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Characterization of pea protein-based bioplastics processed by injection moulding

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ABSTRACT

This study assesses the behaviour of pea protein isolate (PPI) as a potential candidate for the development of biobased plastic materials processed by injection moulding. Around 30–40% of glycerol as plasticizer was required to obtain good processability of PPI/GL blends to produce bioplastics. A mixing rheometer that allows recording of torque and temperature during mixing and a small-scale-plunger-type injection moulding machine were used to obtain PPI/GL blends and PPI-based bioplastics, respectively. Rheological and differential scanning calorimetry measurements were made to guide the selection of suitable conditions for injection and moulding. For injection, we selected a temperature relatively close to the maximum of the loss tangent, but moderate enough to avoid crosslinking effects (50 °C), and for moulding, a high temperature (130 °C) to favour crosslinking in the mould. An increase in the PPI/GL ratio leads to an enhancement of elastic bending and tensile properties of bioplastic specimens, as well as an increase in their ability to absorb mechanical energy before rupturing. On the other hand, the PPI/GL specimens become less transparent. In addition, water uptake of these bioplastics has been found to be very high and fast.

1. Introduction

Over recent years, a huge amount of non-degradable plastic waste has been generated, leaving behind an undesirable human footprint. This environmental problem is worsened by the fact that there is a continuous growth in the demand for plastic products. As a consequence, naturally derived biodegradable polymers (bioplastics) are attracting growing interest as materials that could reduce the environmental impact, this waste, while themselves being made from renewable sources (Shand et al., 2009). Specifically, since 2011, the market for eco-friendly bioplastics has grown exponentially (Byun and Teck Kim, 2014). Proteins (from various sources such as whey, egg, blood meal, soybean, gluten, pea, etc.) and polysaccharides have been proposed as attractive raw materials for the production of bioplastics for a range of applications (di Gioia and Guilbert, 1999; Pommet et al., 2003; Ribotta et al., 2012; Chao et al., 2013). In order to reduce intermolecular forces between polymer chains, protein-based bioplastic processing generally requires a mixing stage with a plasticizer (Gennadios, 2002; Feeney and Whitaker, 1988; Mohammed et al., 2000), which leads to an increase in the mobility of protein chains and a reduction in the glass transition (Matveev et al., 2000; Pouplin et al., 1999).

Regarding type of protein, plant proteins have become fairly attractive for a wide range of potential applications (Plastics Europe, 2008). In particular, legume seeds are cheap sources of protein with a relatively high nutritional value, which make them a very good raw material for the production of protein-based products (De Graaf and Kolster, 1998; Siracusa et al., 2008). However, the worldwide market for bio-based plastic materials is dominated by soy protein (commercially available as soy flour, soy concentrate and soy isolate). This is attributable to its low price, high quality and fairly versatile properties, factors that make it difficult to compete with (Pearson, 1983). However, utilization of pea protein can

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also have economic benefits since its price ($2.5–2.8 Kg^{-1}) is lower than that of other protein isolates like whey protein ($13.5–28 Kg^{-1}) and even soy protein ($3–3.8 Kg^{-1}) (Kowalczyk and Baraniak, 2011). In addition, pea protein offers other advantages such as its lack of genetic modifications in commercial species as well as its relatively low allergenicity and associated rates of feeding intolerance (Directive, 2001/18/EC). In any case, a large part of the literature is focused on soy protein-based films (Kokoszka et al., 2010; Guerrero et al., 2011a; Guerrero et al., 2011b), while data on the use of pea protein is scarce, in spite of its great potential due to its excellent properties (Choi and Han, 2002; Shi and Dumont, 2014).

With regard to processing, protein systems have typically been processed by casting to obtain protein-based films, using an appropriate solvent to transform proteins into a liquid phase. However, only a limited number of plant proteins (gliadin and zein) are soluble in common solvents and using solvents or alkaline solutions increases the cost and makes the process environmentally unfriendly (Reddy and Yang, 2013). In response to this, efforts have been made over recent years to apply classical thermoplastic polymer processing techniques, including thermoforming, extrusion, compression and moulding, to obtain protein-based bioplastic materials (Orliac et al., 2003; Pommet et al., 2003; Liu et al., 2005; Tummala et al., 2006; Jerez et al., 2007; Hernandez-Izquierdo and Krochta, 2008; González-Gutiérrez et al., 2011; Zárate-Ramírez et al., 2011, 2014a). Among the range of thermomechanical techniques used to process plastics, injection moulding is one of the most important for use with thermoplastic or thermosetting polymers to obtain a wide variety of products of different shapes, sizes and functionalities. It seems reasonable to assume that injection moulding could also be used for polymer systems such as proteins which may be of a mixed character (between thermoplastic and thermosetting). However, the use of injection moulding for processing protein-based materials has only recently been considered, and for successful processing of protein/plasticizer blends by this technique, a suitable selection of processing parameters has proven to be essential (Fernández-Espada et al., 2013; Felix et al., 2014, 2015; Martín-Alfonso et al., 2014). Among these parameters, the pre-injection temperature of the cylinder, the injection pressure and the moulding temperature are the most important in this process (Beltrán-Rico and Marcilla-Gomis, 2012). In the case of pea-based bioplastics, injection moulding is still an unexplored approach.

The overall objective of this work is to explore the characteristics of pea protein for the potential development of biobased plastic materials processed by injection moulding. A small-scale plunger-type injection-moulding machine was used in this study to obtain pea protein-based specimens from pea protein/glycerol blends, previously mixed in a mixing rheometer that allows recording of both torque and temperature during the mixing process. Rheological and differential scanning calorimetry (DSC) measurements of these blends were also carried out to obtain information to guide the selection of processing parameters suitable for injection moulding.

2. Material and methods

2.1. Materials

Pea protein concentrate was delivered by Roquette (Lestrem, France). The protein content of pea protein concentrate, determined in triplicate as % $N \times 6.25$ using a LECO CHNS-932 nitrogen micro analyser (Leco Corporation, St. Joseph, MI, USA) (Etheridge et al., 1998), was 89.5 wt%. According to Pearson classification (1983), it may be considered as a protein isolate rather than a protein concentrate because its protein content is ca. 90%. Ash content was determined by heating a small amount of pea protein isolate (PPI) at 150 °C by putting a muffle in an oven and weighing the content after 3 h. The other components of the pea protein isolate include 3.5 wt% ash, 1.4 wt% lipids and 5.1 wt% moisture. Glycerol (GL) was purchased from Panreac Química, S.A. (Spain).

2.2. Sample preparation

Bioplastics were manufactured by a thermo-mechanical procedure including two stages. Firstly, blends were mixed at four different PPI/GL ratios (80/20; 70/30; 60/40 and 50/50) using a two-blade counter-rotating batch mixer, Haake Polylab QC (ThermoHaake, Karlsruhe, Germany), at 25 °C and 50 rpm for 60 min, monitoring the torque and temperature during mixing to obtain a dough-like blend. Secondly, two blends, selected after analysis of the mixing results, were subsequently processed by injection moulding, using a MiniJet Piston Injection Moulding System (ThermoHaake) to obtain bioplastic specimens. The processing conditions are given below, being selected after characterization of the pea protein and its blends. Two moulds were used to prepare two different specimens: (1) a $60 \times 10 \times 1\,mm^3$ rectangular-shaped specimen for dynamic mechanical analysis (DMA) experiments, water absorption capacity and transparency measurements and (2) a dumb-bell-type specimen by ISO 527-1:2012 for tensile properties of plastics.

2.3. Characterization of pea protein isolate

2.3.1. Protein solubility

Protein solubility at different pH values was determined. Aqueous dispersions (ca. 1.00 g protein/40 mL) were prepared and pH of different aliquots was adjusted to alkaline pH values with 6 N NaOH, and to acid pH with 2 N HCl. Samples were homogenized and subsequently centrifuged for 20 min at 10,000×g and 10 °C. The supernatant were collected for protein content determination by means of the Markwell method (Markwell et al., 1978). Solubility was expressed as a percentage (g soluble protein/100 g isolate in sample).

2.3.2. Z potential measurements

Isoelectric point was measured using a "Zetasizer 2000" (Malvern Instruments, U.K.). Therefore, different flour samples were prepared at 1 wt% prepared at pH value with buffers. Prior to analysis, the samples were stirred at 20 °C and, then, samples were centrifuged at 10,000×g for 10 min in a RC5C Sorvall centrifuge (Sorvall Instruments, Wilmington, DE, USA). After that, the samples were measured in triplicate at 20 °C. The zeta potential was calculated from electrophoretic mobility using the Henry equation and the Smoluchowski approximation. The isoelectric point corresponds to the point where the potential value is zero, at which all charges of particles are neutralized (Tan et al., 2008).

2.3.3. SDS-page electrophoresis

Electrophoresis tests were performed using polyacrylamide gels (10%) in presence of sodium dodecyl sulphate (SDS-PAGE) according to Laemmli method (1970). Molecular weights of