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Effect of processing on the viscoelastic, tensile and optical properties of albumen/starch-based bioplastics

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ABSTRACT

The development of biodegradable materials to be used by the plastic industry has been receiving increasing interest over the last few years. In this work, different blends of albumen protein and starch (potato and corn) have been used as raw materials for bioplastics exhibiting high transparency and a suitable mechanical behaviour. In order to study the effect of processing on the mechanical and optical properties of albumen/starch-based bioplastics, three different procedures were followed: (i) compression-moulding-based manufacture, (ii) extrusion, and (iii) combination of both. Dynamic bending (DMTA) and tensile tests, together with %-transmittance measurements demonstrated that the resulting material properties strongly depend upon the selected procedure and its processing conditions. Thus, compression-moulding after blending the ingredients by kneading was seen to produce much more promising results, concerning material transparency and strength, if compared to extrusion. However, results can further be improved by extruding starch and glycerol before blending with the protein.

1. Introduction

In recent years, a great interest has been shown in the production of plastics from renewable resources, which are commonly known as bioplastics. It has been estimated that 4% of the total oil production is used as feedstock for plastics (Rincones, Zeidler, Grassi, Carazzolle, & Pereira, 2009). Consequently, finding alternative renewable raw materials can result in a very significant effect on reducing both our present dependency on fossil oil and environmental pollution (Rosentrater & Otieno, 2006; Tummala, Liu, Drzal, Mohanty, & Misra, 2006).

Biopolymers include polymers extracted directly from biomass, with or without modification, such as starch, cellulose and proteins (Jerez, Partal, Martinez, Gallegos, & Guerrero, 2007a; Queiroz & Collares-Queiroz, 2009). Proteins are heteropolymers comprising more than 20 aminoacids that are able to form numerous intermolecular linkages, and undergo different interactions, thus yielding a great range of functional properties (Gomez-Martinez, Partal, Martinez, & Gallegos, 2009; Pommet, Redl, Morel, Domenek, & Guilbert, 2003). Proteins such as soy protein, wheat gluten, corn zein, and egg albumen, are renewable materials that are produced on an annual kiloton scale, and recent studies have shown their suitability for the manufacture of bioplastics (Gomez-Martinez et al., 2009; Jerez et al., 2007a; Jerez, Partal, Martinez, Gallegos, & Guerrero, 2007b; Kim, 2008; Mohanty et al., 2005; Tummala et al., 2006; Zheng, Tan, Zhan, & Huang, 2003).

Among them, egg white protein (albumen) has traditionally been used by the food industry due to its functional properties, such as gelling, foaming, heat setting and binding adhesion. Jerez et al. (2007b) have recently proved the feasibility of producing highly transparent albumen-based bioplastics, with acceptable mechanical properties, for the manufacture of biodegradable food packaging and other plastic stuff. However, due to its high price and the need for cost-competitive materials, blending with other renewable additives from agricultural sources is sought as a valuable alternative. In that sense, agro-polymers, including cellulose and starch, are abundant biodegradable polysaccharides (Kumar & Singh, 2008), with lower cost than proteins and synthetic additives.

Manufacture of protein-based bioplastics involves the addition of plasticisers, which are molecules with low both molecular weight and volatility that reduce the intermolecular forces and increase the mobility of the polymeric chains (decreasing material glass transition temperature). On the one hand, they endow the very stable three dimensional protein networks with higher plasticity, which eases processability. Hence, heating plasticised proteins above their glass transition produces soft and rubbery materials that can be easily shaped. On the other hand, they increase the flexibility and the extensibility of the final product (Gomez-Martinez et al., 2009; Jerez et al., 2007b) and reduce its brittleness. Therefore, controlling the different processing operations as well as plasticiser nature and content would allow materials with unique properties to be obtained (Pommet et al., 2003).

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Breaking the stabilizing intermolecular bonds (by chemical or physical means) is a crucial step in the production of protein-based bioplastics. Once broken, the mobile polymer chains need to be arranged and oriented into the desired shape. Finally, new intermolecular bonds, which stabilize the new three-dimensional structure, need to be formed (Jerez et al., 2007b). Two possible methods of manufacturing protein-based bioplastics have been reported in the literature: (a) the physico-chemical or casting method (Gennadios, Weller, Hanna, & Froning, 1996), in which the proteins are dispersed in a solvent containing a plasticiser and rupturing agent, then casting the film forming solution and finally drying; and (b) the thermo-plastic/mechanical method (Jerez et al., 2007b), which consists of extrusion/kneading a mixture of proteins and plasticiser to obtain either a bioplastic (thermo-plastic manufacture) or a dough-like material that can subsequently be transformed into a bioplastic by compression-moulding and temperature (thermo-mechanical manufacture).

In a previous paper, feasibility of the development of highly transparent protein/starch-based materials and the effect of bioplastic formulation on their physical and mechanical properties were assessed (Gonzalez-Gutierrez, Partal, Garcia-Morales, & Gallegos, 2010). They proved that further addition of starch has an important effect on reducing elongation at break and the material transparency. In spite of this, the albumen/starch-based biomaterials obtained by Gonzalez-Gutierrez et al. (2010) presented a high degree of transparency if compared to synthetic commodity polymers like LDPE and PP. The main objective of this current work is to show how different processing procedures affect the mechanical and the optical properties of albumen/starch-based bioplastics. With that aim, this paper focuses on the thermo-plastic/mechanical manufacture of bioplastics, which was accomplished either by compression-moulding, extrusion or by a combination of both.

2. Materials and methods

Spray-dried egg white protein (EW, with 73 wt.% protein, 6 wt.% ashes and 8 wt.% moisture) provided by OVOSEC S.A. (Spain), potato starch (PS, 0.1 wt.% protein, 0.5 wt.% ashes and 20 wt.% moisture) supplied by Sudstärke GmbH (Germany), and corn starch (CS, 0.32 wt.% protein and 11.8 wt.% moisture) furnished by Cargill España S.L.U. (Spain) were used as base materials for bioplastics manufacture. Additionally, glycerol (G), from Panreac Química, S.A. (Spain), was selected as plasticiser.

Albumen/starch bioplastics, always having a final composition of 42.5 wt.% albumen, 20 wt.% starch and 37.5 wt.% glycerol, were manufactured by following three different procedures:

(i) "*Thermo-mechanical processing*": The first method includes two stages, mixing of ingredients to obtain a dough-like material, followed by moulding under pressure and heat. Mixing, for 10 min at room temperature, was carried out in the kneading tool (Rheomix 600p) of a torque-rheometer (Polylab, Thermo Haake GmbH, Germany) equipped with two counter-rotating rollers turning at 50 rpm (Jerez, Partal, Martinez, Gallegos, & Guerrero, 2005). After storage for 5 days at room temperature, the resulting material was subjected to compression-moulding, by applying a gauge pressure of 100 bar and a temperature of 120 °C for 10 min in a hot plate press, as described by Jerez et al. (2007b). Two types of moulds were used: one to obtain rectangular 3-mm-thick specimens for both DMTA experiments and transparency measurements, and a second one to obtain type IV-dumbbell specimens (ASTM D638, 2003) for tensile tests.

(ii) "*Extrusion processing*": The second procedure involves mixing of albumen, starch and glycerol, followed by storage and extrusion. Mixing of ingredients and storage was done as above. Extrusion, with a rotational speed of 60 rpm, was performed in a Polylab single screw extruder Rheomex 252p (Thermo Haake GmbH, Germany) equipped with an electrically heated ribbon-shaped die (1-mm-thick) at the exit. Four different temperature profiles were established by fixing temperatures corresponding to the first three zones of the extruder (55, 65 and 80 °C, respectively), while varying the die temperature (90, 100, 120 and 130 °C). The extrudate was later struck with a pneumatic die-cutter (ATS Faar, S.p.A, Italy) into rectangular 1-mm-thick and type IV-dumbbell specimens.

(iii) "*TPS/thermo-mechanical processing*": The third procedure involves manually mixing of glycerol and starch powder at room temperature in a glass beaker. Immediately after, the resulting mixture was subjected to extrusion with a rotational speed of 60 rpm in the device previously described. Feed and conveying zones of the extruder were set at 60 and 80 °C, respectively, while four different temperatures for the mixing zone (90, 100, 110, and 120 °C) were investigated. No die was used at the exit in this procedure. In a last step, the thermoplastic starch (TPS) obtained was cooled down to room temperature, blended by kneading with albumen and, finally, compression-moulded under conditions mentioned in (i).

Dynamic mechanical thermal analysis (DMTA) experiments were performed with a Seiko DMS 6100 (Seiko Instruments Inc., Japan) in double cantilever bending mode on rectangular 50 mm × 10 mm specimens with either 3 or 1 mm thickness. Temperature sweeps were performed at a constant frequency of 1 Hz and strains within the linear viscoelasticity region. The selected temperature ramp was set at 2 °C/min with a temperature range from 30 to 140 °C. Frequency sweeps from 0.01 to 100 Hz were carried out, in the linear viscoelasticity region (LVR), at four different temperatures (30, 70, 90, and 110 °C). All tests were done in triplicate.

Transparency measurements were conducted using a Photometer S-2000 (Selecta, S.A., Spain). %-Transmittance of rectangular 3-mm-thick compression-moulded or 1-mm-thick extruded specimens was measured at a wavelength of 600 nm. Air was used as blank (i.e. 100% transmittance).

Tensile testing at room temperature was carried out in a Shimadzu AG-IS 10kN Universal Testing Machine (Shimadzu Co., Japan). Tensile tests were stroke-controlled with a constant cross head speed of 20 mm/min. According to the standard ASTM D638 (2003), five tests were done for each sample. Elongations were recorded by a Shimadzu Semi-Automatic Extensometer SES-1000.

Differential scanning calorimetry experiments, which allowed starch gelation temperatures to be measured, were performed on starch in glycerol suspensions (weight proportion of 35:65) with a Q100 (TA Instruments, USA). Hermetic aluminium pans containing 10–20 mg samples were used. A heating rate of 10 °C/min was selected. The sample was continuously purged with a nitrogen flow of 50 mL/min.

Additionally, the evolution of starch crystallinity with temperature was monitored by means of an experimental set-up consisting of the electrically heated cell CSS 450 (Linkam Scientific Instruments Ltd., UK) coupled with an optical microscope (Olympus BX51, Japan) fitted with a pair of crossed polarisers.

X-ray diffractograms were recorded at room temperature on a D8-Advance diffractometer (Bruker, Germany), operating at 36 kV and 20 mA, using Cu-Kα radiation (15.406 nm) at 2θ values ranging from 5 to 50°, which covered most of the significant diffraction peaks of the starch crystallites.

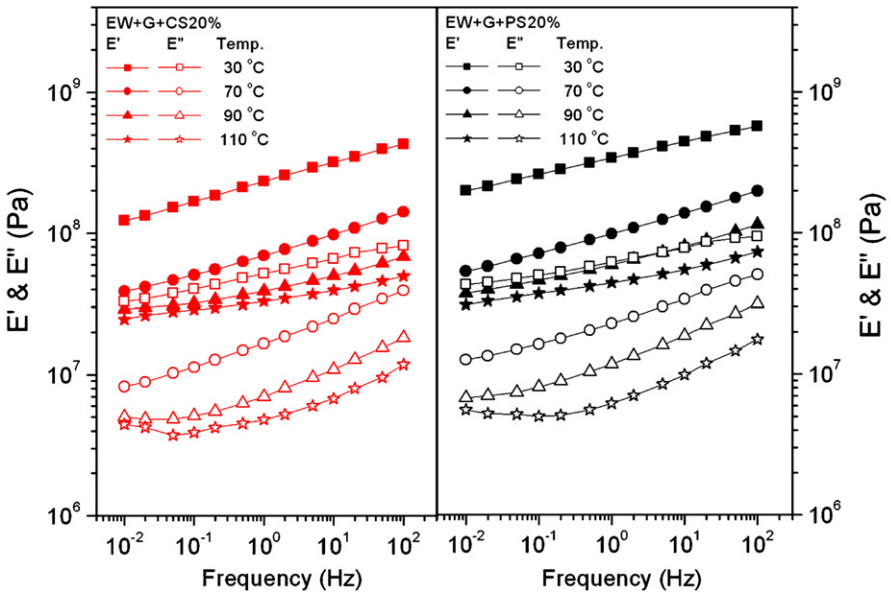

Fig. 1. Frequency dependence of the elastic and viscous bending moduli for 20 wt.% corn or potato starch bioplastics prepared by method (i), at different temperatures.

3. Results and discussion

3.1. Thermo-mechanical processing

The rheological behaviour of albumen/starch-based bioplastics manufactured by procedure (i) was first investigated by means of dynamic bending tests, within the LVR, at several temperatures ranging from 30 to 110 °C, on two selected samples containing 20 wt.% corn or potato starch (Fig. 1). Interestingly, the results obtained are quite similar, regardless the type of starch used, although slightly higher moduli values are found for the sample containing corn starch. It can be observed that both samples show a predominantly elastic response at every temperature tested, with much higher values of the elastic modulus than the viscous one in the entire frequency window studied. An increase in temperature was seen to cause both a decrease in the values of the viscoelastic moduli and notable changes in the shape of the mechanical spectra obtained. Thus, curves at room temperature, in Fig. 1, seem to correspond to the transition from the rubbery to the glassy region, characterised by both moduli showing quite similar slopes. This suggests a highly elastic material and the development of a three-dimensional network structure that involves a large amount of interactions among chain segments (Ferry, 1980). Instead, at the highest temperatures (i.e. above 70 °C), these albumen/starch-based bioplastics show a plateau in E' (and a minimum in E''). This plateau region, extensively described in polymer rheology in terms of an entanglement network formed by the simple topological interaction of polymer chains, would result from polymeric systems behaving like pseudo-gels at frequencies higher (shorter timescale) than the lifetime of the topological entanglements (Ferry, 1980). However, in a variety of biological systems (which include globular proteins and polysaccharides) the plateau observed comes from a situation that falls between a temporary entangled network and permanent covalent crosslinks (Ross-Murphy, 1995). This would be consistent with the molecular structure of an albumen/starch mixture, where hydrophobic interactions, hydrogen bonds, etc. usually do not act at a point on the chain as covalent crosslinks do, but involve more extended "junction zones".

Additionally, dynamic temperature sweeps in bending mode, at temperatures between 30 and 130 °C, were also conducted on the two previous samples. No matter the type of starch involved, comparable results were found. Thus, both curves in Fig. 2a present similar values of the bending complex modulus, $|E^*|$, which continuously decays as temperature increases. A reduction in the decay rate of $|E^*|$, at about 90 °C, can be appreciated; such reduction is related to the gel-glasslike transition temperature of the egg white protein (Nakamura, Hara, Hiramatsu, & Matsumoto, 1999; Sepe, 1997; Takushi, 1998). Instead, tensile tests, in Fig. 2b, reveal different mechanical behaviours influenced by the type of starch used in the bioplastic formulation. On these grounds, corn starch displays higher values of both tensile strength and elongation at break (above 5 MPa and 50%, respectively), if compared to potato starch (4.25 MPa and 35%, respectively). Consequently, at the starch concentration used, the mechanical response at small deformations was seen to be ultimately controlled by the properties of the protein matrix. On the contrary, the type of starch used in the formulation starts to play a larger role when the bioplastics are subjected to large deformations, such as in tensile testing.

The type of starch used in the bioplastic formulation affects not only the tensile properties of the resulting material but also their optical properties. Thus, by looking at the pictures embedded in Fig. 2, it can be seen that the addition of 20 wt.% potato starch leads to a much more transparent material than that formulated by adding the same content of corn starch. Accordingly, the values of %-transmittance of rectangular 3-mm-thick specimens, used as a measure of the transparency of the bioplastics studied, were 17.77 and 3.50%, respectively. Such a notable difference in transparency may be explained by means of calorimetry tests and birefringence experiments.

Differential scanning calorimetry in Fig. 3, conducted on samples of both types of starch, revealed the existence of endothermic events located at their corresponding gelation points, that is, 115 and 120 °C for potato and corn, respectively. This result demonstrates that, in both cases, gelation is certainly to occur at the compression-moulding temperature used (120 °C).

Birefringence experiments in Fig. 4, carried out in an optical microscope equipped with a pair of crossed polarising filters, further confirmed transparency observations, by allowing the reduction of crystallinity to be followed with increasing temperature. At room temperature, semi-crystalline starch granules appear bright with marked birefringent features. As temperature reaches

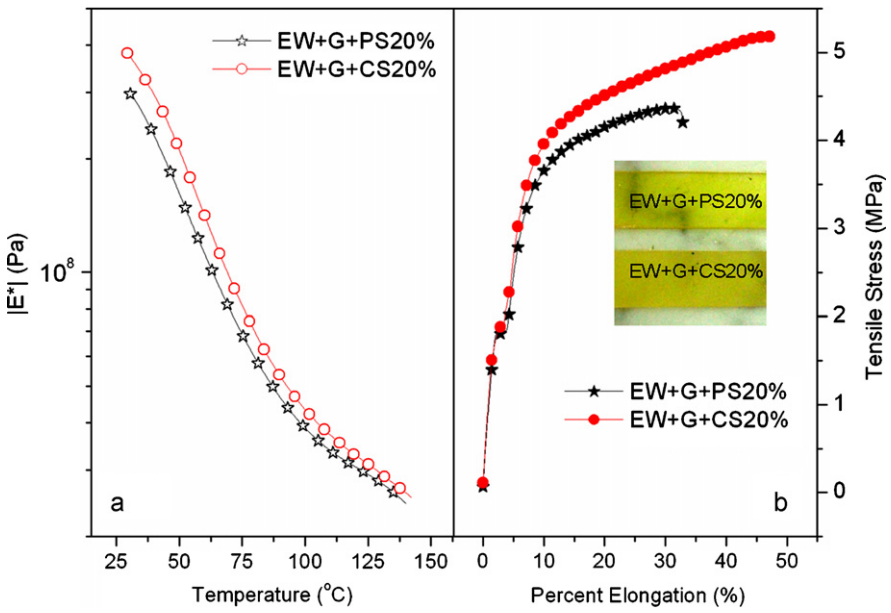

Fig. 2. Evolution with temperature of the complex bending modulus (a) and tensile tests curves (b) corresponding to 20 wt.% corn or potato starch bioplastics prepared by method (i). Inset: visual inspection of their corresponding 3-mm-thick specimens.

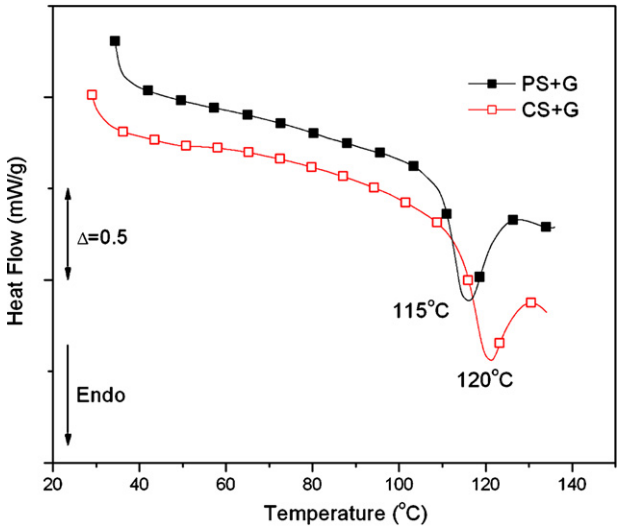

Fig. 3. Differential scanning calorimetry measurements conducted on 2 manually prepared mixtures of potato or corn starch and glycerol.

the gelation point, starch granules break, and crystalline regions are seen with an increasing dark isotropic background. Thus, after 2 min at 120 °C, most of the picture area, for both types of starch, is amorphous. However, it can be observed that, for potato starch, the degree of crystallinity decreases to a larger extent as temperature reaches 120 °C, which would satisfactorily explain the results of transmittance measurements. On the other hand, microscopy observations also might shed light on the tensile behaviour found. Thus, larger potato starch granules mean that a much less homogeneous microstructure was obtained after blending the ingredients. The larger starch granules (even after a partial gelling process) can act as stress concentration points that facilitate the induction and propagation of cracks which subsequently decrease the strength and elongation at break of the resulting bioplastics (Wang, Sun, & Seib, 2001).

3.2. Extrusion processing

Extrusion is a highly efficient way to manufacture and transform plastics at industrial scale. For this reason, it is of major importance to investigate how extrusion affects the properties of

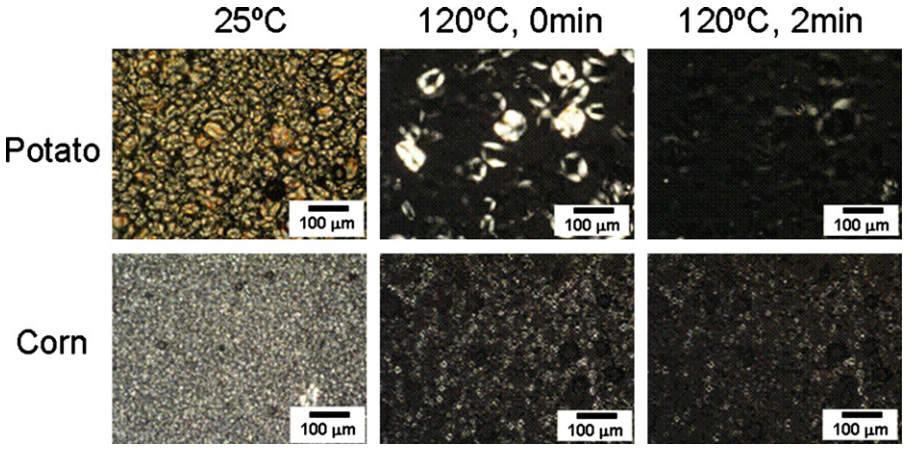

Fig. 4. Birefringence experiments, at room temperature and 120 °C, carried out on 2 manually prepared mixtures of potato or corn starch and glycerol.

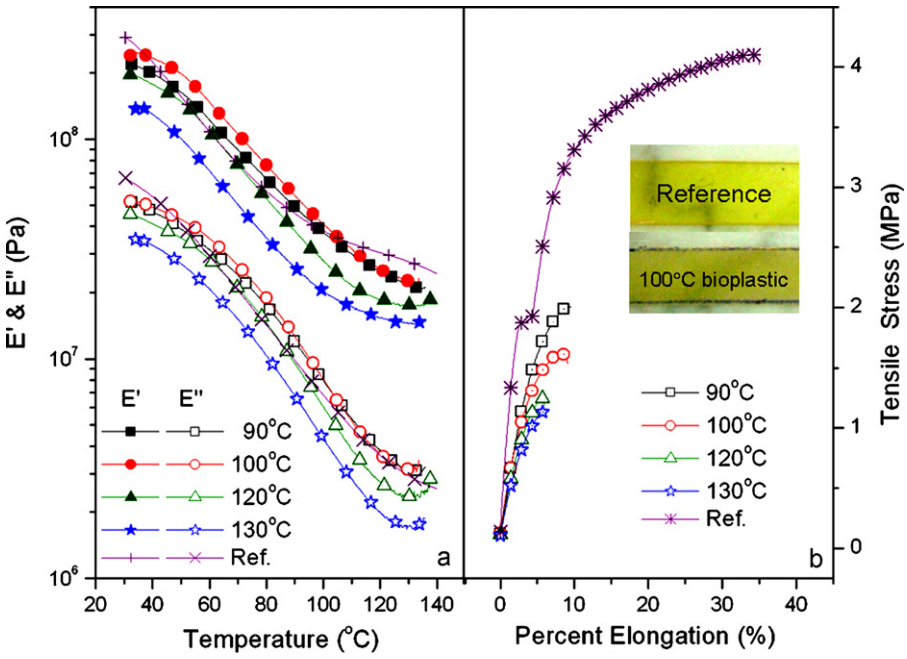

Fig. 5. Evolution with temperature of the elastic and viscous bending moduli (a) and tensile tests curves (b) for 20 wt.% potato starch bioplastics prepared by method (ii), at different temperatures. Inset: visual inspection of selected 1-mm-thick specimen at 100 °C. Reference sample included for comparison.

protein/starch-based bioplastics. Based on the previous study, with potato starch showing more promising results than corn starch as far as optical properties are concerned, potato starch was eventually selected for the preparation of the remaining formulations. Fig. 5a shows dynamic temperature sweeps in bending mode for bioplastics manufactured by procedure (ii), that is, extrusion of a mixture previously prepared by a gentle kneading. Different extruder die temperatures, ranging from 90 to 130 °C, were studied. For the sake of comparison, the 20 wt.% potato starch bioplastic prepared by procedure (i) has been included (referred to hereinafter as "reference" sample). If compared to the reference, the extruded bioplastics display similar viscoelastic response, with E' and E'' steadily decreasing as temperature increases. In addition, these biomaterials show, predominantly, elastic features, with values of E' much higher that E'' in the entire temperature interval studied. Interestingly, die temperature quite notably affects the thermo-mechanical properties of the extrudate, by leading, from 100 °C onward, to a reduction in the values of both viscoelastic moduli with increasing temperature. The reduction was more pronounced at 130 °C. The influence of the die temperature can further be observed by performing large deformation tests, such as tensile tests (Fig. 5b). Thus, an important decrease in the values of tensile strength and elongation at break are found when a higher temperature is set at the extruder exit. Moreover, if compared to the reference bioplastic, with values of the above parameters of about 4 MPa and 35%, respectively, the extruded bioplastics do not even reach, at best, 2 MPa and 10%, respectively.

Extrusion makes the molecular structure of proteins change due to the combined action of heat and high shear (Song & Zheng, 2008). It is believed that, during extrusion, a complete restructuring of the polymeric material occurs in an oriented pattern, defining the final molecular network of the extrudate. Extrusion is known to promote the dissociation and unfolding of macromolecules, which allow them to recombine and crosslink through specific linkages (Allen, Carpenter, & Walsh, 2007; Redl, Guilbert, & Morel, 2003). However, current observations suggest that extrusion might be leading to gel–starch segregation from the denatured protein matrix, originating stress concentration points, which reduce the stress and strain values at rupture during tensile tests. Protein/starch segregation during blending and thermal processing has been previously discussed by Habeych, Dekkers, van der Goot, & Boom (2008) and Vu Dang, Loisel, Desrumaux, & Doublier (2009). Habeych et al. (2008) showed that the structure of the starch/protein blends changed as shear rate was increased; increasing shear rate leads to the orientation of protein flocs in the direction of flow. On the other hand, Vu Dang et al. (2009) observed that starch/protein segregation was accentuated as temperature increased from 90 to 110 °C. It may be concluded, therefore, that extrusion after kneading of the ingredients makes the mechanical properties of the resulting bioplastics notably worse due to starch/protein segregation and protein orientation.

Extrusion also affects material transparency, as deduced from the %-transmittance values in Table 1, and the visual inspection of pictures embedded in Fig. 5. Transmittance measurements conducted on rectangular 1-mm-thick specimens revealed that transparency increases with die temperature, due most probably to temperatures being above gelation point of potato starch. However, when compared to the reference bioplastic, the %-transmittance

Table 1
Values of %-transmittance from tests conducted on 1-mm-thick bioplastic specimens manufactured by procedure (ii), at 4 different die temperatures; and conducted on 3-mm-thick bioplastic specimens manufactured by procedure (iii), at 4 different mixing zone temperatures.

Procedure (ii) (1-mm-thick)	
Die temperature (°C)	%-Transmittance
90	2.45
100	3.50
120	4.10
130	4.37
Procedure (iii) (3-mm-thick)	
Mixing zone temperature (°C)	%-Transmittance
90	14.38
100	19.33
110	3.80
120	3.77

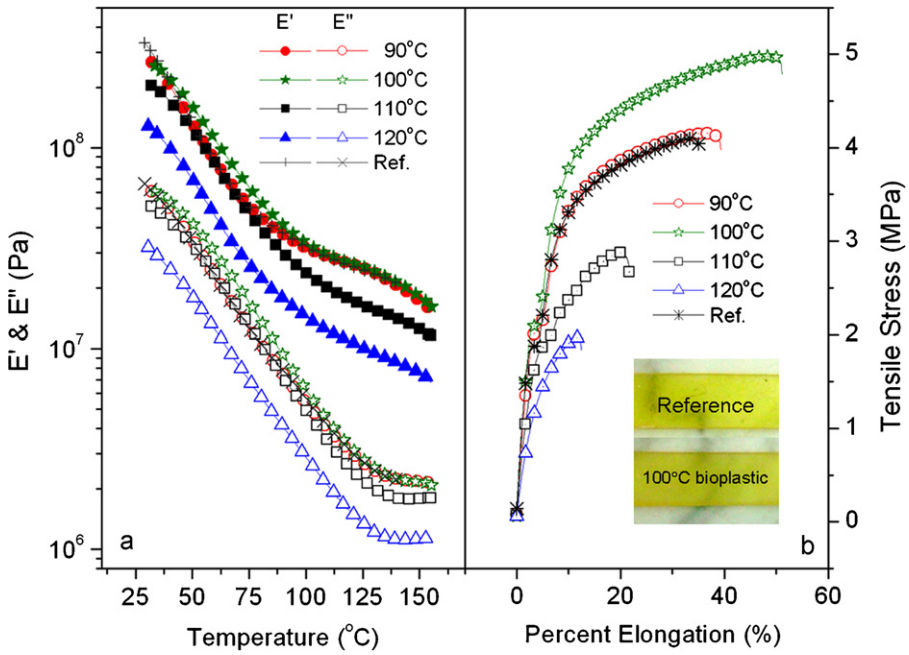

Fig. 6. Evolution with temperature of the elastic and viscous bending moduli (a) and tensile tests curves (b) for 20 wt.% potato starch bioplastics prepared by method (iii), at different temperatures. Inset: visual inspection of selected 3-mm-thick specimen at 100 °C. Reference sample included for comparison.

values are much smaller (17.77% compared to a maximum value of 4.37%), even though the specimens tested are now three times thinner. This dramatic change in transparency might be related to higher orientation of the biopolymer chains caused by extrusion, which would modify the material isotropic state and thus the way light passes through it. In addition, according to Jerez et al. (2007b), the pressure at which material is subjected during its processing plays a relevant role on albumen-based bioplastic optical properties, so that, higher pressures lead to more transparent materials. It has been estimated that the actual pressure applied on the sample during its moulding was about 880 bar, much higher than that reached within the extruder, always below 700 bar. Likewise, insets in Fig. 5 make clear that, if compared to the highly transparent 3-mm-thick compression-moulded specimens, those punched from 1-mm-thick extruded ribbons present a reduced degree of transparency, which hardly allows the marble streaks in the background to be appreciated.

3.3. TPS/thermo-mechanical processing

A third processing method was envisaged, consisting of extrusion of glycerol and starch (with thermo-plasticised starch, TPS, as an intermediate product) followed by the addition of protein, kneading and compression-moulding of the resulting mixture. Four different temperature profiles, by fixing both feed and convey zones temperatures and varying the mixing zone temperature from 90 to 120 °C, by 10 °C-steps, were tested. Dynamic mechanical thermal analysis in bending mode was performed on the four resulting bioplastics, and their corresponding rheological responses compared with that of the reference sample (Fig. 6a). It can be seen that, when potato starch is extruded at the two lowest temperatures (90 and 100 °C), the resulting bioplastics present E' and E'' curves almost identical to those of the reference sample, in the temperature range investigated. Nevertheless, as extrusion temperature increases, the values of both viscoelastic moduli decrease, being quite noticeable at 120 °C.

In a similar way, tensile properties are strongly affected by the conditions set during the manufacturing process. As shown in Fig. 6b, starch extrusion at 90 °C leads to a tensile response very similar to that of the reference bioplastic. However, when TPS is extruded at 100 °C, both tensile strength and elongation at break largely increase (about 5 MPa and 50%, respectively). Higher extrusion temperatures no longer lead to an improvement of the bioplastics mechanical properties; in fact, tensile strength and elongation at break are dramatically decreased.

On the other hand, the transparency of the bioplastics produced by this third method is also greatly affected by the extrusion temperature. Thus, %-transmittance values measured from rectangular 3-mm-thick specimens (Table 1) demonstrated that, as seen in tensile properties, the best response corresponds to an extrusion temperature of 100 °C. In fact, visual inspection of insets in Fig. 6 allows to conclude that both the reference sample and that produced by procedure (iii) at 100 °C present very similar transparency, even higher for the second one, as the transmittance results (17.77 and 19.33%, respectively) confirm.

The observed results in DMTA, tensile tests and %-transmittance measurements hint that, when plasticised starch is extruded prior to blending with protein, the extrusion temperature plays a key role concerning the characteristics of the biomaterial. Hence, it seems that there is an optimum extrusion temperature above which the compatibility of the resulting TPS with the albumen matrix decreases, leading to a large reduction in biomaterial mechanical properties and transparency. During extrusion, starch losses its crystalline structure by the mechanical disruption of molecular bonds, due to the intense shear fields inside the extruder, which in turn can promote a better interaction when further mixed with the protein matrix (Allen et al., 2007); however, a high amount of mechanical and thermal energy transferred to starch during extrusion may also lead to starch fragmentation, degradation or decomposition, which may reduce available bonding sites and affect the performance of the final starch-based bioplastic (Klinger, Meuser, & Niediek, 1986; Liu, Xie, Yu, Chen, & Li, 2009). Therefore, optimization of the extrusion temperature is a crucial factor in the preparation of albumen/starch-based bioplastic with improved mechanical and optical properties.

Fig. 7 presents a qualitative analysis, carried out by means of XRD, on the degree of starch crystallinity destructuring in selected potato starch bioplastics prepared by the three methods studied. It

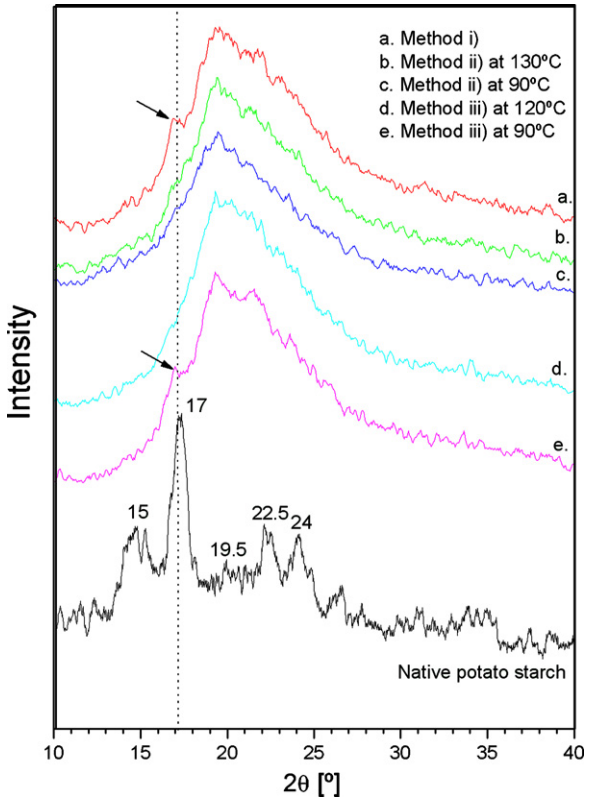

Fig. 7. X-ray diffraction patterns of native potato starch and selected albumen/starch bioplastics prepared by methods (i)–(iii).

can be seen that native potato starch has a typical "B-type" crystal structure, with the strongest diffraction peak located at the 2θ value of 17°, and smaller peaks at 15, 19.5, 22.5 and 24°, which is characteristic of tuber starches (Shujun, Jinglin, & Wenyuan, 2005). Instead of sharp crystal peaks, potato starch bioplastics show broad peaks (characteristic of amorphous materials), suggesting that the inherent granular and crystalline structures of starch were almost completely destructed under the action of high temperature, shear and plasticisers during processing. However, a slight signal of residual crystallinity can still be appreciated in the bioplastic prepared by method (i), shown by a small peak appearing at 17°, as this bioplastic was not processed by extrusion. This fact may be related to the existence of a temperature gradient during bioplastic moulding, with lower temperatures than 120 °C within the moulded material. Accordingly, higher residual crystallinity is likely expected for the corn starch based bioplastic, responsible for its above commented poorer transparency. No peaks were found for the bioplastics prepared by direct extrusion of all the ingredients (method (ii)), neither at 90 nor at 130 °C die temperatures. Finally, the bioplastic prepared by previous extrusion of TPS (method (iii)) at 90 °C presents a small peak at 17°, which disappears as temperature is increased up to 110 °C. Anyway, as was previously commented, high transparency associated to both method (i) and (iii) should primarily be attributed to the high pressures involved in the compression-moulding step rather than the degree of crystallinity destructuring attained.

4. Conclusions

Different blends of albumen protein and starch (potato and corn starch) have been proved to be suitable raw materials for bioplastics exhibiting high transparency and an improved mechanical behaviour. Regardless the type of starch used, DMTA results were quite similar, with samples showing a predominantly elastic response at every temperature tested. Instead, major differences in tensile and optical properties were observed. In that sense, corn starch leads to bioplastics with higher values of tensile strength while potato starch yields more transparent materials.

Both, processing method and temperature selected for the manufacture of albumen/starch-based bioplastics play an important role in their final properties. Thus, materials with good mechanical properties and quite acceptable degree of transparency can be obtained by compression-moulding, which results to be a more effective way to prepare improved albumen/starch-based bioplastics than extrusion. In addition, an adequate combination of extrusion and compression-moulding, by plasticisation of starch prior to mixing with albumen, has proven to further improve albumen/starch bioplastics properties.

Nevertheless, more research is still needed to deeply understand how gelatinized-starch interacts with albumen at the structural level.

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