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From acacia honey monosaccharide content to a new external binary plasticizer applicable in aqueous whey protein films

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ABSTRACT

Plasticizer is an essential adjuvant in food and pharmaceutical film coatings affecting the appearance, mechanical and permeation properties of the final coat. In the present study, film formation and plasticization of native whey proteins (potential future "green" coating agents for pharmaceuticals and food products), were studied with free isolated films. Special attention was paid to the effects of plasticizer, preheating and film forming solution pH on the mechanical stress–strain and moisture permeation properties of whey protein films. Glycerol, binary mixtures of fructose and glucose, and non-crystalline acacia honey were studied as external plasticizers. The type and amount of plasticizer affected the mechanical stress–strain properties of the whey protein films. A short preheating treatment of whey proteins prior to film casting resulted in mechanically strong films with a reduced elongation. The film forming properties of aqueous whey proteins could be modified by adjusting the pH above the isoelectric point of β-lactoglobulin prior to film coating. For effective plasticization, whey protein films required a high amount of monosaccharide containing plasticizer ranging from 80% to 120% (calculated from the protein weight). A new external binary plasticizer having the same ratio of monosaccharides as non-crystalline acacia honey (fructose and glucose 1.67:1) was found to be applicable in aqueous whey protein films.

Keywords: Whey proteins; Film coating; Binary plasticizer; Acacia honey; Mechanical properties; Free films

1. Introduction

Whey proteins are a common by-product of the dairy industry and an ideal source of protein. Native whey proteins consist of β-lactoglobulin, α-lactalbumin, bovine serum albumin (BSA) and some immunoglobulins, with β-lactoglobulin being the major component of whey proteins (approx. 50–60% of the protein). β-Lactoglobulin is a globular protein with known secondary structure (15% α-helix, 50% β-sheet and 15–20% reverse turn) (Creamer et al., 1983; Fox and McSweeney, 1998). No risk of bovine spongiform encephalopathy (BSE) is recognized for proteins of milk origin unlike gelatin, for example.

Applications of milk proteins as an edible film material for food and nutrients are well known but there are only a few reports in the literature on the application of these proteins as pharmaceutical film formers and in film coating processes (Lee and Rosenberg, 1999, 2000a,b; Abu Diak et al., 2007). A literature review on food sciences shows that native whey proteins are considered as good barriers against oxygen at low and intermediate relative humidity (Anker et al., 2002). Gennadios et al. (1993) studied the effects of temperature on the oxygen permeability of edible protein-based films. McHugh and Krochta (1994a,b) evaluated oxygen permeability and mechanical properties of whey protein edible films plasticized with glycerol and sorbitol. The oxygen permeability and tensile properties of the films were found to be compare favorably with those of synthetic film materials. More recently, the use of milk casein protein as a novel film-forming agent for tablet coating has been reported by Abu Diak et al. (2007). Casein coated tablets that had been subjected to post-coating heat

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treatment showed sustained drug release properties at pH 6.8, which may be attributed to casein cross-linking.

Plasticizers are an essential adjuvant in film coating formulations that may greatly affect the mechanical and moisture permeation properties of the final film coating. Effective plasticizers act by decreasing the cohesion forces between film forming molecules (polymer chains), and consequently the mobility of the polymer chains is increased resulting in a more elastic film structure (Banker, 1966; O'Donnell and McGinity, 1997). According to the literature, glycerol at a ratio of 20–60% (calculated from the film former weight) is generally regarded as a plasticizer of choice for whey proteins (McHugh and Krochta, 1994b; McHugh et al., 1994; Sothornvit and Krochta, 2000, 2005; Talens and Krochta, 2005). Glycerol was also found to be a suitable plasticizer for preparing ternary composite edible films based on soy protein isolate (Jia et al., 2009). Talens and Krochta (2005) showed that the incorporation of beeswax produced a plasticizing effect in whey protein:glycerol films. The moisture barrier properties of whey protein:glycerol films improved as a result of the addition of beeswax, which increases the hydrophobic character and decreases of the amount of hydrophilic plasticizer required in the film.

Acacia honey is a free flowing and almost colorless natural fluid. It is composed of approximately 73% of monosaccharides such as fructose and glucose (at a ratio of 1.67:1), and additionally disaccharides (10%), trisaccharides (3%) and water (16%) (Krauze and Zalewski, 1991; Cotte et al., 2003). To date, the application of acacia honey as a plasticizer has not been reported. Acacia honey is one of the few honeys which do not crystallize (Liviu Al et al., 2009). An exceptionally high concentration of fructose in acacia honey results in a low viscosity and a lower tendency to crystallize during storage which could be advantageous from plasticization point of view.

A formulation hypothesis is proposed that externally plasticized whey proteins can have an added value as new film coating alternatives (future "green" coating agents) applicable in the manufacture of pharmaceutical oral solid dosage forms. Today, hydroxypropyl methylcellulose (HPMC) is generally considered as the primary coating material for pharmaceutical tablets. HPMC is a semi-synthetic cellulose ether in which some of the hydroxyl groups are substituted with methyl and hydroxypropyl groups. Although HPMC has many of the desired coating polymer properties, it also has a number of shortcomings such as hygroscopicity, compatibility problems and process limitations associated with the performance of the aqueous film coating (Wong and Bodmeier, 1996).

The main objectives of this study were to investigate film formation of aqueous externally plasticized whey proteins and to evaluate the effects of a new binary plasticizer system containing a relatively high concentration of fructose (i.e. composition close to non-crystalline acacia honey) on film formation and film properties. Special attention was paid to the effects of plasticizer concentration, pH and preheating of the film forming solution on the mechanical and moisture permeation properties of the films. An established externally plasticized HPMC film formulation was used as a reference film.

2. Materials and methods

2.1. Materials

Whey protein films were prepared from an ultrafiltered Heracles whey protein concentrate obtained from Juusto Kaira, Kuusamo, Finland. The composition (w/w) of the whey protein concentrate was as follows: proteins 77%, carbohydrates 10%, fat 5%, water 4%, mineral substances and vitamins 4%. Glycerol (Ph.Eur.), mixture of monosaccharides fructose (Ph.Eur.) and glucose (Ph.Eur.) (1.67:1), and acacia honey (Hunajainen SAM Oy, Söderkulla, Finland) were studied as external plasticizers. Hydroxypropyl methylcellulose (HPMC; Ph.Eur.) plasticized with polyethylene glycol (PEG 400; Ph.Eur.) was used as a reference film. Sodium hydroxide and citric acid (Ph.Eur.) were used for adjusting pH of the coating solutions. Purified water was used as an aqueous solvent.

2.2. Preparation of free films

The study protocol and compositions of the externally plasticized whey protein film forming solutions are summarized in Table 1. With unheated whey protein solutions, the pH was first adjusted to pH 6.6 (2 M NaOH), and the plasticizer was added by mixing with a magnetic stirrer. With preheated solutions, the pH of a solution was adjusted to pH 6.6 (2 M NaOH) prior to heating at +80 ± 2 °C for 20 min. After cooling down (21 ± 2 °C), the plasticizer was added into a solution by mixing with a magnetic stirrer. The water content (16%) of acacia honey was taken into account when calculating the amounts of plasticizers.

The effects of pH on the mechanical properties of the films was studied with the films plasticized with a binary mixture of fructose and glucose (1.67:1), and the pH of the present solutions was adjusted to 3.0, 4.1, 5.2, 6.3, 6.6, 7.4, 8.5, 9.6, 10.7, 11.8 and 12.9. Amounts of the plasticizer in the aqueous solutions of whey proteins (unheated and preheated solutions) were as follows: 60%, 80%, 100%, 120% (expressed as a ratio of plasticizer and whey protein concentrate %, w/w) (Table 1).

The reference HPMC films plasticized with PEG 400 were composed of 10% (w/w) of the polymer and 30% (w/w) of the plasticizer (calculated from the polymer weight). HPMC was dispersed and hydrated in approximately 20–30% of the required amount of purified water (which was pre-heated to 80–90 °C). The remaining cold water was added while continuing to stir with a magnetic stirrer until the solution was clear. Finally, plasticizer was added, and the solution was stirred for a further 45–60 min.

Free films were prepared by a casting/solvent evaporation method. For preparing free films, 10.0 g of the whey protein aqueous solution (10% w/w) or HPMC solution (10% w/w) was carefully poured into polytetrafluoroethylene (Teflon®) molds.

Table 1 – Compositions of the plasticized aqueous solutions of whey proteins studied (unheated and preheated solutions).

Plasticizer	Concentration of the plasticizer from the whey protein concentrate (wt%)			
	60	80	100	120[a]
Glycerol	×	×	×	×
Acacia honey	[b]	×	×	×
Binary mixture of fructose and glucose (1.67:1)	×	×	×	×

[a] Only with a preheated solution.
[b] Only with a unheated solution (limited film formation with preheated solutions).