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Optimization of a thermal process for the production of superabsorbent materials based on a soy protein isolate

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ABSTRACT

Superabsorbent materials have found several applications in fields related to diapers, hygienic tissues or controlled-release in agriculture. In order to produce more environmentally-friendly materials, some efforts have been focused on grafting copolymerization of acrylic derivatives onto a natural compound (e.g. protein, polysaccharide). This manuscript deals with the production of biodegradable superabsorbent materials produced from a Soy Protein Isolate (SPI), in which their water absorbance capacity is modulated only through the modification of the thermal processing. Thus, SPI was blended with a plasticizer (glycerol), using a 1/1 (w/w) SPI-glycerol ratio, and then injection moulded at different mould temperatures (T_{mould}). Subsequently, a dehydrothermal (DHT) treatment was carried out, consisting of the storage of bioplastic produced at 50 °C in an oven for a certain period of time (t_{DHT}). The present study demonstrated that thermal conditions (T_{mould}, t_{DHT}) plays a crucial role in the formation of superabsorbent materials from protein sources like SPI. Mould temperatures as low as 70 °C resulted in materials with a water uptake which defines their superabsorbent character, as long as the t_{DHT} selected is shorter than 10 h. Longer t_{DHT} resulted in a tighter structure with generally higher viscoelastic properties, which was less able to swell and absorb water. A longer moulding stage also lead to a decrease in the water uptake. Thus, thermal processing parameters have been proven to modulate the superabsorbent characteristics of the materials studied, not being necessary any chemical modification of the protein source.

1. Introduction

The massive consumption of petroleum-based plastics has caused a serious environmental issue, as most of the plastics are used in fast-food packaging, being discarded rapidly. Only a 7% of plastic wastes are recycled every year, being the largest volume of those wastes disposed in land-fills or in the oceans (Pathak et al., 2014), altering the ecosystems and causing death and injury to hundreds of thousands of species of marine fauna (Varsha and Savitha, 2011). Those plastics that are either bio based or biodegradable have been named bioplastics, being pointed out as potential substitutes for conventional plastics (Álvarez-Chávez et al., 2012; Mekonnen et al., 2013; Papong et al., 2014).

Even if the industrial production of bioplastics is modest (around 1.7 mt/year in 2014), an increment in their production is expected, forecasting a value of approximately 6.2 mt/year by the end of 2018 (Mostafa et al., 2014). Nevertheless, in order to compensate their reported high production cost, the use of bio-waste to obtain bioplastics has been considered (Morone et al., 2015). To this end, many research works have already used some food industry by-products or wastes, such as wheat gluten (Gómez-Heincke et al., 2017; Gómez-Martínez et al., 2013; Zárate-Ramírez et al., 2014), fish myofibrillar proteins (Cuq et al., 1997), starch (Khlestkin et al., 2018; Privas et al., 2013), soy protein (Félix et al., 2014; Fernández-Espada et al., 2016a), rice protein (Félix et al., 2016) or pea protein (Bourny et al., 2017), for the production of bioplastics. The use of chitosan as ingredient in bioplastics has also been extensively considered, as it confers antioxidative and antimicrobial properties (Gursoy et al., 2018; Kaya et al., 2018).

One of the most remarkable applications for this environmental-friendly materials could be in the field of superabsorbents, materials that can absorb more than ten times (i.e. 1000%) its own weight in water, without losing its shape or integrity (Zohuriaan and Kabiri, 2008). Most of the commercially available superabsorbent materials are composed by a certain amount of low biodegradability acrylic derivatives (Ruiz-Hitzky et al., 2013; Song et al., 2017) and they are

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thoroughly used in a wide range of applications (e.g. agriculture, hygienic tissues, tissue engineering) (Ibrahim et al., 2007; Kim et al., 2008). Some works have pointed out the suitability of some natural polymers in this field, which show better biocompatibility and less toxicity (Mahdavinia et al., 2004).

A soy protein isolate, which may be obtained as by-product of the soybean oil industry, has been used by several authors in the production of bioplastic materials (Kumar et al., 2002; Liu et al., 2010). As soy protein contains an important amount of hydrophilic amino acidic residues (e.g. aspartic, glutamic acid), some authors (Cuadri et al., 2016, 2017; Fernández-Espada et al., 2016a, 2018; Perez-Puyana et al., 2018) have demonstrated its ability to be used as basis for a superabsorbent bioplastic material, achieving water uptake capacity values higher than 3600%. However, either the addition of an hydrophilic ingredient (e.g. nanofillers, salts) or the acylation of the lysine residue of the protein was necessary to achieve the superabsorbent ability.

The production of superabsorbent materials from soy protein only through the adjustment of the processing conditions has not been reported so far. The processing conditions used during the production of bioplastics (e.g. through injection moulding) have proven to be crucial for the final properties of the products, mostly searching for a balance between mechanical properties and water uptake. The interactions between the side chains of amino acids present in the protein molecules may be promoted either during the shaping of the bioplastic at a specific moulding temperature or subsequently submitting the bioplastic to a physical dehydrothermal (DHT) treatment consisting on the exposure of the formed material to a certain temperature. Moreover, the duration of both the moulding and the DHT treatment is also a key parameter in determining the properties of the bioplastic. As the bioplastic structure is reinforced (e.g. through the formation of crosslinking), its water uptake capacity is generally hindered. This has been explained by different authors by a lack of flexibility of the strengthened structure, which eventually prevents its swelling capacity (Bruyninckx et al., 2016, 2015; Jerez et al., 2005).

In the present study, bioplastics were obtained using a lab-scale injection moulding device, followed by a DHT treatment at a moderate temperature (50 °C) for a given time period. The effect of some injection moulding parameters (mould temperature or holding time) and the DHT process duration on the water uptake and viscoelastic properties of the matrices was studied. All of these parameters may alter the inner structure of the bioplastics through the achievement of different degrees of reinforcement of their network structure. Thus, the main objective of the present manuscript was the optimisation of these processing parameters that may help to modulate the swelling of the materials obtained.

2. Experimental

2.1. Materials and sample preparation

2.1.1. Materials

The Soy Protein Isolate (SPI) used (SUPRO 500E (Dupont, USA)) was kindly provided by PROANDA S.A (Spain). The protein content was determined in quadruplicate as % N × 6.25 using a LECO CHNS-932 nitrogen microanalyzer (Leco Corporation, St. Joseph, MI, USA) being 91.8 wt. %. Its ash content is approximately 5.0%, the concentration of lipids is 1.0% and its moisture is around 6.0%. Glycerol was used as a plasticizer in order to improve the processability of the protein isolate to produce homogeneous blends that would be eventually injection-moulded into bioplastics. The glycerol used (Pharma grade) was purchased from Panreac Química S.A. (Spain)

2.1.2. Sample preparation

2.1.2.1. Blending. In this stage, SPI was mixed with the plasticizer in a 1/1 ratio, according to previous studies (Fernández-Espada et al., 2016a). This process was carried out in a two-blade counter-rotating batch mixer Haake Polylab QC (ThermoHaake, Germany), at room temperature and 50 rpm for 10 min.

2.1.2.2. Injection moulding. The injection stage was carried out using a miniJet Piston Injection Moulding System (ThermoHaake, Germany): the blend is first confined in a cylinder at 40 °C (Fernández-Espada et al., 2016a), being injected into a rectangular-shaped mould ($60 \times 10 \times 1\ mm^3$) at a moulding temperature (T_{mould}: 70, 90, 120 °C) as it is pushed by a plunger using an injection pressure equal to 500 bar for 10 s. Then, a holding stage took place for a certain period of time (t_{hold}: 50, 140, 290, 440, 590 s) using a holding pressure of 500 bar.

2.1.2.3. Dehydrothermal treatment (DHT). According to the ASTM D570, in order to determine the water uptake of plastic materials, samples must be dried in the oven at 50 °C for 24 h or until constant weight, prior its water immersion. In our case, the effect of the time length of the storage at 50 °C was studied, using times ranging from 0 to 24 h. The overall drying process has been designated as dehydrothermal treatment (DHT).

2.2. Methods

2.2.1. Water uptake

Water absorption tests were carried out on rectangular probes immersed into distilled water for 24 h. The water absorption percentage was calculated as:

$$\text{Water absorption (wt. \%)} = \frac{\text{wet wt-DHT wt}}{\text{DHT wt}} \times 100. \quad (1)$$

where: DHT wt, is the weight of the specimen after the DHT treatment; and wet wt, refers to the weight of the specimen just after DHT treatment followed by 24 h of water immersion.

At least three replicates of each measurement were performed on samples 24 h after of the bioplastic manufacture and are reported as means and standard deviations.

2.2.2. Cryo-Scanning Electron Microscopy (Cryo-SEM)

Cryo-SEM essays were performed in order to gather information about the microstructure of the selected swelled bioplastics samples as a function of the duration of the holding stage and the DHT treatment. Small pieces of samples (around 2.5 mm) were first immersed in nitrogen slush (−194 °C), and then they were relocated rapidly in the cryo specimen chamber, where they were submitted to an etching stage at −90 °C for 7 min, removing the ice placed on the surface of the samples. Subsequently, samples were gold coated and examined using a ZEISS EVO microscope (United States) at −120 °C. The acceleration operation voltage employed was 8 kV with a beam current of 70 pA. The working distance used was 6 mm, and analyses were performed at ca. 4500× magnification.

2.2.3. Low-pressure mercury intrusion (MIP)

Poremaster-60 GT (Quantachrome Instruments, Germany) was used to determine the pore size distribution of selected freeze-dried samples after swelling through Mercury Intrusion Porosimetry (MIP) at room temperature. To freeze-dry the probes, first they were frozen in a freezer for 2 h (−40 °C), and then were introduced in a LyoQest freeze-dryer (Telstar Technologies, Spain) for 24 h. The porosimeter generates pressure to 60000 psi for pore size analysis from over 950 μ m to 0.0036 μ m pore diameter. It offers two high-pressure and two low-pressure analysis ports to meet the pore size measurement. In the present work, the low-pressure port (0.2 to 50000 psi) was used. The Washburn equation (Washburn, 1921) gives the relationship between the applied pressure and the pore diameter into which mercury will intrude: