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Physicochemical and microstructural characterization of gum tragacanth added whey protein based films

Bade Tonyali[b], Sevil Cikrikci[a], Mecit Halil Oztop[a,*]

[a] Food Engineering Department, Middle East Technical University, Ankara, Turkey
[b] Food Science Institute, Department of Animal Science and Industry, Kansas State University, Manhattan, KS, USA

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ABSTRACT

Edible films of gum tragacanth (GT) with whey protein were fabricated to see how the incorporation of GT influenced whey protein based film properties. Whey protein isolate (WPI) was replaced with GT at different ratios as 0.5, 1, 1.5 and 2% of WPI. Optical, mechanical, permeability and microstructural properties, as well as moisture sorption and solubility behavior of films were measured. The findings indicated that combination of WPI and GT in film formulation led to less strength, more flexible, less soluble films with lower permeability to water and with higher opacity. The results suggested that the addition of GT to WPI could lead to obtain modified WPI based edible films with desirable properties.

1. Introduction

Over the past few decades, films originating from biocompatible and biodegradable polymers have substituted synthetic ones and have received considerable attention from food researchers. Since films formed from polysaccharides, lipids and proteins are generally nontoxic, edible in most cases and also environmentally friendly, they have begun to be preferred to conventional petroleum-based materials (Yang, Wen, et al., 2015). The success and functionality of edible films mainly depend on their color, solubility, permeability and mechanical properties that show differences with composition (López de Lacey et al., 2012; Pérez, Piccirilli, Delorenzi, & Verdini, 2016).

The use of whey protein in film formulation has been common owing to its biodegradable and functional properties. Whey protein isolate (WPI) is a valuable by-product of cheese manufacturing with significant functional properties such as emulsifying and gelling action (Oztop, Rosenberg, Rosenberg, McCarthy, & McCarthy, 2010). It is a globular protein with hydrophobic and thiol groups placed in globular structure and heat induced denaturation of WPI alters its 3D network by opening this structure, exposing sulfhydryl and hydrophobic groups which can interact with other molecules and form strong covalent disulfide intermolecular bonds (Nicolai, Britten, & Schmitt, 2011; Silva, Mauro, Gonçalves, & Rocha, 2016). This ability of WPI makes it very unique in film production since this formation reduces water vapor permeability (WVP) of the films compared to films made by unheated protein (Ebrahimi, Koocheki, Milani, & Mohebbi, 2016).

Edible films from WPI generally exhibit good aroma and oxygen barriers while they show poor mechanical characteristics (Hong & Krochta, 2006). Generally, protein based films need the addition of a plasticizing agent, mostly glycerol, to minimize brittleness and extensibility of the film structure (Gounga, Xu, & Wang, 2010; Hernandez-Izquierdo & Krochta, 2008; Ozdemir & Floros, 2008). Plasticizer is combined within protein matrix, moving the components' chains apart, thereby reducing rigidity (Ramos et al., 2013). Moreover, Gounga et al. (2010) stated that whey protein based films were too brittle to handle when glycerol (Gly) was added below the ratio of 3.6:1 WPI:Gly. Basiak, Galus, and Lenart (2015) kept glycerol concentration at 50% (w/w of materials) for starch-whey protein blend films, and similarly Hassannia-Kolaee, Khodaiyan, Pourahmad, and Shahabi-Ghahfarrokhi (2016) used the glycerol content as 30% (w/w) dry base for whey protein/pullulan films.

Amphiphilic feature of whey protein allows it to interact with other polymers such as polysaccharides, leading to modify its function. The blending of two or more biopolymers could positively affect properties of hydrocolloid solutions and develop physico-mechanical properties of corresponding coatings or films (Phan The, Debeaufort, Voilley, & Luu, 2009). In recent years, various polysaccharides such as hsian-tsao gum (Yang, Li et al., 2015; Yang, Wen, et al., 2015), cassava starch (Jaramillo, Gutiérrez, Goyanes, Bernal, & Famá, 2016) and pea starch-guar gum (Saberi et al., 2016) have been used as novel film-forming polymers for food packaging purposes. Moreover, in addition to whey protein (Basiak et al., 2015; Díaz, Candia, & Cobos, 2016; Hassannia-Kolaee et al., 2016; Pérez et al., 2016; Silva et al., 2016), several proteins such as soy protein (Garrido, Etxabide, Guerrero, & de la Caba,

* Corresponding author at: Middle East Technical University (METU), Universiteler Mah. Dumlupinar Bulvari, No: 1 Cankaya-06800, Ankara, Turkey.
E-mail addresses: tbade@ksu.edu (B. Tonyali), cikrikci@metu.edu.tr (S. Cikrikci), mecit@metu.edu.tr (M.H. Oztop).

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2016; Sui, Zhang, Ye, Liu, & Yu, 2016), grass pea (*Lathyrus sativus*) protein (Ebrahimi et al., 2016) and peanut protein (Li et al., 2015) were used in film studies by combination with/without polysaccharides. However, there is still need for improvement of new film formulations to meet consumer demands about environmental concerns with better properties (Mostafavi, Kadkhodaee, Emadzadeh, & Koocheki, 2016).

GT, also known as katira, is a highly branched, heterogeneous, and anionic polysaccharide consisting of two major fractions; tragacanthin (water soluble) and bassorin (water swellable) representing 60–70% of total gum (Ozel, Cikrikci, Aydin, & Oztop, 2017). It is one of the most acid-resistant gums and includes D-galactose, D-galactronic acid, D-xylose, L-fucose and L-arabinose (Shiroodi, Mohammadifar, Gorji, Ezzatpanah, & Zohouri, 2012). GT could act as a stabilizer, emulsifier, thickener and suspending agent in food products. Mostafavi et al. (2016) investigated the properties of tragacanth-locust bean gum edible blend films and proposed the potential use of these polysaccharides due to their desirable properties. Nevertheless, few studies exist about properties of GT as a film forming material (Ecz & Ktirsi, 1974; Mostafavi et al., 2016; Shrestha, Arcot, & Paterson, 2003).

To best of our knowledge, no attempt has been encountered to study the fabrication of WPI based film combined with GT. Based on the considerations outlined above and the motivation for potential research of edible blend films, the aim of the present study was to fabricate edible films prepared by WPI and GT at different ratios. Physicochemical and microstructural properties of edible film formulations were investigated to understand the interaction between WPI and GT.

2. Materials and methods

2.1. Materials

The polysaccharide GT with around 80–90% carbohydrate, 1–2% protein and maximum 15% moisture (C.E. Roeper GmbH, Hamburg, Germany) was provided by FMC group (FMC BioPolymer, Philadelphia, USA). WPI was supplied from Hardline Nutrition (Hipro Isowhey, Kavi Food Ltd. Co., Istanbul, Turkey). Protein content of WPI was confirmed with Kjeldahl method as 88.5%. Glycerol was obtained from Merck (EMSURE®, ACS, Reag. Ph Eur., Darmstadt, Germany).

2.2. Film preparation

Film forming solutions were prepared by casting method. In only WPI film, 8% (w/w) WPI solution was prepared with distilled water. For GT-WPI blend films, 0.5, 1, 1.5 and 2% of WPI (8%) was replaced with GT (w/w); the formulation is given in Table 1. Since GT is a high molecular weight polysaccharide, such kind of small WPI replacement ratios were selected in samples. With preliminary experiments, it was observed that the uniformity of samples was achieved with the help of microfluidization for these replacement ratios. Firstly, WPI and GT solutions were homogenized separately at 15,000 rpm for 2 min using Ultra Turrax T-18 (IKA Corp., Staufen, Germany) and then combined in a beaker at the magnetic stirrer. Glycerol as a concentration of 4% (w/w) was added to all film forming solutions (100 g) and the solutions were left for stirring for overnight. pH of the solutions was measured as 7.00 ± 0.15. Later, the solutions were kept at water bath (Wisd, Wertheim, Germany) at 90 °C for 30 min to denature the protein. The solutions were then microfluidized at inlet chamber of ISA-N-10M Nano Disperser (Ilshin Autoclave, South Korea) equipment at 50 MPa for 10 passes. After degassing in ultrasonic bath (Jeiotech, Lab Companion, US Portable Cleaners), 7 mL of solutions were poured into polyethylene petri dishes (9 cm in diameter) and dried at 40 °C in an air oven for 16 h. The all peeled edible films were kept in a climate chamber TK 120 (Nuve Test Cabinet, Turkey) at 53 ± 3% relative humidity (RH) at 25 °C for 48 h for conditioning. Then, if necessary, samples were also conditioned in a sealed desiccator at different RH values according to experiment procedure (they were given in each part of method). Photo of a representative film sample was given in Supplementary Section.

Table 1
Film formulations for 100 g solution.

Sample with WPI replacement	WPI (g)	GT (g)	Glycerol (g)
0% (WPI film)	8.00	0	4
0.5%	7.96	0.04	4
1%	7.92	0.08	4
1.5%	7.88	0.12	4
2%	7.84	0.16	4

2.3. Film properties

2.3.1. Physicochemical properties

2.3.1.1. Film thickness and density. The thickness of films was measured with a digital micrometer LOYKA LYK 5202 (Istanbul, Turkey) with a precision of 0.001 mm. To measure the thickness, nine data were taken from one film sample, four from center and five from the perimeter. Three replicates were used and collected data were averaged.

The film density was calculated using the following formula (Ebrahimi et al., 2016):

$$\rho = m/(A \cdot h) \quad (1)$$

where m is the dry mass (g) of film, A is film area (cm^2), h is the thickness (cm) and ρ is the dry matter density of film (g/cm^3).

2.3.1.2. Moisture content and total soluble matter. The moisture content was obtained gravimetrically by drying at 105 °C for 24 h in an oven UNB400 (Memmert GmbH, Schwabach, Germany) (Mostafavi et al., 2016). The moisture content of films was calculated using the following formula:

$$MC\ (\%) = 100\,(M_i - M_f)/M_i \quad (2)$$

where M_i is initial and M_f was the final weight of films, respectively.

For total soluble matter (TSM), analysis method by Garrido et al. (2016) was followed. The film samples were immersed in 50 mL distilled water at room temperature for 24 h. Afterwards, the samples were dried in an oven at 105 °C for 24 h (M_s). Total soluble matter was calculated as follows:

$$TSM\ (\%) = 100\,(M_f - M_s)/M_f \quad (3)$$

where M_s was the weight of film after 24 h.

2.3.1.3. Fourier transform infrared (FTIR) spectroscopy. FTIR spectra of films were analyzed by IR Affinity-1 Spectrometer with Attenuated Total Reflectance (ATR) attachment (Shimadzu Corporation, Kyoto, Japan). The measurements were recorded in 4000–600 cm^{-1} region at 4 cm^{-1} resolution for 32 scans. The analyses were replicated for three times for each film. Before the analysis, the film samples were dried in a desiccator containing dried silica gel for seven days that films reached constant weight and desired state (Basiak et al., 2015; Galus & Lenart, 2013).

2.3.1.4. Moisture-sorption isotherm. Moisture sorption isotherms of films were determined by the method of Silva et al. (2016). The eight salt concentrations at different water activities between 0.09 and 0.92 (NaOH - 0.09; $MgCl_2$ - 0.34; K_2CO_3 - 0.45, $Mg(NO_3)_2$ - 0.53; NaCl - 0.77; KCl - 0.84; $BaCl_2$ - 0.92) were placed into desiccators. The 3 × 3 cm^2 films were put into these desiccators and weighed at certain intervals to the constant weight point. The temperature was kept constant at 25 ± 2 °C. Dry sample weight was obtained by drying the samples at oven at 105 °C. Mathematical modeling of isotherms was conducted by MATLAB using GAB model. The fitted equation is below;