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Bioplastics based on wheat gluten processed by extrusion

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ABSTRACT

Recently, bioplastic have generated an increasing interest as an alternative to conventional plastics. For this reason, their manufacture using the traditional techniques used for the production of plastics, such as extrusion, would help transferring bioplastics production to an industrial scale. In this way, the preparation of wheat gluten bioplastics by extrusion was the main objective of this research, modifying their structure by varying the pH value or by incorporating additives (glyoxal or xanthan gum). These bioplastics were characterized by the measurement of their mechanical properties and their water uptake capacity, proving that the modification of bioplastics cause variations in their properties. Thus, extrusion resulted in a greater gluten-plasticizer compatibility compared to compression, as denoted the temperature ramp tests, especially in the presence of additives (ie. Xanthan gum, glyoxal). Moreover, tensile strength was enhanced at pH 9, probably due to bonding promotion at alkaline conditions. These results demonstrate the great potential of these materials for the replacement of conventional plastics.

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 bioethanol 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).

One of the most used techniques for the production of plastics is extrusion, due to its high mixing and molding efficiency for thermoplastic materials (Pommet et al., 2003). Most of the commercial synthetic plastic films (i.e. polyethylene) are produced in extruders (Hernandez-Izquierdo and Krochta, 2008). The use of this widespread technology with an agricultural renewable raw material, such as wheat gluten, represents an interesting opportunity for the industrial production of bioplastics (Gug et al., 2018; Herniou-Julien et al., 2019; Mathiot et al., 2019; Pommet et al., 2003), helping their

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industrial scale-up (Ferrar et al., 2018). Unlike thermoplastic polymers, wheat gluten protein may undergo some crosslinking reactions upon heating, which would eventually result in an increase in the viscoelastic properties of plasticized gluten-based materials. These structural changes occur at lower temperatures compared to synthetic polymers (Balaguer et al., 2014; Lagrain et al., 2010). In this way, the extrusion of wheat gluten is only possible under certain operating conditions, ranging from the point at which protein chains begin to flow to the point where they start to aggregate.

In the extrusion of wheat gluten proteins, certain key parameters must be considered in order to have optimal operating conditions, such as plasticizer content, mechanical energy input, applied shear, as well as operating time, temperature and pressure. Therefore, the degree of aggregation, molecular conformational changes and chemical crosslinking that occur along the extrusion process can be determined by these parameters. In this respect, it is important not only to select an adequate temperature window to obtain a moderate viscosity, which facilitates the processing of the protein/plasticizer blend, but also to ensure a proper aggregation of protein molecules that allows the formation of a homogeneous material, without exceeding thermal conditions leading to degradation. On the one hand, the lowest temperature is defined by the glass transition temperature of the protein, which is required to allow the material to achieve its final shape (Ullsten et al., 2009). On the other hand, the upper temperature limit is defined by either an extensive aggregation or the thermal degradation of the protein. Thus, wheat gluten materials are generally processed between 80 and 130 °C, with their properties depending on those operating conditions (Redl et al., 2003).

Another parameter to be considered when replacing conventional plastics with any alternative bioplastic is their final properties, such as their mechanical characteristics and water uptake capacity. Within this scope, several techniques have been investigated to reinforce bioplastics and improve their characteristics (Rasheed et al., 2018; Thammahiwes et al., 2018, 2017). In this manner, studies can be found where the pH of the bioplastics has been modified (Cortes-Trivino and Martinez, 2018), altering the net charge of the protein system as it moves further away from the isoelectric point. Thus, a pH shift may enhance certain bioplastic properties, such as Young's modulus or absorption capacity, as it strongly influences the nature of intermolecular interactions. Another procedure investigated to improve the quality of bioplastics is the inclusion of different additives in the system (Cieśla et al., 2006; Erdohan and Turhan, 2005; Gounga et al., 2007; Parris et al., 1995; Siracusa et al., 2008; Turkoz et al., 2018). The addition of polysaccharides into a protein matrix, with both of them being complex heteropolymers, may promote the formation of non-covalent interactions and intermolecular linkages between them (Turgeon et al., 2003). For this reason, protein-polysaccharide mixtures may present a wide range of structures with different rheological and physical-chemical properties that may allow the tailoring of the final properties of the bioplastic material (Coughlan et al., 2004; Gómez-Martínez et al., 2009; López-Castejón et al., 2016; Schmitt et al., 2009, 1998; Turgeon and Beaulieu, 2001; Zaleska et al., 2000). Although some gums, such as xanthan gum, have proved to be stable over a wide pH and temperature range, as well as to enzymatic degradation or in the presence of salts (Sworn, 2009; Vega et al., 2015), all these factors may alter the protein-polysaccharide interactions. Since xanthan gum is an anionic polymer, depending on whether the pH is below or above the protein isoelectric point (IEP), attractive or repulsive electrostatic interactions between the protein and the polysaccharide are expected (Gosh and Bandyopadhyay, 2012). On the other hand, the incorporation of crosslinking additives, such as aldehydes (e.g. glyoxal), to wheat gluten protein-based bioplastics has proved to promote covalent crosslinking both intra- and intermolecularly in wheat gluten protein (Zárate-Ramírez et al., 2014b). However, Bruyninckx et al. (2016) have recently shown that an increase in crosslink density does not always lead to enhanced mechanical properties of gluten-based bioplastics. These authors postulated that crosslinks between protein segments may lead to a positive reinforcement of the protein network, although but they may also force some kind of unfavorable configurations that could prevent the formation of further physical entanglements, thus compromising the overall network quality.

Taking into account all these parameters, the overall aim of this research was to process biodegradable protein-based bioplastics with wheat gluten by extrusion, comparing this with the compression molding method and determining the influence of the pH modification and the addition of xanthan gum (polysaccharide) and glyoxal (aldehyde) to them. In this way, their rheological properties and water uptake capacity were 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 percentage of water required to maintain the initial ratio WG:GL (25:9). These modifications were carried out following the same procedure used in previous papers (Zárate-Ramírez et al., 2014b) (Zárate-Ramírez et al., 2014a).

The mixing process was carried out under adiabatic conditions at 50 rpm for 10 min approximately. Other authors have also used this mixing step (Ottenhof and Farhat, 2004; Türe et al., 2012; Ullsten et al., 2009) in order to facilitate the thermomechanical processing through extrusion (Chantapet et al., 2013; Ottenhof and Farhat, 2004), thermo or compression molding (Jerez et al., 2007; Sun et al., 2008) and injection molding (John et al., 1998). All of them, traditional polymer processing techniques that can improve the industrial escalation of this bioplastic. However, the properties

of the final dough-like material blends may affect their subsequent processing. Thus, it is very convenient to monitor parameter such as, torque and temperature throughout the mixing time.

2.2.2. Extrusion of gluten/plasticizer bioplastics

The dough-like materials after the mixing step were introduced into a Rheomex 302p screw extruder (Thermo-Haake, Germany) coupled to the mixer. This extruder has a spindle barrel diameter of 19 mm with a total length of 830 mm. In addition, it has an electric heating system at four zones (feed, nozzle and two in the mixing zone) from where the temperature profile indicated in Table 1 was established for the different blends (based on previous studies). The nozzle used was of laminar geometry, and the spindle speed applied was 30 rpm.

2.2.3. Die cutting

The material obtained after the extrusion step was subjected to punching to obtain bioplastic specimens with different dimensions: rectangular probes (50 × 10 × 3 mm) and type IV probes ("ASTM D638-14: Standard Test Method for Tensile Properties of Plastics," 2014).

2.2.4. Compression molding of gluten/plasticizer blends

Different bioplastic specimens (rectangular and type IV) of the reference formulation (WG/GL/W at pH 6) were also processed by compression molding in order to make a comparison with those specimens prepared by extrusion (and die-cutting). In this case, the blends were subjected to compressing molding at 130 °C and 9 MPa for 10 min, following a procedure previously described (Zárate-Ramírez et al., 2014a, 2014b, 2011).

2.2.5. Conditioning of moisture content of gluten/plasticizer specimens

All the probes obtained by extrusion and die cutting or by compression molding were subjected to a conditioning step for 2 weeks before testing into recipients at 53% relative humidity (RH) to reach moisture equilibrium at room temperature. After this conditioning period, the actual moisture content was determined maintaining each sample for 24 h at 105 °C ((AOAC), 2003).

2.3. Characterization of gluten/plasticizer bioplastic specimens

2.3.1. Dynamic mechanical temperature analysis (DMTA)

DMTA tests were carried out with a dynamic-mechanical strain analyser RSA3 (TA Instruments, USA) with a dual cantilever bending geometry. The tests were performed on rectangular probes from −30 to 130 °C at a heating rate of 3 °C·min^{-1}. The frequency was kept constant at 1 Hz and a strain between 0.01 and 0.3 was used (i.e, well within the linear viscoelastic region). Results were obtained for the elastic (E′) and viscous (E″) moduli and loss tangent (tan δ).

2.3.2. Uniaxial tension tests

The Insight 10 kN Electromechanical Testing System (MTS, USA) was used to perform the tensile measurements, according to ASTM D638 ("ASTM D638-14: Standard Test Method for Tensile Properties of Plastics," 2014). So, type IV probes were subjected to an extensional rate of 22 mm min^{-1} at room temperature, recording the strain at break (ε_{max}), maximum tensile stress (σ_{max}) and Young's modulus (E).

2.3.3. Water absorption tests

Water absorption tests was carried out following the ASTM D570-98 norm ("ASTM D570-98: Standard Test Method for Water Absorption Of Plastics," 2005), where rectangular probes were immersed in 300 mL of distilled water for 24 h at room temperature.

2.4. Statistical analysis

The data were presented as mean ± standard deviation (SD) of at least three (water uptake capacity and DMTA tests) or six (tensile tests) determinations. A probability value of $p < 0.05$ was considered significant.

3. Results and discussion

3.1. Batch mixing of gluten/plasticizer samples

Fig. 1 shows the torque (M) and temperature (T) profiles obtained by the systems WG/GL/W with different modifications during the mixing step. As may observed in Fig. 1A, all systems show an increase in the mixing torque up to a maximum value, followed by an asymptotic decrease. The torque profile for the blend prepared with XG shows a delay time in its evolution over the other blends, as well as a displacement towards higher values. Both effects can be also observed in the thermal profile (Fig. 1B). These results might be caused by the higher mobility induced by the presence of water, which exhibits a higher plasticising efficiency than the XG dispersion. The plasticising efficiency is generally based on the ability of an ingredient to decrease the glass transition temperature, T_g, resulting in a softening of the structure (Verbeek and van den Berg, 2010). Water is an efficient plasticizer for proteins as it enters easily the protein network, preventing protein-protein interaction and thereby promoting chains mobility. It must be considered that when a hydrophilic compound like XG is present, the large number of hydroxyl groups present within its structure show a great affinity to bind water. The high-water binding capacity of XG reduces the amount of free water available, which retards the movement of particles along mixing (Noorlaila et al., 2017). Moreover, the energy dissipation is higher for modified blends as the change (pH or additives) contributes a higher viscosity to the medium. This behaviour is also found in data reported in the literature (Redl et al., 2003). Thus, in absence of water, torque and temperature profiles typically show an induction stage (Jerez et al., 2005; Redl et al., 2003), whereas the induction period vanishes when water is used in combination with other plasticizer (Zárate-Ramírez et al., 2011). It seems that water plays the same role as temperature as reported by Pommet et al. (2003) who did not find such induction stage at temperatures above 40 °C.

In view of the results from the mixing-rheometry test the selected mixing time for the preparation of the different blends was 10 min. This mixing time seems to be long enough to ensure a proper homogenization degree since it is much longer than the time at which the torque peak is located and temperature remains moderate, indicating that crosslinking reactions still play a minor role.

Table 1
Temperature profile used during the extrusion of the dough-like materials of wheat gluten (WG), glycerol (GL), water (W) and different percentages of xanthan gum (XG, 0 and 1.5 wt%).

Systems	Feed (°C)	Mixing zone 1(°C)	Mixing zone 2(°C)	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

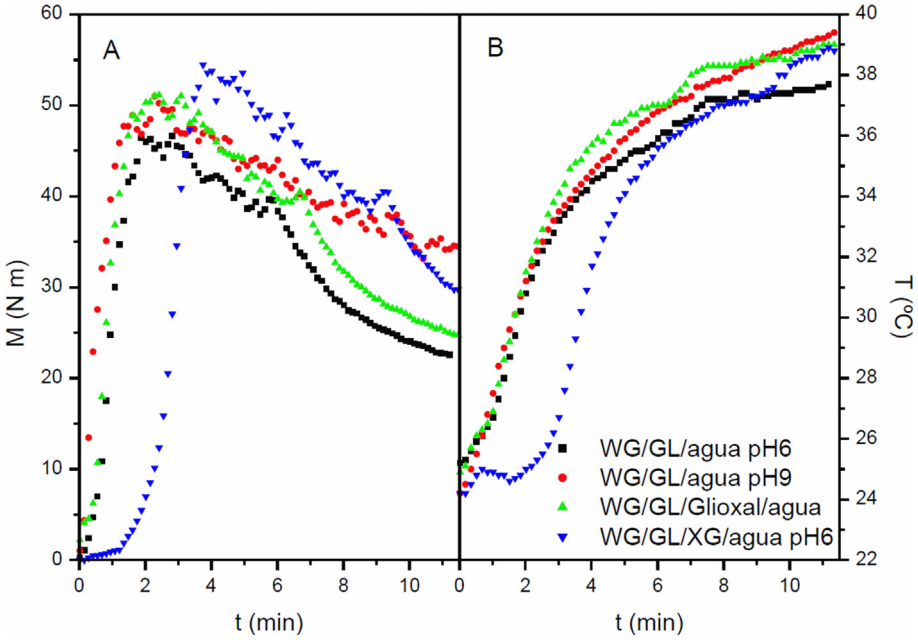

Fig. 1. Torque (A) and temperature (B) profiles along mixing. WG: Wheat gluten. GL: Glycerol. GXAL: Glyoxal. XG: Xanthan gum.

3.2. Extrusion of gluten/plasticizer bioplastics

The dough-like blends, once mixed, were introduced in an extruder as mentioned in section 2.2.2. Fig. 2 shows the appearance of the bioplastic sheets after passing through the extrusion or compression molding. As can be seen, the modification of compression molding to extrusion (Fig. 2A' and 2A) made a smooth change in the colour of the bioplastic. In addition, the change of pH to that of the extruder reference matrix WG/GL/W (Fig. 2B and A, respectively) made its appearance more homogeneous, with no surface roughness. This same behaviour was observed with the incorporation of XG to the sample (Fig. 2D). When GXAL was incorporated (Fig. 2C), apart from the homogenization of its surface, there was also a significant browning effect conferred by GXAL itself, which was due to occurrence of Maillard reactions.

3.3. Characterization of gluten/plasticizer bioplastic specimens

3.3.1. Dynamic mechanical temperature analysis (DMTA)

Fig. 3 shows the flexural storage modulus (E′) and loss tangent (tan δ) values from DMA tests, carried out by means of dual cantilever bending geometry, for modified WG/GL/W bioplastics (pH variation, addition of XG or GXAL) processed by extrusion. This figure also includes the results for the reference systems (WG/GL/W at pH 6) prepared either by extrusion or compression molding. It can be observed that, regardless of the composition of the specimen, E′ had a similar evolution for all systems as temperature rose up from −30 to 100 °C, undergoing a dramatic decrease up to a plateau value at 100 °C. Later, there was a pronounced increase when temperature was further increased for the sample with XG. This increase in elastic properties at temperatures higher than 100 °C when XG is present indicates that it is possible to process those systems at a molding temperature higher than 130 °C in order to achieve an enhanced microstructure, which would result in higher E' values.

In Fig. 3B, tan δ profiles display two well-defined peaks for all the systems. These maximum peaks were identified in a previous research for systems containing wheat gluten as biopolymer and glycerol/water as plasticizer (Zárate-Ramírez et al., 2011). The first peak may coincide with the characteristic glass transition of the plasticizer blend, affected by some fraction of wheat gluten protein, whereas the second peak was attributed to a glass transition of the plasticized wheat gluten (Jerez et al., 2005; Sun et al., 2008, 2007). The change from compression molding processing to extrusion causes an approach between the two peaks. A further approach takes place when any of the additives is incorporated into the bioplastic, suggesting a greater degree of compatibility between phases in the presence of the additives included. Therefore, extrusion proves to be a more effective processing technique for the production of gluten bioplastics, regarding the compatibility among ingredients. Moreover, extrusion shows the advantage of being a continuous process compared to the discontinuous compression molding.

The high values of E' for bioplastics with gum and the overlap of the tan δ peaks for specimens with GXAL and XG, indicate that the shear and the relatively high temperatures inside the extruder favour a greater degree of crosslinking and compatibilization of the systems that incorporate these components, compared to those that are free of additives. In fact, the shear can decrease the activation energy of the crosslinking reactions and facilitate the interaction between the reactive groups of the additives and those of the protein chains, while the high profiles of temperature would help fix the structure of the bioplastic matrix (Domenek et al., 2003; Redl et al., 2003).

3.3.2. Uniaxial tension measurements

Fig. 4 shows the values of the parameters obtained from tensile tests for the different bioplastics studied. This figure collects the maximum strain (ε_{max}), the maximum stress (σ_{max}) and the Young's modulus (E) values. First, the change from compression molding to extrusion processing produced an increase in ε_{max} and E values, but a decrease in σ_{max} values. On the other hand, regarding the different bioplastics made by extrusion, the WG/GL/W specimen prepared at pH 9 showed the highest values of σ_{max} and ε_{max}. This behaviour may be due to the fact that the alkaline pH favours the aggregation of wheat gluten proteins and the formation of

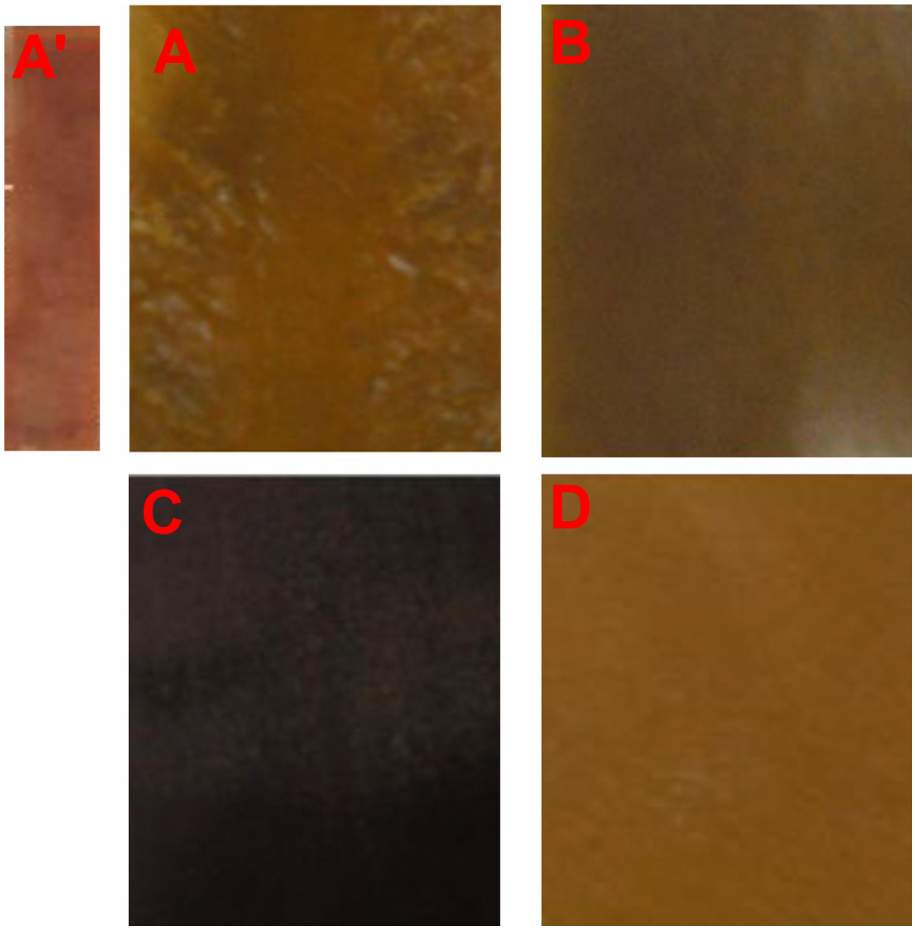

Fig. 2. Bioplastics obtained with wheat gluten (WG), glycerol (GL), water (W), glyoxal (GXAL) and xanthan gum (XG) through compression molding and extrusion. A': WG/GL/W by compression molding. A: WG/GL/W by extrusion. B: WG/GL/W pH9. C: WG/GL/GXAL-W. D: WG/GL/XG-W.

bonds through SH-SS exchange, oxidation of SH groups, lanthionine formation (LAN) and/or Maillard reactions (Gerrard and Brown, 2002; Olabarrieta et al., 2006). The slightly darker extrusion profiles obtained at pH 9 seems to support this later mechanism. Therefore, the alkaline medium would allow the formation of a wheat gluten matrix with a good degree of crosslinking, being more stable and with stronger intermolecular interactions between components. Secondly, the high temperatures used for the formation of sheets with GXAL and XG lead to a high polymerization, giving rise to bioplastics with low values of σ_{max} and ε_{max}, which are more pronounced for the bioplastics containing GXAL (WG/GL/GXAL-W).

Mechanical properties of wheat gluten bioplastics here presented are well below that reported for some typical commercial polymeric materials, like polypropylene (E: 1.5–2 GPa) or epoxies (E: 2–3 GPa) (Lagrain et al., 2010), and even lower than low molecular weight polyethylene (LDPE. E: 250 MPa) ("ASTM D638-14: Standard Test Method for Tensile Properties of Plastics," 2014) but bring biodegradability or a dependency on a renewable resource as advantages. However, they still need to prove they are cheaper to produce than their petrochemical counterparts to successfully penetrate in the plastic market (Patni et al., 2014).

3.3.3. Water absorption tests

The parameters obtained from water absorption tests is showed in Fig. 5. Thus, the 2 and 24 h water uptake capacity values and the soluble matter loss are represented. As can be observed, the use of extrusion instead of compression molding lead to a clear improvement for the water uptake capacity after 2 h but to a reduction after 24 h. When comparing the different bioplastics made by extrusion, the WG/GL/W system at pH 9 presented a noticeable improvement in water uptake (particularly after 24 h) over the reference (WG/GL/W at pH 6 by extrusion), whereas the rest of specimens showed a moderate decrease in values as compared to the reference, being the GXAL system which yielded the lowest values. It is worth pointing out that among the extruded systems, the specimen showing higher WUC was one of the systems processed under milder thermal conditions and was also the system displaying the lowest Young's modulus. On the other hand, the bioplastics with additive (GXAL or XG) have a crosslinked structure that would give less space to the interaction with water molecules, resulting in lower percentages of water uptake capacity.

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-

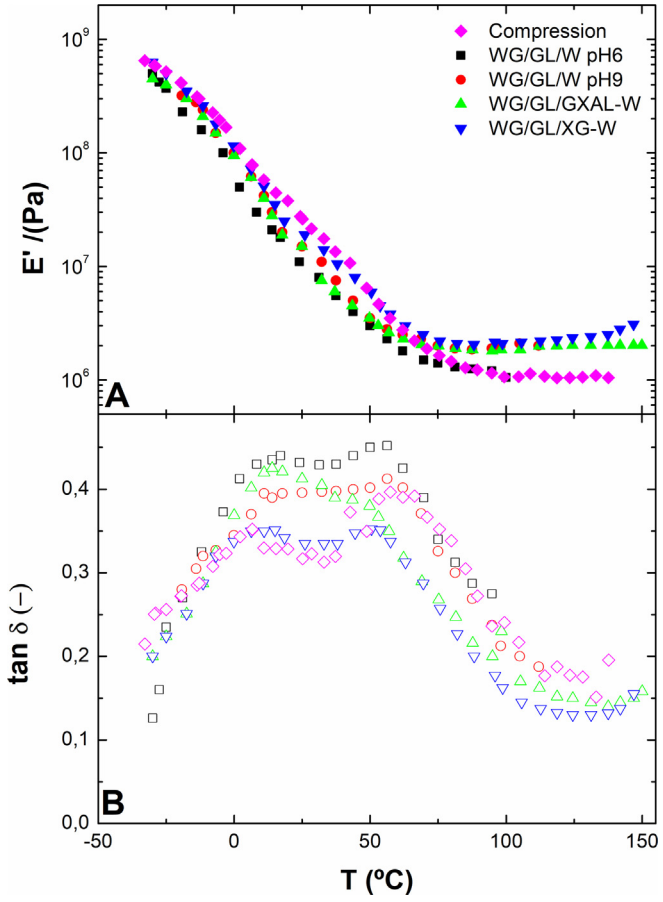

Fig. 3. Values of elastic flexural modulus E' (A) and loss tangent tan δ (B) from DMA temperature ramp measurements for the different bioplastics obtained. WG: Wheat gluten. GL: Glycerol. W: Water. GXAL: Glyoxal. XG: Xanthan gum.

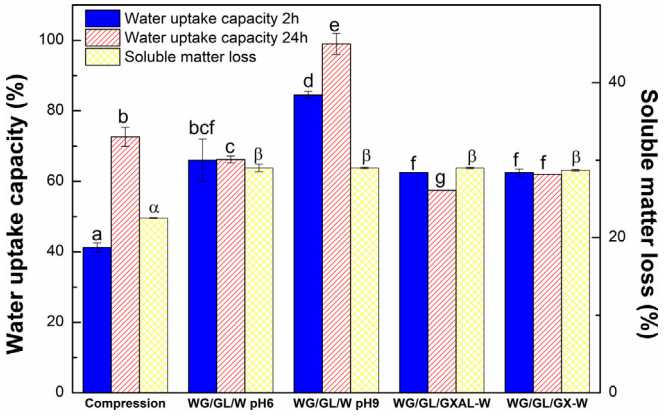

Fig. 5. Water uptake capacity and soluble matter loss obtained for samples subjected to immersion for 2 and 24 h of immersion. WG: Wheat gluten. GL: Glycerol. W: Water. GXAL: Glyoxal. XG: Xanthan gum.

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 may be due to a greater level of aggregation/crosslinking and structural alignment within the sheets in the flow direction of the extrusion.

Different results were obtained when the effect of pH or the presence of additives (glyoxal and xanthan gum) were studied. Therefore, it was observed that a change of pH to a more alkaline pH improved the water uptake capacity of the bioplastics. Although this took place at the expense of mechanical properties such as Young's modulus, the physical integrity was clearly maintained. However, when bioplastics were produced with additives (GXAL

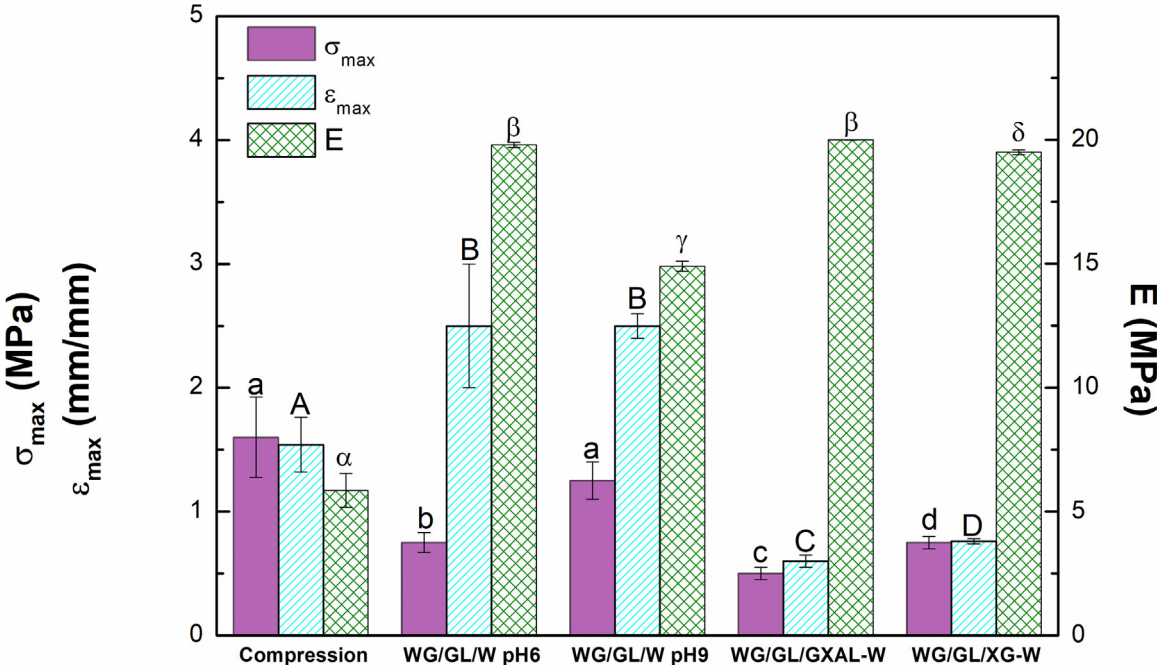

Fig. 4. Representative parameters (σ_{max}, ε_{max} and E) obtained from tensile strength tests performed on the different samples processed by compression molding and extrusion. WG: Wheat gluten. GL: Glycerol. W: Water. GXAL: Glyoxal. XG: Xanthan gum.

and XG), a higher polymerization occurred due to the high temperatures used, giving rise to bioplastics with mechanical and absorption properties which slightly differ from those of the reference system (WG/GL/W at pH 6 by extrusion). So, the presence of additives resulted in materials that were generally less deformable and, consequently, presented a limited swell-ability, retaining a lower amount of water.

These results prove the great potential presented by wheat gluten-based bioplastics processed through extrusion for the replacement of conventional plastics. The use of the most frequently used technique for plastic processing may facilitate the bioplastic production at an industrial scale.

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