface, there was also a significant browning

275 effect conferred by GXAL itself, which was due to occurrence of Maillard reactions.


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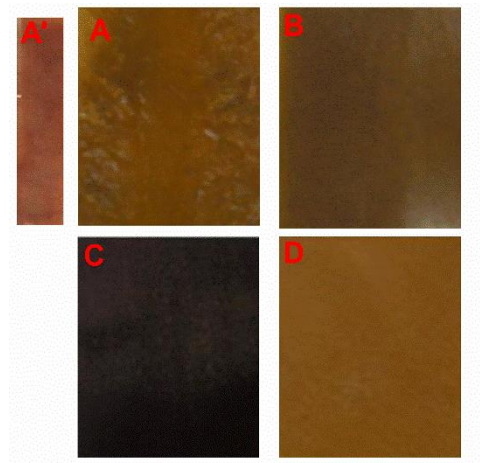
Figure 2: Bioplastics obtained with wheat gluten (WG), glycerol (GL), water (W), glyoxal (GXAL) and xanthan gum (XG) through compression moulding and extrusion. A': WG/GL/W by compression moulding. A: WG/GL/W by extrusion. B: WG/GL/W pH9. C: WG/GL/GXAL-W. D: WG/GL/XG-W.

3.3. Characterization of gluten/plasticizer bioplastic specimens

281 3.2.1. Dynamic Mechanical Temperature Analysis (DMTA)

282 Figure 3 shows the flexural storage modulus (E') and loss tangent (tan δ) values from

283 DMA tests, carried out by means of dual cantilever bending geometry, for modified

284 WG/GL/W bioplastics (pH variation, addition of XG or GXAL) processed by extrusion.

285 This figure also includes the results for the reference systems (WG/GL/W at pH 6)

286 prepared either by extrusion or compression molding. It can be observed that, regardless

287   of the composition of the specimen, E' had a similar evolution for all systems as

288   temperature rose up from -30 to 100 ℃, undergoing a dramatic decrease up to a plateau

289   value at 100 ℃. Later, there was a pronounced increase when temperature was further

290   increased for the sample with XG. This increase in elastic properties at temperatures

291   higher than 100℃ when XG is present indicates that it is possible to process those

292   systems at a molding temperature higher than 130 ℃ in order to achieve an enhanced

293   microstructure, which would result in higher E' values.
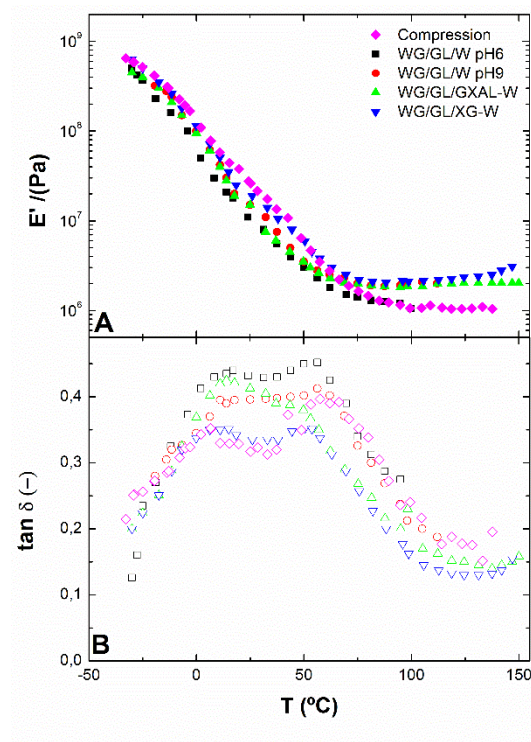
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295   **Figure 3:** Values of elastic flexural modulus E' (A) and loss tangent tan δ (B) from DMA temperature ramp

296   measurements for the different bioplastics obtained. WG: Wheat gluten. GL: Glycerol. W: Water. GXAL: Glyoxal.

297   XG: Xanthan gum.

298   In Figure 3B, tan δ profiles display two well-defined peaks for all the systems. These

299   maximum peaks were identified in a previous research for systems containing wheat

300   gluten as biopolymer and glycerol/water as plasticizer (Zárate-Ramírez et al., 2011).

301   The first peak may coincide with the characteristic glass transition of the plasticizer

302   blend, affected by some fraction of wheat gluten protein, whereas the second peak was

303 attributed to a glass transition of the plasticized wheat gluten (Jerez et al., 2005; Sun et

304 al., 2008, 2007). The change from compression molding processing to extrusion causes

305 an approach between the two peaks. A further approach takes place when any of the

306 additives is incorporated into the bioplastic, suggesting a greater degree of compatibility

307 between phases in the presence of the additives included. Therefore, extrusion proves to

308 be a more effective processing technique for the production of gluten bioplastics,

309 regarding the compatibility among ingredients. Moreover, extrusion shows the

310 advantage of being a continuous process compared to the discontinuous compression

311 molding.

312 The high values of E' for bioplastics with gum and the overlap of the tan δ peaks for

313 specimens with GXAL and XG, indicate that the shear and the relatively high

314 temperatures inside the extruder favour a greater degree of crosslinking and

315 compatibilization of the systems that incorporate these components, compared to those

316 that are free of additives. In fact, the shear can decrease the activation energy of the

317 crosslinking reactions and facilitate the interaction between the reactive groups of the

318 additives and those of the protein chains, while the high profiles of temperature would

319 help fix the structure of the bioplastic matrix (Domenek et al., 2003; Redl et al., 2003).

320   3.2.2. Uniaxial tension measurements

321 Figure 4 shows the values of the parameters obtained from tensile tests for the different

322 bioplastics studied. This figure collects the maximum strain (ε_{max}), the maximum stress

323 (σ_{max}) and the Young's modulus (E) values. First, the change from compression

324 molding to extrusion processing produced an increase in ε_{max} and E values, but a

325 decrease in σ_{max} values. On the other hand, regarding the different bioplastics made by

326 extrusion, the WG/GL/W specimen prepared at pH 9 showed the highest values of σ_{max}

327 and ε_{max}. This behaviour may be due to the fact that the alkaline pH favours the

328 aggregation of wheat gluten proteins and the formation of bonds through SH-SS

329 exchange, oxidation of SH groups, lanthionine formation (LAN) and/or Maillard

330 reactions (Gerrard and Brown, 2002; Olabarrieta et al., 2006). The slightly darker

331 extrusion profiles obtained at pH 9 seems to support this later mechanism. Therefore,

332 the alkaline medium would allow the formation of a wheat gluten matrix with a good

333 degree of crosslinking, being more stable and with stronger intermolecular interactions

334 between components. Secondly, the high temperatures used for the formation of sheets

335 with GXAL and XG lead to a high polymerization, giving rise to bioplastics with low

336 values of σ_{max} and ε_{max}, which are more pronounced for the bioplastics containing

337 GXAL (WG/GL/GXAL-W).
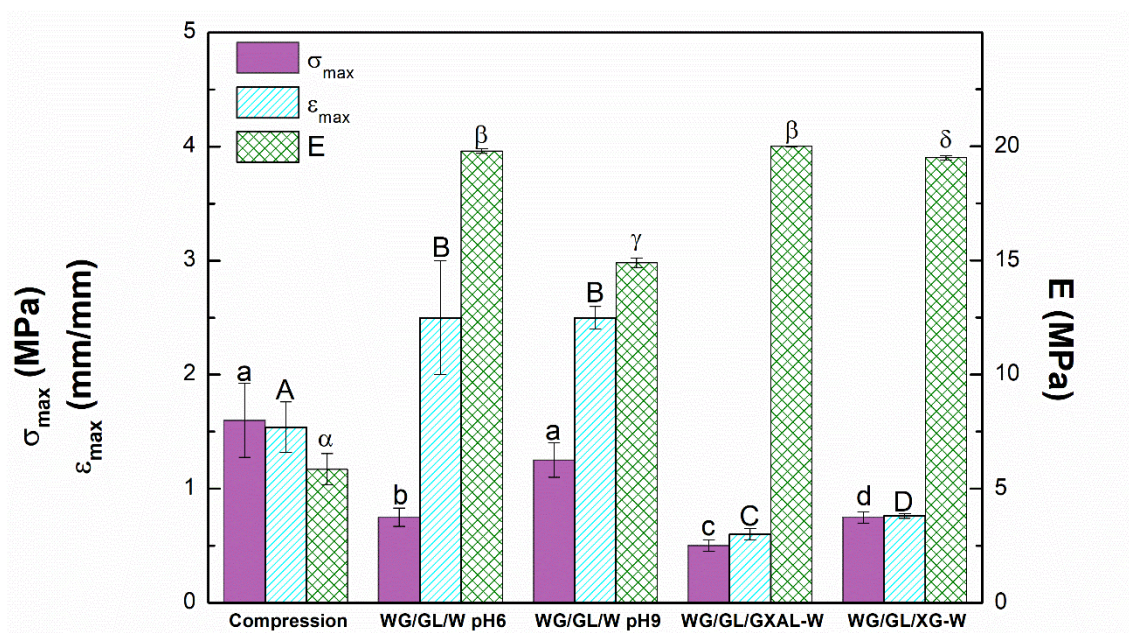
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339 **Figure 4:** Representative parameters (σ_{max}, ε_{max} and E) obtained from tensile strength tests performed on the different

340 samples processed by compression moulding and extrusion. WG: Wheat gluten. GL: Glycerol. W: Water. GXAL:

341 Glyoxal. XG: Xanthan gum.

342 Mechanical properties of wheat gluten bioplastics here presented are well below that

343 reported for some typical commercial polymeric materials, like polypropylene (E: 1.5-2

344 GPa) or epoxies (E: 2-3 GPa), (Lagrain et al., 2010) and even lower than low molecular

345   weight polyethylene (LDPE. E: 250 MPa) ("ASTM D638-14: Standard Test Method for

346   Tensile Properties of Plastics," 2014) but bring biodegradability or a dependency on a

347   renewable resource as advantages. However, they still need to prove they are cheaper to

348   produce than their petrochemical counterparts to successfully penetrate in the plastic

349   market (Patni et al., 2014).

350   3.2.3. Water absorption tests

351   The parameters obtained from water absorption tests is showed in Figure 5. Thus, the 2

352   and 24 h water uptake capacity values and the soluble matter loss are represented. As

353   can be observed, the use of extrusion instead of compression molding lead to a clear

354   improvement for the water uptake capacity after 2h but to a reduction after 24 h. When

355   comparing the different bioplastics made by extrusion, the WG/GL/W system at pH 9

356   presented a noticeable improvement in water uptake (particularly after 24 h) over the

357   reference (WG/GL/W at pH 6 by extrusion), whereas the rest of specimens showed a

358   moderate decrease in values as compared to the reference, being the GXAL system

359   which yielded the lowest values. It is worth pointing out that among the extruded

360   systems, the specimen showing higher WUC was one of the systems processed under

361   milder thermal conditions and was also the system displaying the lowest Young's

362   modulus. On the other hand, the bioplastics with additive (GXAL or XG) have a

363   crosslinked structure that would give less space to the interaction with water molecules,

364   resulting in lower percentages of water uptake capacity.

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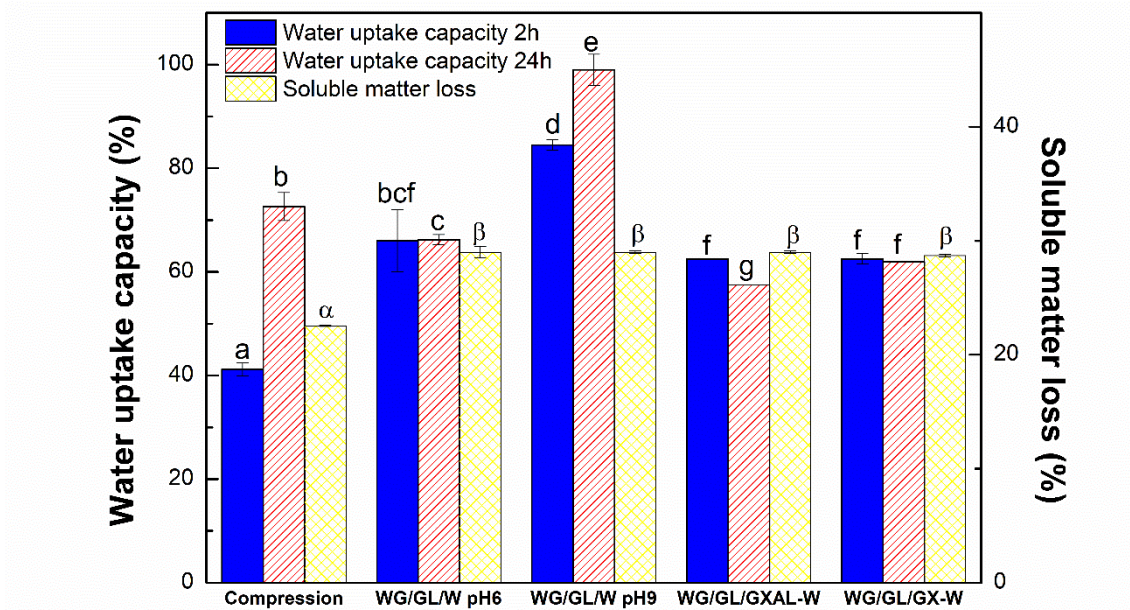
Figure 5: Water uptake capacity and soluble matter loss obtained for samples subjected to immersion for 2 and 24 h of immersion. WG: Wheat gluten. GL: Glycerol. W: Water. GXAL: Glyoxal. XG: Xanthan gum.

As for the soluble matter loss, this was lower when the bioplastic was made by compression molding. This fact together with the lower water uptake capacity denotes that a more closed structure is achieved when the bioplastics are made through compression molding. In addition, significant differences were not found between the different systems elaborated by extrusion.

4. Conclusions

In order to face the environmental issues related to the ubiquitous presence of plastic materials, it is interesting to assess the industrial production of bioplastic materials through well-stablished technologies, such as extrusion or compression.

Firstly, it was observed that extrusion gave rise to bioplastics with greater compatibility between their components when compared to compression molding, assuming an improvement both in mechanical properties and water uptake capacity. These results

381   may be due to a greater level of aggregation/crosslinking and structural alignment

382   within the sheets in the flow direction of the extrusion.

383   Different results were obtained when the effect of pH or the presence of additives

384   (glyoxal and xanthan gum) were studied. Therefore, it was observed that a change of pH

385   to a more alkaline pH improved the water uptake capacity of the bioplastics. Although

386   this took place at the expense of mechanical properties such as Young's modulus, the

387   physical integrity was clearly maintained. However, when bioplastics were produced

388   with additives (GXAL and XG), a higher polymerization occurred due to the high

389   temperatures used, giving rise to bioplastics with mechanical and absorption properties

390   which slightly differ from those of the reference system (WG/GL/W at pH 6 by

391   extrusion). So, the presence of additives resulted in materials that were generally less

392   deformable and, consequently, presented a limited swell-ability, retaining a lower

393   amount of water.

394   These results prove the great potential presented by wheat gluten-based bioplastics

395   processed through extrusion for the replacement of conventional plastics. The use of the

396   most frequently used technique for plastic processing may facilitate the bioplastic

397   production at an industrial scale.

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