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Protein/glycerol blends and injection-molded bioplastic matrices: Soybean versus egg albumen

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ABSTRACT: Two well-known proteins have been selected in order to produce bioplastics through injection molding: a soy protein isolate (SPI) and an egg white albumen concentrate (EW). Each of them has been thoroughly mixed with glycerol (40 wt %) and the blend then obtained have been characterized by means of rheological and thermomechanical techniques, which allowed the optimization of the processing moulding conditions (cylinder temperature, 60°C–65°C; mould temperature, 120°C; post-injection pressure, 500–600 bars). Once bioplastics were obtained, their thermomechanical and tensile properties, as well as their water uptake capacity and transparency were evaluated. Bioplastics containing EW showed higher values in the elastic and loss moduli, E' and E'', from −30°C to 130°C, than the corresponding SPI bioplastic. However, they both showed qualitatively the same evolution with temperature, where E' and E'' decreased up to a plateau at high temperatures. When examining their tensile and water uptake properties is found that SPI bioplastics are more ductile and present enhanced water uptake behavior over EW bioplastics, which on the other hand possess higher Young's modulus. SPI seems to provide tougher bioplastics, being an excellent option for potential superabsorbent applications, whereas EW would suit for those applications requiring higher mechanical properties. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 42980.

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INTRODUCTION

Even if petroleum-based plastics are profusely used, many drawbacks result from their use. For example, the production of those plastics generates important wastes that are not easily degraded. It is important to notice that plastic industry has gone through a continuous growth for more than 50 years, with a global production in 2013 of 299 million tones. Packaging represents the largest market sector where plastics are used, followed by the building and construction sector. In spite of its ubiquitous presence in everyday life, a low recycling ratio (26%) has been reported.[1] It is because of these negative attributes of conventional plastic use that attention is being focused on environmentally friendly plastics from alternative sources.[2]

Bioplastics have been produced from different sources, like proteins, lipids, and polysaccharides.[3–5] Protein-based bioplastics are getting much attention these days, as they are a plausible choice for many applications where traditionally synthetic polymers have been used, both for economical and ecological reasons. Proteins like wheat gluten,[6–12] soybean protein,[13–16] egg white albumen (EW),[2,17] rice protein,[18] bloodmeal protein,[19] or spirulina[20] represent a renewable raw material source produced at a global scale from which suitable bioplastics have been produced.

Anyway, there is still a lot of work ahead in order to improve mechanical and physical properties of protein-based bioplastics. They generally display tensile properties similar to those of synthetic polymers (e.g., HDPE), representing an attractive bioplastic source, as many of them are low-cost materials, annually renewable, and readily available.[18] Jerez *et al.*[18] pointed out how water uptake capacity of bioplastics may vary from 40% to 320%. However, depending on their future applications, possible inconveniences may be found, as good hygroscopic properties normally are paired with lower elastic properties. Thus, although some advances have been made in order to minimize those disadvantages, more research is needed to evaluate both positive and negative properties of protein-based bioplastics in order to support their suitability for a wide variety of applications.[21]

Recent studies show how egg albumen presents antibacterial properties, due to the presence of lysozyme,[22] which may be useful in medicine and pharmacology. Moreover, when compared with other common proteins like gluten, egg white has

proved to be an adequate raw material in the obtaining of highly transparent bioplastics with suitable mechanical properties for the manufacture of biodegradable food packaging and other plastic products. Blends of this protein with other products from agricultural sources, biodegradable and of lower cost than protein and synthetic additives have been recently proposed.[23]

Soybean proteins consist of mainly 7S and 11S globulins, being the former a trimer and the latter being composed by six subunits.[24] Soybean proteins may be transformed into biodegradable plastics when mixed with a plasticizer.[25,26] Potential applications of soybean-based bioplastics have been reported, like spoons, toys, or food packaging.[27–29] However, these soybean bioplastics have showed low mechanical strength and high moisture absorption.

The present study focuses on the rheological and thermal characterization of two different protein/glycerol blends: one based on EW and another on soybean protein. Through that characterization, an optimization of the processing parameters to be used in injection molding to obtain bioplastic matrices is made. Then, the main objective of this study is the comparison of the injection-molded bioplastics produced at the selected conditions for both proteins. Their thermomechanical and tensile properties, as well as their transparency and water uptake capacity (from air or water environment) will be discussed. Moreover, their suitability for different applications will also be considered.

EXPERIMENTAL

Materials and Sample Preparation

Soy protein isolate (SPI, 89.7 wt % protein content, 5.8 wt % moisture content, SUPRO 500E) was obtained from Protein Technologies International, Inc. (the United States). EW (80.0 wt % protein content, 8 wt % moisture content) was provided by PROANDA Proveedora Andaluza Sociedad Limitada. Glycerol (GL) from Panreac Quimica Sociedad Limitada Unipersonal (Spain) was used as plasticizer.

The SPI/GL and EW/GL blends were properly manufactured by a thermomechanical procedure that consisted of two stages. Firstly, those blends containing 60 wt % SPI or EW concentrate and 40 wt % glycerol were mixed in a two-blade counter-rotating batch mixer Haake Polylab QC (ThermoHaake, Karlsruhe, Germany) at room temperature and 50 rpm for 10 min, at adiabatic conditions. Secondly, the dough-like materials obtained after mixing were subsequently processed by injection molding using a Mini-Jet Piston Injection Molding System II (ThermoHaake, Karlsruhe, Germany) to obtain bioplastic specimens. Three molds were used to prepare three type of specimens: (1) a 55 × 10 × 1 mm rectangular-shaped specimen, to be used for both dynamic mechanical temperature analysis (DMTA) experiments and transparency measurements, (2) a dumb-bell-type specimen defined by ISO 527-2:1993 for determining the tensile properties of plastics, and (3) a 25 × 1.5 × 20.5 mm circular-shaped specimen to be used for water uptake capacity determinations.

Thermogravimetric Analysis (TGA)

TGA was carried out on a TGA instrument (Q5000, TA Instruments) under a nitrogen atmosphere at 100 mL/min, from 20°C to 600°C using a continuous heating rate of 10°C/min. The weight of the sample was always approximately 10 mg.

Dynamic Mechanical Properties

DMTA tests were carried out with a RSA3 (TA Instruments, New Castle, DE). When studying the thermomechanical properties of the unprocessed blends obtained after mixing, tests were always carried out in compression mode using cylindrical plates. Temperature ramp tests were carried out at constant frequency (6.28 rad/s) and strain (between 10^{-4} and 3×10^{-3}, within the linear viscoelastic region) from −30°C to 130°C. The selected heating rate was 3°C/min. All the samples were coated with Dow Corning high vacuum grease to avoid water loss. The mechanical spectra of the blends for both systems, SPI/GL and EW/GL, were obtained at the selected temperature at a constant stress within the linear region from 0.01 to 20 Hz.

On the other hand, when examining the processed bioplastics, rectangular probes were used in tension mode (dual cantilever bending). Temperature ramp tests for bioplastics follow the same procedure as blends.

Each sample was analyzed at least in duplicate.

Mechanical Property Measurements

The tensile properties of injection-molded soy and albumen-bioplastics were measured using a MTS Insight 10 kN (the United States), according to standard method ASTM D638 (2003). The crosshead speed was 1 mm/min, and at least six replicates were tested for each sample.

Water Uptake

Water uptake capacity of circular probes (25 × 1.5 mm^2) was measured from immersion in water, as well as from sorption from the surrounding atmosphere at different relative humidity (RH) values.

From immersion in water, water absorption tests, according to UNE-EN ISO 62:2008, were carried out on the circular probes immersed into distilled water for 24 h, water uptake percentage was calculated as:

$$\text{Water uptake} = \frac{m_2 - m_1}{m_1} \times 100 \quad (1)$$

where: m_1 is the initial weight of the probe immediately weighed after being dried in an oven at 50°C for 24 h and cooled in a desiccator; and m_2 refers to the weight of the probe just after 24 h of water immersion.

Moreover, soluble matter loss was estimated as:

$$\text{Soluble matter loss} = \frac{m_1 - m_3}{m_1} \times 100 \quad (2)$$

where: m_1 is the initial weight of the probe immediately weighed after being dried in an oven at 50°C for 24 h and cooled in a desiccator; and m_3 refers to the final weight of the wet sample after 24 h of drying in an oven at 50°C.

At least three replicates of each measurement were performed 24 h after the bioplastic manufacture. Reported results correspond to average values and standard deviations.

From the saturated surrounding atmosphere, water uptake was calculated as expressed in eq. (1), though in this case: m_2, is the

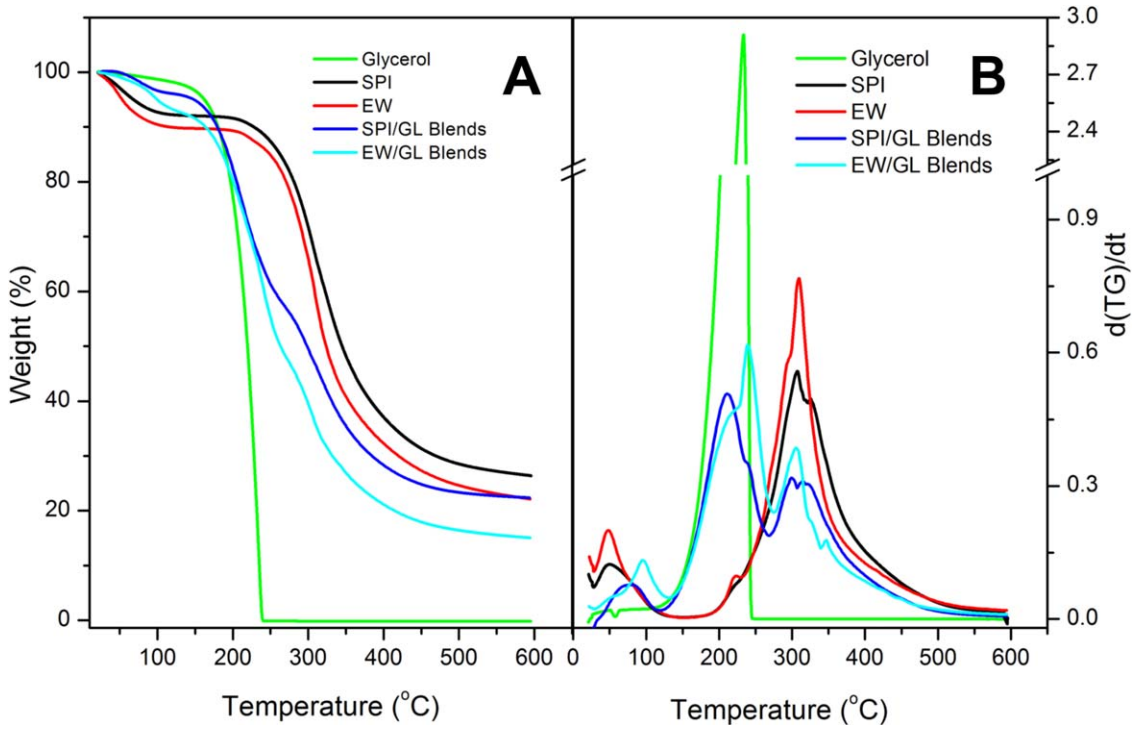

Figure 1. Thermal gravimetric analysis tests for SPI/GL and EW/GL blends, as well as for their components individually (**A**), and their corresponding derivative signals (**B**). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

weight of the probe just after 1 week in a sealed container equilibrated at a constant RH. Four RH values were selected: 100%, 75%, 53%, and 33%, obtained by saturation over distilled water and salt solutions [NaCl, $Mg(NO_3)_2$ and $MgCl_2$], respectively.

At least two replicates of each measurement were performed 24 h after the bioplastic manufacture. Reported results correspond to average values and standard deviations.

Transparency

Transparency measurements were done by means of a Genesis 20 spectrophotometer (Thermo Scietific, the United States). Transmittance (%) of rectangular specimens was measured using a wavelength of 600 nm. Reported results correspond to average values and standard deviations.

RESULTS AND DISCUSSION

Protein/Glycerol Blends

Thermal Gravimetric Analysis (TGA). Thermal stability of the SPI/GL and EW/GL blends, as well as of their components individually, was evaluated through TGA tests. The results are shown in Figure 1. As may be observed, the TGA profile for glycerol initially shows a smooth weight loss starting at about 120°C, associated with the small amount of water present, that is followed by a rather steeper loss, displaying a marked peak at 234°C in the derivative signal [Figure 1(B)] that corresponds to the evaporation of glycerol. Yunos and Rahman[30] also reported a similar TGA profile with evaporation of glycerol in the range between 200°C and 300°C. EW and SPI showed similar TGA and d(TG)/dT profiles. The derivative profile showed a first peak at about 48.5°C due to moisture loss, being more pronounced for EW protein. In both cases protein degradation starts at about 220°C, but the peak for EW develops faster and becomes narrower, displaying a peak at 309°C, which suggests a slightly higher thermal stability for SPI. These results are similar to those found previously for EW[2,31] and SPI.[32–34] The double peaks for SPI also indicates that the 7s protein (peak at 308°C) shows a slightly faster degradation kinetics than 11s fraction (peak at 325°C), as described by Güttler.[35] Some authors reported TGA profiles with thermal events at 294°C and 307°C for ovalbumin[36] and lyzosyme,[37] respectively, in agreement with the profiles reported in this study. The former authors also reported a moderate thermal event at 224°C that was attributed to some loss associated with ovalbumin melting. This thermal event has been also detected in this study for the whole albumen, as well as in other articles.[2,31] The TGA profile for glycerol shows a rather apparent thermal degradation peak at 233°C, which coincides with the results reported by literature (e.g., Jones *et al.* 2013 that found a peak at 225°C). The position of this peak is highly dependent on the water content of glycerol.[38]

As for protein/GL blends they showed in both cases three stages of weight loss during heating. In the first stage, the weight loss below 130°C is mainly attributed to the evaporation of the absorbed moisture.[39–41] The temperature at maximum weight-loss corresponding to moisture evaporation is 78.8°C and 94.7°C for SPI/GL and EW/GL, respectively. Subsequently, the weight loss that takes place during the second stage, from 130°C to 270°C or 275°C for SPI/GL and EW/GL, respectively, seem to be attributed to the evaporation of glycerol.[30,37,39] Then, it is at higher temperatures when the protein degradation mainly

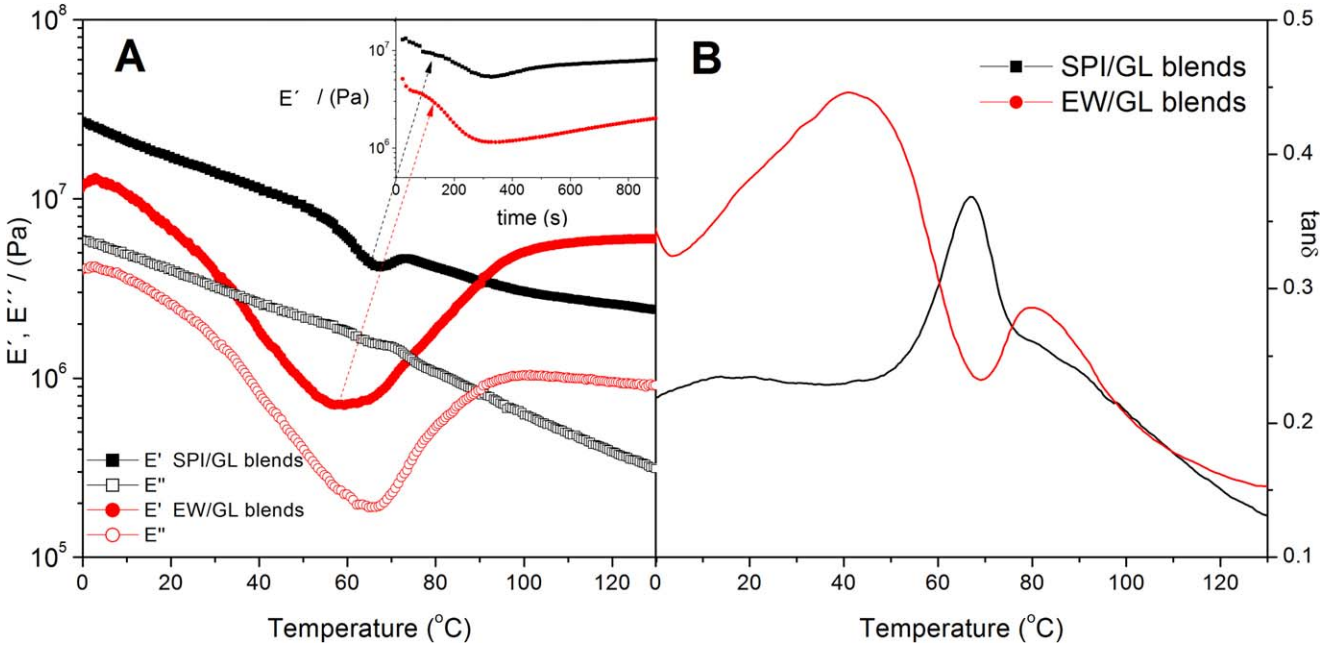

Figure 2. E', E'' (A) and tanδ (B) responses from DMTA in compression mode for SPI/GL and EW/GL blends prior to the injection molding. Frequency: 1 Hz. Heating rate: 3°C/min. Insert figure shows time sweep tests carried out at 65°C and 60°C for SPI/GL and EW/GL, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

occurs, with a maximum at a temperature around 300°C.[2,32,40,41] In fact, both blends show this maximum at a temperature around 300°C–310°C.

It is possible to observe some differences when comparing TGA results for blends and their individual components. Moisture seems to be lost at higher temperatures for protein/GL blends than for protein samples, which may be explained on basis of a greater amount of water binding taking place in the blends through hydrogen bonding with both glycerol and the protein. Moreover, the peaks corresponding to the plasticizer and the protein seem to approach each other in blends, when compared with those of the individual components. Chen *et al.*[32] explained this effect through hydrogen bonding taking place between the protein and glycerol in the blends.

Dynamic Mechanical Analysis (DMA) by Compression Mode. Temperature ramp DMA compression tests for the SPI/GL and EW/GL blends to be processed through injection molding are shown in Figure 2. Both samples show a predominantly elastic response ($E' > E''$) over the whole temperature range. At low temperatures and up to around 60°C–65°C, both systems show analogous response, with both the elastic and loss moduli, E' and E'', decreasing progressively with temperature, although it is remarkable how EW/GL blend shows a much more dramatic decrease than SPI/GL [Figure 2(A)]. The decrease in the mechanical properties as temperature rises is often related to mobility increase in the biopolymer chains as well as to the breakage of hydrogen bonds. For EW/GL, E' and E'' start to increase from 60°C up to plateau values at around 110°C. This increase may be explained on basis of covalent bonds forming between different segments of the protein surface (e.g., disulphide bonds), which would eventually result in the formation of entanglements strengthening the elastic gel network.[42] Conversely, for SPI/GL, after E' reaches its minimum value at 65°C, and after a slight increase in E', both E' and E'' keep decreasing continuously with temperature. It should be noticed, however, that the decreasing rate found for E' becomes slower in the high temperature regime. As a consequence of these different temperature profiles, it is found how in the 0°C–90°C temperature range, SPI/GL blends show higher thermomechanical properties than EW/GL. However, from 90°C upward, it is the EW/GL blend which shows higher E' and E'' values. The reason of this may rely on the higher potential of EW proteins to establish disulphide bonds when compared with soybean proteins. Thus, previous work showed that the amount of disulphide bonds and sulfhydryl groups is higher for EW.[43] This has been related to the presence of some aminoacids such as methionine and cysteine in ovalbumin, which is the only egg protein that contain —SH groups.[44]

Figure 2(B) shows the tan δ profiles for both blends as they are heated. SPI shows one peak at about 67°C that seems to be related to a glass-like transition of the SPI/GL blend, being consistent with the E' thermal profile. The profile for EW is quite different, showing two peaks at 41°C and 79°C. The first one takes place before the minimum value observed for E' [Figure 2(A)], leading to some thermal-induced structural softening that is related to a glass transition, whereas the second peak, which takes place after the minimum in E', is associated with the strengthening of the gel-like blend. The evolution of DMA results may be explained on account of two different processes taking place along heating: an increase in mobility as the transition from glass-like to rubber-like behavior takes place and, on the other hand, an enhancement of the aggregation between protein segments. This second event is particularly apparent for

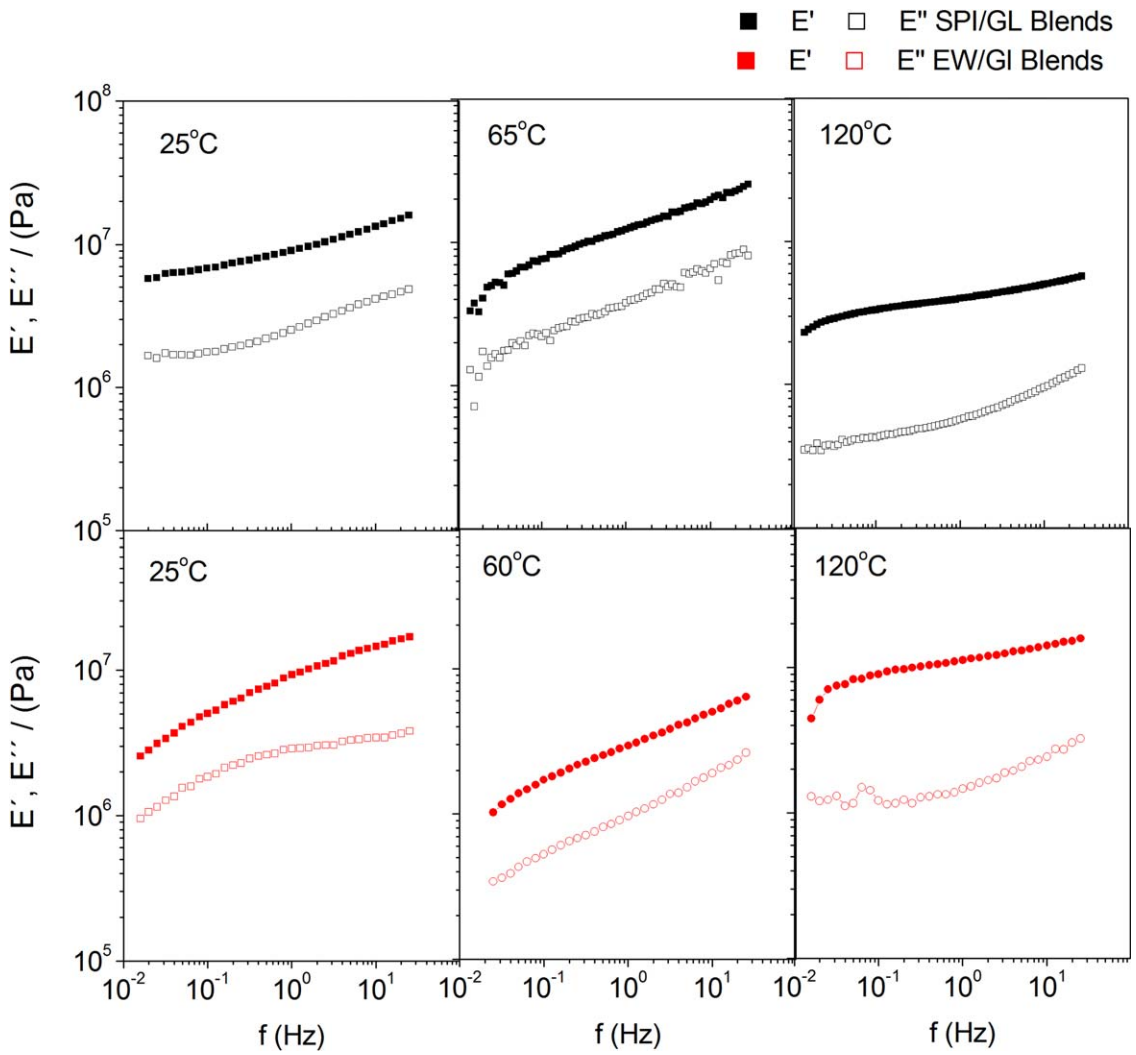

Figure 3. Mechanical spectra (E', E'' vs. frequency) for SPI/GL and EW/GL blends prior to the injection molding at three different temperatures: 25°C (A), T_{cyl} (B), and 120°C (C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

EW/GL blends, while it seems to be restricted for SPI/GL blends.

From results shown in Figure 2, some injection molding processing conditions may be selected. Generally, it might be concluded that the cylinder temperature (T_{cyl}) would be optimal when the minimum for E' is found. At that point, the blend has achieved its maximum softening degree and the flow from the cylinder into the mould would be facilitated. This seems to be the case for EW/GL blend, as its moduli are much higher (up to one order of magnitude) at temperatures different from the minimum ($T_{cyl} = 60$°C). However, this criterion must be changed for SPI/GL blend since the minimum in E' corresponds to the high temperature regime at which tan δ value is much lower. Instead, 65°C was selected as the temperature for the cylinder since it is close to the tan δ peak achieved for this blend. Moreover, SPI/GL shows higher values for E' and E'' than EW/GL at T_{cyl}, which would in the end result in the need of a higher pressure (600 bars) for SPI than for EW (500 bars). Finally, the mould temperature has been set on 120°C for both systems. At that temperature, EW/GL blends have already achieved a plateau for E' and E''. Similar results have been reported by González-Gutierrez *et al.*[23] for EW/starch specimens.

Moreover, time sweep tests were carried out at T_{cyl} to determine the optimal time (t_{opt}) that samples should stay in the cylinder prior to proceeding with the injection into the mould [insert figure in Figure 2(A)]. Initially, there is a softening of the structure resulting in a decrease of both moduli up to the minimum that defines t_{opt}, from which the samples structures start to strengthen, even though gently, as covalent interactions may take place. The value of parameter t_{opt} is around 200 s for both blends.

Frequency sweep tests were carried out at constant stress within the linear range at 25°C, T_{cyl} and 120°C (T_{mould}) for a further characterization of these blends prior to injection molding. The results obtained are plotted in Figure 3.

In all cases, considering the nature of the blends studied, mechanical spectra show elastic responses which dominate over the viscous ones ($G' > G''$). These results are in good agreement with those shown in Figure 2. Both blends exhibit

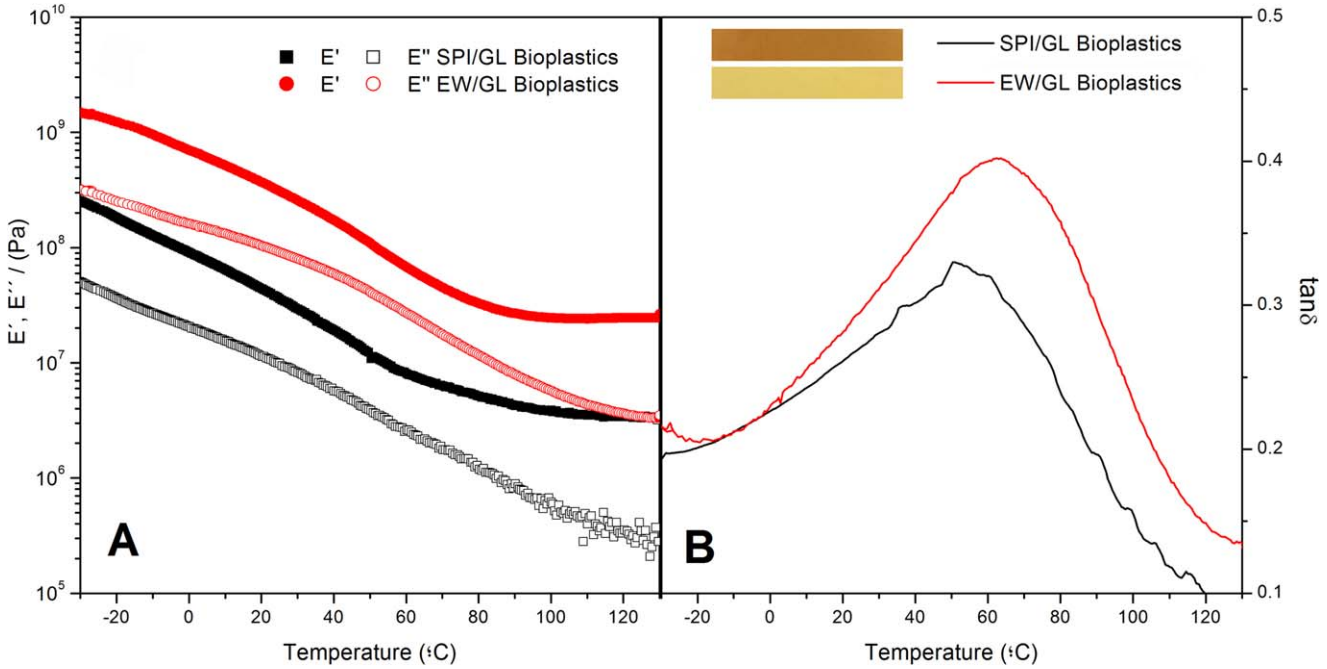

Figure 4. E', E'' (A) and tanδ responses from DMTA in tensile mode (dual cantilever bending) for SPI/GL and EW/GL bioplastics. Frequency: 1 Hz. Heating rate: 3°C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

thermorheological complex behaviors since time–temperature superposition is not possible. However, the mechanical spectra from small amplitude oscillatory compression measurements for both blends follow different patterns with increasing temperature. Thus, EW/GL blends display minimum for both moduli at 60°C [coinciding with those minimum values shown in Figure 2(A)], followed by an evolution toward a mechanical spectrum typical of a reinforced gel network (showing lower slope with frequency for both moduli, as well as lower tan δ values) with higher values for E' and E''. On the other hand, the mechanical spectra of SPI/GL blends are quite similar at 25°C and 65°C and both moduli undergo a marked decrease by increasing temperature up to 120°C. Interestingly, even though E' and E'' are much lower for SPI/GL blends than for EW/GL at this temperature, the shapes of the mechanical spectra are similar in both cases, also showing similar tan δ values over the whole frequency range. These results may be explained in terms of the effect that temperature exerts on the interaction among protein segments. It is generally accepted that hydrophobic interactions, which are responsible for protein–protein aggregation, as well as disulphide bonding are promoted by heating to temperatures above 100°C. However, the increase in temperature also disrupt electrostatic and hydrogen bonding.[33,45] In the case of SPI/GL blends, these later interactions exert a dominant effect on the viscoelastic response, which leads to lower values for E' and E'' obtained at 120°C, although some covalent bonds are also expected to participate, thus explaining the decrease in tan δ values. On the other hand, the building-up effect is more apparent for EW/GL blends, which suggests that its behavior is dominated by hydrophobic and disulphide bonding. The differences between both proteins must be related to the higher surface hydrophobicity and free sulfhydryl content found for EW protein.[46] In addition, heating has been reported to favor exposure of sulfhydryl groups located at EW protein surfaces.[47]

Protein/Glycerol Bioplastics

Dynamic Thermomechanical Analysis by Uniaxial Tensile Mode. Temperature ramp tests for the SPI/GL and EW/GL bioplastics processed through injection molding are shown in Figure 4. The evolution of E' and E'' along heating is qualitatively similar for both systems, though some differences may be pointed out. Thus, as temperature increases, EW/GL bioplastics show a decrease up to a plateau value reached at a temperature around 100°C. E'' also decrease progressively with temperature, though at a slower rate at high temperatures, showing also a trend to reach a plateau value [Figure 4(A)]. The occurrence of a plateau value for both moduli suggests that EW-based specimens exhibit a certain thermoset character.

SPI/GL bioplastics display much lower values of both moduli in the whole temperature range than those processed from EW/GL blends, which is consistent with their respective viscoelastic responses at high temperature. The trend to the plateau value for SPI systems is less clear, particularly for E''. The evolution of the loss tangent is also similar for SPI and EW-based bioplastics, showing maximum values in both cases, which are found at around 50°C and 60°C for SPI and EW, respectively. Again, an explanation of the differences between both systems, which is reflected in the values of the moduli rather than in the loss tangent, may be given in terms of the degree of hydrophobic and disulphide bonds being higher for egg albumen systems.

Tensile Properties. The average values for the maximum tensile strength (σ_m), the fracture strain (ε_f), and the Young's modulus (E) for SPI/GL and EW/GL bioplastics are displayed in Figure 5. The toughness (U_T) measures the capacity of the specimen to

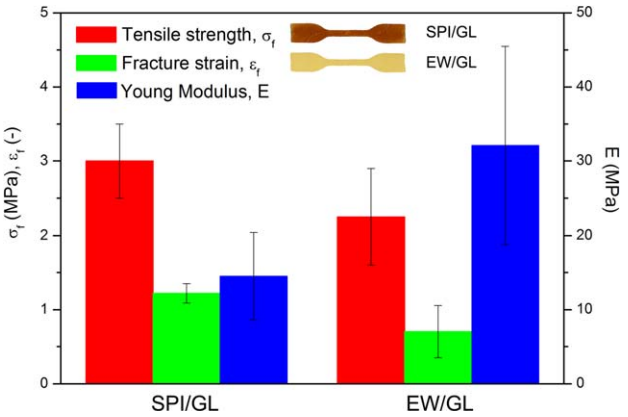

Figure 5. Tensile parameters for SPI/GL and EW/GL bioplastics processed through injection molding with an injection temperature of 65°C and 60°C, respectively, an injection pressure of 500 and 600 bars, respectively, and a molding temperature equals to 120°C, for both of them. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

absorb energy per unit volume before fracture. This parameter can be determined by integrating the stress–strain curve:

$$U_T = \int_0^{\varepsilon_f} \sigma d\varepsilon$$

EW/GL bioplastics are more fragile than SPI/GL bioplastics, as the maximum tensile stress and fracture strain are higher for the latter. Moreover, EW/GL possesses a higher Young's modulus, which is consistent with the better elastic response found from previous DMTA tests. In addition, SPI/GL specimens exhibit higher toughness than EW/GL (3.5 ± 0.5 MJ/m^3 compared with 0.91 ± 0.07 MJ/m^3). This means that the SPI-based bioplastics can absorb more energy per unit volume before rupturing.

Tensile parameters (σ_m, ε_f, E) found in the present study for EW and SPI are in good agreement with those found elsewhere.[41,46,47]

Water Uptake and Vapor Sorption. Inset table in Figure 6 shows the water uptake and the water-soluble matter loss obtained from water absorption measurements obtained after immersion of bioplastics for 24 h in distilled water.

Water uptake capacity is clearly greater for SPI/GL bioplastics, with an average value of 200% compared with the poorer value obtained for EW/GL bioplastics (~40%). The fact that albumen bioplastics show a lower water uptake capacity than soybean-based samples, has been previously related to a higher degree of structuration in the albumen protein matrix, as crosslinking is more favored in the albumen protein matrix than in the soybean matrix, which results in a more rigid bioplastic, less prone to swelling.[15,48] In fact, the amount of free sulfhydryl for EW is about 24 times the amount corresponding to SPI,[15] which must lead to a higher contribution of disulphide bonds to the bioplastic network. Moreover, previous work also pointed out that EW show higher hydrophobicity than SPI that also would support these results.

Similar results have been obtained for SPI bioplastics processed through different methods. Thus, values around 180%–200% have been previously reported for water uptake capacity of SPI bioplastics processed through extrusion[49] or compression.[50]

From the soluble matter loss results shown in the same inset table, it may be seen that although the values are close, SPI shows significantly higher loss than EW specimens. Presumably these soluble matter losses (37% and 35.5%, respectively) might correspond mainly to the glycerol initially contained in the bioplastics (~40%), which is known to be highly hydrophilic. Anyway, the presence of some amount of protein in the matter loss not strongly associated to the network structure should not be neglected.

Figure 6 shows the evolution of the relative increase in weight due to water vapor sorption as a function of the relative moisture content. The plot corresponding to SPI-based bioplastic follows the typical "S-shaped" curve of a sorption isotherm for a hygroscopic material. As for the EW bioplastics a quite similar behavior can be observed up to 53% RH, showing the onset of the S-shaped curve that is eventually truncated by reaching a saturation point, such that no evolution takes place above 75% RH. This shape shown by EW is in agreement with the well-known Langmuir adsorption isotherm, derived for adsorption in a unimolecular layer.[51] This different behavior suggests that EW lead to much less hydrophilic bioplastic materials. Moreover, the different shape found in the water vapor sorption profile may be related to different mechanisms for both proteins, a multilayer adsorption for SPI and a monolayer adsorption for EW. Multilayer adsorption has been associated to macroporous substrates, while monolayer adsorption has been related to microporous solids, which may be related to the higher water

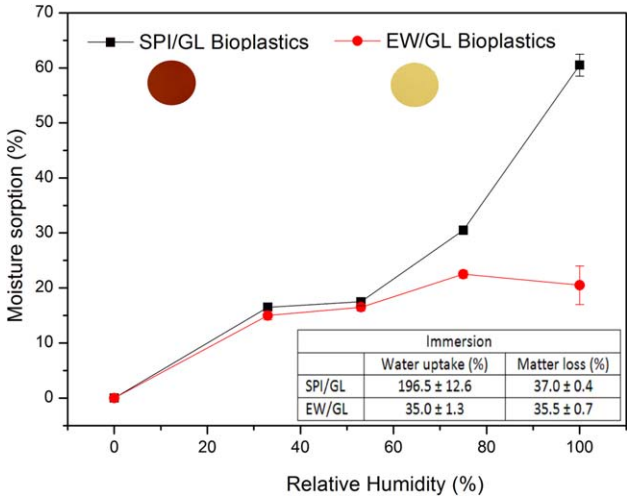

Figure 6. Water vapor sorption for SPI/GL and EW/GL bioplastics processed through injection molding with an injection temperature of 65°C and 60°C, respectively, an injection pressure of 500 and 600 bars, respectively, and a molding temperature equals to 120°C, for both of them. Inset Table: Water uptake and the water-soluble matter loss obtained after immersion of bioplastics for 24 h in distilled water. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

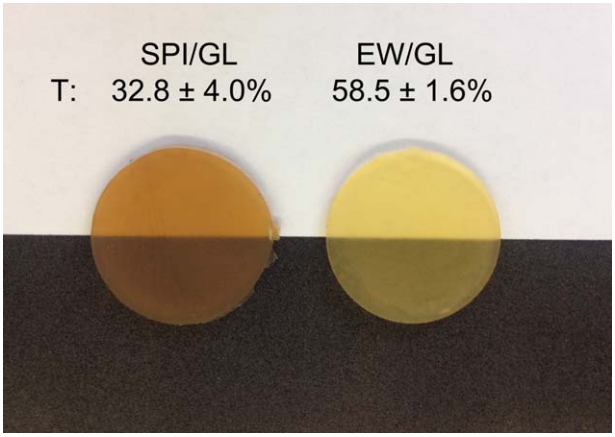

Figure 7. Physical appearance of SPI/GL (left) and EW/GL (right) bioplastics processed through injection molding, respectively, an injection pressure of 500 and 600 bars, respectively, and a molding temperature equals to 120°C, for both of them. Transmittance (*T*) was obtained at 600 nm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

uptake displayed by SPI.[52] Moreover, when results at 100% RH are compared with water uptake capacity values obtained previously through immersion, it is noticeable that the latter is 3 and 1.8 times higher than the former for SPI and EW, respectively. The reason of the greater difference found for SPI may lay in these differences in morphology as well as in its above commented higher hydrophilic character.

Transparency Measurements. Bioplastics produced through injection molding show different colors and transparency, depending on the protein source. Thus, EW/GL bioplastics are light yellow, and SPI/GL bioplastics are light brown or amber tinge. For SPI-based compression-molded bioplastics, Paulk and Ogale[53] reported that a compaction temperature of 175°C resulted in a dark-brown film with evident degradation of the material. Cunningham *et al.* (2000) found semitransparent amber tinge soybean probes at 150°C through compression.

As may observed in Figure 7, EW/GL bioplastics show higher transparency than SPI/GL. Specifically, when measuring the transmittance (*T*) through the sample, and considering air as reference ($T = 100\%$), the albumen bioplastic presented a T value that is 26% higher than that corresponding to soybean bioplastic. In general, the clarity of the films may be improved with increasing processing temperature.[54]

CONCLUSIONS

From the results obtained in this study it may be concluded that SPI possesses a more thermoplastic character than EW protein. This difference in behavior is expected to lead to a wider processing window for SPI/GL blends, which in turn would contribute to look for those conditions promoting injection-molded bioplastic matrices with a higher hydrophilic character. On the other hand, if higher reinforced matrices were required, which may be desirable in certain applications, EW-based blends should be selected for injection molding. It is worth mentioning that these EW bioplastics are more transparent, elastic, harder and more fragile than SPI bioplastics for the same protein/plasticizer ratio, even when they are produced with a lower energy cost, as they can be produced at lower injection pressures. These differences are related to the higher sulfhydryl content of egg white, which allows a higher degree of structuration when subjected to high pressure/temperature.

In addition, the higher hydrophilic character of SPI bioplastics is responsible for its remarkable enhancement in water uptake capacity (either in air or water media) over EW bioplastics. This would make soybean an excellent candidate to produce protein-based bioplastics for different potential applications where the absorption of water is critical (e.g., superabsorbent materials).

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