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Development of albumen/soy biobased plastic materials processed by injection molding

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ABSTRACT

Biobased plastics from renewable polymers constitute a highly interesting field for relevant industrial applications such as packaging, agriculture, etc., in which thermomechanical techniques (i.e. extrusion, compression molding, etc.) are increasingly being used. In spite of the potentials of injection molding in the manufacture of shaped products it is still scarcely used with biopolymers. This study evaluates injection molding as an alternative to produce biobased materials from blends prepared in a mixing rheometer, using different albumen/soy ratios and glycerol as the plasticizer. Viscoelastic measurements and DSC of protein/glycerol blends were used to select suitable processing conditions. Physicochemical properties of injection-molded probes were characterized through dynamic mechanical thermal analysis, tensile strength, water uptake and transmittance tests. Occurrence of shear-induced effects over mixing was confirmed by extractability analysis of protein concentrates and blends, particularly for soy-based systems. Both proteins and their mixtures yield injection-molded bioplastics, although showing lower mechanical properties than LDPE standards.

1. Introduction

Plastic materials are currently considered very important materials due to their exceptional properties and performance over other materials such as metal and wood (Plastics Europe, 2008). In fact, according to a recent report, the demand for plastic will continue to rise following a trend that has increased since 1950s (Plastics Europe et al., 2008). Nowadays, the substitution of petroleum-based plastics with bio-based plastics is seen as a promising alternative because it will reduce the dependency of plastics on fossil fuels and the pressure on landfills from plastic solid wastes (Alvarez-Chavez et al., 2012). In recent years there has been a great interest to utilize renewable biomass in the manufacture of high-quality, cost-competitive and biodegradable consumer goods as a means to reduce the consumption and the dependence on petrochemical feedstock and to diminish environmental pollution (Rosentrater and Otieno, 2006; Tummala et al., 2006). In particular, packaging films and containers made of natural biodegradable polymers represent a particular interest due to their compostability, since most of these products have a relative short service life ending up in landfills. In this sense, protein-based materials have been proved to be completely degrading in 50 days when buried in farmland soils (Domenek et al., 2004).

Proteins, lipids and polysaccharides have been proposed as biopolymers sources for many years (Averous, 2004; De Graaf, 2000; Hernández-Izquierdo and Krochta, 2008; Irissin-Mangata et al., 2001; Siracusa et al., 2008). Regarding proteins, most studies have used plant proteins such as zein, wheat gluten or soybean to manufacture bioplastics (Cuq et al., 1998; Gomez-Martinez et al., 2013; Jerez et al., 2005; Kim, 2008; Zheng et al., 2003). Moreover, some works have been focused on animal proteins such as milk proteins, collagen, gelatin, etc. (Cuq et al., 1998; Pommet et al., 2003).

Soy protein is the major coproduct of soybean oil and is one of the cheapest proteins in nature (Tian et al., 2012). In fact, soy proteins have commonly been used for food and animal feed for many years. However, soy protein is a new polymer for biodegradable resins. Soy protein polymers are macromolecules that contain a number of amino acids and side chains that can be used in the manufacture of plastic (Sun et al., 1999). The mechanical properties of soy protein based plastics can be controlled and optimized by adjusting the initial moisture content as well as some processing parameters such as the molding temperature and/or pressure (Wang et al., 2007; Liang et al., 1999; Mo et al., 1999; Jane and Wang, 1996; Pateau et al., 1994). However, the application of soy protein plastics is limited because of its low strength (Tummala et al., 2006) and high moisture absorption (Liu et al., 2005). Therefore, it can be concluded that the most effective method is to blend soy protein with another biodegradable polymer. Currently, soy-based blends for plastic applications include polyphosphate (Otaigbe and Adams, 1997), polyesters (Graiver et al., 2004; Liu

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et al., 2004), polyurethane (Tian et al., 2010) or natural fibers (Liu et al., 2005). On the other hand, no reports on the enhancement of soy-based plastic materials by using a combination with other proteins have been found.

Egg white protein (albumen), traditionally used by the food industry, has recently proved the feasibility to produce bioplastics (Jerez et al., 2007b). Moreover, if compared to 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 (González-Gutiérrez et al., 2010).

A protein-based material could be defined as a stable three-dimensional macromolecular network stabilized and strengthened by hydrogen bonds, hydrophobic interactions and disulfide bonds (Pommet et al., 2003). However, as proteins themselves do not have sufficient plasticity to be handled and brittle properties are typically found in bioplastics, a plasticizer is required. The role of plasticizers in reducing the glass transition temperature and providing mobility to polymeric chains has been extensively described (Irissin-Mangata et al., 2001; Matveev et al., 2000; Pouplin et al., 1999). Due to its excellent properties, glycerol is among the most commonly used plasticizers for biopolymer-based biodegradable materials.

Protein/plasticizer blends (bioplastics) can be processed using existing plastic processing technologies: from the physic-chemical or casting method (Gennadios, 2002) to thermo-plastic/mechanical method (compression molding or extrusion) (Jerez et al., 2007a; González-Gutiérrez et al., 2011). However, a relevant technique such as injection molding, which is among the most common processing methods used with synthetic polymers, has not been found to be used for protein-based bioplastic applications. The potential use of protein-based injection molding to produce many kinds of shaped products will entail new arguments in favor of considering these biopolymer materials as an alternative to synthetic plastics for different applications.

The overall objective has been to study plasticized albumen/soy biobased plastic materials processed by injection molding. To achieve this objective, different albumen/soy ratios plasticized with glycerol have been processed. In addition, some variables such as temperature and residence time in the pre-injection mixing chamber, as well as the temperature of the mold have been also analyzed in order to select suitable processing parameters for protein-based injection molding.

2. Material and methods

2.1. Materials

Commercial spray-dried albumen (AP) was provided by OVOSEC S.A. and soy protein isolate (SPI) was supplied by Protein Technologies International (SUPRO 500E, Leper, Belgium). The protein content of both products was determined in quadruplicate as % N × 6.25 using a LECO CHNS-932 nitrogen microanalyzer (Leco Corporation, St. Joseph, MI, USA) (Etheridge et al., 1998) being 83 wt.% for AP and 91 wt.% for SPI. Glycerol (GL), from Panreac Química, S.A. (Spain), was used as protein plasticizer.

2.2. Sample preparation

Blends containing 60 wt.% protein, with different AP/SPI ratios as shown in Table 1 and 40 wt.% glycerol (GL) were mixed in a two-blade counter-rotating batch mixer (Brabender Plastograph, Germany). A suitable proportion of 40% of glycerol as plasticizer agent has been selected in order to obtain an adequate viscosity for blends. Lower protein/plasticizer ratio led to more incompatibles systems in which the blend was hardly processable and final molded pieces exhibited glycerin exudation which indicated an excess of plasticizer agent. On the other hand, a higher ratio led to higher blend viscosity which made injection rather difficult.

Table 1
Formulations of protein (albumen and soy protein isolate)/plasticizer blends.

Protein concentrate 60% (wt.%)		Plasticizer 40% (wt.%)
Albumen (AP) (wt.%)	Soy protein isolate (SPI) (wt.%)	
100	0	Glycerol (GL)
75	25	
50	50	
25	75	
0	100	

Mixing process was carried out at 25 °C and 50 rpm for ca. 10 min (Jerez et al., 2005) to obtain a dough-like material at neutral pH. The final pH value was measured by a Crison pH 25 pH meter in combination with a puncture electrode (Crison Instruments S.A., Barcelona, Spain).

The dough-like materials obtained after the mixing process were subsequently processed by injection molding using a MiniJet Piston Injection Molding System (ThermoHaake, Karlsruhe, Germany) to obtain bioplastic probes. The most suitable processing variables, such as injection temperature and pressure, as well as residence time in the pre-injection mixing chamber, were selected after performing temperature ramp and time sweep tests to the dough-like materials. Two types of molds were used to prepare the probes: a 60 × 10 × 1 mm rectangular shape mold for both DMTA experiments and transparency measurements and a Dumpbell type probe defined by ISO 527-2:1993 for Tensile Properties of Plastics.

2.3. Characterization

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 at 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. Protein extractability

Samples were extracted in different extraction media (2.5 mL): distilled water; a denaturing agent solution (Method A); a solution of denaturing and reducing agents (Method B). All the materials were extracted for 2 h at 20 °C by magnetic agitation (approximately 400 rpm). Method A used a 0.086 mol L^{-1} Tris-base, 0.045 mmol L^{-1} glycine, 2 mmol L^{-1} EDTA, 10 g L^{-1}, 5 g L^{-1} Sodium Dodecyl Sulfate (SDS) pH 8 buffer. In method B, proteins were dissolved in the same buffer containing 10 g L^{-1} Dithiothreitol (DTT). Dispersions were centrifuged at 10,000× g for 15 min at 15 °C and protein content was determined by a LECO CHNS-932 nitrogen microanalyzer. Similar methods were previously used by the authors with protein gels (Romero et al., 2011). Protein solubility was determined from supernatant and expressed as 100× protein content in the supernatant/total protein content. Three