



## Biodegradable Whey Protein Edible Films as a New Biomaterials for Food and Drug Packaging

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### Abstract

Food packaging extensively uses plastic films and containers of petroleum-based polymers for their excellent functional properties and competitive price. Plastic packaging has become a central focus of waste reduction efforts, particularly in aesthetic terms of damage to flora and fauna. Presently, consumers require greater quality and longer shelf lives for their foodstuffs, while they demand a reduction in the quantity of packaging materials used. In the present study, polyethylenglycol (PEG), glycerol, and olive oil were incorporated into whey protein concentrate (WPC) through emulsification to produce films. Whey protein films were prepared by dispersing 10% whey protein concentrate in tap water and plasticized with different levels of glycerol, PEG or olive oil. The emulsion films were evaluated for mechanical properties, water vapor permeability (WVP) and opacity. Increasing the levels of glycerol or PEG in the films resulted in a decrease in modulus and tensile strength. Increasing glycerol content of the films at oil/protein ratios of 0.2 and 0.4 led to slight increases in elongation. Increasing the oil/protein ratio further resulted in a decrease in elongation for all films. No significant difference in WVP and opacity was observed between films made from mixtures of various proportions of whey protein concentrate-glycerol with increasing PEG (addition) at all levels of the plasticizer. These results suggest that a whey protein based edible films is a viable alternative packaging process for food and improvement of shelf life.

*Keywords:* Edible films; Food packaging; Gas permeability; Mechanical properties; polyethylenglycol.

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### 1. Introduction

Food packaging extensively uses plastic films and containers of petroleum-based

polymers for their excellent functional properties and competitive price. Plastic packaging has become a central focus of waste reduction efforts, particularly in aesthetic terms of damage to flora and fauna. Presently, consumers require greater quality and longer shelf lives for their foodstuffs, while they

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demand a reduction in the quantity of packaging materials used. Concerns about the environmental pollution caused by plastics have led to attempts on the part of researchers and industries to develop biodegradable plastics by incorporating degradable components such as starch.

Development of edible and biodegradable films using natural biopolymers such as proteins, polysaccharides and lipids could also be useful in alleviating the landfill burden by replacing synthetic non-biodegradable packaging in some applications. Whey obtained as a by-product in cheese, is produced in large quantities and has excellent functional properties and could potentially be used for edible films. Barrier and mechanical properties of whey protein isolate based films have been studied by some researchers, but generally they have been studied at 25 °C and 100% relative humidity (RH) gradient [1-4]. Utilization of the excess whey in the form of whey protein concentrate (WPC) could effectively alleviate the whey disposal problem by their conversion into value-added products, such as edible films and coatings.

Edible films and coatings derived from whey protein have been investigated for their barrier and mechanical properties. This investigation also focused on the actual applications of whey protein films as coatings on food systems. Whey protein films produce transparent, bland, flexible, water-based edible films with excellent oxygen and aroma barrier properties at low relative humidity [4]. However, they have poor moisture barrier properties due to their hydrophilicity and/or to the level of plasticizer added to filmogenic solutions. Incorporation of hydrophobic compounds such as fatty acids, monoglycerides and waxes to a film solution to reduce the water vapor permeability of protein films has been studied.

Olive oil is applied in this study which is a complex compound made of fatty acids,

vitamins, volatile components, water soluble components and microscopic bits of olive. The flavonoid polyphenols in olive oil are natural anti-oxidants which have been shown to have a host of beneficial effects to prevent oxidation [5].

The aim of this study was to study the effect of adding lipid to film-forming solution and polyethyleneglycol (PEG) and glycerol content on water vapor permeability (WVP), film opacity, and the mechanical properties of whey protein/PEG emulsion films.

## 2. Materials and methods

### 2.1. Materials

Whey protein concentrate (85% protein) was supplied by Arla Co. (Denmark); olive oil was obtained from Etko Co. (Manjil-Iran); and PEG 400 and glycerol were from Merck. Magnesium sulfate (6 H<sub>2</sub>O) (Merck) was used for formation of a saturated salt solution (50% relative moisture).

### 2.2. Film formation

Heat-denatured WPC films were prepared according to the method described by Show *et al.* [6]. Aqueous solution of 10% (w/w) WPC was prepared and was stirred continuously on a magnetic stirrer at room temperature for 2 h. To prepare heat-denatured films, WPC solutions were heated at 90 °C for 30 min. in a water bath. Heated solutions were cooled to room temperature and adjusted to pH 7.0 with drop-wise addition of 1 N NaOH. Glycerol was added to film-forming solutions to give glycerol: protein (Gly:Pro) ratios (w/w) of 0.2 and 0.3 and this ratio was kept constant throughout the study. PEG was added to the 2 h heat denatured WPC solution containing glycerol, to give PEG:Pro ratios (w/w) of 0.0, 0.2, 0.3 and 0.4. Before being cast, final solutions were degassed under vacuum to remove any dissolved air. Films were cast by pipetting 12 g whey protein solution onto rimmed, smooth plates (100 mm id) resting on a leveled granite slab. For

each property studied, different numbers of replicates were prepared. The films were allowed to dry at room temperature over 24-48 h. Films were peeled from the plates and stored for 24 h at  $50\pm 5\%$  RH and  $23\pm 2$  °C.

### 2.3. Film thickness

Thickness of film was measured with caliper micrometer (FEINMESSZEUG Fabric SUHL-DDR.0-2.5 mm) at 5 random positions of the film, following WVP and preceding tensile tests. WVP and mechanical properties were calculated based on average thickness.

### 2.4. Tensile test conditions

A universal Testing Machine was used to measure the tensile properties of the film according to the standard testing method [6]. The Universal Testing Machine was operated with a 5 Newton load cell and with self-alignment grips (Model STANTAM, SMT-20) in a room controlled to  $25\pm 2$  °C and  $75\pm 5\%$  RH. Self-alignment grips consist of one fixed end and one movable end to provide perfect alignment when load is applied. The grips are lined with thin rubber faces to prevent sample slippage and they are air-actuated to prevent sample breakage. The initial gauge separation was fixed at 58 mm and crosshead speeds were 100 mm/min. At least 10 strips of each film type were analyzed and percent elongation at break (EL) tensile strength at break (TS) and elastic modulus (EM) were

calculated as outlined in ASTM (1985).

### 2.5. Water vapor permeability measurement of films

The WVT was determined according to the method described by Gontard *et al.* [7]. A container with silica gel was closed with a sample of edible film firmly fixed on top. Then, the container was placed in desiccators with saturated sodium chloride at a temperature of  $25\pm 2$  °C. The films were weighed daily for 10 days. The WVT was calculated according to Eq. (1):

$$WVT = w \times x / A \quad (1)$$

where 'WVT' is Water Vapor Transmission ( $\text{g H}_2\text{O mm.cm}^{-2}$ ), 'x' is the average thickness of the film (mm) and 'A' is the permeation area ( $\text{cm}^2$ ).

### 2.6. Statistical analysis

All experiments were repeated three times. Data were analysed by ANOVA using the general linear model (GLM) [8]. Significant differences between means were determined by the least significant difference (LSD) test.

## 3. Results and discussion

### 3.1. Film formation

All film formulations formed peelable films. Upper surface of those films containing oil were shiny and had oil droplet (Figure 1).

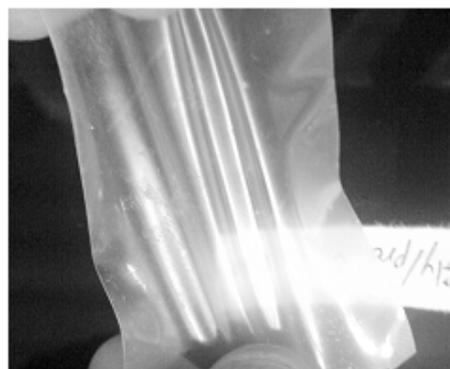


Figure 1. Whey protein composite films.

### 3.2. Mechanical tests and physical properties of WPC composite films

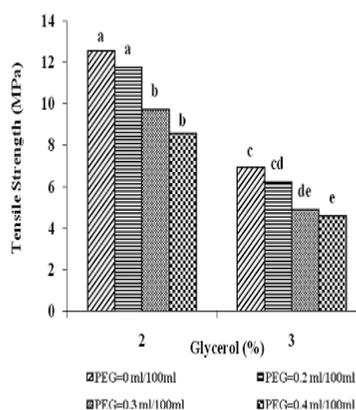
Increasing the levels of glycerol or PEG in the films led to decreases in elongation modulus (EM) and tensile strength (TS). Increasing glycerol content of films led to increases in elongation (EL). Increasing the oil/protein ratio further resulted in a decrease in EL for all films. No significant difference in WVP was observed between films made from mixtures of various proportions of WPC-glycerol with increasing PEG addition at all levels of plasticizer (Figures 2-5) [9].

Increasing soya oil concentration led to increases in EL and decreases in TS and EM but did not affect the WVP of WPI-soya oil composite films. Incorporation of lipid into protein films resulted in lower tensile strength at break, indicating that they became weaker and non-homogeneous [7]. Laminate whey protein-lipid films decreased the WVP 70 times [10]. The tensile tests showed that the lipid functioned as an apparent plasticizer by enhancing the fracture properties of the emulsion films, and this effect increased with homogenization. Percentage of elongation at break markedly decreased as PEG concentration increased, thus the flexibility of

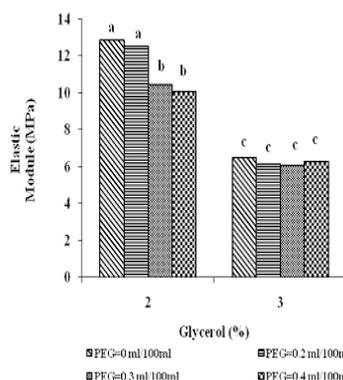
whey protein emulsion films was reduced.

Opacity was found to be largely dependent on the concentration of lipid material in the film in the first week of storage time. After the first week of storage time all the films were opaque [7].

There was a relationship between the level of glycerol and oil in WPI composite films and the measured physical properties of the films [9]. For example, the WVP values obtained in this study were found to be affected more by the level of glycerol than the level of soya oil and this was reflected in the fact that the glycerol term of the derived model was significant whereas the oil term was not. Highly plasticized films have such a poor moisture barrier properties that minor decreases in film WVP, due to increases in oil concentration, are obscured. In agreement with the present findings, WVP of WPI films did not change with increasing emulsified triolein content or film orientation [2, 11]. They suggested that creaming of the lipid phase needed to occur in order to effectively decrease film WVP and that creaming is only likely if emulsion particles exceed 1  $\mu\text{m}$  in diameter. The lack of an effect of film orientation on WVP in this study suggests



**Figure 2.** Tensile strength changes of film formulations with 2 and 3% glycerol with different concentrations of polyethyleneglycole. Different letters denote significant differences ( $p>0.5$ ) through the Duncan test.



**Figure 3.** Elastic modulus changes of film formulations with 2 and 3% glycerol with different concentrations of polyethyleneglycoles. Different letters denote significant differences ( $p>0.5$ ) through the Duncan test.

that although some creaming may have occurred during film drying it was not sufficient to affect film WVP. Both glycerol and oil were shown to affect film extensibility. Milk fat fraction enhanced the plasticizing effects of glycerol in WPI films. They reported decreases in strength and elastic modulus with increasing lipid concentration for a variety of WPI/lipid composite films. They suggested that increasing lipid concentration weakened the strength of the protein phase. The decreases in TS and EM with increasing glycerol content may be attributed to increases in protein intermolecular spacing, thereby decreasing film strength and stiffness [11]. Opacity was found to be largely dependent on the concentration of lipid material in the film. The opacity of the films may be attributed to oil droplets dispersed throughout the protein network, the level of which increased with increasing proportion of emulsion in the film forming solution [7].

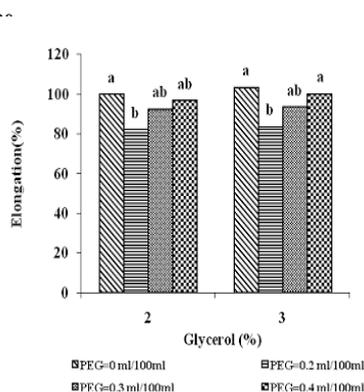
WVP and mechanical properties of whey protein isolate (WPI) and WPI-lipid emulsion films dried at different conditions [12]. The effect of lipid particle size on WVP and mechanical properties has been shown to depend on lipid content and film orientation during WVP measurements. As lipid content

increased, a decrease in lipid particle size improved the WVP of the WPI/ beeswax emulsion films, probably due to an increase in protein immobilization at the lipid-protein interface as lipid content became more important in the film [13].

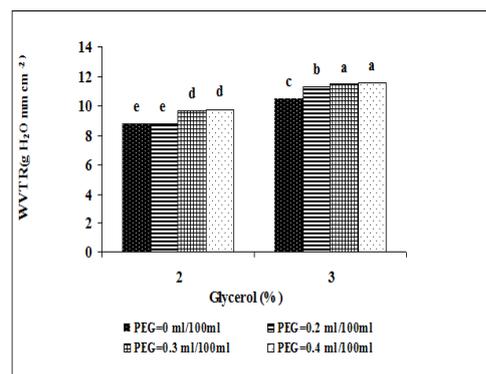
At pHs above or below the isoelectric point (pI) of proteins, WVP of emulsion films decreased. Increasing soya oil concentration led to increases in the percentage of EL, glass transition ( $T_g$ ) temperature, and decreases in MC, TS, and EM, but did not affect the WVP of films. Increasing levels of glycerol led to increases in the percentage of EL, MC and decreases in TS, EM,  $T_g$  and film opacity [9].

## 5. Conclusions

A potential for altering the whey protein films through the addition of olive oil was observed. The addition of olive oil to WPC films led to decreases in the films' mechanical properties. The incorporation of lipid into protein films resulted in lower TS at break, indicating that they became weaker and non-homogeneous. This could be explained by the fact that the protein phase has higher TS than the lipid phase. Percentage of EL decreased as olive oil concentration increased; thus, the flexibility of whey protein emulsion



**Figure 4.** Elongation changes of film formulations with 2 and 3 % glycerol with different concentrations of polyethyleneglycole. Different letters denote significant differences ( $p > 0.5$ ) through the Duncan test.



**Figure 5.** Water vapor transmission rate changes of film formulations with 2 and 3% glycerol with different concentrations of polyethyleneglycole. Different letters denote significant differences ( $p > 0.5$ ) through the Duncan test.

films was reduced. This may be attributed to non-continuous film matrix formation probably because of the presence of lipid globules. No significant difference in WVP was observed between films made from mixtures of various proportions of WPC-glycerol with increasing olive oil (addition) at all levels of the plasticizer; it is because highly plasticized films have such poor moisture barrier properties that minor decreases in film WVP are obscured. Addition of PEG had no significant effects on the mechanical properties but increased the films WVP in higher levels.

### Acknowledgement

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