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Synergistic interactions of locust bean gum with whey proteins: Effect on physicochemical and microstructural properties of whey protein-based films

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ABSTRACT

Locust bean gum synergistic interactions with whey proteins are widely described in terms of functional properties. The aim of this work is to assess how these interactions affect whey protein-based film properties. Blended films were manufactured using whey protein isolate (WPI), four different concentrations levels of locust bean gum (LBG) and two different thermal treatments. A rheological study was performed to assess interaction between WPI and LBG. The influence of glycerol on WPI/LBG interactions was also verified. Barrier, mechanical, and optical properties, as well as microstructure, solubility and moisture sorption behavior of films were evaluated. The results show that interaction between WPI and LBG and more severe heat treatments provide stronger, more flexible and less soluble films with lower permeability to carbon dioxide and oxygen and lower transparency. These findings suggest that the addition of locust bean gum to WPI can be used to tune the properties of WPI-based edible films to meet specific food packaging and edible coating needs.

1. Introduction

Plastics have been increasingly used as packaging materials all over the world. However, due to their non-biodegradability, the interest in packaging from biodegradable biopolymers has been growing in the last years. Proteins (such as caseinates, gelatin, whey protein) and polysaccharides (starch, chitosan, galactomannans and pectin) are biopolymers widely studied because they usually present good adherence to fruits and vegetables surfaces and good barrier properties to gases such as oxygen and carbonic gas (Han & Gennadios, 2005). These biopolymers are presented as possible substitutes in petrochemical-based packaging for specific applications.

Whey protein isolates and concentrates result from the industrial separation of the protein fraction from whey and are by-products of cheese manufacture with excellent functional properties. The functionality and performance of edible films depends on their barrier and mechanical properties (Cerqueira et al., 2011). Edible films from whey protein isolates have shown good oxygen and aroma barriers but generally show poor mechanical properties (Hong & Krochta, 2006; Pérez-Gago & Krochta, 2002). A minimal content of plasticizer like glycerol is needed to reduce brittleness of the protein-based films, increasing extensibility of film (Gounga, Xu, & Wang, 2007; Ozdemir & Floros, 2008). Kokoszka, Debeaufort, Lenart, and Voilley (2010) studied the influence of different glycerol concentrations (30, 40 and 60% (w/w), of WPI) in films from whey protein isolate (WPI) and observed that film barrier properties are better with 40% (w/w, of WPI) of glycerol. Whey proteins have an amphiphilic character. This feature allows them to interact with different kind of molecules. It is thus possible to modify the functional properties of whey proteins by the addition of other components, such as polysaccharides (Rocha, Teixeira, Hilliou, Sampaio, & Gonçalves, 2009). In contrast to casein, WPI is a globular protein with hydrophobic and thiol groups located inside the globular structure. The denaturation, caused by heat treatment,

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opens the globular structure of protein, exposes sulfhydryl and hydrophobic groups that can interact with other molecules and form strong covalent dissulfide intermolecular bonds (Nicolai, Britten, & Schmitt, 2011).

Galactomannans are heterogeneous polysaccharides commonly used in the food industry, mostly obtained from the endosperm of dicotyledonous seeds of numerous plants. Galactomannans present the advantage of forming viscous solutions at relatively low concentration and being little affected by pH, heat and ionic strength (Cerqueira et al., 2011; Dakia, Blecker, Robert, Wathelet, & Paquot, 2008; Goycoolea, Morris, & Gidley, 1995; Sittikijyothin, Torres, & Gonçalves, 2005). Locust bean gum (LBG) is a kind of galactomannan, also known as carob gum, found in the endosperm of fruit pod of the carob tree, compatible with others gums, thickening agents and proteins, usually used to increase the elasticity and strength of the gel (Barak & Mudgil, 2014; Fernandes, Gonçalves, & Doublier, 1991; Gonçalves, Sittikijyothin, Silva, & Lefebvre, 2004). LBG is partially soluble in water at ambient temperature, however the heat is necessary to achieve best water binding capacity (Maier, Anderson, Karl, Magnuson, & Whistler, 1993; Pollard & Fischer, 2006).

Edible films from LBG present high water vapor permeability and elongation-at break values range similar to cellophane films, being indicated by some authors as alternatives to synthetic materials (Bozdemir & Tutas, 2003; Cerqueira, Souza, Teixeira, & Vicente, 2012).

Mixtures of whey protein and anionic polysaccharides had presented positive effects on functional properties of gels (Baeza, Sanchez, Pilosof, & Patino, 2005; Beaulieu, Turgeon, & Doublier, 2001; Ibanoglu, 2002; Ibanoglu, 2005; Neirynck et al., 2007; Sun, Gunasekaran, & Richards, 2007). Interaction between whey proteins and galactomannans have also been referred. For instance, Rocha et al. (2009) found interaction between whey protein concentrate (WPC) and locust bean gum (LBG) at pH 7.0 and observed that a small amount of LBG in the presence of salt leads to a big enhancement in the gel strength. Several authors have been studied blends of proteins and polysaccharides as edible film forming agents in order to increase the mechanicals and barrier properties (Arvanitoyannis & Biliaderis, 1998; Arvanitoyannis, Psomiadou, & Nakayama, 1996; Arvanitoyannis, Psomiadou, Nakayama, Aiba, & Yamamoto, 1997; Lee, Park, Lee, & Choi, 2003; Osés et al., 2009). However, though several authors have studied edible films containing WPI with promising results (e.g. Pierro, Sorrentino, Mariniello, Valeria, & Porta, 2011; Pereira, Souza, Cerqueira, Teixeira, & Vicente, 2010; Ramos, Fernandes, Silva, Pintado, & Malcata, 2012; Seydim & Sarikus, 2006), few have reported on polysaccharide/whey protein blended films (e.g. Brindle & Krochta, 2008; Coughlan, Shaw, Kerry, & Kerry, 2004; Yoo & Krochta, 2011) and, to best of our knowledge, no investigation was performed about properties of edible films containing WPI and locust bean gum.

This study aims to evaluate the effect of LBG addition on barrier, optical and mechanical properties, microstructure, solubility and sorption isotherms of whey protein isolate (WPI) films. A preliminary rheological study was performed at pH 7.0 to assess if the WPI/LBG interactions persist upon the addition of glycerol (the most common plasticizer used in the WPI-based film formulation). Films were prepared without or with two different LBG amounts and two different thermal treatments, at pH 7.0.

2. Materials and methods

2.1. Materials

Whey Protein Isolate (WPI), LACPRODAN DI-9224, kindly supplied by Arla Foods Ingredients (Viby, Denmark), was used as the protein source. This isolate contains a minimum of 93.5% total protein content (74% α-lactoglobulin, 18% β-lactalbumin and 6% bovine serum albumin), maximum content of 0.2% lactose and fat, approximately 0.5% sodium, 1% of potassium and 0.1% calcium, as specified by Arla Foods Ingredients.

Locust bean gum (LBG) (>75% galactomannan content) was kindly supplied by Danisco Portugal (Faro, Portugal).

Glycerol was supplied by Merck (Germany) and other chemicals were supplied by Sigma, Co (St. Louis MO, USA).

2.2. WPI/LBG solutions

The stock solution of 1% (w/w) LBG was prepared by stirring the appropriate amount of dry LBG powder dispersed in distilled water for 1 h, at room temperature. After that, the solution was heated with stirring, for 30 min at 80 °C. After cooling, the non-dissolved material was removed by centrifugation at 20,000 g for 30 min. The final concentration was determined from dry matter content.

WPI mixed solutions were prepared by weighing the appropriate amount of WPI powder, adding the required amounts of LBG stock solution, glycerol (used as plasticizer) and NaCl solution (20% w/w) to a final salt concentration of approximately 50 mM to ensure constant ionic strength, and completing to the final volume with distilled water. The mixtures were stirred again during 2 h, at room temperature. The pH was then adjusted to 7.0 with NaOH 1 M and the solution was stirred for 2 h more.

2.3. Rheological measurements

The films can be formed through different mechanisms including coacervation and gelation followed by solvent evaporation. WPI denaturate upon heating and gel which is the usual mechanism used for producing WPI films through solvent casting. Flow would interfere with the gelling mechanism and would impose severe damage to the sample. Therefore, small amplitude oscillation tests were chosen to study the gel formation process, which is important for the film formation. Mixtures of WPI (10% w/w) and LBG (0, 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5% w/w) were prepared for rheological characterization with or without glycerol as plasticizer. For the mixtures with plasticizer, glycerol was added until a final concentration of 4% (w/w) in the solution. Measurements were performed with a controlled stress rheometer AR-G2 (TA Instruments, New Castle, USA) fitted with parallel-plate geometry (40 mm diameter, gap 800 μm). The mixture was poured onto the plate of the rheometer and covered with paraffin oil to prevent water loss. Samples were heated to 80 °C, at the rate of 2 °C/min, equilibrated for 3 h at 80 °C and cooled from 80 °C to 20 °C with the same rate of 2 °C/min. Mixtures were then equilibrated for 30 min at 20 °C to obtain non time dependent dynamic shear modules. Frequency of 1 Hz was maintained constant and all experiments were performed in the linear viscoelastic region (previously tested) using a target strain of 0.5%.

The experiments were carried out in triplicate with the results reported as the measurements averages.

2.4. Film preparation

Solutions were prepared as described above, being the final concentrations in the film forming solutions 5% (w/w) for WPI and 2% (w/w) for glycerol. Four different LBG concentration (0, 0.025, 0.05% and 0.1%) were tested. After the 4 h stirring period, the mixtures were heated to denature the protein fraction. Two different heat treatments were used: 1) the mixtures were heated until 75 °C and immediately cooled back to room temperature; 2)