Improvement of mechanical and water absorption properties of plant protein based bioplastics

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Abstract

Bioplastics deriving from plant proteins are becoming an increasingly popular source of raw material for plastic products since they are not only biodegradable but renewable resources. However, these bioplastics require improved mechanical and water absorption properties to be suitable for many applications, such as packaging. For this reason, this study considers potato and rice proteins as a new source for the manufacture of bioplastics. The proteins were mixed with different glycerol concentrations followed by thermomoulding at temperatures from 60 to 180 ºC. The resulting bioplastic is characterized in terms of thermo-mechanical properties, water absorption and molecular weight distribution. Compared to well-known wheat gluten, these bioplastics required higher temperatures for their thermomoulding. However, both of them were more structured materials and exhibited less water absorption (e.g. as low as 9 wt.%) than those obtained for wheat gluten blend. Potato protein-based bioplastics showed complex modulus values comparable to synthetic polymers such as Low Density Polyethylene (LDPE).

Keywords: Rice protein; potato protein; bioplastics; rheology; water absorption; molecular weight properties.

1. Introduction

Bioplastics formulated with plant proteins are becoming an increasingly popular source of raw material for plastic products since they are not only biodegradable but they are also made from renewable resources such as polysaccharides, lipids and proteins (Mooney, 2009; Song & Zheng, 2008; Phillips, A. L., 2008, Wirsenius, Azar & Berndes, 2010). Currently, many bioplastics are still in the developmental stage, but important applications are beginning to emerge in the areas of packaging, food production and medicine (Mooney, 2009; Chen & Tan, 2006; Van de Velde & Kiekens, 2002). Some bioplastics can even directly replace synthetically derived materials in traditional applications, whereas others possess unique properties that could open up a range of new commercial opportunities.

Their suitability for many applications such as biodegradable films, food packaging or plastic stuffs will depend on material mechanical and water absorption properties. Wheat gluten is a good example of a protein which has been investigated for its thermoplastic properties (Zhong & Yuan, 2013; Jerez et al., 2005a). However, this protein is also highly hygroscopic, which renders it inappropriate for this type of application (Gomez-Martinez et al., 2009; Jerez et al., 2005a). In addition, a critical reason to take into consideration is the potential consumers with celiac disease which comprises approximately 1% of the worldwide population (Renzetti et al., 2012). The use of gluten based bioplastics in food packaging might be risky or even dangerous to their health; the gluten would be in direct contact with food which is a big inconvenience in this case. For this reason, other gluten free alternatives as raw materials should be considered for the manufacturing of bioplastics. In this regard, potato and rice isolates, vegetable proteins that are by-products of the starch industry, are naturally hypoallergenic, meaning that it is entirely free from any gluten.

Potato protein has a high content of amino acids with hydrophobic functional groups and its lysine content is much higher than that of other types of protein (Waglay; Karboune & Alli, 2014; Refstie & Tiekstra, 2003). Potato protein can be used as an additive of the feed ingredients, in application of health food, in many food products as emulsifiers and emulsion stabilizers (Waglay; Karboune & Alli, 2014; Singh & Kaur, 2009; Van Koningsveld et al., 2006) and can also be used as nitrogen sources for industrial fermentation. Rice protein is high in the sulfur-containing amino acids, cysteine and methionine. This protein could be extracted from rice bran which is an inexpensive, underutilised milling co-product of rough rice (Tang, et al., 2003).

Despite the broad available literature about protein based bioplastics, the use of potato or rice proteins as raw materials for manufacture of bioplastics by a thermo-mechanical procedure has so far little studied (Rattanatham et al., 2011; Felix et al., 2016). The purpose of the present study was to evaluate the potential of both proteins isolates as a new source for the production of bioplastics. These bioplastics were obtained by thermomechanical processing that involves a mixing stage followed by thermomoulding, as previously described elsewhere (Gomez-Martinez et al., 2009; Sun, Song & Zheng, 2008; Jerez et al., 2005a; Mangavel et al., 2004; Pommet et al., 2003). The effect of glycerol concentration used as plasticizer, and thermoulding conditions (between 60 to 180ºC) on both rice and potato protein based bioplastics was studied. The resulting materials were characterized in terms of thermo-mechanical properties, water absorption and molecular weight distribution.

2. Materials and methods

The bioplastics prepared in this work were composed of rice (R), potato proteins (P) and, as a reference protein, wheat gluten isolates (WG) and glycerol (G) as plasticizer. The proteins were provided by Ferrer Alimentación S.A. (Spain). The composition of rice isolate (R) was about 79 wt.% protein, 5 wt.% lipids, 16 wt.% carbohydrates and 2.0 wt.% ashes. Its moisture content was 12 wt.% on dry basis. Potato isolate (P) is mainly composed by 82 wt.% protein, 1.0 wt.% lipids and 0.5 wt. ashes. Its moisture content was 10 wt.% on dry basis. Wheat gluten isolate composition was about 83 wt.% protein, 3 wt.% lipids, 10 wt.% carbohydrates and 1.0 wt.% ashes. Its moisture content was 8 wt.% on dry basis. Glycerol (G) was provided by Prolabo S.A. (Spain).

Bioplastic compounds were mixed in a Polylab torque-rheometer equipped with a Rheomix 600p kneading tool (Thermo-Haake GmbH, Germany). This device recorded evolution of temperature and torque along glycerol-protein isolate mixing. Neither heating nor cooling was supplied to the kneading chamber (69 cm^3 volume, filled with 56g of sample to 85% of its full capacity) during compounding. The process consisted in mixing protein (fine powder) with plasticizer (liquid), by means of two rollers (37.5 mm diameter and 47 mm length) counter-rotating at 50 rpm. The mixing time t_{mix} was stopped at 15 min. Subsequently, the resulting blends were compression-moulded into rectangular specimens (50 mm length, 10 mm width, 3 mm thick) by applying a gauge pressure of 100 bar for 10 min at six different temperatures, 90, 100, 120, 140, 160 and 180ºC (Jerez et al., 2005a,b). These temperatures were above the highest temperature reached during the mixing process. Finally, specimens were allowed to cool down to room temperature inside the hot-plate press before removing from the mould. Afterwards, bioplastics were stored at 53% relative humidity (RH) before testing. Two formulations were studied, containing 33 and 43wt.% glycerol. For sake of simplicity, samples will be identified by the protein source and plasticizer concentration, e.g. potato protein based bioplastics containing 33% and 43% will be referred to as P33 and P43, respectively. Similarly, samples R33, R43, WG 33 and W43 will identify rice and gluten based bioplastics.

Dynamic Mechanical Thermal Analysis (DMTA) experiments were performed with a Seiko DMS 6100 (Seiko Instruments, Japan), using 50x10x3 mm^3 samples in double cantilever bending mode, according to the ASTM standard method D5023–01 (ASTM, 2001b). Storage modulus E' (elastic response) and loss modulus E'' (viscous response) were determined by this technique as a function of temperature. From these data, the complex modulus (E*) was calculated as $|E^*|^2 = |E'|^2 + |E''|^2$. Temperature sweeps were carried out at a constant frequency of 1 Hz, being the applied strain always below 0.025% to assure that all tests were within linear viscoelasticity (LVE) region. A heating ramp of 2 ºC/min was set between 30 and 180 ºC. As a reference, low density polyethylene (LDPE) was measured for comparison with bioplastics.

Water absorption measurements were based on ASTM standard method D570-98 (ASTM, 2001). Bioplastic samples were dried in an oven, at 50ºC for 24 h, and cooled down in a desiccator before weighing (W_0). 50mg of every sample were submerged in 50 ml distilled water for a constant period of 24 h. Water on the surface of the samples was removed, and the samples were weighed again (W_1). The remaining water, containing glycerol and soluble proteins, was dried in order to quantify the weight of soluble matter (W_{sol}). The water absorption (Ab) was calculated as follows:

$$Ab = \frac{\left(W_1 - W_0 + W_{sol}\right)}{W_0} x100 \qquad [1]$$

The molecular weight of wheat gluten, rice and potato protein bioplastics was performed by sodium dodecyl sulphate-polyacrylamide gel electrophoresis (SDS PAGE) under reducing conditions as described by Da Silva and Taylor (2004), but using a 4-12% acrylamide gradient gel prepared as described by Byaryhanga et al. (2005). The reducing agent used was 2-Mercaptoethanol, which further denatures the proteins by reducing disulfide linkages, thus overcoming some forms of tertiary protein folding, and breaking up quaternary protein structure (oligomeric subunits).

At least three replicates (n) were carried out for each test. Standard deviations were calculated for some selected parameters from water uptake capacity and DMTA. The data were presented as average ($\bar{x}$) ± standard deviation (SD=$[\sum_n (x_n - \bar{x})^2 /(n - 1)]^{1/2}$).

3. Results and discussion

3.1 Effect of mixing process

The mixing process is an important step during manufacturing of protein based bioplastics, in which protein and plasticizer have to be efficiently blended to obtain a material with suitable mechanical properties (or, alternatively, rheology) at the end of the process. The torque and temperature profiles recorded during mixing process of rice (R33, R43) and potato (P33, P43) proteins with 33 and 43 wt.% glycerol are shown in Figure 1. A decrease in torque down to zero was found for all rice protein blends (R33, R43), which became even more evident as the glycerol content increased. On the other hand, the evolution of torque for potato protein blends (P33, P43) shows that the torque values were slightly higher than those recorded for the rice protein blends (Figure 1 A). Furthermore, the temperature variation during the mixing for these samples did not register a continuous increase, as found for other proteins such as wheat gluten (Jerez et al., 2005a), remaining close to 19ºC for rice protein blends (R33, R43) and below 22 ºC for P43 (Figure 1 B). Similarly, a slight increase in temperature of up to 36ºC is observed for a lower glycerol concentration in the potato based blend P33. In any case, this temperature can be considered very low when compared to the temperature reached for wheat gluten samples (Jerez et al., 2005a, Gomez-Martinez et al., 2009), which might suggest a low thermal dissipation of energy and small extent of microstructural changes induced in the protein molecules during mixing, probably due to poor protein-glycerol interactions. This is probably associated with the low molecular weight of both proteins as compared to, for example, wheat gluten (Oszvald et al., 2008). Such a lack of interactions between protein and plasticizer, related to the gentle shear and temperature conditions, allowed the mixing process to be stopped, after 15 min, while the plasticizer-protein dough still showed a suitable rheology (Figure 1A). Subsequently, it was necessary to apply a post-thermal treatment at higher temperature and pressure, in order to improve the interactions between the protein and plasticizer.

Therefore, the low mixing temperatures recorded would avoid denaturation or modification of the protein, reported to be close to 80ºC by Gorinstein et al. (1996) for rice protein, which in some cases could affect further material processing. Similarly, thermal denaturation (unfolding) of native potato protein is reported between 55-75 ºC (Van Koningsveld, 2001), temperature range considerably higher than the temperature recorded during mixing (36 ºC). In both cases, the lack of protein denaturation led to a low viscous (deduced from low mixing torque values measured) dough, adequate for further thermo-mechanical processing.

3.2 Effect of thermo-moulding process

The evolution of the complex modulus and tan δ with temperature as a function of the thermosetting temperature for rice protein based bioplastic with 33 wt.% glycerol is shown in Figure 2. A decrease in the complex modulus (E*) with temperature is observed. First, E* underwent a change in the slope, which occurs at a range of temperature between 74 and 106 ºC (Figure 2A). After this, samples exhibited different behaviour depending on the thermosetting temperature. In this sense, a plateau region in E* was found for samples thermoset below 140 ºC, and this event tended to appear at higher temperatures as the thermosetting temperature increased. Conversely, this plateau region was less evident as thermosetting temperature increased up to 160 ºC, and at the end of the plateau the complex modulus decreased. On the other hand, for samples thermoset at 180 ºC, there was no plateau region, but a continuous decrease in the complex modulus was observed in the temperature range studied. The evolution of tan δ with temperature for rice protein based bioplastic with 33 wt.% glycerol at different thermosetting temperatures shows a maximum in tan δ at a temperature close to 57 ºC for sample thermoset at 90 ºC, and 71 ºC for sample thermoset at 180 ºC (Figure 2B). This maximum is located at higher temperature as thermosetting temperature increased. Also, a decrease in tan δ values is observed as thermosetting temperature increased for samples thermoset below 160 ºC above which a significant increase in tan δ values is reached. In addition, a minimum in tan δ at a temperature close to 160 ºC for sample thermoset at 90 ºC, is found. This minimum appeared at lower temperature as thermosetting temperature increased and did not show up for sample thermoset at 180 ºC. Instead, this sample showed a flattening between 137 to 160 ºC, after which tan δ curve decrease.

The influence of rice protein on the development of the bioplastic network structure was compared to the structure development in wheat gluten bioplastic with 33 wt.% glycerol and thermoset at 120 ºC, as shown in Figure 2. Wheat gluten plasticized with glycerol (henceforth WG/G) was selected as the benchmark because its viscoelastic properties have been widely studied. According to Jerez et al. (2005a), the evolution of the viscoelastic functions for a WG/G sample showed three regions as temperature increased. First, E* decreased to a plateau region (from 20 to 80 ºC) and a maximum in tan δ around 30 ºC. Second, a plateau region appeared from 100 to 160 ºC. Finally, above 160 ºC, a decrease in the E* was observed and a minimum in tan δ occurs above 125 ºC. The rice protein samples displayed E* values greater than the benchmarked sample up to the first region (from 20 to 80 ºC), but beyond 80 ºC, the reference sample exhibited about the same value at the plateau region. The maximum peak in loss tangent for the rice protein samples was reached at higher temperature (around 50 ºC) than the reference. Although the minimum in loss tangent was at about the same temperature as compared with the benchmarked sample, the values in tan δ were significantly higher for rice protein samples than for the WG/G sample.

Figure 3 shows the changes in complex modulus and loss tangent with temperature for rice protein based bioplastic with 43 wt.% glycerol, submitted to different thermomoulding temperatures. The complex modulus of the rice protein bioplastics decreased with temperature in the same way as rice protein blends with 33 wt.% glycerol, and also exhibited a change in the slope in E*, which occurred at temperatures around 100 ºC. Moreover, after the change in the slope in the complex modulus, samples thermoset at 120 and 180 ºC tended to display a plateau region, whereas a gradual decrease in the slope of the complex modulus was observed for the sample thermoset at 160 ºC. A maximum of loss tangent at lower temperatures appeared as the thermosetting temperature increased. The samples also became more elastic (lower loss tangent) as the thermosetting temperature increased, except for the sample thermoset at 180 ºC (Figure 3 B). An increase in the complex modulus, between 30 and 75 ºC, was observed as the thermosetting temperature increased (from 90 to 140 ºC). However, an increase in the thermomoulding temperature from 160 to 180 ºC led to a decrease in E*.

Therefore, the viscoelastic properties of rice-based bioplastics were affected by glycerol content and thermomoulding temperature treatment. We identified two groups of behaviour, a first group with rice protein samples thermoset at temperature below 140 ºC and the second one with samples thermoset at temperature above 140 ºC. For samples in the first group, it was observed that an increase in glycerol concentration led to a decrease in E* and glass transition temperature (calculated from the loss tangent peak), although the values at the maximum peak in tan δ were not affected. At the same time, an increase in the thermomoulding temperature led to a slight increase in E*, which was most evident in the sample with the highest glycerol content. In addition, the glass transition temperature occurred at a range of temperatures between 60–70 ºC, while a slight decrease in the values at the maximum peak in tan δ was observed. The rice protein samples for the second group, by contrast, showed a significant decrease in E*, coupled with an almost constant glass transition temperature and a slight increase in the values at the maximum peak in tan δ. The complex modulus and glass transition temperatures for these samples did not vary with glycerol concentration and thermomoulding temperature.

This behaviour could suggest an optimum temperature interval for the rearrangement and alignment of the protein network, in this way promoting the protein-plasticizer interaction and giving more flexibility to the material. According to Ellepola & Ma (2006) rice protein has relatively high thermal stability indicating that it could retain its functionality during the thermomouding process. These samples also showed a higher viscoelastic modulus than wheat gluten based bioplastic but almost one decade lower than those found for LDPE (Figure 2 and 3).

Figure 4 shows the evolution of the complex modulus and tan δ with temperature as a function of the thermosetting temperature for potato protein based bioplastic with 33 wt.% glycerol. The complex modulus of the potato protein based bioplastic decreased with temperature as expected. Moreover, a change in the slope in E* was observed. This event occurred within a temperature range of 102-109 ºC for samples thermoset at temperatures higher than 120 ºC, whilst a change in the slope in E* at 75 ºC was observed for the sample thermoset at 90 ºC. There were slight increases in E* values in the glassy region for samples thermoset below 140 ºC after which E* slightly decreased. The evolution of tan δ with temperature for potato protein based bioplastic with 33 wt.% glycerol did not show a minimum value in the loss tangent but a protuberant peak which appeared at a temperature of 75 ºC for sample thermoset at 90 ºC, and at c.a. 85 ºC for sample thermoset at 180 ºC. This sample also showed higher values in tan δ than other thermosetting temperatures. Non-significant variation in tan δ values for samples thermoset below 160 ºC was observed.

The influence of potato protein on the development of the bioplastic network structure was compared to the structure developed in wheat gluten bioplastic with 33 wt.% glycerol after thermosetting at 120 ºC, as shown in Figure 4. The benchmark (i.e. the wheat gluten sample) showed E* values lower than the potato protein samples across almost the whole range of temperatures studied. These values are more than an order of magnitude higher for potato protein bioplastics than for wheat gluten at low temperature, close to the glassy region (close to 10^{9} Pa). In addition, the maximum in loss tangent for the potato protein samples always appeared at a higher temperature (90 ºC) than the benchmark (30 ºC).

Figure 5 shows the evolution of complex modulus and loss tangent with temperature for potato-protein based bioplastics with 43 wt.% glycerol. The complex modulus of the potato protein bioplastic decreased with temperature and showed a change in the slope in E* at a temperature range of 108 to 117 ºC. A gradual decrease in the slope of the complex modulus was also observed. In addition, an increase in thermosetting temperature first led to a slight increase in complex modulus values in the glassy region although it then led to a decrease at T >140 ºC. A maximum peak in tan δ around 80ºC for samples with 43 wt.% was found, excepting the sample thermoset at 90 ºC (with a peak in tan δ at 96ºC).

The viscoelastic properties of potato protein-based bioplastic did not seem to be too affected by plasticizer concentration or thermosetting treatment as compared to wheat gluten and rice protein bioplastics. The potato protein-based bioplastics had higher complex modulus value (close to 10^9 Pa) and similar to those found for LDPE (Figure 4 and 5). Also, tan δ peaks for potato protein samples were located at higher temperature than the maximum reached for wheat gluten-based bioplastic and rice systems, indicating that the potato protein blend is more resistant to high temperatures. This behaviour is indicative of a more structured material, with a higher degree of crosslinking.

3.3 Characterization of molecular weight distribution

In the manufacture of protein-based bioplastics, it is important to understand the composition of the protein and its characteristics, and also how the protein might behave under processing conditions. Understanding these factors is a means of predicting and accounting for possible interactions or reactions between proteins, and the effect of the plasticizers and other components of bioplastics.

The molecular weight of wheat gluten, rice and potato protein bioplastics was performed by sodium dodecyl sulphate-polyacrylamide gel electrophoresis (SDS PAGE) under reducing conditions (Figure 6). The results obtained were compared with a protein standard consisting of 12 protein bands in the range of 2.5 – 200 kDa. This reference (Lane 1 in Figure 6) allows accurate molecular weight estimation of the protein sample over a wide molecular weight range.

SDS PAGE under reducing conditions showed that the well-known gluten protein bioplastic (Lane 4 in Figure 6) contained bands at 36, 45 and 52 kDa, which corresponded to the alpha, beta and gamma-gliadins, respectively. This range of molecular weight could be also related to the low molecular weight of glutenins (LMW-GS, 20-45 kDa) (Kasarda et al., 1983), which, in our case, might be overlapping. Both proteins tend to be rich in asparagine, glutamine, arginine or proline, serine, methionine and isoleucine (Masci et al., 1995; Lew, Kuzmicky &Kasarda, 1992).

In rice protein-based bioplastic (Lane 3 in Figure 6), one large band at 14 kDa can be distinguished. Ogawa et al. (1987) found that rice protein consists of three polypeptide subunits with apparent molecular weight distributions of 10, 13 and 16 kDa. The reason why three bands cannot be found in this sample may be that they are so close that they could not be distinguished from each other. Previous studies have mentioned that 13 and 16 kDa are cysteine rich (the sulphur amino acid), which means that this protein might tend to interact and aggregate under thermal conditions (Hibino et al., 1989; Ogawa et al., 1987). Therefore, these three polypeptide subunits might be responsible for the high modulus exhibited in viscoelastic behaviour of rice protein based bioplastics. It is known in the case of wheat gluten based bioplastics that thermomoulding treatment leads to protein aggregation which results in an increase in E* (Gómez-Martinez et al., 2009). By contrast, in the case of rice protein, E* decreased for blends thermoset above 140 ºC as is observed in Figure 2 and 3. It seems that the high temperatures during thermomoulding might help to improve the protein-plasticizer interaction, giving more flexibility to the material (Ellepola & Ma, 2006). Moreover, rice glutelin is extremely insoluble in water because of its hydrophobic, hydrogen and disulfide bonding (Hamada, 1996; Juliano, 1985). In addition to the rice protein sample characterization, this sample exhibited one band at 21 kDa close to the band (25 kDa) cited by many authors for rice albumins which have a wide range of molecular weights (Houston & Mohammed 1970). However, according to Juliano (1972), the major component of the glutelin is located at 18–20 kDa and thus close to the band we found.

The potato protein-based bioplastic (Lane 2 in Figure 6) contained a group of proteins at 6, 16, 21 and 45 kDa. The first three bands mentioned might be identified by protease inhibitors. A characteristic of this protein is that it is small, cysteine rich (comprising a large number of disulphide bridges) and heat-resistant (Pouvreau et al., 2005a,b; Van Koningsveld, 2001). This fact might promote the aggregation of the protein under thermal conditions and may play an important role in the viscoelastic behaviour properties of this material. Therefore, this factor may explain the high values of E* and tan δ peaks located at high temperature (see Figure 2 and 3). Also, thanks to this individual protein the potato protein blend was more resistant to high temperatures than wheat gluten bioplastics and rice protein systems. According to Pouvreau et al. (2005a,b), protease inhibitors is an individual protein with heat-resistant properties which might explain the low sensitivity of these blends to be affected by the thermosetting temperature as compared to wheat gluten and rice protein samples. The 45 kDa band might be identified as patatin which is a hydrophobic protein (Park et al., 1983). In addition, two weak bands at high molecular weights 54 and 66 kDa were found. These types of oligomers represent about 12 wt.% of the protein present, such as lectin (Pouvreau et al., 2001; Allen et al., 1996).

3.4 Water absorption

Previous results have shown the type of protein used and thermomechanical treatment can lead to different thermo-mechanical behaviour and, likewise, different water uptake capabilities should be expected. Water absorption is an important parameter to be controlled when material application or processing is required (Rouilly et al., 2005; Jerez et al., 2005a, 2007). Figure 7 shows the water absorption values for rice and potato protein-based bioplastics manufactured with different glycerol content at different thermosetting temperatures.

The observed water absorption values for rice protein based bioplastics with 33 wt% glycerol showed a continuous decrease with increasing thermosetting temperature, from 90 to 180ºC (Figure 7A). Thus, samples thermoset above 160ºC exhibited the lowest water absorption, about 20%. Conversely, at 43 wt% glycerol content, absorption tended to decrease with higher thermosetting temperatures until these reached 140ºC. This behaviour agrees with the highest values of E* for this blend (see Figure 3), after which it increased to around 33 wt.%.

Figure 7B shows the water absorption values for potato protein-based bioplastics manufactured at different thermosetting temperatures and different glycerol concentrations. The water absorption values for the samples with 33 wt.% glycerol decrease for samples thermoset below 140 ºC which registered the lowest absorption value (9 wt.%), after which sample gave higher values with increased thermosetting temperatures. These results are entirely consistent with the values in the complex modulus observed at these thermosetting temperatures (see Figure 4). By contrast, potato protein-based bioplastics with 43 wt.% glycerol did not show a clear trend with thermosetting temperature. This blend exhibited the minimum value in water absorption with the sample thermoset at 180 ºC (13 wt.%).

On the whole, water absorption variability among replicates for both proteins decreased as temperature thermosetting increased, coupled to the progressive thermal denaturation of proteins. In any case, the obtained results pointed out that both protein isolates led to materials significantly more hydrophobic than the reference gluten-derived bioplastics, which typically exhibit water absorption values in the range 80-90 wt.% (Gomez-Martinez et al., 2009; Jerez et al., 2007).

In general, thermomoulding treatment leads to protein denaturation which results in an increase of hydrophobicity, due to exposure of hydrophobic groups that are folded inside the intact native protein molecule (Mine, 1997), showing that E* increases as water absorption decreases (Gomez-Martinez et al., 2009; Jerez et al., 2007). By contrast, rice and potato protein samples did not show the same tendency. Both proteins however exhibited water absorption values lower than 50 wt.%, these values are low compared to those obtained for wheat gluten blend (Gomez-Martinez et al., 2009). This behaviour is probably due to the presence of glutelin in the rice protein and the patatin in potato protein, which are not present in wheat gluten (Figure 6-Line 4). They are extremely insoluble in water because of its hydrophobic, hydrogen and disulfide bonding (Oszvald et al., 2008; Hamada, 1996; Juliano, 1985; Park et al., 1983). Therefore, these two polypeptide subunits may play an important role in reducing the water absorption for these two bioplastics. This fact was more evident in the absorption properties of the potato protein which brings the lowest water uptake as well as a narrower range of these values compared to rice protein-based bioplastics.

Conclusions

The resulting blends from potato and rice proteins, as new raw materials to manufacture bioplastics, have exhibited suitable viscoelastic and water absorption properties to be potentially used as food packaging.

The mixing process hardly induces protein-plasticizer interactions, being required a post-thermal treatment at higher temperature and pressure to obtain a material with suitable properties. Potato protein-based bioplastics had a complex modulus value similar to those found for LDPE. The viscoelastic properties of rice protein-based bioplastic were affected by glycerol content and thermomoulding temperature treatment. In contrast, potato protein-based bioplastic did not seem to be affected.

Both proteins exhibited water absorption values lower than 50 wt.%, although potato protein based bioplastic showed the lowest water absorption (9 wt.%). These values are significantly lower than those obtained for wheat gluten blends. In this regard, glutelin in the rice protein, and the protease inhibitors and patatin in potato protein, may play an important role in both viscoelastic behaviour and water absorption properties of rice and potato protein bioplastics.

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FIGURES

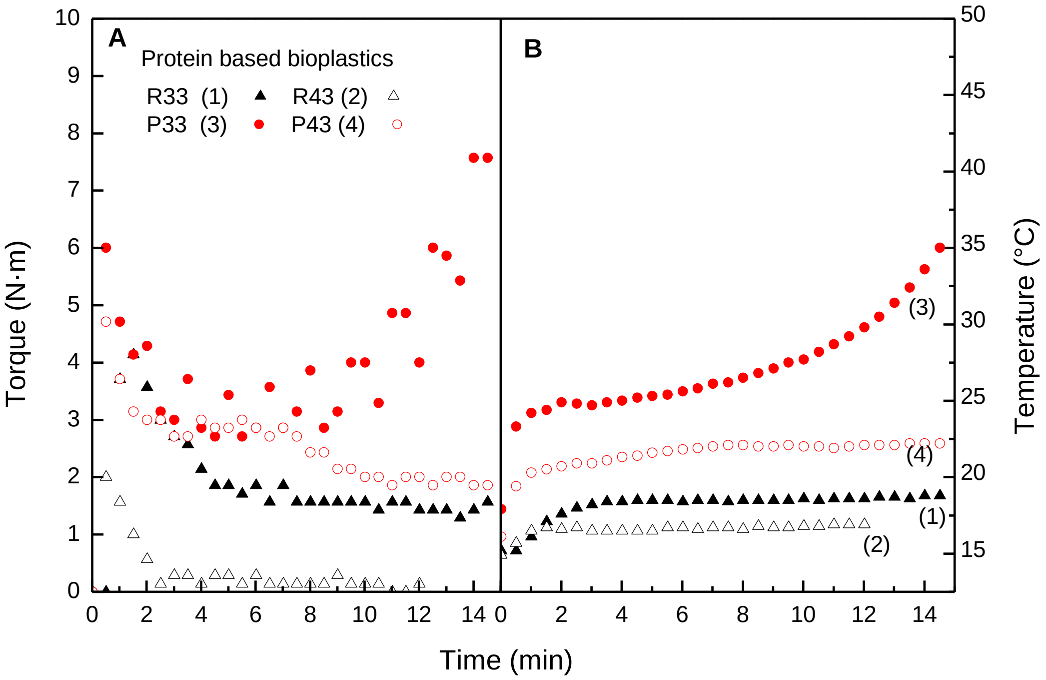

Figure 1. Evolution of torque (A) and temperature (B) during the mixing process for rice and potato protein-based bioplastic with varying glycerol content.

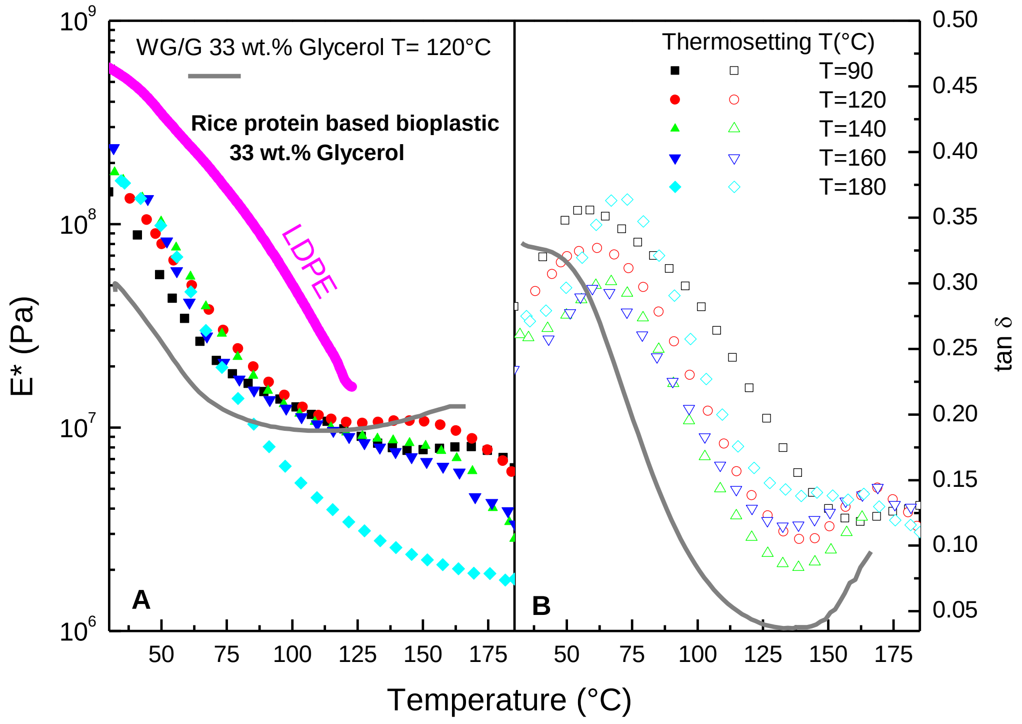

Figure 2. Dynamic mechanical thermal analysis results, complex modulus E* (A) and tan δ (B) for rice protein based bioplastic with 33 wt.% glycerol (R33) at different thermosetting temperatures.

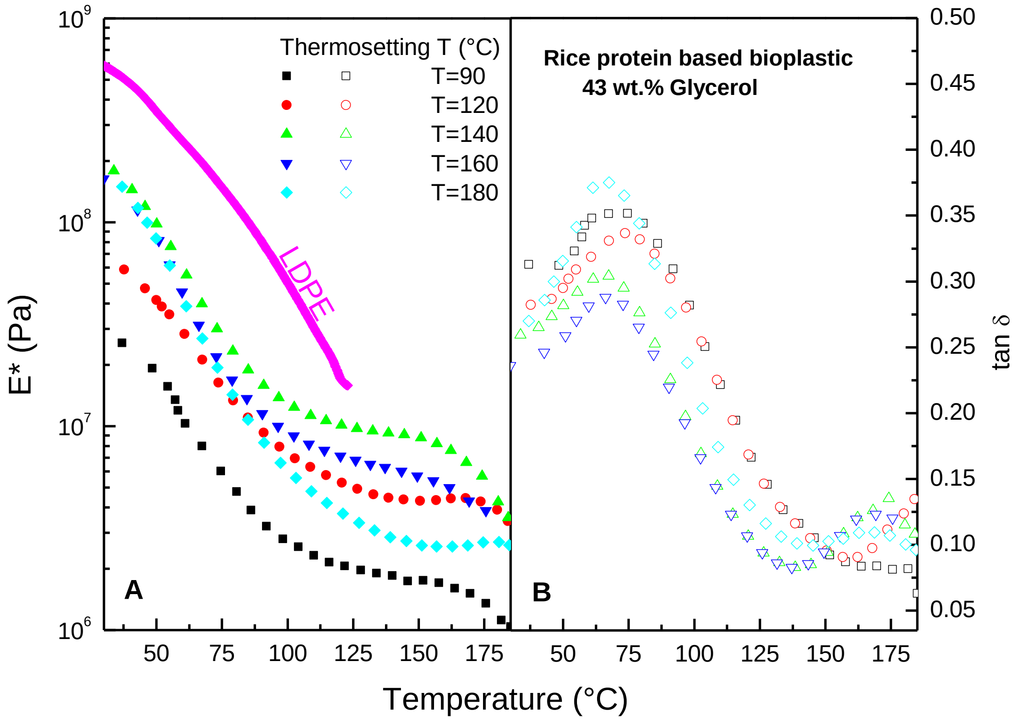

Figure 3. Dynamic mechanical thermal analysis results for the complex modulus E* (A) and tan δ (B) for rice protein based bioplastic with 43 wt.% glycerol (R43) at different thermosetting temperatures.

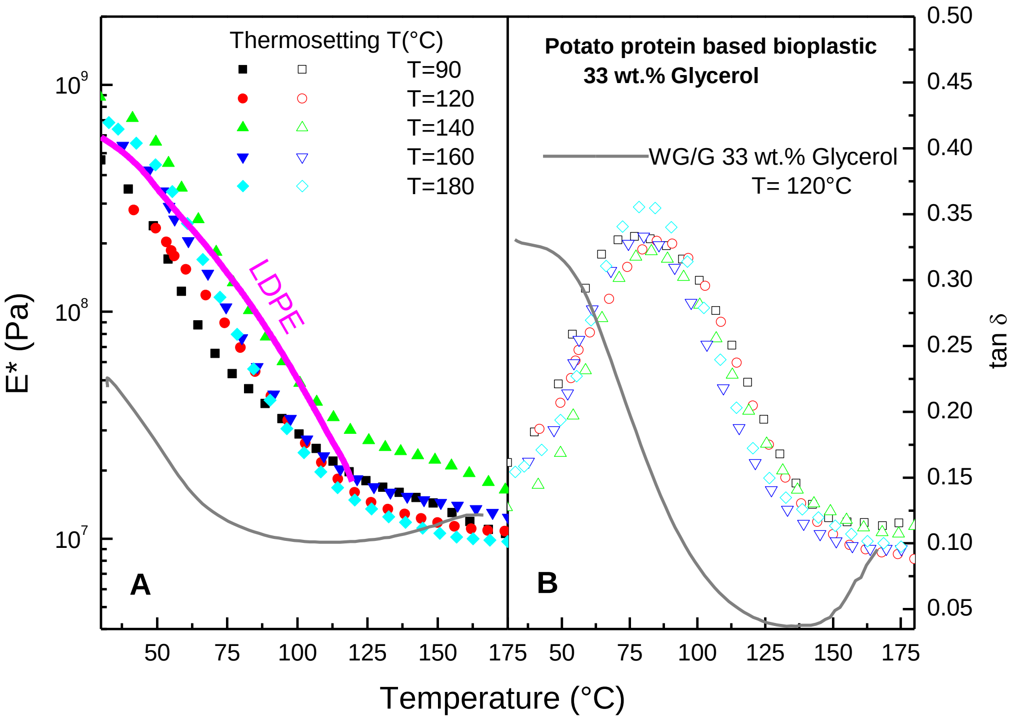

Figure 4. Dynamic mechanical thermal analysis results, complex modulus E* (A) and tan δ (B) for potato protein based bioplastic with 33 wt.% glycerol (P33) at different thermosetting temperatures.

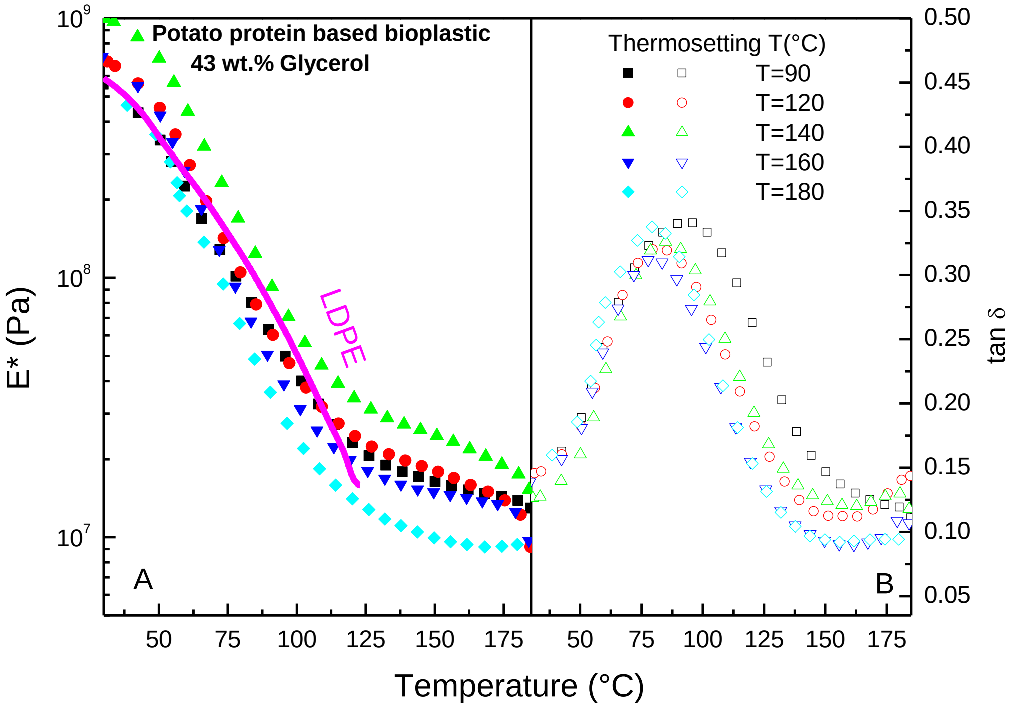

Figure 5. Dynamic mechanical thermal analysis results showing the complex modulus E* (A) and tan δ (B) for potato protein based bioplastic with 43 wt.% glycerol (P43) at different thermosetting temperatures.

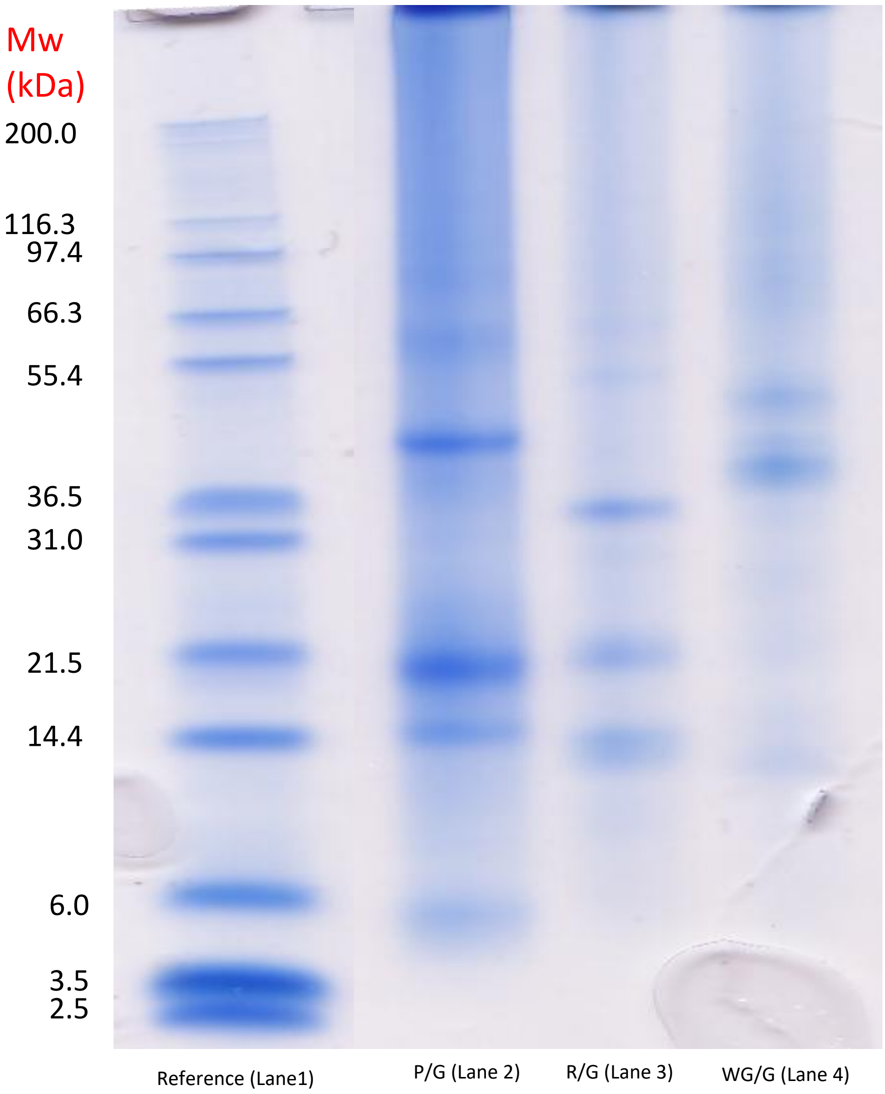

Figure 6. SDS-PAGE for wheat gluten, rice and potato protein based bioplastics, under reducing conditions. Lane 1: reference, lane 2: potato protein/glycerol(P/G), lane 3: rice protein/glycerol(R/G) and lane 4: wheat gluten/glycerol (WG/G) under reducing conditions.

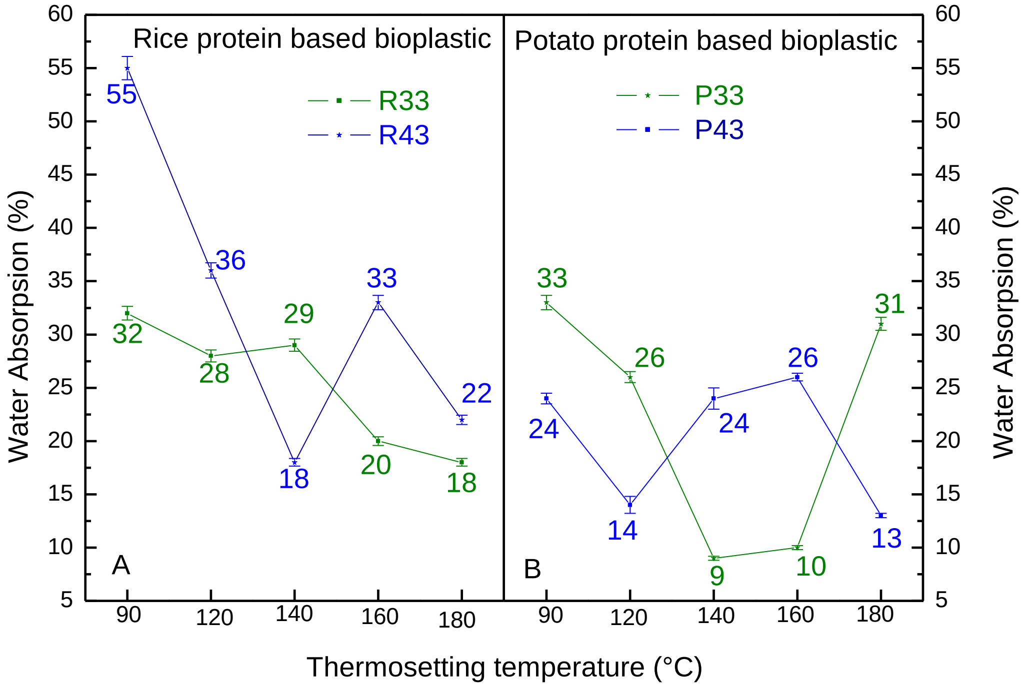

Figure 7. Water absorption for rice and potato protein bioplastics plasticized with different glycerol concentrations, at different thermosetting temperatures