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Water vapour permeability, thermal and wetting properties of whey protein isolate based edible films

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ABSTRACT

This study deals with the effect of whey protein isolate (WPI) and glycerol (GLY) used as a plasticizer on some physical properties of cast whey protein isolate (WPI) films. Films were prepared from heated (80 °C for 30 min) aqueous solutions of WPI at 7, 8, 9 and 10% (w/w), GLY (40%, w/w, of WPI) and WPI at 8% (w/w), GLY (30, 40, and 60%, w/w, of WPI). For all types of films, water vapour permeability for four relative humidity differentials (30–100%, 30–84%, 30–75%, and 30–53%), surface and thermal properties were measured. Varying the proportion of WPI and GLY in edible films had some effect on water vapour permeability, wetting and thermal properties of WPI films. A cumulative effect of both glycerol and protein content was observed on the water vapour permeability increase. Indeed film barrier properties are much better for the lowest WPI (7%) and GLY (40%) contents. GLY increases the degradation temperature and favours film surface wettability whereas protein content did not affects thermal properties of films.

1. Introduction

A variety of renewable biopolymers such as polysaccharides, proteins, lipids and their composites, derived from plant and animal resources have been investigated for the development of edible/biodegradable non-petrochemical-based packaging materials and edible coatings (Cuq, Gontard, & Guilbert, 1998; Debeaufort, Quezada-Gallo, & Voilley, 1998; Gennadios, Rhim, Handa, Weller, & Hanna, 1998; Guilbert, Gontard, & Gorris, 1996; Kester & Fennema, 1986; Krochta & De Mulder-Johnston, 1997; Rhim & Ng, 2007). Components of edible films and coatings can be divided into three categories: hydrocolloids, lipids and composites. Hydrocolloids include proteins and polysaccharides, such as starch, alginate, cellulose derivatives, chitosan, and agar. Lipids include waxes, acylglycerols, and fatty acids. Composites contain both hydrocolloid components and lipids. Composite film structure could be dried emulsions, or bilayers. The choice of materials for a film or a coating is largely dependent on its desired function (Cha & Chinnan, 2004).

Various whey protein products have been developed over the past decades, often with a specific application field. One such product is whey protein isolate (WPI), either produced by ion-exchange and subsequent ultrafiltration (UF) or microfiltration and UF. According to the American Dairy Products Institute, the protein content should be at least 90% on an "as is" basis (Dierckx & Huyghebaert, 2002; Horton, 1998).

The use of the whey protein for the production of films has received a large amount of attention in the last few decades. This is quite understandable, since these films are edible, biodegradable, based on a waste stream from the cheese industry, and have interesting mechanical properties. Some detailed reviews have been written on this subject (Gennadios, 2002; Khwaldia, Perez, Banon, Desobry, & Hardy, 2004; Krochta, Baldwin, & Nisperos-Carriedo, 1994).

The making of protein-based films generally requires the incorporation of a minimal content of plasticizer to reduce its brittleness. Film plasticizers function by weakening intermolecular forces between adjacent polymer chains. This results in an increased film extensibility and flexibility, with a decreased elasticity, mechanical resistance, and barrier property of the films. The most common plasticizers used are polyols and mono-, di-, and oligosaccharides. Glycerol, as a plasticizer, has been incorporated into most hydrocolloid films. It is a high boiling point plasticizer that is water-soluble, polar, nonvolatile, and protein miscible. These properties make glycerol a suitable plasticizer for use with a compatible water-soluble polymer (Banker, 1966). The residual water within a film also acts as a plasticizer for hydrophilic films and may explain why proteinaceous films become more brittle in low moisture conditions. In addition, many plasticizers have a strong flavour and high cost. The plasticizer:polymer ratio is a key parameter in determining the functional properties of a film (Coupland, Shaw, Monahan, O'Riordan, & O'Sullivan, 2000).

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The formation of flexible hydrocolloid films requires two essential ingredients: a film-forming polymeric material to provide structural support, and a plasticizer to reduce brittleness. Plasticizers, such as glycerol and sorbitol, are used generally for whey protein-based edible films to enhance the film flexibility and extensibility (Kaya & Kaya, 2000; Mate, Frankel, & Krochta, 1996; McHugh & Krochta, 1994; Osés, Fernandez-Pan, Mendoza, & Maté, 2009). In films manufactured from whey protein isolate, increasing levels of glycerol and sorbitol have been reported to increase film extensibility and reduce film strength (McHugh, Aujard, & Krochta, 1994; Ozdemir & Floros, 2008). The hydrophilic nature of the plasticizer (nature and amount) significantly affects the moisture barrier ability of protein films. Similar results were noted by Shaw, Monahan, O'Riordan, and O'Sullivan (2002) when the concentration of GLY was 50%, 60% and 70% (w/w) in WPI films, WVP increased slightly when the GLY amount increased in film-forming solutions. Bodnar, Alting, and Verschueren (2007) reported that the WVP barrier values increased with increasing GLY concentration. The main and probably sole explanation of this behaviour was demonstrated for WPI–GLY and WPI–Sorbitol by Osés et al. (2009), but also for fish muscle proteins by Sobral, Santos, and Garcia (2005). The higher the glycerol content, the higher the moisture content. Moreover, plasticization by water reduces the protein–protein interactions, favours the polymer chain mobility, increases the free volume and as a result increases moisture diffusion. Indeed, Karbowiak et al. (2006c) showed that the diffusivity of small molecules, such as water or fluorescein, in carrageenan-based edible films only depends on the water content whatever the concentration of the plasticizer.

Contrarily to the barrier properties, very little information regarding the surface and thermal properties of whey films containing different ratios of glycerol is published.

In general, protein films cast from an aqueous solution are not promising water barriers. The added value for these barriers needs to be found in other characteristics. Miller and Krochta (1997) wrote about the possibility of using whey protein films as barriers against oxygen or aroma migrations. From these studies, it follows that the barrier properties are strongly reduced when the films are exposed to high relative humidity. In this respect it can be envisaged that the added value of whey protein films as a barrier can be found in the form of (macro) encapsulation. These capsules are then designed to extend the shelf life of the encapsulated material by, e.g., preventing oxidation. When they come into contact with water, or an environment with high water activity, the barrier properties change and the contents of the capsule will be released in a controlled way. However, most of the research is devoted to the barrier properties of the films in a dry state (Bodnar et al., 2007). Within the current study the focus is also on the permeability of the whey protein films in an aqueous environment, 100% relative humidity. Thermal and surface properties can also be determined to improve the use of whey films and their application in food packaging.

The objective of this study was to investigate the influence of varying proportions of whey protein isolate (WPI) and glycerol (GLY) on the water vapour permeability, wettability and thermal properties of films formed from WPI.

2. Materials and methods

2.1. Reagents and chemicals

The WPI BiPRO (~90% protein) was obtained from Davisco Foods International Inc. (La Sueur, MN, USA). Anhydrous glycerol (98% purity) was supplied by Fluka Chemicals (Seelze, Germany) and used as a plasticizer in order to improve the mechanical properties of whey protein isolate films. Three saturated salt solutions (Prolabo, Fontenay-sous-Bois, France) were used to fix the water activity (a_w) at 25 °C: magnesium nitrate giving 0.53 a_w, sodium chloride giving 0.75 a_w, and potassium chloride giving 0.84 a_w.

2.2. Preparation of WPI films

Film-forming solutions were prepared by slowly dissolving WPI in distilled water (7, 8, 9, 10%, w/w) under a 700 rpm constant magnetic stirring for 10 min. The natural pH 7 did not need to be adjusted. No additional salts were added. Subsequently, the solutions were heated on a magnetic plate at 80 °C for 30 min to denature the whey protein, then cooled to room temperature and various amounts of GLY (30–60%, w/w) were added to plasticize the films. The cooling required several minute to remove naturally most of the air bubbles incorporated during stirring. Solutions were poured onto a series of Petri dishes (diameter 14 cm). To control the film thickness, the quantities of each film-forming solution poured onto a plate were the same, fixed at 14 mL. The solutions were dried for 10 h at 25 ± 1 °C and 30 ± 2% relative humidity (RH) in a ventilated chamber (KBF 240 Binder, ODIL, Dijon, France). After this time, the dried solutions formed easily detachable films. The dried films were then peeled-off and conditioned again at 30% RH and 25 °C for 48 h prior to testing. Compositions of the films are presented in Table 1.

2.3. Measurement of film thickness

The film thickness was measured with an electronic gauge (Multi Check FE, Sodexim, Tourcoing, France) having a precision of 1 μm. The electronic gauge was calibrated at 25, 51, 127 or 260 μm using standards prior to film thickness measurements. Five thickness measurements were taken of each film, one at the centre and four around the perimeter, and the mean was used in the calculations.

2.4. Differential scanning calorimetry

Differential scanning calorimetry (DSC) tests were performed using a Perkin Elmer DSC-7 (Perkin Elmer, Courtaboeuf, France). An empty capsule was used as an inert reference. The sample weight ranged between 10 and 15 mg. The heating and cooling rates were fixed at 10 °C min^{-1}. The following temperature program ranging between 25 and 110 °C was used: heating from 25 to 110 °C, cooling to 25 °C, heating to 110 °C, and finally cooling to 25 °C. Prior to the experiment, the DSC was calibrated using indium samples for which the phase transition temperatures are well-known. The initial temperature of degradation (denaturation), T_d, temperature at maximum degradation rate, T_{max} and the apparent enthalpy of fusion, ΔH_f, were computed from each first run of the thermal curve according to Ryan et al. (2008). Two measurements per film were obtained.

Table 1
Compositions of film-forming suspensions of edible films based on whey protein isolate.

Film[a]	WPI (g)	GLY (g)	Water (g)
7WPI 40GLY	7	2.8	90.2
8WPI 30GLY	8	2.4	89.6
8WPI 40GLY	8	3.2	88.8
8WPI 50GLY	8	4.0	88.0
8WPI 60GLY	8	4.8	87.2
9WPI 40GLY	9	3.6	87.4
10WPI 40GLY	10	4.0	86.0

[a] The format gives weight of whey protein isolate (WPI) in 100 g total and the relative percentage of glycerol (GLY), e.g., 7WPI 40GLY: means 7 g of WPI with the equivalent of 40% (by weight) of glycerol.