Food Packaging and Shelf Life 16 (2018) 122–128

Contents lists available at ScienceDirect

Food Packaging and Shelf Life

journal homepage: www.elsevier.com/locate/fpsl

Physicochemical and microstructural properties of whey protein isolate-based films with addition of pectin

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ARTICLE INFO

Keywords:
Whey protein isolate
Pectin
Edible films
Biopolymer interactions
Film properties

ABSTRACT

The interest in edible packaging films as a possible substitute for petrochemical-based films has been growing over the last years. Blends of proteins and polysaccharides can be an alternative to enhance edible film properties. This work aims to develop whey protein isolate (WPI) films with pectin (PEC) addition by complex coacervation method and to evaluate the effect of polysaccharide addition on film properties. Blended films were elaborated using WPI and four concentrations of PEC. Interaction between WPI and PEC was evaluated through ζ-potential. Solubility, moisture sorption behavior, optical, barrier and mechanical properties and microstructure of films were evaluated. The results showed that PEC electrostatically interacted with WPI at pH 3.0, reducing the ζ-potential to values close to zero. The interaction between compounds increased the opacity, solubility and permeability to water vapor, but decreased the flexibility and tensile strength of WPI films. With the increase of pectin concentration, the electrostatic interaction was reduced and the non-complex pectin that, was present in excess, improved the mechanical properties of films.

1. Introduction

The interest in edible packaging films as a possible substitute for petrochemical-based films has been growing over the last years. Polysaccharides and proteins are the most used biopolymers to manufacture edible films (Donhowe & Fennema, 1994; Kester & Fennema, 1986). Blends of protein and polysaccharide in specific solution conditions (protein/polysaccharide ratio, ionic strength and pH of solution) and in certain amount can result in protein-polysaccharide complexes that will form films with advantageous physical properties (Murillo-Martínez, Pedroza-Islas, Lobatto-Calleros, Martinez-Perez, & Vernon Carter, 2011).

Blends of protein and polysaccharide in the solution result in phase separation that can be associative (attraction between polymers) or segregative (repulsion between polymers). During associative separation the biopolymers of opposite charges can crosslink through electrostatic interaction and form one rich phase in biopolymers (coacervate) and the other one in solvent. This separation is also known as complex coacervation (De Kruif, Weinbrecka, & De Vries, 2004; Eghbal et al., 2016).

The electrostatic interactions between biopolymers can be evaluated through electrophoretic mobility which is automatically converted into zeta potential. When the interaction between protein and polysaccharide reaches the maximum, zeta potential of the solution approaches zero indicating that there has been reduction of the electrostatic free energy (Eghbal et al., 2016).

The complex coacervation can be applied to prepare composite edible films, aiming to improve functional and physico-chemical properties of the films (Farris et al., 2011). Di Pierro, Sorrentino, Mariniello, Giosafatto, and Porta (2011) noticed that addition of chitosan reduced the oxygen permeability of whey protein isolate (WPI) film. Eghbal et al. (2016) observed that complex coacervation between sodium caseinate and pectin improved mechanical properties of the films. Farris et al. (2011) reported that electrostatic interaction between gelatin and pectin resulted in more resistant films to break than the ones obtained from gelatin only.

Whey protein is a residual product from cheese manufacturing with excellent functional properties, however, for a long time viewed as material of little value. Separation of the whey protein fraction can result in two products: whey protein isolate (WPI) and concentrate (WPC), being that WPI presents protein content above 90% w/w in dry basis (Ramos et al., 2013) and it is constituted basically by 65% β-lactoglobulin, 25% α-lactalbumin and 8% bovine serum albumin (Khwaldia, Perez, Banon, Desobry, & Hardy, 2004). Its application as

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https://doi.org/10.1016/j.fpsl.2018.03.005
Received 15 June 2017; Received in revised form 6 March 2018; Accepted 20 March 2018

edible film has been intensively studied by diverse researchers which observed that WPI films present good oxygen barrier properties and transparency but show poor mechanical properties (Pérez-Gago & Krochta, 2002; Ramos et al., 2013; Schmid et al., 2012; Schmid, Pröls, Kainz, Hammann, & Grupa, 2017)

Pectin (PEC) is a linear polysaccharide, negatively charged, soluble in water and usually obtained from peel and pulp of citric fruits and apples. Their basic structure includes galacturonic acid partially esterified by methoxyl groups. Depending on the methoxylation grade, pectin is classified as high methoxyl (50–80%) and low methoxyl (25–50%) pectin (Thakur, Singh, & Handa, 1997).

Recently, some authors have studied WPI + pectin (PEC) interaction. Krzeminski, Prell, Weiss, and Hinrichs (2014) and Zhang and Vardhanabhuti (2014) studied interaction between WPI and HMP (high methoxyl pectin) and found that at low pH the two biopolymers interact by complex coacervation forming large particle sizes of several micrometers. Krzeminski et al. (2014) related that WP-HMP based systems revealed very dense aggregated structures. Thongkaew, Hinrichs, Gibis, and Weiss (2015) suggested that WPI + PEC particles may be useful as carriers of functional components or as structuring agents in a variety of foods. However, studies about elaboration of WPI-PEC coacervate films and its properties are still scarce in the literature

This study aimed to develop whey protein isolate (WPI) films with pectin addition by complex coacervation method and to evaluate the effect of polysaccharide addition on barrier, optical and mechanical properties; microstructure, solubility and sorption isotherms of the WPI films.

2. Materials and methods

2.1. Materials

Whey Protein Isolate (WPI), LACPRODAN DI-9224, containing 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, was kindly supplied by Arla Foods Ingredients (Viby, Denmark). High methoxylated amidated pectin (GRINDSTED® PECTIN RS 461 – DM = 70%) was kindly supplied by Danisco (Cotia, Brazil). Glycerol was supplied by Sigma, Co (St. Louis MO, USA).

2.2. WPI/PEC Solutions

Films constituted only by WPI or by WPI + PEC (in different concentration) were developed for the purpose of this study.

Stock solution of 6% (w/w) PEC was prepared by dispersion of dry PEC powder in distilled water, with stirring, at 50 °C until complete dissolution. After that, the solution was cooled at room temperature and reserved. Aqueous stock solution of 8% WPI were prepared by dispersion WPI powder in distilled water with posterior stirring for one hour at room temperature.

Film solutions were prepared adding appropriated amount of WPI stock solution, required amounts of PEC stock solution, glycerol and NaCl solution (20%w/w) to ensure a constant ionic strength with final salt concentration of approximately 50 mM. The mixtures were stirred at room temperature during 2 hours. Four different PEC concentrations (0, 0.5, 1% and 2%) were tested. After 2 hours of stirring, solutions without PEC had pH adjusted to 7.0 with NaOH 20% (v/v) and the solutions with PEC addition had pH adjusted to 3.0 with HCl 20% (v/v). It was not possible to obtain continuous WPI films without PEC at pH 3.0 because they present ruptures and brittle areas and for this reason they were not studied. So, the final volume was completed with distilled water and the solution was stirred for 2 hours more, at room temperature. Kokoszka, Debeaufort, Lenart, and Voilley (2010) compared the influence of different glycerol concentration (30, 40 and 60% (w/w), of WPI) in WPI films and observed that 40% (w/w, of WPI) of glycerol provided films with better barrier properties. So, the prepared solutions presented final concentrations in the film forming solutions of 5% (w/w) for WPI, 2% (w/w) for glycerol (used as plasticizer) and different PEC concentrations (0, 0.5, 1% and 2%).

2.3. Film preparation

After four hours stirring period, the mixtures were heated at 75 °C for 10 min and then cooled back to room temperature, to denature the protein fraction.

Films were prepared by casting method where 200 g of each film forming solution were poured onto tray (25 × 15 cm). Films were dried in a climate chamber (BT 71, Biothec, Brasil) for 72 h at 30 ± 2 °C. In order to carry out the analyses, the dried films were equilibrated in desiccator contained magnesium nitrate- 6-hydrate saturated solution (53% relative humidity) at 25 °C for one week.

2.4. Zeta potential

The average electrical charge (ζ-potential) of the WPI and WPI-PEC solution were determined using a commercial dynamic light scattering and micro-electrophoresis device (Malvern Zeta mNano ZS, Malvern Instruments, Worcestershire, UK). Samples were diluted with deionized water to a final protein concentration of 0.3% w/w. The analysis was determined in triplicate.

2.5. Characterization of WPI + PEC films

2.5.1. Film thickness

The thickness of the films was measured at 10 different points for each film using a digital micrometer (Mitutoyo, Japan).

2.5.2. Water solubility

The film solubility in water was determined according to the method reported in the literature (Cuq, Gontard, Cuq, & Guilbert, 1996 and Silva, Mauro, Gonçalves, & Rocha, 2016. The solubility was determined according to Eq. 1, being that (W_0) is the weight of disks from the dried films before immersion in water at 25 °C, with agitation (60 rpm) and (W_f) is the weight of these disks after 24 h of solubilization and drying in a vacuum oven (TE-395, Tecnal, Brasil) at 60 °C and 10 kPa until constant weight.

$$S = \frac{W_0 - W_f}{W_0} \times 100 \quad (1)$$

2.5.3. Moisture sorption isotherms

Pieces of films (30 × 30 mm) were used to plot sorption isotherms according to the static gravimetrical method proposed by Jowitt et al. (1987). Samples were weighed in triplicate, placed in small jars containing different saturated aqueous salt solutions corresponding to water activity intervals between 0.11 and 0.90 (LiCl; CH_3COOK; $MgCl_2$; Mg $(NO_3)_2$; NaBr ; $SrCl_2$; NaCl; KCl; $BaCl_2$) and placed in a temperature-controlled chamber maintained at 25 °C. The equilibrium moisture content was measured gravimetrically, drying to constant weight using a vacuum oven at 60 °C and 10 kPa. The Guggenheim-Anderson-de-Boer (GAB) model (Eq. 2) was adjusted to the experimental data using the non-linear regression module of Statistic 7.0 software (Statsoft, Tulsa, OK, USA).

$$X = \frac{X_m . C . K . a_w}{(1 - K . a_w)(1 - K . a_w + C . K . a_w)} \quad (2)$$

where, a_w - water activity, dimensionless; X - equilibrium moisture content (% dry basis); X_m - moisture content of monolayer (% dry basis) (water content corresponding to saturation of all primary adsorption sites by one water molecule); C - Guggenheim constant and K - corrective constant (Van den Berg & Bruin, 1981).