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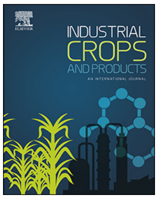

Development of soy protein-based matrices containing zinc as micronutrient for horticulture

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ABSTRACT

Protein-based bioplastics may be regarded as novel biopolymer matrices based on renewable natural components. Due to technological, economic and environmental benefits, these biopolymer matrices are highly attractive for the incorporation and subsequent release of micronutrients that are essential for the development and health of plants, avoiding the typical excesses of conventional fertilizers. In addition, soy protein isolate (SPI) seems to be an adequate resource for the manufacture of natural-based superabsorbent materials due to its hydrophilic character and excellent processability when combined with a plasticizer. The objective of this work is to develop soy protein-based bioplastic matrices loaded zinc sulphate monohydrate with potential applications in horticulture. With this aim, the micronutrient loading level and water absorption are the most important properties to assess. The effect of the presence of a selected micronutrient (zinc) at different concentrations in the soy protein-based matrix was assessed, evaluating the mechanical properties, water uptake capacity, microstructure and loading level of zinc. The results confirm that important amounts of an essential micronutrient for a plant (Zn) can be incorporated into bioplastic matrices, modifying water absorption, mechanical and microstructural properties. In any case, the results obtained in this work open up a great potential for the use of this matrices as a supplying source of micronutrients for horticultural crop applications.

1. Introduction

Plastics are one of the most important and most used consumer products in human life. Almost everything used in society is made of plastic or contains plastic, so plastics are used in a great variety of applications, such as, packaging, construction, electronic devices, houseware, etc. Due to this great use, the world´s production of plastics reached 322 million tons in 2015, when China led the market (27.8% of production), followed by Europe (18.5%) (Plastics Europe, 2016). However, this high production of plastic products has significant disadvantages derived from their low biodegradability, which leads to high contamination, and their extremely low renewability, since most of them come from fossil sources (Bledzki and Jaszkiewicz, 2010). In 2014, recycling and recovery of plastic reached 69.2%, while the rest of this percentage is still discarded in landfills, causing garbage accumulation (Plastics Europe, 2016). For these reasons, plastics are being gradually replaced by bioplastics.

The term bioplastics refers to either those polymeric materials which are obtained from renewable sources, or those which exhibit a natural degradability that helps eliminate garbage accumulations. A particularly interesting group is constituted by those bioplastics which present both characteristics, such as proteins and polysaccharides (Flieger et al., 2003). The world´s production of bioplastics reached 1.5 million tons in 2015, with an estimated increase to 6 million tons in the next years (European Bioplastics, 2015). Some of their applications include agriculture, biomedicine, food industry and packaging (Flieger et al., 2003). In this context, the interest in bio-based plastics has greatly increased due to their excellent potentials derived from their low cost, if they are manufactured with residual/waste biomass, high availability and excellent biodegradability.

Generally, bioplastics are composed of a polymeric matrix, a plasticizer and, in certain cases, some specific additives. Bioplastics based on proteins have been extensively studied in the literature (Araújo et al., 2018; Cuadri et al., 2018, 2017, 2016; Felix et al., 2016; Félix et al., 2016, 2014; Fernández-Espada et al., 2016a, 2016b; Gómez-Martínez et al., 2009, 2013; Perez-Puyana et al., 2016; Ramakrishnan et al., 2018; Sharma and Luzinov, 2013; Zárate-Ramírez et al., 2014). In particular, soybean is one of the most used biopolymer raw materials for bioplastics production, as it is a renewable and affordable source. For example, Fernández-Espada et al. (2016a) used soybean to achieve

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superabsorbent matrices due to its hydrophilic character derived from its high content of glutamic and aspartic acid, which make it more hydrophilic than other proteins, whereas Cuadri et al. (2018, 2017, 2016) benefit from its high content in lysine to introduce some functional carboxylic groups, thereby enhancing its hydrophilic character. There are several soy products with different protein content. Among them, the soy protein isolate (SPI) contains at least 90 wt.% protein; although more expensive, it gives the best results due to the greater amount of protein and less moisture (Mo et al., 1999). Plasticizers are low molecular weight agents that have the ability to increase protein chain mobility, reducing the number of inter and intramolecular interactions and decreasing the glass transition temperature. Glycerol (Gly) is the most widely used from this group (Bourny et al., 2017; Guerrero et al., 2010; Matveev et al., 2000). A wide variety of additives are often used to improve the processability and/or the final properties of bioplastics (Bourny et al., 2017).

The properties of these soy-based matrices (bioplastic) can be controlled by the SPI/Gly ratio, the processing conditions and technologies used. Protein-based bioplastics can be processed by using existing processing technologies, from the physicochemical to thermomechanical methods. Among these thermomechanical techniques, injection moulding is one of the most important and suitable process for systems that may exhibit a mixed (thermoplastic and thermoset) character such as proteins. However, this technique needs a previous mixing process in order to obtain a readily injectable protein-plasticizer blend (Reddy, 2015).

In the agricultural sector, the use of these materials would bring great advantages due to their null toxicity and high biodegradability (Guo et al., 2015), as well as the extra contribution of nutrients after their degradation (Saenghirunwattana et al., 2014). Besides, these materials are able to absorb and retain water from the environment, maintaining their integrity without dissolving, even though they can suffer a marked increase in volume (Fernández-Espada et al., 2016a). All of these advantages make these materials an attractive potential candidate for the incorporation of essential micronutrients for the development and health of plants in horticulture. Micronutrients are elements needed by plants in small quantities. There are seven essential micronutrients in horticulture: Boron, Copper, Iron, Zinc, Manganese, Molybdenum and Chlorine. Among them, Zinc has an important role in the growth and development of plants (Uchida, 2000). The incorporation and subsequent controlled release of micronutrients would contribute to avoid the typical excesses of conventional fertilization, while increasing the efficiency of assimilation by the plant. In addition, being able to store water and dispose it during crop growth would increase water-use efficiency of plants (Mortain et al., 2004). The present work is focused on the development of soy protein-based matrices loaded with a soluble micronutrient for their potential use in horticulture. For this purpose, the most important property to evaluate is the micronutrient loading level followed by the water uptake capacity. Zinc cation was selected as the micronutrient, and it was introduced in salt form in the mixing stage, along with SPI and glycerol. Then, bioplastic systems were obtained by injection moulding, at selected conditions, evaluating the water uptake capacity, the mechanical properties and particularly the zinc loading level. It is worth pointing out that mechanical properties of zinc-loaded bioplastics only have a relative importance for their horticulture applications. However, a minimal level of mechanical properties is necessary to ensure physical stability of these bioplastics. In addition, the microstructure of the freeze-dried matrix and their loading level of zinc have also been studied.

2. Experimental

2.1. Materials

Soy protein isolate (SPI, with min. 91 wt.% protein and 6 wt.% moisture) was supplied by Protein Technologies International (SUPRO 500E, Belgium). Glycerol (Gly) was used as a plasticizer and zinc micronutrient was incorporated into the matrix as zinc sulphate monohydrate ($ZnSO_4{\cdot}H_2O$, MN), which were both purchased from Panreac Química Ltd. (Spain).

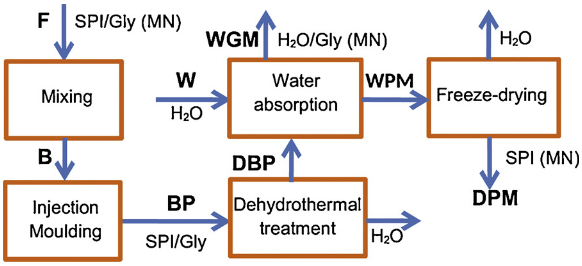

Fig. 1. Processing stages for the preparation of soy/glycerol and soy/glycerol/micronutrient matrices. F: soy, glycerol (and micronutrient) flow. B: moulding blends. BP: bioplastics after injection moulding. DBP: bioplastics after dehydrothermal treatment. W: water. WGM: water with glycerol and micronutrient which leave the matrix. WPM: matrix with water. DPM: matrix without water.

2.2. Preparation of bioplastic matrices

The procedure for the preparation of matrices consisted of several stages, as can be seen in Fig. 1.

First of all, SPI and Gly (ratio 1:1) with different percentages of $ZnSO_4{\cdot}H_2O$ (0.0, 2.5, 5.0, 10 and 15 wt.%), maintaining this SPI/Gly (1:1) ratio constant (Table 1), were mixed in a two-blade counter-rotating mixer Polylab QC (ThermoHaake, Germany) at room temperature and 50 rpm for 10 min, under adiabatic conditions, following the same protocol as in previous studies (Felix et al., 2016; Fernández-Espada et al., 2016a). A detailed description of this equipment and its operational conditions may be found in the literature (Dealy, 1983; Van Wazer et al., 1963). At this stage, torque (M) and temperature (T) measurements were taken during mixing time.

In the second stage, SPI/Gly or SPI/Gly/MN blends (B) obtained after mixing were subsequently processed by injection moulding using a MiniJet Piston Injection Moulding System II (ThermoHaake, Germany) to obtain soy protein-based bioplastic matrices (BP). In this stage, the processing parameters were selected on the basis of a previous study (Fernández-Espada et al., 2016a), taking into account the specific requirements of this current study. As a result, the selected values were: cylinder temperature (40 °C), mould temperature (90 °C), injection pressure (600 bar, 20 s) and post-injection (holding) pressure (200 bar, 300 s). These moulding conditions will be referred to as 40/90. Subsequently, the bioplastic matrices were subjected to a dehydrothermal treatment that consisted in a heating stage in a conventional oven at 50 °C for 24 h to obtain dried bioplastic matrices (DBP). This stage involves some network strengthening and, therefore, is necessary to maintain the physical integrity of the matrices in the subsequent stage of absorption with water. The next step was an absorption process performed in a closed vessel with 300 mL of distilled water (W) for 24 h. In this stage, the glycerol, with some micronutrient, and even protein, was released into the water (WGM). Finally, the wet protein matrices after absorption (WPM) were introduced into a freeze-drying

Table 1
Percentages and nomenclature of the different soy/glycerol/micronutrient (SPI/Gly/MN) blends in the mixing stage.

Nomenclature	SPI (wt.%)	Gly (wt.%)	$ZnSO_4{\cdot}H_2O$ (wt.%)
0.0%	50.00	50.00	0
2.5%	48.75	48.75	2.5
5.0%	47.50	47.50	5.0
10%	45.00	45.00	10
15%	42.50	42.50	15