



Effect of Different Formulations on Mechanical and Physical Properties of Calcium Alginate Edible Films

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Abstract

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Background: Environmental problems of the plastic materials used in food packaging and the demand for food quality improvements lead to the development of packaging in natural materials. Edible films such as calcium alginate extend the shelf life by acting as a selective barrier against moisture and oxygen. The main objective of this study was to explore a calcium alginate based edible film to improve the quality and extend the shelf life of food products.

Methods: Tests of physical properties including water vapor permeability (WVP) and oxygen transmission rate (OTR) and mechanical properties including tensile strength (TS) and elongation at break (E) of two calcium alginate based formulations (dextrose monohydrate based and maltodextrin based) were done in triplicate. Data were investigated using SPSS (16.0). Significant differences in the results were detected by the Mann-Whitney U test.

Results: There was no significant difference in mechanical properties and WVP of these two formulations, though WVP values related to the dextrose monohydrate based formulation were slightly higher than those of the maltodextrin based formulation. A significant decrease was observed in OTR of the maltodextrin based formulation compared to the dextrose monohydrate based formulation.

Conclusion: There was no significant difference in mechanical properties (TS and E) and WVP between these two formulations; however, a significant reduction was observed in OTR of the maltodextrin based formulation compared to the dextrose monohydrate based formulation. Therefore, the last was more suitable as a barrier to oxygen.

Introduction

The increasing concerns of consumers about environmental issues are changing the trend in packaging from synthetic to natural materials. Therefore, the demand for higher quality foods has contributed to the development of packaging made with natural sources such as polysaccharides, proteins and lipids. Many researchers have focused on the incorporation of plant extracts into films,

edible coatings and bio-based packaging materials (Del Nobile et al., 2008; Ghasemlou et al., 2013; Norajit et al., 2010; Oussalah et al., 2006; Rojas-Graü et al., 2007). Edible films can extend the shelf life and quality of foods by being a selective barrier against moisture and oxygen. They also reduce lipid oxidation by controlling oxygen transmission and volatile compounds which are effective in producing undesired odor and flavor. Microbial contamination in ready-to-eat food products (refrigerated

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meats and intermediate moisture foods) is the main cause of food spoilage and food-borne disease (Cárdenas et al., 2008; Cutter, 2002; Devlieghere et al., 2004). Edible coatings either individually or with antimicrobial agents, inhibit bacterial growth on food surfaces, therefore which retarding food spoilage (Ouattara et al., 2000).

Alginate, a polysaccharide extracted from brown seaweeds (Phaeophyceae) is a common gel-producing agent in food technology (Mancini and McHugh, 2000). Alginate is a salt of alginic acid. It is a polymer of β -D-mannuronic acid (M) and α -L-guluronic acid (G) which provides unique properties including thickening, stabilizing, suspending, film forming, gel producing, and emulsion stabilizing (Rhim, 2004). Hydrophilic alginate films are poor moisture barriers but the use of calcium in film formulation reduces these films' water vapor permeability (WVP), making them insoluble in water (Olivas and Barbosa-Cánovas, 2008).

Plasticizers are used to modify the physical and mechanical properties of films (Rhim, 2004). The addition of plasticizers to the main ingredients of film or their dispersion result in the separation of polymer chains, reduction of structure rigidity, and increased flexibility of the alginate film (Guilbert and Biquet, 1996). Also, plasticizers can reduce brittleness, decrease hydrogen bonds between polymer chains and increase intermolecular spaces. Water may also be a plasticizer in hydrophilic coatings like alginate (Sothornvit and Krochta, 2000).

Rhim (2004) studied physical and mechanical properties of sodium alginate, evaluating its water resistance after treatment with calcium chloride using two methods. The WVP, tensile properties and solubility of methylcellulose edible films were evaluated (Turhan and Şahbaz, 2004). The effects of garlic oil addition on physical and antimicrobial properties of edible alginate films were studied (Pranoto et al., 2005) and the antimicrobial and impermeability properties of edible alginate apple puree films in the presence of essential oils and oil compounds were also reported (Rojas-Graü et al., 2007).

The objectives of the present study were to evaluate physical properties including film thickness, water vapor permeability (WVP), oxygen transmission rate (OTR) and mechanical properties including tensile strength (TS) and elongation at break (E) in two different formulations of alginate film.

Materials and methods

Ingredients and reagents

Sodium alginate (BDH Co, UK), maltodextrin (DE 10.2, Applichem Co, UK), D-glucose monohydrate, calcium chloride, carboxyl methyl cellulose, glycerol, silica gel, glacial acetic acid, chloroform, titrisol solution of

0.01 N sodium thiocyanate (Merck, Germany), starch indicator solution, soybean oil sample without antioxidant (Parsghoo Vegetable Oil Co.) and grease were used.

Instruments

Special cups designed for WVP measurement, a rim with a gasket and screws, caliper, micrometer, analytical scale (with readability of 0.0001), oven, water still (GFL 2104, Germany), surgical scalpel No. 24 (Health Care, China), 30×20 cm plexiglass sheets, medium and small magnets, a heater stirrer (Tajhizfan, Iran), an instron machine (Zwick, Germany) and a stomacher 400 circulator (Seward, USA) were also used.

Film preparation

To make a dextrose monohydrate based film, 5 g sodium alginate powder was mixed with 45 g dextrose monohydrate dry granules. The mixture was dissolved in 270 ml distilled water at ambient temperature (25 °C). In order to achieve a homogenous solution, the mixture was poured into a bag and blended for 10 min at 200 ×g. Then the solution was transferred to a beaker and stirred on a heater stirrer for 4 h to remove trapped air. 50 ml aliquots of the solution were placed on 30×20 cm plexiglass sheets which had been coated with cellophane. The solutions were spread on the cellophane by a glass rod to reach a uniform area, making a thin layer. The sheets were dried in ambient conditions (23±2 °C and 50±5% RH) for 48 h. The film was then removed from the cellophane and dipped in a solution containing 2.75 g calcium chloride and 0.9 g carboxyl methyl cellulose in 49 ml distilled water for 30 min and allowed to dry for 24 h in ambient conditions. To make a maltodextrin based film, 5 g sodium alginate powder was mixed with 45 g dry maltodextrin. About 20 g glycerol was added to the mixture and dissolved in 210 ml distilled water. Further steps were as described for dextrose monohydrate based film.

Film thickness determination

The thickness of each film was randomly measured by a digital micrometer (0-20 mm) with a resolution of 0.001 mm at five places in triplicate and their mean were used to calculate WVP (Rhim, 2004).

Determination of TS and E

Mechanical tests were performed according to the American Society for Testing and Materials (ASTM) D882 standard method (ASTM, 2002a) and Longares et al. (2004) by Instron machine (Z 2.5, Zwick, Germany) in ambient conditions as described above. The films were cut into 70×30 mm strips using a surgical scalpel and

fastened to the 17.23 mm arms of the machine before applying a force of 500 N. Tensile properties were reported using instron software in two main parameters; stress at break point in MPa and strain in mm.

Determination of WVP

WVP was tested according to the method of McHugh et al. (1993) which is a modified version of the ASTM E96 standard method (ASTM, 2002b). The ASTM E96 method measures WVP in hydrophobic polymer films, where resistance to mass transfer in the gaseous phase (through both sides of the film on the cup) is insignificant. In the method modified for hydrophilic films, the role of water vapor partial pressure in the air gap between the film and water in the cup has been considered. Both methods are based on gravimeter. Here, films were cut into pieces using a surgical scalpel to match the cup opening. About 10 ml distilled water was poured into each cup and the gap between the water surface and the film was measured. The film was fixed to the cup opening by grease and sealed by a rim, gasket and screws. Then, the cups were weighed and equilibrated for 2 h in desiccators to reach a linear correlation between weight loss and time. Each cup was weighed at 3 h intervals 5 times for 24 h. Weight loss over time was measured and WVP was calculated as follows:

$$WVP = WVTR_{\chi} / (p_3 - p_2)$$

$$p_2 = P - (P - p_1) \exp(RT \Delta z WVTR / PD)$$

Where χ is average thickness of the film, p_3 is water vapor partial pressure inside the chamber (atm) and p_2 is corrected water vapor partial pressure next to the film inside the cup (atm). P is the total atmospheric pressure (atm), p_1 is the partial pressure at the surface of the desiccant in the cup, R is the universal gas constant ($\text{cm}^3 \text{atm/g mol K}$), T is the absolute temperature during the test (K), Δz is the air gap inside the cup (cm), and D is the diffusion coefficient (cm^2/s) (McHugh et al., 1993).

The cups were 5.5 cm in outer diameter, 3.5 cm in inner diameter, 2.5 cm in height, edge width of 1 cm and opening area of 23.75 cm^2 . The air gaps between the surface of the distilled water and the edge of the film were as follows. For the dextrose monohydrate based film (0.42 mm thick), water depth in triplicate cups on day 1 was 2 cm, 1.8 cm and 2.1 cm. On day 2 those depths were 1.9 cm, 1.6 cm and 2 cm, respectively. For the maltodextrin based film (0.32 mm thick), water depth in the triplicate cups on day 1 was 2.1, 1.9 and 2 cm. On day 2, those depths were 2, 1.8 and 1.9 cm.

Determination of oxygen transmission rate

The comparative quality test was done by the method of Ou et al. (2005) with a slight modification to deter-

mine OTR. The test was based on the determination of peroxide value changes in antioxidant-free fresh sheep fat samples. In order to determine OTR, 10 g fresh antioxidant-free fat samples were transferred to each cup and the openings were covered by the film samples. Afterwards, the cups were maintained at $40 \text{ }^\circ\text{C}$ in the oven for 12 days. Peroxide value was calculated according to the method of Ou et al. (2005) for each sample on the final day.

Statistical analysis

A complete block model was used in SPSS 16.0 to investigate the mechanical and physical properties of two different films in triplicate. Significant differences were determined by the Mann-Whitney U test.

Results

There was no significant difference ($p > 0.05$) between the two films in E, TS or WVP. However, bar charts suggest that maltodextrin based films had relatively high E (Fig. 1), relatively low TS (Fig. 2) and relatively low WVP (Fig. 3). Maltodextrin based films also had relatively low OTR ($p < 0.05$; Fig. 4).

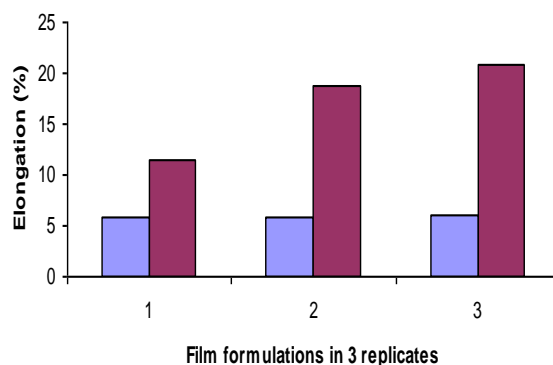


Fig. 1: Elongation of two different film formulations measured by Instron

Film formulation of dextrose monohydrate based ■
 Film formulation of maltodextrin based ■

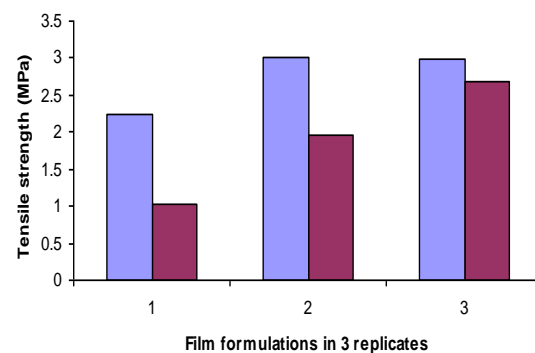


Fig. 2: Tensile strength of two different film formulations measured by Instron

Film formulation of dextrose monohydrate based ■
 Film formulation of maltodextrin based ■

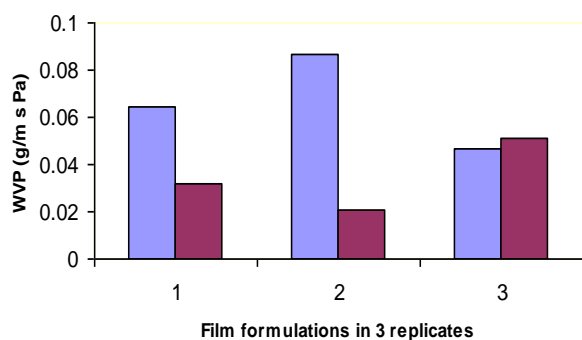


Fig. 3: WVP of two different film formulations

Film formulation of dextrose monohydrate based ■
 Film formulation of maltodextrin based ■

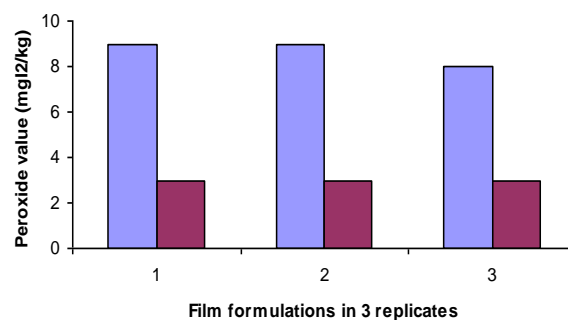


Fig. 4: Peroxide values in two different formulations which represents oxygen transmission rate

Film formulation of dextrose monohydrate based ■
 formulation of maltodextrin based ■

Table 1: Comparison of mechanical properties and WVP of some edible films

Film	RH (%)	Plasticizer	TS (MPa)	E (%)	WVP (g/m s Pa)	References
Calcium-alginate	50	None	2.73	5.8	6.5×10^{-2}	Present study
Calcium-alginate	50	Glycerol	1.89	17	3.4×10^{-2}	Present study
Calcium-alginate	56	Sorbitol	65.9	2.5	2.1×10^{-10}	Olivas and Barbosa-Cánovas (2008)
Calcium-alginate	56	Glycerol	64.7	2.8	4.2×10^{-10}	Olivas and Barbosa-Cánovas (2008)
Calcium-alginate	98	Sorbitol	18.4	6.6	3.5×10^{-10}	Olivas and Barbosa-Cánovas (2008)
Calcium-alginate	98	Glycerol	24.1	7.9	5.4×10^{-10}	Olivas and Barbosa-Cánovas (2008)
Soy protein isolate	50	Ferulic acid	1.4	86.4	3.02×10^{-11}	Ou et al. (2005)
Calcium-alginate	50	Glycerol	85.9	3.8	1.0×10^{-9}	Rhim (2004)
Calcium-alginate	50	Oregano essential oil	31.1	3.7	2.7×10^{-9}	Benavides et al. (2012)
β -Lactoglobulin	50	Sorbitol	2.7-10.6	24.7-65.8	-	Sothornvit and Krochta (2000)
β -Lactoglobulin	50	Glycerol	4.9-16	11.3-76.4	-	Sothornvit and Krochta (2000)

Discussion

Table 1 compares the present study's observations on mechanical properties and WVP with those of previous studies. Similar results were reported by Olivas and Barbosa-Cánovas (2008) using different plasticizers including fructose, glycerol, sorbitol and polyethylene glycol (PEG8000) and also there was no significant difference between the films containing glycerol and those containing other plasticizers. Of course, as RH was increased (76% and 85% RH), significantly higher TS and lower E were observed in the films containing glycerol, compared to sorbitol and fructose ($p < 0.05$). According to Pranoto et al. (2005), garlic oil addition to the film formulation had the same effect on TS and E. Also, Turhan and Şahbaz (2004) found that using ethanol and polyethylene glycol (PEG400) in the formulation could decrease TS in methylcellulose (MC) based films. High TS was related to several hydrogen bonds between MC chains. These

bonds contributed to cohesiveness and low flexibility of unplasticized films. As PEG was entered into the MC network, a competition for hydrogen bonding occurred between MC-MC and MC-PEG. As a result, direct interactions between MC chains were reduced because of hydrogen bond formation with PEG and slightly by a blocking effect of high molecular weight PEG. Therefore, an increase in PEG concentration significantly increased hydrogen bond formation which led to decreased TS and increased E. Rojas-Graü et al. (2007) found that using essential oils and oil compounds could significantly decrease TS and increase E; however, no significant difference was observed in this study after adding glycerol as a plasticizer.

Contrary to our findings, Rhim (2004) reported an increase in TS and a decrease in E after treating films with calcium chloride. Increasing CaCl_2 solution's concentration and immersion time or developing cross link for-

mation between carboxyl groups of alginate and calcium ions led to these changes.

Although, the formulations studied by Benavides et al. (2012) and Galus and Lenart (2013) were different from this study, it means TS and E were higher and WVP was lower than the present findings. Rhim (2004) found that WVP was increased with the addition of extra glycerol. WVP values mostly depended on the method of preparation. In other words the variations of films prepared by mixing were not significant compared to the control; but in a film prepared by immersion, there was a significant decrease arising from the cross linking of alginate and calcium ions. Apparently, ionic cross linking would also reduce polymer movements and water vapor transmission through the film network. Although no significant difference was observed in WVP at the present study, a trend of WVP variation in based films was observed.

Similar to the present study, Tapia et al. (2008) reported that glycerol could be used as a plasticizer in film formulation. Plasticizers increase polymer chains' movements by filling gaps in the polymer network. Accordingly, plasticizers could result in low brittleness, increase hydrophilicity and increase transmission of gas and water vapor. Glycerol enhances films' resistance to water vapor transmission at concentrations between 1.5-1.75% (v/v), but it shows a reverse effect at higher concentrations. It has been stated that the addition of plasticizers also modifies films' properties and increase WVP by decreasing the number of intramolecular bonds between polymer chains; however, the films containing fructose and sorbitol have lower WVP than unplasticized films (Guilbert and Biquet, 1996). Regarding the high brittleness of unplasticized films, they might contain small pores that would increase water vapor transmission rate. There was no significant difference in WVP between the films containing glycerol and unplasticized ones. Rodriguez et al. (2006) noted that there was no significant difference in WVP between starch films containing glycerol as plasticizer and unplasticized films which verified our finding. The addition of plasticizers to the polymer matrix could increase WVP. For instance, PEG400 is incorporated in the polymer matrix and decreases cohesive forces between methyl cellulose chains. As a result, empty space and then movement increase and water molecules are able to disperse freely; therefore, WVP is increased (Turhan and Şahbaz, 2004). WVP changes for maltodextrin based film were similar to those reported by Pranoto et al. (2005) after using 0.4% (v/v) garlic oil in alginate films' preparation, while there was no significant difference, which might happen due to hydrophobic properties of garlic oil that contributed to intramolecular interactions in the alginate film network and increased transmitted humidity by the film.

Using essential oils and oil compounds has no effect on WVP, probably because they are terpene-like compounds and are not lipids (Rojas-Graü et al., 2007). Significant reductions in the OTR of maltodextrin based formulation films can be explained by noting that alginate film is affected by multivalent cations' concentration in the gel (like calcium), cation addition rate, exposure time to cations, pH, temperature and other ingredients like hydrocolloids. Calcium ions connect to alginate polymer chains by ionic hydrogen bonds (Miller and Krochta, 1997). Rojas-Graü et al. (2007) showed that alginate-apple puree films were efficient barriers against oxygen. Permeability of this film was half of pectin-apple puree films, which meant the carbohydrate used in formulation affected OTR. A slight decrease was observed in OTR by adding 0.5% (w/w) lemon grass and citral. Therefore, it was expected that maltodextrin addition would have a major effect and glycerol would play a minor role in OTR reduction in the second formulation compared to the other one in the present study. OTR reduction led to reduction in fat oxidation (rancidity), oxidation of myoglobin (browning), sublimation of volatile compounds, and preventing entrance of volatile compounds from the environment.

Conclusion

There was no significant difference in mechanical properties (TS and E) and WVP between the two films studied here; however, a significant reduction in OTR was observed in maltodextrin based films in comparison with dextrose monohydrate based films. As a result, maltodextrin based film containing added glycerol was more suitable as a barrier to oxygen.

Conflicts of interest

None declared.

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