Food Hydrocolloids 44 (2015) 407–415

Contents lists available at ScienceDirect

Food Hydrocolloids

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

Sodium caseinate films containing linseed oil resin as oily modifier

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ARTICLE INFO

Article history:
Received 29 April 2014
Accepted 15 October 2014
Available online 30 October 2014

Keywords:
Sodium caseinate
Linseed oil based resin
Films
Emulsion

ABSTRACT

Modified sodium caseinate films were prepared by casting of film forming emulsions prepared by adding different contents of a linseed oil based resin (LOR) into the aqueous protein solution. Infrared spectroscopy of the formed films revealed that physical interactions between the main component of the film and the oily modifier were developed. The films were also characterized in terms of water vapor permeability, water absorption, optical, mechanical and thermal properties. Water vapor permeability and equilibrium moisture content decreased with the addition of LOR, reaching their minimum values (59% reduction in WVP and about 70% reduction in EMC, respect to the corresponding values of the neat SC film) with the incorporation of 10 and 15 wt% of LOR, respectively. As expected, contact angle measured using a polar solvent and opacity increase (respect to the neat SC film) when the lipid modifier is used in the formulation, although the increment in the last property is lower than the reported in similar works. The presence of LOR decreased tensile modulus and strength but the elongation at break is not significantly affected.

1. Introduction

Naturally renewable films, based on biopolymers such as proteins, polysaccharides, lipids or their combination, have attracted a continuously increasing research interest over the last two decades because of the wide field of potential applications, their low cost, great availability as well as their biodegradable character that avoid ecological imbalance and esthetic deterioration of nature (Bonilla, Atarés, Vargas, & Chiralt, 2012; Matsakidou, Biliaderis, & Kiosseoglou, 2013; Pavlath & Orts, 2009; Tharanathan, 2003).

Specifically, sodium caseinate (SC), a family of phosphoserylated proteins (α_{s1}-, α_{s2}-, β-, κ-caseins) (Holt & Sawyer, 1993), presents film-forming ability, either on its own (Schou et al., 2005), or in combination with polysaccharides (Kristo & Biliaderis, 2006; Pereda, Aranguren, & Marcovich, 2008) and/or hydrophobic compounds (Fabra, Perez-Masia, Talens, & Chiralt, 2011; Pereda Aranguren, & Marcovich, 2010). Due to the structure and amino acid composition of caseins, it is likely that hydrogen bonds, electrostatic interactions and most probably hydrophobic forces are involved in the formation of casein-based edible films (Schou et al., 2005).

This protein, in general, produces flavorless, tasteless, flexible and biodegradable films with good gas barrier properties (Cuq, Gontard, Aymard, & Guilbert, 1997; Park & Chinnan, 1995). In addition, it provides nutritional value to the final product if used as an edible coating, it is water soluble and may additionally act as an emulsifier due to its surface activity, heat resistance and water-holding properties (Khwaldia, Perez, Banon, Desobry, & Hardy, 2004). Because of all of these characteristics, sodium caseinate presents potential use in different applications, that can include their direct use in food packaging (Pavlath & Orts, 2009) or as a barrier coatings on paper packaging materials (Khwaldia, Arab-Tehrany, & Desobry, 2010; Khwaldia, Basta, & Houssni El-Saied, 2014).

However, water-soluble hydrocolloid films present poor water barrier properties (Quezada-Gallo, 2009). A number of studies have been published on the incorporation of hydrophobic substances into the biopolymer film matrix, such as vegetable oils (Pereda, Aranguren, & Marcovich, 2010), essential oils (Zinoviadou, Koutsoumanis, & Biliaderis, 2009), waxes (Perez-Gago & Krochta, 2001) and fatty acids, to bring about a decrease in film water vapor permeability (WVP). The incorporation of hydrophobic materials can effectively modify the properties of protein films, as reported by Krochta, Hudson, and Avena-Bustillos (1990) for their films made of SC and acetylated monoglycerides that had a 41% reduction in water vapor transmission rate in comparison with control films (without lipid). However, the emulsification of the initial biopolymer-oil mixture is required, to obtain a uniform droplet distribution with small-sized droplets so as to increase the tortuosity factor and enhance, effectively, the water barrier

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http://dx.doi.org/10.1016/j.foodhyd.2014.10.016
0268-005X/

performance of the film (Debeaufort, Martinpolo, & Voilley, 1993; Fabra, Perez-Masia, et al., 2011; McHugh & Krochta, 1994; Perez-Gago & Krochta, 2001; Vargas, Perdones, Chiralt, Chafer, & Gonzalez-Martinez, 2011).

The affinity of hydrophobic modifiers with the protein that forms the film can be improved by chemical modification of the oils. In this way, vegetable oil can be reacted with glycerol (transesterification) followed by esterification with maleic anhydride, to produce a maleinated monoglyceride (Mosiewicki, Aranguren, & Borrajo, 2005). This final oil based resin presents lower molecular weight and higher polar structure in comparison with the original oil.

In this study, a linseed oil based resin was chosen as the lipid additive. Linseed oil, also known as flax seed oil, is a clear to yellowish oil obtained from the dried ripe seeds of the flax plant (*Linum usitatissimum*, Linaceae). As a renewable resource from agriculture, the use of the linseed oil in industrial products has received much attention. In particular, this oil has been widely used as a drying oil in the painting industry since it contains a high percentage of linolenic acid, with 3 unsaturations per fatty acid chain (Formo, Jungermann, Norris, & Sonntag, 1985; Mallégol, Lemaire, & Gardette, 2000; Yang & Luo, 2013).

Although the properties of films based on caseinates have been studied in several publications, there are very few published data on sodium caseinate films modified with alternative oil based resins. The aim of the present study is, therefore, to report the properties of films based on sodium caseinate (SC) and a linseed oil based resin (LOR) made by casting of film forming emulsions.

2. Materials and methods

2.1. Materials

Sodium caseinate (SC) powder, containing 88.9 wt.% protein (the rest being lactose, lipids, attached moisture, and ashes), was obtained from Lactoprot Deutschland GmbH (Germany). The average protein molecular weight is 22,600 g/mol (Audic and Chaufer, 2005). Linseed oil based resin (LOR) was obtained from non-refinated linseed oil (Grainer S.A., Entre Rios, Argentina) by glycerolysis and maleinization reactions (Mosiewicki et al., 2005).

2.2. Methods

2.2.1. Linseed oil resin (LOR) preparation

The LOR was prepared in two-steps reaction: 1) transesterification of linseed oil with glycerol to obtain mainly monoglycerides, b) chemical reaction of the monoglycerides with maleic anhydride to produce a final resin with maleated half esters. The details of synthesis and characterization of LOR were published previously (Mosiewicki et al., 2005). The main component of this linseed oil-based resin is the monoglyceride bis maleate, which chemical structure is represented in Scheme 1. However, the resin also contains minor proportions of diglyceride mono maleate, monoglyceride monomaleate, glycerol mono and bis maleate, and glycerol tris maleate (Mosiewicki et al., 2005).

2.2.2. Preparation of the film forming emulsion

Sodium caseinate aqueous solutions with protein concentrations of 2.5% (w/v) were prepared by dissolving the sodium caseinate powder in distilled water and stirring continuously for 3 h at room temperature. Then, the lipid fraction was incorporated in LOR/protein weight ratios of 0.05, 0.1, 0.15 and 0.2, and stable emulsions were achieved by using both homogenizer (Ultra-Turrax, 3 min treatment) and ultrasonic (Elma- Elmasonic P, 4 times of 5 min each) treatments. The film-forming dispersions were defoamed under rest for 1 h at room temperature.

2.2.3. Film preparation

Films were prepared according to the usual casting method, i.e. 45 g of the film-forming dispersions were poured into each Teflon Petri dish (diameter = 14 cm) and dried at 35 °C for approximately 10 h in a convection oven. After water was evaporated, the obtained films were peeled off from the plates and kept in a closed reservoir at 50% relative humidity (RH) and constant temperature (23 ± 2 °C) for 3 days.

2.3. Characterization of the film forming emulsions

2.3.1. Transmission optic microscopy (TOM)

The film forming emulsions were analyzed by TOM, using a microscope (Leica DMLB) coupled to a video camera (Leica DC100). For this purpose, a drop of the selected emulsion was mounted between glass-holder and glass-cover and pictures were taken at different magnifications.

2.4. Characterization of the films

2.4.1. Film thickness

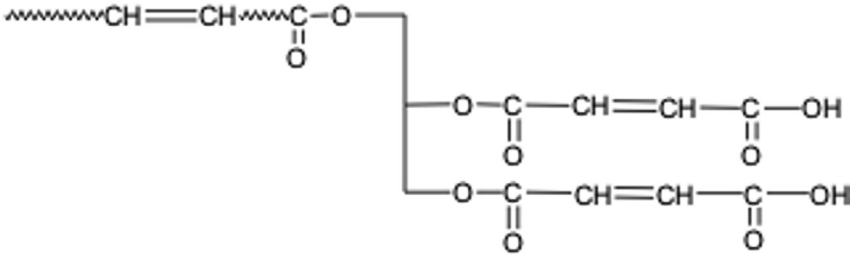
The film thickness was measured with a 0–25 mm manual micrometer with an accuracy of ±0.01 mm in four random locations for each film.

2.4.2. Infrared spectroscopy

FTIR spectra of the films were recorded using the attenuated total reflection method (ATR) in a Genesis II (Mattson) Fourier transform infrared spectrometer. The oil was examined by transmission using smeared samples on NaCl windows. In both cases, the spectra were recorded over a range of 600–4000 cm^{-1} with a resolution of 2 cm^{-1} and averaged over 32 scans.

2.4.3. Opacity and color properties

The color of the films was determined with a NoviBond Colorimeter RT500 (Neu-Isenberg, Germany) with an 8 mm diameter measuring area. A white standard color plate for the instrument calibration was used as a background for color measurement of the films. Results were expressed as L^*, a^* and b^* (lightness 'L', red-



Scheme 1. Structure of the monoglyceride bis maleate.