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Effect of plasticizer and storage conditions on thermomechanical properties of albumen/tragacanth based bioplastics

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ABSTRACT

The effects of composition of the plasticizer fraction and storage conditions on the physical and thermomechanical properties of egg albumen/tragacanth gum based bioplastics were studied. Thus, glycerol (G) and water (W) were used as plasticizers at different G/W ratios (1:0, 3:1, 1:1, 1:3, 0:1), keeping the biopolymer fraction always at 60% (w/w). Tragacanth gum was included in the formulation for its well-known hydrophilic character, as possible future applications of these bioplastics may be moisture dependent (e.g. modified atmosphere packaging). Moreover, properties of bioplastics stored at room temperature under no control of relative humidity were different of those obtained when bioplastics were equilibrated a 53% relative humidity (RH) atmosphere. This is reflected in the DMTA and tensile tests results, for which water loss in the samples with the highest water contents (1:3, 0:1) involves very significant increases in viscoelastic moduli and tensile strength when equilibrated at 53% RH. Glycerol presence when no RH control was taken promotes water uptake, probably due to an interaction between both plasticizers, which eventually lead to a greater plastic region in the tensile tests.

1. Introduction

Proteins, biopolymers directly extracted from biomass, are composed of more than 20 different aminoacids that, through numerous intermolecular linkages and interactions, yield a great range of functional properties (Gómez-Martínez et al., 2009; Pommet et al., 2003). In that sense, different types of proteins like wheat gluten, corn zein, soy protein, etc., have recently shown suitability for the manufacture of bioplastics (Zárate-Ramírez et al., 2014; Gómez-Martínez et al., 2013, 2009; Kim, 2008; Mohanty et al., 2005; Tummala et al., 2006; Zheng et al., 2003).

Protein-based bioplastics generally include plasticizers and, sometimes, a disrupting agent in their formulation (Sothornvit and Krochta, 2005; Pommet et al., 2005). Plasticizers, like glycerol or water, are molecules with low molecular weight and volatility that facilitate the bioplastic processing by reducing the intermolecular forces between the polymeric chains, increasing their mobility. With this regard, three main steps must occur during the formation of protein-based bioplastics: (a) breaking of the stabilizing intermolecular bonds; (b) orientation of mobile polymer chains in the desired shape; and (c) formation of new intermolecular bonds that stabilize the three-dimensional network. Furthermore, a procedure in which a dough-like material is obtained by either kneading or extruding a protein/plasticizer blend is referred to as "thermo-plastic". If the resulting material is further subjected to both heat and pressure, the procedure is called "thermo-mechanical" (Jerez et al., 2007a). Hence, an adequate selection of composition and

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processing parameters may lead to materials with unique properties (Pommet et al., 2003).

Egg white albumen is a protein mainly composed of ovalbumin (54 wt.%), a monomeric phosphoglycoprotein with four free sulfhydryl groups buried in the protein core. Denaturation of albumen by heat results in the exposure of those groups, accompanied by a decrease in its total content due to oxidation to disulfide bonds (Van der Plancken et al., 2005). Consequently, proteins chains unfold and entangle with neighbouring chains and new bonds arise, making texture change. Due to its functional properties, egg white albumen has traditionally been used by the food industry as gelling, foaming, heat setting and binding agent. As a novel alternative to the food industry, recent work by Jerez et al. (2007a, 2007b), Gonzalez-Gutierrez et al. (2010), González-Gutiérrez et al. (2011) and Fernández-Espada et al. (2013) has revealed the feasibility of producing highly transparent bioplastics from egg white albumen. If compared to other common proteins, those bioplastics showed suitable mechanical properties for the manufacture of biodegradable food packaging and other plastic stuffs by application of thermo-mechanical methods.

However, high hydrophilic bioplastics may be required in modified atmosphere packaging (MAP) applications, as oxygen scavenging and CO_2 emitting processes are moisture dependent, and only occur after water has been absorbed from the food product or package atmosphere. For this reason, tragacanth gum, a hydrophilic dried exudate obtained from the stems and branches of Asiatic species of Astragalus, may be included in the formulation. Tragacanth gum is a very complex heterogeneous anionic polysaccharide of high molecular weight (Weiping and Branwell, 2000) consisting of two main fractions: (a) a water-insoluble component called bassorin, which has the capacity to swell and form a gel; and (b) a water-soluble component called tragacanthin (Balaghi et al., 2010). Tragacanth gum, accepted since 1961 as GRAS (generally recognized as safe, according to FDA) at the level of 0.1–1.3 wt.% (Anderson, 1985), has been used for many years as a stabilizer, thickener, emulsifier and suspending agent in the food, pharmaceutical, cosmetic, textile and leather industries, as well as in technical applications. It presents high viscosity in aqueous solution at low concentration, good suspending action, high stability to heat and acidity and effective emulsifying properties. It is also pourable and has creamy mouth feel and good flavour-release properties (Weiping and Branwell, 2000), and very long shelf life (Levy and Schwarz, 1958). Preliminary studies carried out have pointed out the effect of tragacanth gum on increasing water absorption of the resulting protein-based material.

Moreover, previous results revealed a certain degree of incompatibility between glycerol and the protein matrix, which may result in its substantial migration to the bioplastic surface. The inclusion of tragacanth gum may prevent this, as it has also shown to prevent glycerol migration. In fact, tragacanth gum has been used along with glycerol and water as a tablet binder in the pharmaceutical or cosmetic fields (Weiping and Branwell, 2000).

Based on above observations, this research studies the effect of plasticizer on the water uptake capacity and thermo-mechanical/tensile properties of albumen/tragacanth bioplastics obtained by a thermo-mechanical treatment. Hence, different formulations derived from a fixed albumen + tragacanth/plasticizer ratio (60:40), but varying the water/glycerol proportion within the plasticizer, were studied. A comparison between fresh samples and those being stored under relative humidity (RH) control was also established.

2. Materials and methods

2.1. Materials

Spray-dried egg white albumen (designated EW; with 73 wt.% protein, 6 wt.% ashes and 8 wt.% moisture) provided by OVOSEC S.A. (Spain) was used as base material for bioplastics manufacture. On the other hand, tragacanth gum (designated TG) (39–42% carbon content) was supplied by Sigma–Aldrich (USA). In relation with the plasticizers, glycerol, from Panreac Química, S.A. (Spain), and distilled water were designated G and W, respectively.

Table 1 – Formulation of the protein-based bioplastics.

	TG-free formulations	TG-containing formulations				
	G/W	G/W				
	1:1	0:1	1:3	1:1	3:1	1:0
EW (wt.%)	60	40	40	40	40	40
TG (wt.%)	0	20	20	20	20	20
W (wt.%)	20	40	30	20	10	0
G (wt.%)	20	0	10	20	30	40

As far as formulations are concerned, a biopolymer/plasticizer ratio of 60:40 was set, with the protein/gum ratio within the biopolymer fraction being fixed as 2:1, and the glycerol/water ratio within the plasticizer varying as 1:0, 3:1, 1:1, 1:3 and 0:1. These formulations allowed the effect of the plasticizer on the water uptake capacity and mechanical properties to be evaluated. Moreover, the influence of tragacanth addition was evaluated by comparing some of these formulations with their counterparts where the protein was the only component within the biopolymer fraction. Table 1 provides the final formulations in terms of wt.% of each ingredient.

With regard to the bioplastics manufacture, this was accomplished by a thermo-mechanical process, which includes two stages:

(a) Mixing of ingredients: it was carried out for 10 min in the kneading tool (Rheomix 600p) of a torque–rheometer (Polylab, Thermo Haake GmbH, Germany) equipped with two counter-rotating rollers turning at 50 rpm (Jerez et al., 2005). Temperature, starting at 25 °C, was allowed to naturally evolve over this period (no heating/cooling) (Table 2).
(b) Compression-moulding: the resulting dough-like material was subjected to pressure of 100 bar and temperature of 120 °C for 10 min in a hot-plate press, as described by Jerez et al. (2007b). Two types of moulds were used: one to obtain rectangular 3-mm-thick specimens for both DMTA and water uptake capacity measurements; and a second one to obtain type IV-dumbbell specimens (ASTM D638, 2003) for tensile tests.

After preparation and before testing, these samples were either wrapped in plastic film and stored in sealed glass containers at room temperature (no RH control) or placed in desiccators at relative humidity of 53% with a saturated solution of $Mg(NO_3)_2{\cdot}6H_2O$ at room temperature (RH control). Samples were always stored for 24 h prior any test was conducted.

2.2. Methods

2.2.1. Water uptake

Water uptake tests, according to ASTM D570 (2005), were carried out on rectangular probes (50 mm × 10 mm × 3 mm) immersed into distilled water for 24 h. Three replicates were done for each sample, and the water uptake percentage calculated as:

$$\text{Water uptake(wt.\%)} = \frac{\text{wet wt.} - \text{reconditioned wt.}}{\text{conditioned wt.}} \times 100 \quad (1)$$