Food Hydrocolloids 60 (2016) 353–363

Contents lists available at ScienceDirect

Food Hydrocolloids

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

Microstructure and functional properties of sorbitol-plasticized pea protein isolate emulsion films: Effect of lipid type and concentration

Dariusz Kowalczyk [a, *], Waldemar Gustaw [b], Emil Zięba [c], Sławomir Lisiecki [d], Joanna Stadnik [e], Barbara Baraniak [a]

[a] Department of Biochemistry and Food Chemistry, University of Life Sciences in Lublin, Skromna 8, 20-704 Lublin, Poland
[b] Department of Fruits, Vegetables and Mushrooms Technology, University of Life Sciences in Lublin, Skromna 8, 20-704 Lublin, Poland
[c] Confocal and Electron Laboratory, Interdisciplinary Research Center, John Paul II Catholic University of Lublin, Al. Kraśnicka 102, 20-718 Lublin, Poland
[d] Center of Bioimmoblisation and Innovative Packaging Materials, Faculty of Food Sciences and Fisheries, West Pomeranian University of Technology, Szczecin, Poland
[e] Department of Meat Technology and Food Quality, University of Life Sciences in Lublin, Skromna 8, 20-704 Lublin, Poland

ARTICLE INFO

Article history:
Received 8 October 2015
Received in revised form
1 April 2016
Accepted 5 April 2016
Available online 7 April 2016

Keywords:
Emulsion films
Anhydrous milk fat
Candelilla wax
Lecithin
Oleic acid

ABSTRACT

The aim of this work was to compare the effect of increasing concentrations of anhydrous milk fat (AMF), candelilla wax (CNW), lecithin (LEC) and oleic acid (OLA) on the physicochemical and morphological properties of sorbitol-plasticized pea protein isolate (PPI) edible emulsion films. The lipids were incorporated into film-forming solutions at 0, 0.5, 1.0, 1.5, and 2.0%. It was found that among the tested lipids, only AMF and CNW reduced water vapour permeability (WVP) of the films, most likely due to their ability to increase film surface hydrophobicity. The greatest effect on the WVP reduction was achieved with CNW. The WVP of PPI films incorporated with 2.0% CNW was 2.5 times lower than that of the control. The incorporation of lipids into PPI films caused an increase in oxygen permeability. LEC destroyed the continuous structure of film matrix and caused an increase in film wettability and solubility. Increasing the amount of lipids in the films led to a decrease in mechanical strength. CNW-added films tended to have the best toughness properties. Unlike the solid lipids, OLA did not reduce the film transparency and showed a plasticizing effect, making the films more extensible. The addition of 2.0% OLA caused phase separation leading to the formation of discontinuity zones during film drying. Films with CNW had remarkably higher transparency compared to those of containing other solid lipids. All the resulting films were effective UV barriers. Surface microstructure of the emulsion films was influenced by the lipid type and lipid volume fraction.

1. Introduction

There is a growing body of literature that recognises the importance of using agricultural polymers for the preparation of biodegradable packaging. It is because increasing consumer awareness about the non-renewable character of petroleum-based polymers and escalating problems with plastic packaging waste. Depending on the origin of the raw material, as well as processing parameters and fabrication route, bio-based packaging can be decomposed both *in vitro* and *in vivo* (i.e. may be edible) which opens up new opportunities for the food processing industry. Up to now, at least a few specific applications of edible packaging have got special attention: casing, superficial coatings, food wrappers, water-soluble bags for pre-portioned foods that are not removed for cooking, layers separating various components in complex food products, microcapsules, controlled-release systems for food additives and drugs.

Protein-based bioplastic materials have a long-established tradition. Film obtained from soymilk, known as 'yuba' in Japan, has been used throughout East and Southeast Asia since ancient times (Shurtleff & Aoyagi, 2012). Casein plastics (trade name Galalith) were commercially exploited at the beginning of the 20th century (Lokensgard, 2010). Collagen and gelatin have been used for more than 50 years in the manufacture of artificial casings and drug capsules, respectively. Recent developments in the field of edible films have led to a renewed interest in usable potential of

* Corresponding author.
E-mail address: dariusz.kowalczyk@up.lublin.pl (D. Kowalczyk).

http://dx.doi.org/10.1016/j.foodhyd.2016.04.006
0268-005X/

various proteinaceous substances.

Legume seeds are considered as an inexpensive source of high-quality proteins, which make them suitable for the production of protein concentrates and isolates with a high level of functionality. Pea (*Pisum sativum* L.) is the main protein crop cultivated in the European Union (FAO 2013). Currently, pea protein isolate (PPI) is easily available on the market and gets a lot of attention, especially as a perfect option for those with certain food intolerances. According to Commission Directive 2007/68/EC, pea, unlike soyabean, cereals containing gluten, eggs, fish, peanuts, milk, lupin and products thereof, is not the common cause of allergies and feeding intolerance. Previous studies have indicated that pea proteins can be utilized to prepare edible films with water vapor permeability (WVP) and physical characteristics similar to those obtained from soy proteins, whey proteins, or zein (Choi & Han, 2001; 2002). Various film-forming variables have been examined to determine their effect on the properties of PPI-based films (Kowalczyk & Baraniak, 2011; 2012; Kowalczyk, Gustaw, Świeca, & Baraniak, 2014). The results showed that optimal conditions to form films with satisfactory characteristics to be utilized in food industry are plastification with low levels of sorbitol (instead of glycerol), neutral pH and the thermal treatment (90 °C, 20 min) of FFS. PPI films produced at these conditions exhibit the highest tensile strength (Kowalczyk et al., 2014), transparency and the lowest WVP (Kowalczyk & Baraniak, 2011).

Proteins are good film-formers and excellent oxygen, aroma and lipid barriers at low relative humidity, however, due to hydrophilic nature, they are poor moisture barriers compared to synthetic films. Additionally, hydrophilic plasticizers necessarily incorporated into protein films to decrease brittleness and avoid cracks in the polymeric matrix, usually decrease WVP. The combination of proteins with lipid materials to form emulsion films is an efficient approach to improve the film functionality. It is partially because of hydrophilic-lipophilic (amphipathic) character of proteins. So far, numerous studies have shown that the moisture barrier properties of emulsion films depend on the polarity and the degree of saturation of lipids, location, volume fraction, lipid-polymer interactions, and drying conditions (Pérez-Gago & Krochta, 2005).

This paper focuses on the characterization and optimization of physical properties of the emulsion PPI-based films, through modulating filmogenic formulations by lipid type and concentration. Four commonly used lipid materials, such as anhydrous milk fat (AMF), candelilla wax (CNW), lecithin (LEC) and oleic acid (OLA), showing a wide range of physio-chemical properties, were selected for this study. Compared to fatty acids and hydrogenated or crystalline triglycerides, waxes are superior moisture barriers (Kamper & Fennema, 1984; Kester & Fennema, 1989), thus are very useful in producing films with reduced WVP. A recent study, however, demonstrated that the addition of CNW into film formulations allows the improvement of the moisture barrier properties of films, but only those cast from unstable wax-in-water mixtures (Kowalczyk & Baraniak, 2014). Destabilization of emulsion produces films with a laminar structure, which tends to improve the barrier properties (Morillon, Debeaufort, Blond, Capelle, & Voilley, 2002). Shellhammer and Krochta (1997) demonstrated that incorporation of milk fat fraction into whey protein films reduced WVP more efficiently than the plant waxes. In contrast, Khwaldia, Banon, Desobry, and Hardy (2004) found that AMF did not improve WVP of casein films, but even deteriorated the barrier properties when it was used at high concentration. So far, very little attention has been paid to the effect of lipid surfactants on the functional properties of biopolymeric films. Andreuccetti, Carvalho, Galicia-García, Martínez-Bustos, and Grosso (2011) demonstrated that addition of LEC, likely due to hydrophobic nature of its constituents, produced a significant reduction in the solubility and WVP of gelatin-based films. Liquid fats are less effective in reduction of WVP compared to solid fats, but on the other hand, the films with liquid lipids exhibit better transparency (Fernández, de Apodaca, Cebrián, Villarán, & Maté, 2007), thus OLA was also used in this study.

All of the studies reviewed here indicate that the effect of lipids on the properties of protein films cannot be generalized and remains the complex subject. Thus, the objective of our study was to investigate how the lipid type and lipid volume fraction affects water affinity, barrier, optical and mechanical properties of PPI films plasticized with sorbitol. The findings are discussed in terms of the surface properties (microstructure and wetting) of the films.

2. Materials and methods

2.1. Materials

The following materials were used: pea protein isolate Propulse (ProFlo) (82.0± 2.0% protein; PPI) from Parrheim Foods Co. currently Nutri-Pea Limited (Portage la Prairie, MB, Canada), anhydrous milk fat from Mlekovita (Wysokie Mazowieckie, Poland), lecithin SOLEC™ FS-B (phospholipids min. 96%) from The Solae Company (St. Louis, Missouri, USA), D-sorbitol (min. 99.5%), candelilla wax and oleic acid (90%) from Sigma Chemical Co. (St. Louis, MO, USA).

2.2. Preparation of PPI-based films

Emulsion films were obtained from 10% (w/w) aqueous PPI solutions containing 5% (w/w) sorbitol and various amounts of lipids (0.5–2.0% w/w). Film-forming solution (FFS) without added lipids served as the control. The mixture of PPI, sorbitol and distilled water was neutralized to pH 7.0 (with concentrated NaOH solution) and heated in a water bath at 90 °C for 20 min with constant stirring. Before the end of heating, the lipid was added, and the hot solution was emulsified with a homogenizer (H-500, Pol-Eko Aparatura, Poland) at 20,000 rpm for 5 min. The FFSs were cooled to 25 °C (at constant stirring), rehomogenized (14,000 rpm, 1 min), degassed, and cast on leveled polystyrene Petri dishes (Nunc, Roskilde, Denmark). A constant amount of 1.65 g of total solids was cast onto an area of 145 cm^2 in order to maintain film thickness. FFSs were dried at room temperature (25 ± 1 °C) for ~24 h. The freestanding films were peeled manually.

2.3. Viscosity measurements

The apparent viscosity of FFSs was analyzed using a RS 300 rheometer (ThermoHaake, Karlsruhe, Germany), equipped with a concentric cylinder system with a rotating bob and a fixed cup, at 20 °C and a constant shear rate of 10 s^{-1} for 120 s.

2.4. Light and scanning electron microscopy (SEM)

The photographs of dispersed PPI (10% (w/w) aqueous suspension) were taken using an inverted microscope (Olympus IX70, Tokyo, Japan) equipped with Nomarski differential interference contrast optics and a digital camera (DP-12, Tokyo, Japan). The morphology of film surface was tested using a scanning electron microscope (Zeiss Ultra Plus, Oberkochen, Germany). The samples were dusted with chromium before viewing. Imaging of samples was performed in high vacuum (5×10^{-3} Pa), using a secondary electron detector at 7 kV. SEM images were analyzed with Zeiss AxioVision Rel. 4.8 digital image processing software.