

## Effect of the injection moulding processing conditions on the development of pea protein-based bioplastics

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**ABSTRACT:** Bioplastic materials from renewable polymers, like proteins, constitute a highly interesting field for important industrial applications such as packaging, agriculture, etc., in which thermo-mechanical techniques are increasingly being used. Pea protein-based bioplastics can be made through a mixing process followed by an injection moulding. The objective of this study was to investigate the influence of different injection parameters (moulding time and injection pressure) on the properties exhibited by the final bioplastics obtained. A dynamic mechanical analysis and tensile strength measurements were performed, along with water absorption capacity and transparency tests. The results indicated that the major differences between bioplastics obtained at different moulding times are in transparency and in the Young's Moduli, exhibiting lower values as moulding time increases. On the other hand, modifying the injection pressure lead to more consistent bioplastics which differed mainly in the elastic component ( $E'$  profiles) and in the strain at break. Furthermore, the water uptake was more than 100% in almost all the different bioplastics processed because of its hydrophilic character, so they could be considered as potential sources for absorbent material. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43306.

**KEYWORDS:** biodegradable; blends; coatings; proteins; rheology

Received 15 October 2015; accepted 4 December 2015

DOI: 10.1002/app.43306

### INTRODUCTION

Proteins, polysaccharides, and lipids are suitable raw materials for the production of bioplastics.<sup>1–3</sup> In particular, starch is widely used as a packaging material, usually mixed with biodegradable polyesters.<sup>4</sup> Regarding proteins to manufacture bioplastics, research studies have investigated not only plant proteins such as zein, wheat gluten, and soybean,<sup>5–7</sup> but also, in some cases, animal proteins, such as milk proteins, collagen, gelatine, etc.<sup>8,9</sup> However, pea protein has increasingly become an adequate raw material because of its price and excellent properties.<sup>10–12</sup> Protein concentrates have been widely used as raw materials, but those bioplastics obtained simply by the action of pressure and temperature. However, the combination of intermolecular disulphide bonding, hydrogen bonding, hydrophobic interactions, and electrostatic forces between proteins chains typically leads to a fragile and brittle protein structures.<sup>13</sup> For that reason, protein concentrates are generally mixed with a plasticizer.

With regard to plasticizers, they are used in order to reduce intermolecular forces among polymer chains,<sup>14,15</sup> reducing the cohesion within the matrix and facilitating the mobility of protein chains.<sup>16</sup> The use of hydrophilic plasticizers with low molecular weight improves the flexibility of the final bioplastics

obtained, but they cannot support a lower mechanical stress. The most effective plasticizer, for biopolymers, is water because reduces the glass transition temperature facilitating the processing. Without water addition, the degradation temperature would be easily reached before bioplastics would be finally processed.<sup>17</sup> Besides water, glycerol is a plasticizer widely used in thermomechanical processing of proteins.<sup>8,18</sup> Its effect is related to the facility of glycerol to be inserted inside the three-dimensional structure of biopolymers.<sup>19</sup>

Considering the processing method, classical thermoplastic polymer processing techniques (extrusion, compression moulding, etc.) have been used to obtain different protein-based bioplastic materials.<sup>20–22</sup> Among these thermomechanical techniques, injection moulding is one of the most important and suitable processes for systems that may exhibit a mixed character such as proteins,<sup>23–26</sup> but it needs a previous mixing process in order to obtain a suitable protein-plasticizer blend. It is important to select the optimum injection parameters (injection pressure and moulding time),<sup>27</sup> but also the temperature in the pre-injection cylinder, high enough to reduce the viscosity of the blend (facilitating the subsequent injection) and leading to heating changes the three-dimensional structure of proteins (protein unfolding and denaturation) by disrupting hydrogen

bonds and nonpolar hydrophobic groups.<sup>28</sup> Regarding protein films, resulting electrostatic interactions, hydrogen bonding, van der Waals forces (noncovalent forces), and covalent disulfide bridges can improve the matrix stability.<sup>29</sup> However, it is important to avoid so high temperature in the cylinder to avoid protein cross-linking by covalent intermolecular disulfide bonds or even protein degradation.<sup>25</sup> Furthermore, exposure to alkaline conditions, particularly when coupled to thermal processing, induces formation of nondisulphide covalent cross-links, such as dehydroalanine, lysinoalanine, and lanthionine.<sup>30,31</sup> On the other hand, it is important to control the conditions in the packing stage and in the previous injection process, selecting the appropriate conditions to ensure an optimum injection speed related with the lowering speed of the piston, allowing the blend to be inserted into the mould. Depending on the conditions selected, the bioplastics fabricated would exhibit adequate properties to consider them for specific applications. In this way, not only preparation conditions are important, but only other components in the formulation such as plasticizers, pH, chemicals, enzymes, nanocomposites, lipids and as well as cross-linking by irradiation.<sup>32</sup>

The main objective of this work was to explore the potential development of biobased plastic materials from pea protein processed by injection moulding and to study the influence of injection conditions in the packing stage (moulding time and injection pressure) on their mechanical properties. Furthermore, a mechanical characterization (water absorption and transparency measurements) was useful to evaluate the effects of the modification of the injection parameters on the final bioplastics properties. A small-scale-plunger-type injection moulding machine was used in this study to obtain pea protein-based specimens from pea protein/glycerol blends, previously mixed by means of a mixing rheometer that allows the torque and temperature to be recorded during mixing process.

## MATERIAL AND METHODS

### Materials

Pea flour was provided by Roquette (Lestrem, France). Its protein content, obtained in quadruplicate as % N  $\times$  6.25 using a LECO CHNS-932 nitrogen microanalyzer (Leco Corporation, St. Joseph, MI, USA) was so close to 90% ( $89.5 \pm 0.7\%$ ) that it can be considered as a protein isolate (PPI).<sup>32</sup> Besides, microanalysis results revealed a sulphur content of  $0.45 \pm 0.02\%$ , related to the presence of methionine and cysteine and its importance on generating cross-linking. The ash and lipids content of the protein isolate were  $3.5 \pm 0.2\%$  and  $1.4 \pm 0.6\%$ , respectively. Besides, the pea protein isolate presents a moisture content close to 5% ( $5.1 \pm 0.1\%$ ). Glycerol (GL) with residual water content  $\leq 0.3\%$  was purchased from Panreac Química, S.A. (Spain).

### Characterization of Blends

**Rheological Measurements.** Dough-like blends were characterized by small amplitude oscillatory shear (SAOS) measurements, using a controlled-strain rheometer (ARES, TA Instruments, USA). A plate-plate geometry (dia: 40 mm) with a rough surface has been used, selecting a gap between plates of 2 mm. Low viscosity Dow Corning 200 fluid was used as sealant to

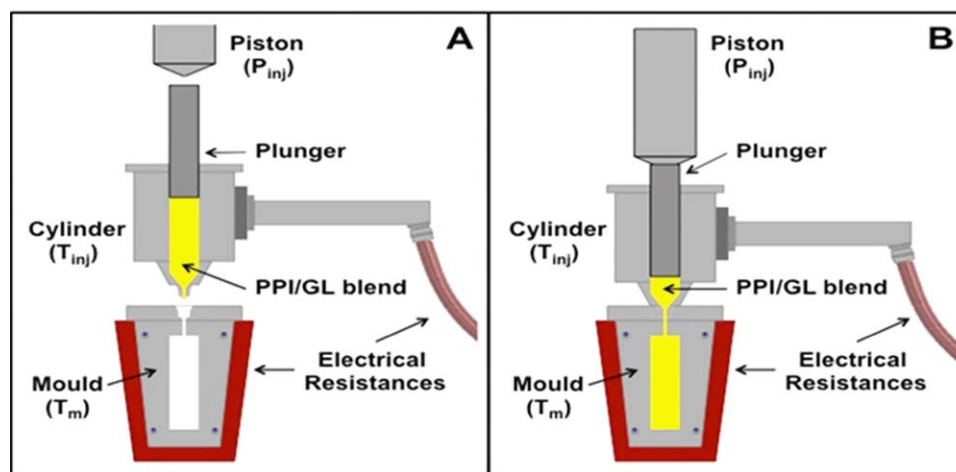
avoid sample drying. Strain sweep SAOS tests were also performed in order to establish the linear viscoelasticity range. Temperature ramp tests were carried out at  $5^\circ\text{C}/\text{min}$  from  $20^\circ\text{C}$  to  $100^\circ\text{C}$ . In these measurements, complex viscosity ( $\eta^*$ ) was monitored at a constant frequency of 6.28 rad/s. All the systems studied had the same thermo-rheological history before performing any rheological test.

### Preparation of Bioplastics

Bioplastics with a 60PPI/40GL ratio (lower protein/plasticizer ratios would lead to an excess of plasticizer that yields too low consistent blends to be properly processed and an increase of this ratio would produce some shear-induced cross-linking effects leading to excessively brittle specimens) were manufactured by a two-stage thermo-mechanical procedure. Firstly, the selected blend was mixed using a two-blade counter-rotating batch mixer, HaakePolylab QC (ThermoHaake, Karlsruhe, Germany), at  $25^\circ\text{C}$  and 50 rpm for 60 min, monitoring the torque and temperature during mixing to obtain a dough-like blend. Secondly, bioplastics were obtained by an injection moulding process in a MiniJet Piston Injection Moulding System (ThermoHaake) using the blends previously prepared. A schematic illustration of the injection moulding cell can be observed in Figure 1: before injection (A) and after injection took place (B). The selected conditions for the pre-injection cylinder were  $50^\circ\text{C}$  (see Preparation and Characterization of Blends Section) and a residence time of 100 s. As mentioned above, the temperature should not be increased excessively but in addition the residence time should not be too long in order to prevent thermally induced protein cross-linking effect before the injection stage. On the other hand, as for the mould processing conditions, the mould temperature was  $130^\circ\text{C}$  and different moulding times were selected (100, 200, and 300 s) to investigate their effect on the properties of the final bioplastics obtained. It was also important to avoid exposition to high temperatures for a long time in order to avoid protein degradation. In addition, different injection pressures (100, 300, 500, and 900 bar) were also evaluated. A pressure value of 200 bar was selected for the packing stage, to ensure a suitable flow of blend and moulding of specimens. These conditions should allow the development of protein cross-linking to achieve the final network structure. Some injection conditions as the injection pressure or the moulding time were modified in order to study their influence on the properties of the final bioplastics obtained. Two moulds were used to prepare two different specimens: (1) a  $60 \times 10 \times 1$  mm rectangular-shaped specimen for dynamic mechanical analysis (DMA) experiments, water absorption and transparency measurements and (2) a dumb-bell-type specimen by ISO 527-1:2012 for tensile properties of plastics. Bioplastics were stored at room temperature and 50% RH for at least five days in order to reach equilibrium.

### Characterization of Bioplastics

**Dynamic Mechanical Analysis (DMA).** DMA tests were carried out with a RSA3 (TA Instruments), on rectangular probes using dual cantilever bending. Strain sweep tests were also performed in order to establish the linear viscoelasticity range. The selected heating rate was  $5^\circ\text{C}/\text{min}$  and the temperature range covered was from  $-30^\circ\text{C}$  by the use of an air chiller connected to the



**Figure 1.** Diagram of the lab-scale plunger-type injection moulding device: (A) Before injection; (B) After injection. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

forced convection oven (Polycold, TA Instruments) to 130 °C. Linear viscoelastic modulus ( $E'$ ) and  $\tan \delta$  ( $E''/E'$ ) were monitored at constant strain (0.05%, within the linear viscoelastic region) and frequency (6.28 rad/s). All the samples were coated with Dow Corning high vacuum grease to avoid water loss and showed the same thermo-rheological history.

**Tensile Strength Measurements.** Tensile tests were performed by using the Insight 10 kN Electromechanical Testing System (MTS, Eden Prairie, MN, USA), according to ISO 527-2:1993 for Tensile Properties of Plastics. Young's Modulus, strain at break and maximum tensile strength were evaluated using type IV probes and an extensional rate of 10 mm/min at room temperature.

**Water Absorption Capacity.** Water uptake capacity of bioplastics was measured according to the standard method for determining water absorption in plastics ASTM D570, 2001. Rectangular specimens of 60 × 10 × 1 mm were used. The specimens were subjected to drying (conditioning) in an oven at 50 ± 2 °C for 5–6 h to determine dry weight, then introduced into distilled water and weighed after 24 h immersion. Finally, it was subjected to drying (reconditioning) again and weighed to determine the soluble material loss. All the experiments were performed in triplicate at room temperature. According to the methodology used, water absorption capacity and soluble material loss were determined by the following equations:

$$\text{Water uptake} = \frac{\text{Wet Weight} - \text{Initial DryWeight}}{\text{Initial DryWeight}} \cdot 100 \quad (1)$$

$$\% \text{ Loss of soluble material} = \frac{\text{Initial Dryweight} - \text{Final Dryweight}}{\text{Initial Dryweight}} \cdot 100 \quad (2)$$

**Color Determination.** A Colorimeter CM-700D (Konica, Japan) was used to measure the color of the bioplastics. According to EN ISO 11664-4, the CIE standards are used to calculate color differences. It is described by a three-dimensional coordinate system ( $L^*$ ,  $a^*$ , and  $b^*$ ) that locates a color in a color space. The parameter  $L^*$  refers to the lightness of the color ( $L^* = 0$  indicates black and  $L^* = 100$ , white). Parameters  $a^*$  and  $b^*$  can be either positive

or negative: Parameter  $a^*$  extends from green ( $-a^*$ ) to red ( $+a^*$ ) and  $b^*$  from blue ( $-b^*$ ) to yellow ( $+b^*$ ).

**Transparency Measurements.** Transparency measurements were performed on a Genesys-20 (Thermo Scientific, USA) spectrophotometer. In this device, the transmittance (%) of rectangular specimens, 1 mm thickness, at a selected wavelength of 600 nm is measured. Air is used as blank (100% transmittance). In order to compare the transparency of different bioplastics, a transmittance index ( $I_T$ ) was used:

$$I_T = \frac{\% \text{ Transmittance}}{\% \text{ Transmittance of reference bioplastic}} \quad (3)$$

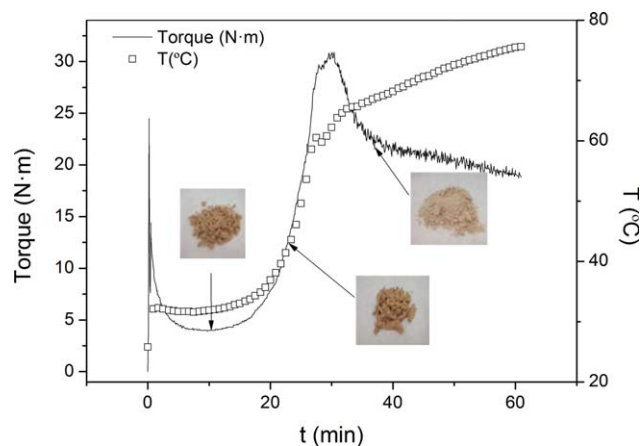
#### Statistical Analysis

At least three replicates of each measurement were carried out. Statistical analyses were performed with  $t$  tests and one-way analysis of variance (ANOVA,  $p < 0.05$ ) by means of the statistical package SPSS 18 (IBM, Chicago, IL, USA). Standard deviations from some selected parameters were calculated.

## RESULTS AND DISCUSSION

### Preparation and Characterization of Blends

As indicated above, mixing is the first stage in the thermochemical processing of the protein-based bioplastics studied. The 60PPI/40GL ratio was an adequate proportion because doughs with a higher or lower content in protein would not be suitable for processability because they were too consistent or the final bioplastics exhibit glycerol exudation, respectively (results not shown). Besides choosing an appropriate protein/plasticizer ratio, a suitable selection of the mixing conditions is very important, however it is not always easy. An extensive mixing was required to obtain a homogeneous dough-like blend, but long mixing periods must be avoided to limit shear induced structuration effects. For that reason, both torque and temperature values were monitored as a function of mixing time for the 60PPI/40GL system (Figure 2). The profile shows a maximum torque value followed by a continuous decrease and a tendency to reach an eventual constant value, whereas the temperature exhibited a constant increase over the mixing time.



**Figure 2.** Evolution of mixing torque and temperature over the mixing process for the 60PPI/40GL blend. Pictures of the resulting blends at different mixing times are inserted. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

From the torque and temperature profiles, it may be deduced that a balance for the mixing time, long enough for a suitable homogenization degree but short enough to avoid premature cross-linking reactions of protein chains is needed. Therefore, three different mixing times were studied: one related to the minimum torque (10 min), another when the increase in torque was produced (21 min), and the third when the torque was stabilized (38 min). That one was rejected because an increase in temperature occurs in relation to possible cross-linking effects.

An interesting parameter that may be considered in this stage is the Specific Mechanical Energy (SME) input for mixing, which is the energy provided by the mixer per unit mass, defined as follows<sup>33</sup>:

$$\text{SME} = \frac{\omega}{m} \int_0^{t_{\text{mix}}} M(t) dt \quad (4)$$

where  $\omega$  represents the rotational speed (in rad/s) of the mixer,  $m$  is the total sample mass that is introduced (in kg),  $M$  (in N·m) is the torque, and  $t_{\text{mix}}$  (in s) is the mixing time. This parameter was calculated for the different mixing times, obtaining 611 and 873 kJ/kg for 10 and 21 min, respectively. The mixing time finally selected was the lowest (10 min) to avoid cross-linking effects and because of its lower SME value.

Figure 3 shows the complex viscosity ( $\eta^*$ ) obtained from small amplitude oscillatory shear measurements for 60/40 and 70/30 PPI/GL blends. The objective of these measurements was to select a suitable temperature ( $T_{\text{inj}}$ ) to achieve moderate rheological properties to facilitate injection to the mould from the pre-injection cylinder, making it possible to obtain bioplastics with higher reproducibility and efficiency. The viscoelastic behavior of the two plasticized blends is quite similar, with a pronounced initial decrease in viscosity with temperature and, after reaching a minimum value ( $T_{\text{min}}$ ), a marked increase. This behavior may be explained in terms of two opposite effects: a thermally induced structural relaxation, which dominates below 60 °C, and an enhancement of the network structure related to occurrence of thermally induced protein cross-linking, which

becomes dominant at the highest temperature values. Therefore, the pre-injection cylinder temperature ( $T_{\text{inj}}$ ) has to be close but lesser to 70 °C.

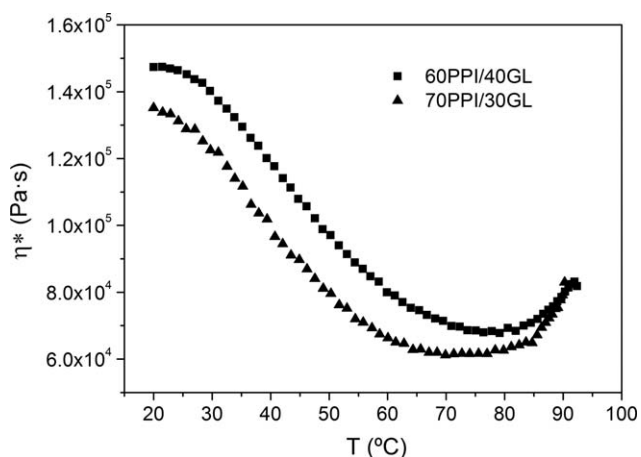
Therefore, the system may be described as a dispersion of PPI in a continuous phase formed by a solution of protein in glycerol, since the protein concentration in the PPI/glycerol blends is much higher than that one corresponding to its solubility in glycerol. The blends are rather stable since both the concentration of the disperse phase and the viscosity of the continuous phase is fairly high. Some CLSM images shown for albumen protein/glycerol blends seem to support this description.<sup>9</sup> However, thermomechanical processing of protein/glycerol blends to obtain bioplastics typically leads to formation of a gel-like protein network and glycerol is embedded within the network.<sup>5,24,25</sup>

In fact, CLSM images of bioplastics based on egg albumen, processed by injection moulding under similar conditions to the present study, has recently shown occurrence of phase segregation where the glycerol-rich phase is randomly dispersed as filler all over the protein matrix.<sup>34</sup> Some recent SEM images obtained with soy protein isolate-based bioplastic samples also support this description (unpublished results).

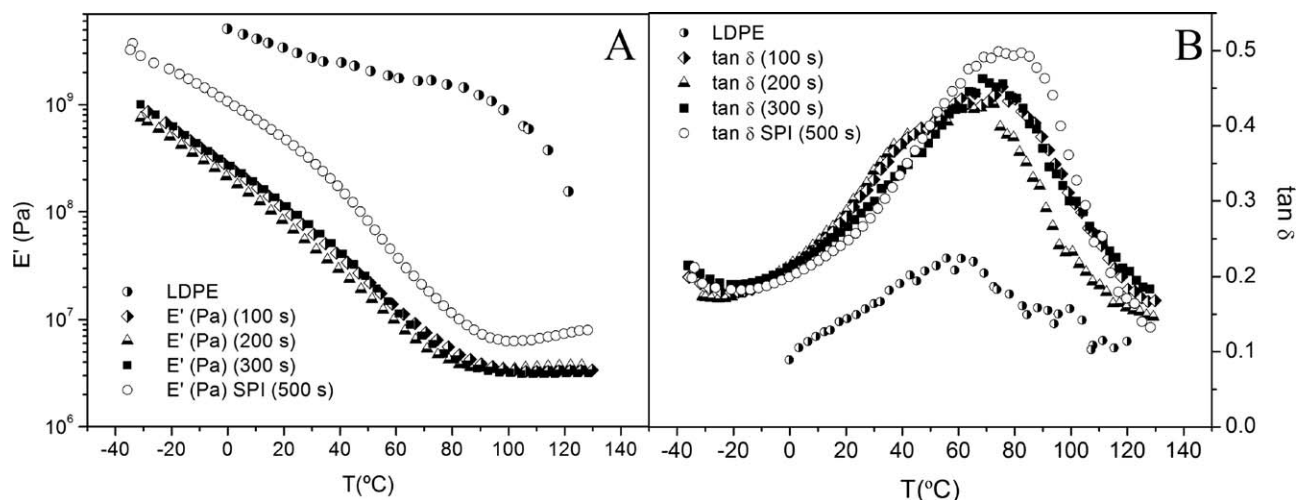
### Characterization of Bioplastics

#### Effect of Moulding Time. Dynamic mechanical analysis.

Figure 4 shows the evolution of the elastic component ( $E'$ ) (A) and  $\tan \delta$  (B) with temperature for different systems by changing the moulding time (100, 200, and 300 s). The profile for  $E'$  values exhibited a drastic drop of the values until 75 °C at which they remained constant. The analysis of  $E'$  did not give enough information because  $E'$  values for these systems are quite similar. Comparing the profile exhibited by PPI-based bioplastics compared to the profile from Soy-based (SPI) bioplastics showed an increase in  $E'$  values for the latter may be because of a better structuration of soy-based bioplastics. Furthermore, the profile for a synthetic polymer such as LDPE was also included having a different tendency, with much higher  $E'$  values and a turning point at 70 °C. However, the profiles for  $\tan \delta$  (ratio of loss modulus to storage modulus), related to the glass transition temperature value and the compatibility of the bioplastics,<sup>35</sup> allowed to select an adequate value for moulding



**Figure 3.** Complex viscosity ( $\eta^*$ ) over heating at constant rate (5 °C/min) for 60/40 and 70/30 PPI/GL ratios.



**Figure 4.** Results from mechanical tests carried out for 60PPI/40GL biobased specimens obtained at different moulding times (100, 200, and 300 s): (A) Storage modulus ( $E'$ ) and (B) loss tangent ( $\tan \delta$ ) values from Dynamic Mechanical Thermal Analysis (DMTA) temperature ramp measurements performed at constant frequency (6.28 rad/s) and heating rate (3 °C/min). Values for LDPE and Soy biobased specimens (SPI) were also included.

time because the ideal profile should exhibit only one peak according to an appropriate compatibility between plasticizer and protein. The profiles obtained for the lowest moulding times (100 and 200 s) showed a tendency to a second peak whereas the results for the bioplastic fabricated with the highest moulding time (300 s) exhibit only one peak. For that reason, it can be deduced that a higher moulding time produces a better compatibility between plasticizer and protein.

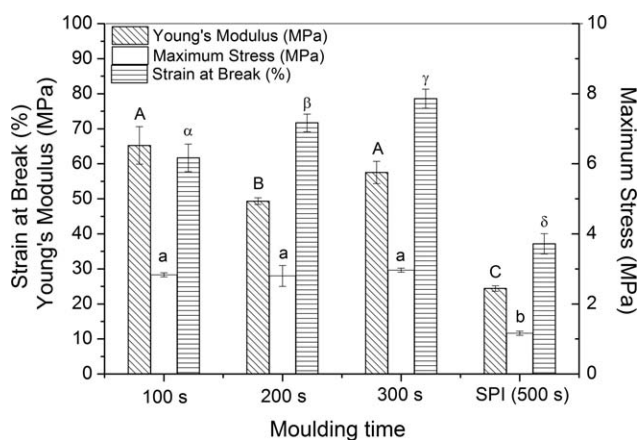
**Tensile strength measurements.** In Figure 5 appears the values for Young's Modulus, strain at break, and maximum tensile strength for the systems processed at different moulding times (100, 200, and 300 s). The stress–strain curves obtained have the typical profile that consists of a initial high sloped linear region followed by a plastic region where the slope is continuously decreasing until a sudden decrease in stress that corresponds to the rupture of the sample (results not shown).

The moulding time did not reveal an influence on the Young's Modulus because values at 100 and 300 s did not exhibit significant differences. Furthermore, the similarities in the maximum tensile strength values were coincident with the slight differences found for  $E'$  values in Figure 4. However, an increase in moulding time produced an increase in the strain at break, possibly because of a better alignment of the different protein fractions with time. In addition, the tensile properties of PPI-based bioplastics are better than those obtained from soy protein (SPI). In any case, all the bioplastics obtained exhibited lower tensile properties than synthetic polymers as LDPE, being the Young's Modulus, maximum tensile strength and strain at break as much as the 20%, 30%, and 45%, respectively, of the values for ASTM normalized LDPE (ASTM D638).

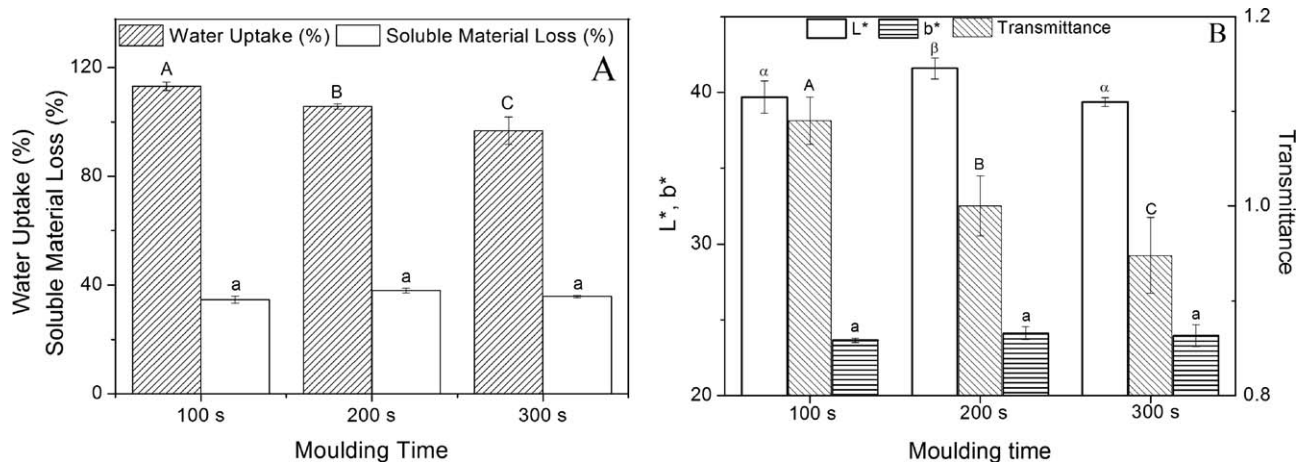
**Water absorption capacity and color/transparency measurements.** In Figure 6 it can be observed the variation of water absorption [Figure 6(A)] and transparency [Figure 6(B)] with moulding time. Soluble material loss was also measured.

For the three systems, soluble material loss is close to 40% coinciding with the content in glycerol of the bioplastics. Besides

this, the amount of water the specimens were capable of absorbing depends on moulding time because the higher the time was, the lower the water uptake was (110% for the system obtained at 100 s and ca. 100% for the specimens produced at 200 and 300 s), because of the higher framing of the system. On the other hand, Figure 4(B) shows the evolution of the two most useful color parameters ( $L^*$  and  $b^*$ ) with moulding time. They correspond to the brightness and to the yellow/green axis in the color space respectively. The  $b^*$  value is similar at different moulding times so PPI-based bioplastics obtained present nearly the same yellowish color. Thus, a color difference between the bioplastics was not visible, although the  $L^*$  value reaches a maximum at 200 s, so brighter bioplastics are obtained at intermediate moulding times. Furthermore, transparency of the systems was also measured. It can be seen how the transparency decreased as the moulding time. Furthermore, the more opaque, the more crystalline the specimens were



**Figure 5.** Young's modulus, maximum stress and strain at break from tensile strength measurements carried out for 60PPI/40GL biobased specimens obtained at different moulding times (100, 200, and 300 s). Values for Soy biobased specimens (SPI) were also included. Columns with different letters are significantly different ( $P \leq 0.05$ ).



**Figure 6.** (A) Evolution of water absorption capacity (%) after immersion for 24 h and soluble material loss (%) and (B) Color standards and transparency measurements: lightness ( $L^*$ ), yellow/blue value ( $b^*$ ), and transmittance carried out for 60PPI/40GL biobased specimens obtained at different moulding times (100, 200, and 300 s). Columns with different letters are significantly different ( $P \leq 0.05$ ).

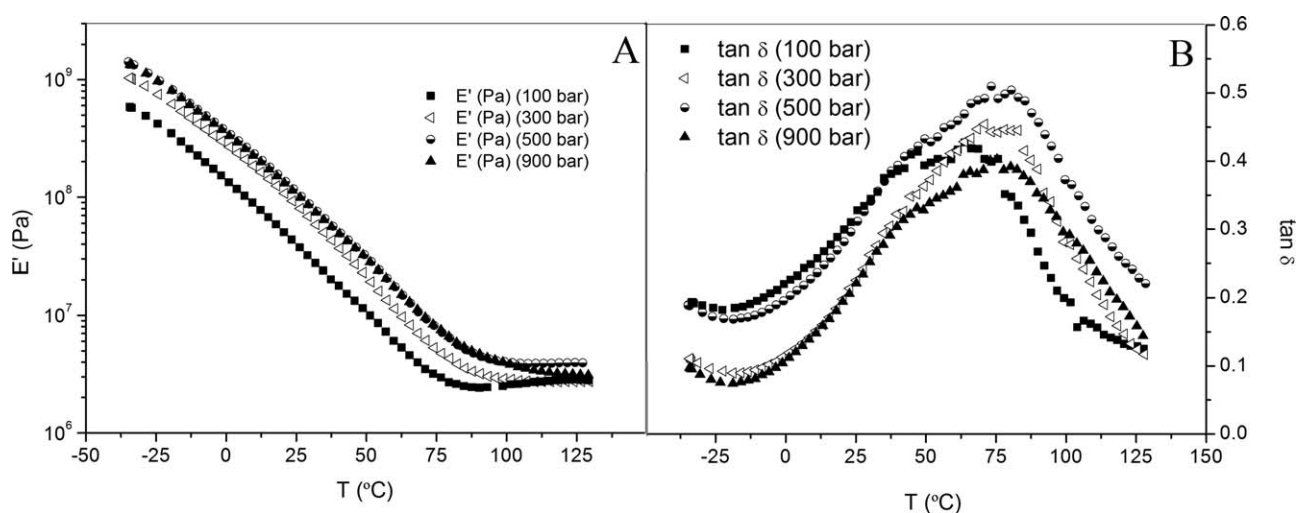
because of the fact that crystalline zones disperse the light avoiding its free transmission.<sup>23</sup>

The differences were not very important because of the importance of nonprotein components in transparency (the three systems have the same formulation). However, once again, the system with the highest moulding time presented a more organized structure (more crystalline), evidenced by a lesser transmittance index.

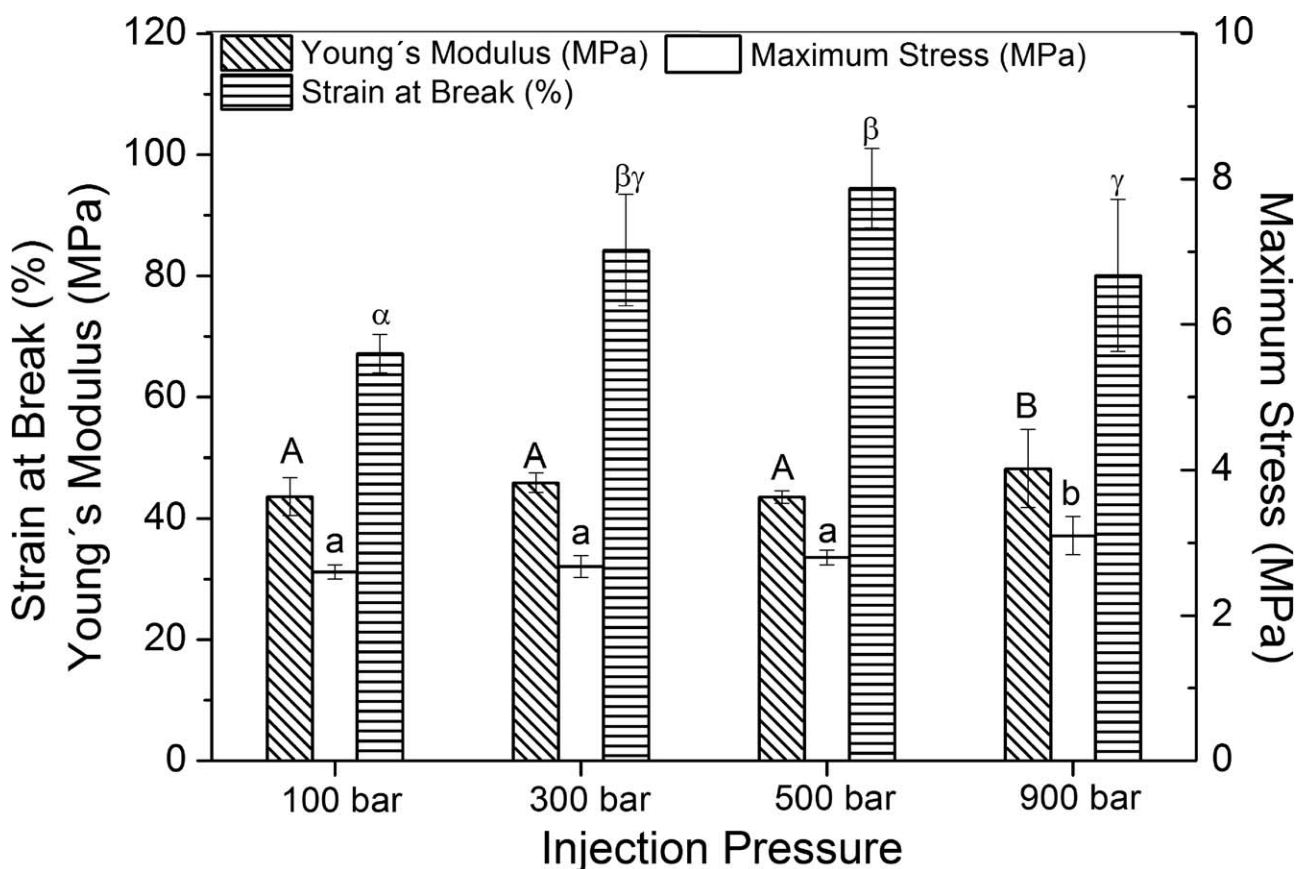
**Effect of Injection Pressure. Dynamic mechanical analysis.** Figure 7 shows the evolution of  $E'$  (A) and  $\tan \delta$  (B) from  $-30^\circ\text{C}$  to  $130^\circ\text{C}$  for four systems with different injection pressures (100, 300, 500, and 900 bar). These systems exhibit the same profile to those obtained with different moulding time. Increasing injection pressure showed a significant increase of  $E'$  values, and no change in the elastic component could be seen up to 500 bar. It was important to point out that the sys-

tem processed with the lowest injection pressure appeared to exhibit a thermosetting potential. Furthermore, the profiles of  $\tan \delta$  were quite similar for all the systems, showing a broad peak that could be produced by the huge variety of protein fractions that pea protein presents. Once again, the  $E'$  values for SPI-based bioplastics are higher to those obtained from pea protein. However, these values became similar when the PPI bioplastics are processed at higher injection pressures (500 and 900 bar).

**Tensile strength measurements.** Figure 8 shows Young's Modulus, strain at break and maximum tensile strength for the bioplastics obtained at different injection pressures (100, 300, 500, and 900 bar). Once again, no significant changes took place in Young's Modulus or maximum strength by changing the injection pressure. However, an increase in the strain at break was observed when the injection pressure increases, excepting for the system with the highest injection pressure (900 bar) at



**Figure 7.** Results from mechanical tests carried out for 60PPI/40GL biobased specimens obtained at different injection pressures (100, 300, 500, and 900 bar): (A) Storage modulus ( $E'$ ) and (B) loss tangent ( $\tan \delta$ ) values from Dynamic Mechanical Thermal Analysis (DMTA) temperature ramp measurements performed at constant frequency (1 Hz) and heating rate ( $3^\circ\text{C}/\text{min}$ ).

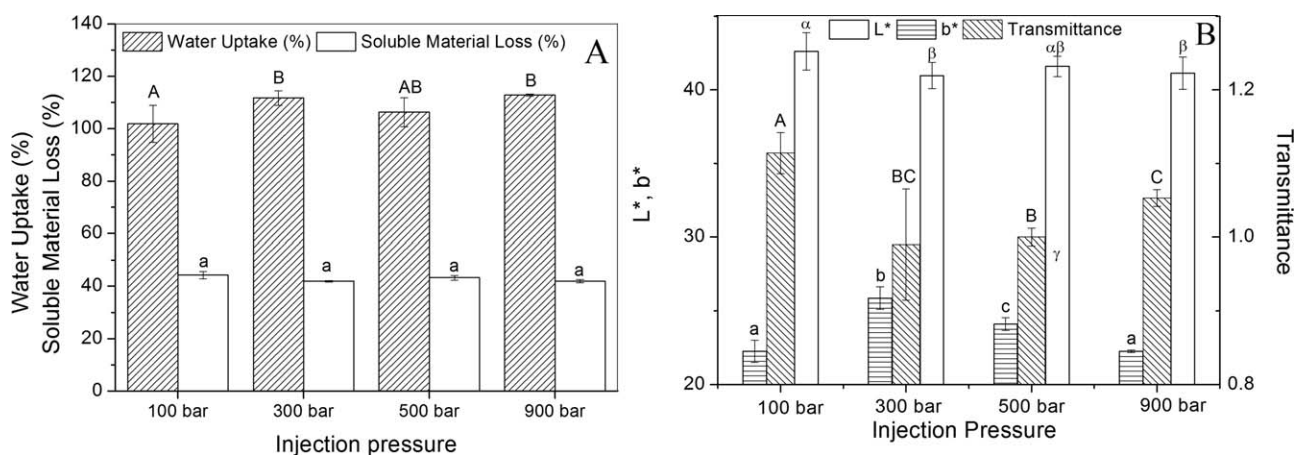


**Figure 8.** Young's modulus, maximum stress and strain at break from tensile strength measurements carried out for 60PPI/40GL biobased specimens obtained at different injection pressures (100, 300, 500, and 900 bar). Columns with different letters are significantly different ( $P \leq 0.05$ ).

which the strain at break tended to decrease, that may be produced because very fragile bioplastics could be obtained with too high pressure.

**Water absorption and color/transparency measurements.** Water absorption and soluble material loss of the four different specimens (100, 300, 500, and 900 bar) obtained are shown in Figure

9(A). Figure 9(B) includes the color and transparency measurements of the bioplastics according to their injection pressure. As it can be seen, soluble material loss was ca. 40% for all the systems (similar to glycerol content as it happened in the other systems studied). Comparing water uptake, in an overall aspect, the differences in the values obtained seem negligible. As it can be seen in Figure 9(B), the profile for  $b^*$  exhibited a marked



**Figure 9.** (A) Evolution of water absorption capacity (%) after immersion for 24 h and soluble material loss (%) and (B) Color standards and transparency measurements: lightness ( $L^*$ ), yellow/blue value ( $b^*$ ) and transmittance carried out for 60PPI/40GL biobased specimens obtained at injection pressures (100, 300, 500, and 900 bar). Columns with different letters are significantly different ( $P \leq 0.05$ ).

tendency: reaching a maximum at 300 bar followed by a progressive decrease at higher injection pressure. The more positive the  $b^*$  value, the more yellow the bioplastic is, so an increase in the injection pressure (starting at 300 bar) produced less yellow bioplastics. On the other hand, the brightness ( $L^*$ ) and transparency of the bioplastics had an opposite profile because  $L^*$  became lower with an increase in the injection pressure until 500 bar at which it became constant. However, the transparency increased with injection pressure from 300 to 900 bar, may be because of a worse organization of the protein fractions when the pressure was increased, obtaining a more amorphous structure. However, the specimen made with the lowest injection pressure (100 bar) showed the higher transparency, possibly because the pressure was not high enough to induce a crystalline framework in the bioplastic. Thus, the brightness and the crystallinity could be related as the pattern is similar. So, in general, increasing injection pressure produced less crystalline and yellow bioplastics.

### CONCLUDING REMARKS

In the light of the results, a byproduct of the pea agroindustry (pea protein isolate) could be useful to obtain bioplastics. Considering their properties, these bioplastics would be suitable candidates in certain applications to substitute conventional petroleum plastics.

An increase in moulding time induced a progressive decrease in water absorption and transparency of the specimens (as they become more crystalline). The only mechanical parameter showing an increase with moulding time was the strain at break.

An increase in pressure led to an enhancement of bending properties and of the tensile strain at break, as well as a slight displacement of the loss tangent peak towards higher temperature. Water absorption was hardly affected by pressure while transparency and brightness showed a minimum at intermediate injection pressure. A certain injection pressure was necessary to obtain bioplastics with suitable properties, but it was not useful to increase it because the properties were not optimized or even causing drawbacks (lower strain at break values) to the final bioplastics.

The effects of moulding time or injection pressure did not produce considerable improvements in the results exhibited by the bioplastics although, interestingly, an increase in the strain at break was observed. Furthermore, water uptake of these bioplastics exhibited relatively high values. However, pea protein-based bioplastics show worse mechanical properties than LDPE standards and consequently, further research is required in this field.

### ACKNOWLEDGMENTS

This work is part of a research project sponsored by MINECO, "Ministerio de Economía y Competitividad", from the Spanish Government (Ref. MAT2011-29275-C02-02/01) and by the Andalusian Government, (Spain) (project TEP-6134). The authors gratefully acknowledge their financial support. The authors also acknowledge the Microanalysis Service (CITIUS-Universidad de

Sevilla) for providing full access and assistance to the LECO-CHNS-932 (TA instruments).

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