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Development of rice protein bio-based plastic materials processed by injection molding

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ABSTRACT

Rice protein concentrate (RPC) has been evaluated as a potential candidate for the development of bio-based plastic materials processed by injection molding. Around 30% of glycerol (GL) as plasticizer and other additives (sodium bisulfite as a reducing agent as well as glyoxal and L-cysteine as cross-linking agents) were required to obtain good processability of RPC/GL blends to produce bioplastics. A mixing rheometer that allows recording of torque and temperature during mixing and a small-scale-plunger-type injection molding machine were used to obtain RPC/GL blends and RPC-based bioplastics, respectively. Rheological measurements were taken to guide the selection of suitable conditions for injection and molding. For injection, we selected a temperature relatively close to the glass transition temperature, but moderate enough to avoid crosslinking effects (87 °C), while for molding, we selected a higher temperature (130 °C) to favor crosslinking in the mold. However, other processing parameters (e.g., injection pressure) also need to be optimized. Final products (bioplastics) are plastic materials from renewable polymers (rice proteins) with both adequate properties for important industrial applications such as packaging, agriculture, etc. and high biodegradability when subjected to composting conditions. Adding each of the aforementioned additives leads to final specimens with different mechanical properties, as shown by dynamic mechanical temperature analysis and tensile strength measurements.

1. Introduction

Over 300 million tons of petroleum-based or gas-based polymers are produced worldwide each year, mostly being used in the production of synthetic non-biodegradable plastics for a wide variety of applications in almost all areas of daily life (agriculture, packaging, construction, transport, electrical and electronic devices, etc.) as well as in the process industry (chemical, food, aerospace, pharmaceutical, etc.) (DiGregorio, 2009; Halden, 2010). However, due to recent concerns about depletion of fossil resources and environmental problems related to the lack of biodegradability of most of these plastic materials, efforts have been made to replace conventional oil- and gas-based plastics with others based on hydrocarbons derived from renewable resources such as biomass. In fact, the transition from a fossil-based economy to a bio-economy is an important target of the European Union 2020 Strategy.

Bio-based plastics represent a broad spectrum of materials that may be synthesized by living organisms (i.e., naturally produced bio-based polymers, such as proteins or polysaccharides) or may be derived from renewable resources in their monomer form, requiring a chemical transformation for conversion to a polymer (e.g., PLA from lactic acid). According to the European Bioplastics Organization, the former group can be defined as plastics based on renewable resources (bio-based), whereas the later should be described as biodegradable and/or compostable plastics. Recently, interest in the use of bioplastics has been shifting from compostable/biodegradable materials towards bio-based materials (Peelman et al., 2012; Verbeek and van den Berg, 2010). Currently, bioplastics is still a nascent market that is starting to emerge, capturing the plastics market at a growth rate of 30% annually (Reddy et al., 2013).

Protein is among the most promising bio-based resources for bioplastics, since protein-based materials tend to form three-dimensional macromolecular networks, stabilized and strengthened by hydrogen bonds, hydrophobic interactions, and disulfide bonds (Thomas et al., 2013). Typically, the manufacture of protein-based bioplastics involves chemically-, thermally-, or pressure-induced protein denaturation as a first stage. Due to the diversity in the assembling of protein networks and to their unique structures, a large variety of biodegradable materials can be produced, offering a wide range of functional properties (Verbeek and van den Berg, 2010).

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Globally, rice cultivation covers 145 million hectares, mostly in Asia (the leading producers of rice in the world being India, China, Thailand and Bangladesh). In the European Union, the area dedicated to this crop is some 410,000 ha, mostly in the Mediterranean area (Ferrero and Tinarelli, 2007). The rice industry typically produces a large amount of by-products, like rice proteins, that may have a negative environmental impact. Specifically, it is estimated that 100 million tons of rice residues and by-products are generated each year (Li et al., 2010).

Currently, rice residues are treated as waste products incinerated for energy purposes (Arvanitoyannis and Tserkezou, 2008; Li et al., 2010; Madrid et al., 2013) or are normally used as animal feed (Njie and Reed, 1995; Yun et al., 2005) because of the poor solubility. However, protein hydrolyzates are prepared in order to increase its solubility and its use for nutritional supplementing or functional enhancement (Guo et al., 2013). One of the most interesting potential uses of these products is the manufacture of bioplastics, solving a problem of environmental pollution. However, although various different protein concentrates have been used to manufacture bioplastics (Cuq et al., 1998; Gomez-Martinez et al., 2013; Jerez et al., 2005; Kim, 2008; Zheng et al., 2003), few studies have investigated the use of rice flour in the production of thermoplastic flour materials (Khamtong and Lumdubwong, 2012). Furthermore, the use of mixtures of these proteins with synthetic additives has been proposed to obtain good mechanical properties (Hernández-Muñoz et al., 2004; Min et al., 2008; Pickering et al., 2012; Sun et al., 2007; Zárate-Ramírez et al., 2014) for the manufacturing of biodegradable plastics, for example, food packaging (Peelman et al., 2013; Siracusa et al., 2008).

Protein/plasticizer blends (bioplastics) can be processed using existing processing technologies, from the physicochemical or casting methods (Gennadios, 2002) to thermomechanical methods (compression molding, thermomolding and extrusion) (Gonzalez-Gutierrez et al., 2011; Jerez et al., 2007). However, injection molding, which is among the most common processing methods used with synthetic polymers, has been very little used for protein-based bioplastic applications (Félix et al., 2014). If the potential of protein-based injection molding to produce many kinds of shaped products could be demonstrated, this would strengthen the arguments in favor of considering these biopolymer materials an alternative to synthetic plastics for multiple applications. Before thermoprocessing a bioplastic, it is necessary to obtain a dough, which is a mixture of protein concentrate and plasticizer (Suyatma et al., 2005). The role of the plasticizer is to reduce the glass transition temperature (T_g) and provide mobility to polymeric chains (Irissin-Mangata et al., 2001), reducing electrostatic and hydrophobic interactions (Lee et al., 2013) and, therefore, it should be a polar and low weight molecule (Vieira et al., 2011), such as glycerol (GL).

Our overall objective was to evaluate the potential development of high quality biodegradable rice protein bio-based plastic materials (bioplastics) processed by injection molding with good thermo-mechanical properties and high biodegradability compared to petroleum-derived plastics. To achieve this objective, rice protein concentrate (RPC) was processed with GL and other chemical components, we refer to as additives, to obtain RPC/GL/additive blends using a mixing rheometer that allows the torque and temperature to be recorded during mixing. The additives assessed were sodium bisulfite (SB) as a reducing agent as well as glyoxal (GLX) and L-cysteine (Cys) as cross-linking agents. On the one hand, rheological and differential scanning calorimetry (DSC) measurements of these blends were carried out to obtain information about the suitable processing parameters for injection molding operations and, on the other hand, mechanical properties of the final bioplastics were evaluated.

2. Materials and methods

2.1. Materials

RPC from rice husks, containing ca. 80 wt% protein, was provided by Remy Industries (Leuven-Wijgmaal, Belgium). The protein content of this concentrate, determined in quadruplicate as % N × 6.25 using a LECO CHNS-932 elemental analyzer (Leco Corporation, St. Joseph, MI, USA) (Etheridge et al., 1998), was 78.2 wt.%. GL, SB, GLX and Cys were purchased from Panreac Química, S.A. (Spain).

2.2. Sample preparation

We manufactured blends with various different RPC/GL ratios and additives at the following concentrations: 0.3 wt% SB, 3.0 wt% GLX and 1 wt% Cys, based on experience in other studies (Zárate-Ramirez et al., 2014; Sun et al., 2007). For this, we followed a two-stage thermo-mechanical procedure. Firstly, selected blends were mixed in a Haake Polylab QC two-blade counter-rotating batch mixer (ThermoHaake, Karlsruhe, Germany) at 50 rpm for 60 min, starting at 25 °C, and monitoring the torque and temperature during mixing to obtain a dough-like material. Secondly, this dough-like material was processed by injection molding using a MiniJet Piston Injection Molding System (ThermoHaake) to obtain bioplastic specimens. Two molds were used to prepare two types of specimens: (1) a 60 × 10 × 1-mm rectangular-shaped specimen for dynamic mechanical temperature analysis (DMTA) experiments, and (2) a dumbbell-shaped specimen as recommended in ISO 527-1:2012 for tensile testing of plastics.

2.3. Characterization of RPC

2.3.1. Free and total sulfhydryls

Free and total sulfhydryl groups (SH and SS, respectively) of protein samples were determined using the method developed by Beveridge et al. (1974) and Thannhauser et al. (1984), respectively. Samples were suspended (1 mg/mL) in 0.086 mol/L Tris–HCl, 0.09 mol/L glycine, 4 mmol/L EDTA, and 8 mol/L urea, with pH 8 buffer. Dispersions were stirred at 25 °C for 10 min at 500 rpm in a thermomixer and then centrifuged at 15,000 × g (10 min, 10 °C). Supernatant was incubated with Ellman's reagent (4 mg DTNB/mL methanol) and 1 mL NTSB was used in the case of the total sulfhydryls. Absorbance at 412 nm was measured in a Genesys-20 spectrophotometer (Thermo Scientific, Waltham, MA, USA). The content was calculated as follows:

$$\mu\text{molSH/g} = 73.53 \times A_{412} \times D/C$$

where A_{412} is the absorbance at 412 nm, C is the sample concentration (mg/mL), D is the dilution factor (5 and 10 are used for SH and SS, respectively), and the constant 73.53 is calculated as $10^6/(1.36 \times 10^4)$ (10^6 being for the conversion from molar basis to μM/mL basis and from mg solids to g solids and 1.36×10^4 the molar absorptivity). The SS content was calculated by subtracting the SH content from the total SH group content and dividing the result by 2. The protein concentration of extracts was determined by the Bradford method (Bradford, 1976).

2.4. Characterization of blends

2.4.1. DSC

These experiments were performed with a Q20 calorimeter (TA Instruments, New Castle, DE, USA), using 3- to 8-mg samples, in hermetic aluminum pans. A heating rate of 10 °C/min was selected. The sample was purged with a nitrogen flow of 50 mL/min.