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Research Article

EFFECT OF GLYCEROL CONCENTRATION ON PHYSICAL PROPERTIES OF COMPOSITE EDIBLE FILMS PREPARED FROM PLUMS GUM AND CARBOXY METHYL CELLULOSE

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ABSTRACT
In this study a novel edible film plasticized with glycerol was prepared from plums gum and carboxy methyl cellulose. The mechanical, gas permeability and thermal properties of blends films Incorporated with four levels of glycerol (5%, 10%, 15%, and 20% w/w) as plasticizer were determined. The aim of this study was to better understand the possibility of preparing composite edible film on the basis of plums gum, carboxy methyl cellulose (CPG) and glycerol and influence of glycerol contents on the behavior of the physical properties of composite films. Water vapor permeability of the films was found to decrease as the glycerol content increased from 5% to 20% w/w in the formulation, resulted in improvement of films flexibility and significantly lower tensile strength and higher elongation at break. The results of the present study demonstrated the benefit of using plums gum as a natural gum to prepare edible films.

Keywords: *Plums Gum, Physical Properties, Glass Transition, Edible Film*

INTRODUCTION

Using biopolymer-based films have been raising interest in recent years, because of general concerns of limiting natural resources as feedstock for, and environmental effects caused by non-biodegradable plastic-based packaging materials. Such demands have caused increased interest in edible and biodegradable films that potentially are used to extend the shelf life and improve the quality of food (Ramos *et al.*, 2013).

The main film-forming materials are polysaccharides, proteins and lipids (Falguera *et al.*, 2011); also the blend of these biopolymers with other biopolymers, glycerol, polyethylene glycol (as a plasticizer), hydrophobic substances, natural gums and antimicrobial compounds has been widely used to improve the physical, organoleptic and nutritional properties of edible films (Vasconez *et al.*, 2009). Potential applications of edible films and coatings have been widely reviewed (Falguera *et al.*, 2011). In recent years, the market of edible films and coating has enjoyed significant growth which is expected to continue in future, so the search for better formulations of these films with improved characteristics from diverse sources is inevitable (Luduena *et al.*, 2007).

Plant gums (PG) have been used in a variety of applications such as in food emulsifiers, stabilizers, thickeners, pharmaceuticals, cosmetics and textiles. Natural gums are polysaccharides of natural origin, capable of causing a large increase in a solution’s viscosity. Gums and other kind of saccharide materials are known to have been used as binding media, sizing agents. Actually, carbohydrates are contained in a variety of materials used as support, binders and varnishes in painted objects (Lluveras *et al.*, 2011).

Plasticizer is required for edible films to overcome film brittleness. Plasticizers could reduce the intermolecular forces and increase the mobility of polymer chains, therefore improving the flexibility and extensibility of the films (Hsien *et al.*, 2008).

Carboxymethyl cellulose (CMC) is used as a highly effective additive to improve product quality and processing properties in food stuffs, cosmetics and pharmaceuticals, paper and textile industries.

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Although there are a few papers on the CMC bio composite properties (Karami *et al.*, 2011), no specific studies have been reported about combined effect of natural gum (PG) and CMC. To the best of our knowledge, there is no published study regarding characterization of edible films made from PG.
Therefore, the aims of the present study were to investigate the effect of different proportions (5-20% w/w) of glycerol as plasticizers type on mechanical, gas permeability and thermal properties of composite biodegradable CPG films (Ghanbarzadeh *et al.*, 2010).

MATERIALS AND METHODS

Materials

Plums gums were purchased from a contracted farmer (Babolsar Province, Iran). Glycerol which was used as plasticizer and ethanol were purchased from Merck Corporation. Carboxy methyl cellulose with average molecular weight of 41,000 (food grade) was purchased from Caragum Parsian Corporation (Tehran, Iran).

Method

Method of Coating Solution Preparation

About 5 g PG washed with washed with tap water, rinsed with distilled water, and then air-dried (40°C, 48 h). Aqueous PG was prepared using distilled water (water to PG weight ratio of 100:5). Next, the solutions were filtered. Film solution was prepared by slowly dissolving 5% PG, different level glycerol as a plasticizer (5- 20% (w/w) under constant stirring (750 rpm) at 35°C for 15 min. Finally, the emulsion was placed into an ultrasonic to remove air bubbles.

Method of Film Preparation

About 70 mL of the emulsion was poured on to teflon coated plates (40* 40 cm) which is obtained from local workshop in Iran. To control film thickness, the amount of solution poured was the same (300 mL) in each test, resulting in films with 0.08±0.01 mm thickness, measured by a micrometer. We used a thin solution to avoid flow and viscous limitations, and used a carefully leveled table for each sample. Five determinations were made at random positions. The samples were then dried at 35°C in an oven to cast the films.

Determination of Physical Properties of the Films

Solubility in Water

Solubility in water was determined as the weight of the film that is dissolved after in distilled water. A circular film sample was cut from each sample, dried at 100 ± 2°C for 24 h in a laboratory oven, and weighed to determine the initial dry weight.
The solubility in water of the different films was measured by immersion test in 50 ml of distilled water for five hours at 25°C. After that, the remaining pieces of film were taken out and dried at 100 ± 2°C. The weight percentage of the total soluble matter (TSM) of the final films was calculated using Equation 1. TSM tests for each type of films were carried out in three replicates and average was reported (Slavutsky *et al.*, 2012).

$$\%\mathrm{TSM} = \frac{[\text{Initial dry weight}] - [\text{Final dry weight}]}{[\text{Initial dry weight}]} \times 100 \qquad eq(1)$$

Water Vapor Permeability Rate (WVP)

WVP properties of the films were carried out using the standard test method (ASTM E96-95, 1995). Glass vial, with an average diameter of 0.8mm and a depth of 2cm, were accordingly used to determine WVP of films. The films were cut to a diameter slightly larger than the diameter of the vial. Each vial was placed in a desiccator containing saturated Mg $(NO_3)_2.6H_2O$ solution, which provided constant RH of about 52% and 25°C.
The vials were weighed every 24 h and water vapor transport was determined by the weight loss of the vials. Changes in the weight of the vial were recorded as a function of time. Slopes were calculated by linear regression (weight change versus time) and water vapor transmission rate (WVTR) was calculated by dividing slope of the curve by the transfer area (m^2) WVP (g m^{-1} h^{-1} Pa^{-1}) as equation (2) (Alexandre *et al.*, 2009).

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$$\mathrm{WVP} = \frac{\mathrm{WVTR}}{\mathrm{P}(\mathrm{R_1}-\mathrm{R_2})} \qquad \mathrm{eq}(2)$$

In equation (2), P is the saturated vapor pressure of water (Pa) at the test temperature (25°C), R_1 is the RH in the desiccator, R_2 is the RH in the vial and X is the film thickness (m). All measurements were performed in three replicates and average was reported.

Oxygen Permeability (O_2P) of Films

O2P was measured at 25°C and 50 ± 1% RH according to the standard method ASTM D3985 (ASTM D 3985-3995, 1995). Each film was placed on a stainless steel mask with an open testing area of 0.0144 $\mathrm{m.}^2$

Films were placed into the test cell and exposed to oxygen (***O_2***) flow. Gases at similar absolute pressures and flow rates passed on either side of the sample film. Pure oxygen passed on one side of the sample. Oxygen permeated from the side with high concentration, through the film and into the oxygen-deficient carrier gas stream. After leaving the sample chamber, the carrier gas passed through an oxygen sensor to measure the oxygen concentration in the carrier gas. The analysis was performed in duplicate (ASTM D 3985-3995, 1995).

Mechanical Properties

Ultimate tensile strength and strain to break of the films were determined at 24 ±1°C and52 ± 1% RH using a tensile tester (Elma, Tehran, Iran) according to ASTM standard method D882-91 (ASTM D 882-891, 1996). Three dumb bell forms (10 cm×1 cm) were cut from each of the samples and mounted between the machine grips. The initial grip separation and cross-head speed were set to 50 mm and $2\mathrm{mm.min}^{-1}$.

Differential Scanning Calorimetry (DSC)

The thermal properties of the films were carried out using a Differential Scanning Calorimeter (DSC) made by Setaram (Caluire, France).The sample was placed into a sample pan of the DSC. Samples were scanned at a heating rate of 10°C/min from -50°C to 150 °C. Nitrogen gas was purged at a flow rate of 20 ml/min. An empty aluminum pan was used as reference. In order to determine thermal properties, second heat ramps were used (Alexandre *et al.*, 2009).

Statistical Analysis

The raw results of the tests were analyzed statistically by ANOVA procedure in SPSS (version 20, Chicago, IL USA) software. Duncan's multiple range test ($p<0.05$) was used to detect differences among mean values of film properties.

RESULTS AND DISCUSSION

Film Solubility in Water

Solubility in water is a major property of edible films that is related to the structural properties of film and the presence of components in the films, since potential applications may require water insolubility to enhance product integrity and water resistance.

Table 1 shows the effect of incorporating various concentrations of glycerol on the physical properties of CPG films.

The amount of water present in composite films provides an indication of the films hydrophilicity, the more hydrophilic films being those that present the highest values of moisture content. At the same condition films with greater glycerol content exhibited a lower solubility in water ($p<0.05$). As can be seen in Table 1, the incorporation of glycerol decreased water solubility of CPG films with respect to the control film.

Addition of glycerol at a level of 20% w/w reduced the water solubility value. Thus, might interact with water and interrupting the network by hydrogen bonds, reducing the cohesiveness of the natural gum matrix and increasing its solubility in water (Ghanbarzadeh *et al.*, 2011), (Altiok *et al.*, 2010). Tunc and Osman obtained similar results for methylcellulose films (Tunc *et al.*, 2007).

Furthermore, our results showed that the water solubility of CPG films incorporated with 20% wt various concentrations of glycerol decreased significantly ($p < 0.05$) from 20.24% to 14.11% (Table 1).

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Table 1: Film solubility and moisture content of CPG films obtained with different glycerol concentration

Glycerol Concentration (%w/w)	Thickness (mm)	Moisture content (%)	Solubility in Water (%)
0	0.062	24.26	20.24
5	0.063	22.04	18.58
10	0.065	21.10	17.24
15	0.069	17.62	15.18
20	0.062	16.02	14.11

Water Vapor Permeability

The water vapor permeability (WVP) is the most important and extensive property of edible films because of its connections to degenerative reactions (Acosta *et al.*, 2013). Figure 1 shows the water vapor permeability (WVP) values of different composite films. The WVP of composite films changed significantly ($p < 0.05$) depending on the glycerol concentration used. Glycerol had greatest effect on the amount of water permeated through the film. In fact, WVP of composite films declined significantly with the increase of glycerol, up to 20%wt. according to Figure 1. WVP of the control films was 6.81×10^{-7}g/m.h.Pa and decreased to 1.42×10^{-7}g/m.h.Pa for10% glycerol containing films. The hydrophobic or hydrophilic nature of biopolymers and presence of voids in their structure have a considerable influence on the WVP of resulting films (Ghasemlou *et al.*, 2011). The film containing 20% glycerol exhibited the lowest WVP value. Decreased WVP by incorporation of glycerol was in agreement with the results reported for polymer blends which are studied for packaging applications (Ghasemlou *et al.*, 2011). Farahnaky and coworkers obtained similar results for films made of wheat starch and glycerol (Farahanaky *et al.*, 2013).

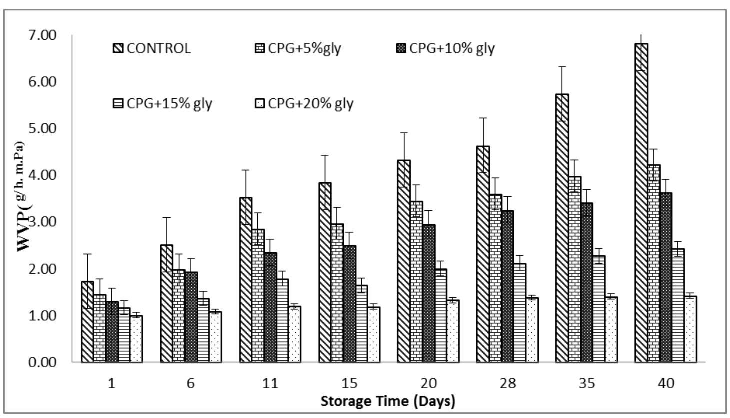

Figure 1: Effect of glycerol concentration on WVP of CPG films (p<0.05))

Oxygen Permeability of the Films

Oxygen permeability of the CPG films with and without glycerol is summarized in Table 2. The O_2P of the control CPG film was 39.82 ± 0.25 ml. day/ m^2, by increasing glycerol to 20% w/w this value decreased to 20.56 ± 0.25 ml day/m^2, resulting in better oxygen barrier properties of CPG films, by increasing more glycerol, oxygen permeability increased.

The films without glycerol exhibited the highest values of O_2P among all films tested ($P < 0.05$). These results, as with WVP values, could be due to the hydrophilic nature of glycerol. The result in agreement with Farahnaky and coworkers which found that the lowest water vapor permeability for the films with 20 and 30% wt. glycerol (Farahanaky *et al.*, 2013).

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Table 2: Effect of glycerol concentration on oxygen permeability of CPG films (p<0.05)

Glycerol concentration (%w/w)	Thickness (mm)	Oxygen permeability ml .day/m^2
0	0.062	39.82
5	0.063	33.43
10	0.065	31.16
15	0.064	27.04
20	0.062	20.56

Tensile Strength and Percentage of Elongation

Tensile strength and percentage of elongation are two significant properties in packaging material. Effect of glycerol concentration on tensile properties of pure CPG composite films was investigated. Figures 2 and 3 show the relationships between glycerol content and the tensile properties of the CPG films. Improvement was seen by addition of glycerol. The results show improvement of mechanical strength with the increase of glycerol. According to these figures, glycerol addition of up to 20% increases the mechanical parameters (UTS and %E) for all films compared to the control. In control film the UTS and elongation were 20.84 MPa and 2.38% and in composite film with 20% glycerol there were 14.76 MPa and 2.82% respectively. The films which did not contain glycerol had a poor result, In general, the composite film with (10% w/w) glycerol had higher (P<0.05) values of this parameter. It seems that the addition of glycerol improves film strength due to the strong interaction between glycerol and CPG, resulting from reduced free volume and molecular mobility of the polymer (Saderi *et al.*, 2005).

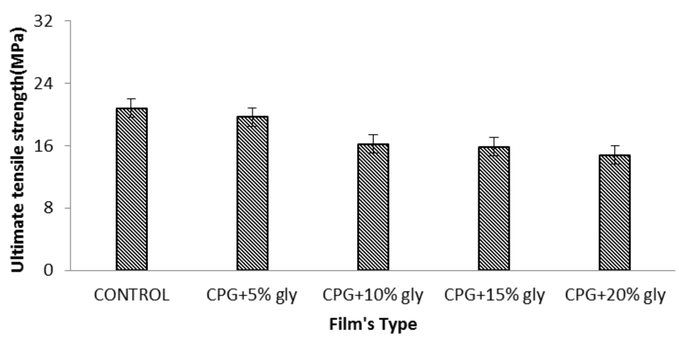

Figure 2: Ultimate tensile strength (UTS) of the CPG films as a function of glycerol (p<0.05)

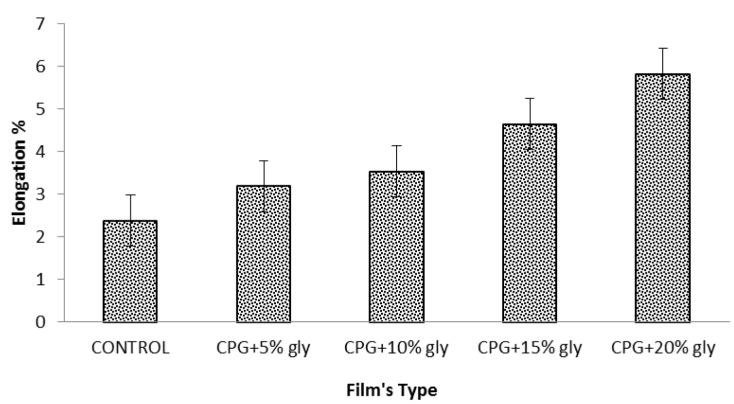

Figure 3: Elongation at break of the CPG films as a function of glycerol (p<0.05)

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The similar effects on mechanical properties of adding plasticizers, such as increases in elongation and decreases in tensile strength, have been broadly discussed in the literature (Tajik *et al.*, 2013), (Abdorreza *et al.*, 2011). In fact Plasticizers interfere with polymer chains: they decrease intermolecular forces, soften the rigidity of the film's structure and thus help to improve the flexibility of the films (Abdorreza *et al.*, 2011).

Thermal Properties

The effect of glycerol concentration in CPG films on the thermal properties was studied by DSC. The initial temperature of degradation, temperature at maximum degradation rate and apparent enthalpy were measured using the first DSC scan for all the films. Below Tg, films are rigid and brittle, whereas above it films become flexible (Ghasemlou *et al.*, 2011), (Altoik *et al.*, 2010). Table 3 shows the glass transition temperatures (Tg) and melting temperatures (Tm) of the CPG-based films with different glycerol concentrations. The glass transition temperature (Tg) is the temperature at which the material undergoes a structural transition from a glassy state to a more viscous rubbery state (Tajik et.al. 2013). The findings of this study indicate that control films(CPG) had a Tg value of about (11.7°C), Tm (58.42°C) and ΔH of (52.83). Incorporating glycerol (0 to 20% w/w) into the CPG films significantly increased Tg, Tm andΔH. Glycerol in CPG films makes films more hydrophilic and maintains a higher moisture content compared to control films when conditioned at the same humidity (RH %) and temperature. Composite film containing 2% glycerol had a Tg value of about (36± 0.5°C), Tm (90± 0.5°C) and ΔH of (95.48). Significant increase in Tg values with increasing glycerol content, shows that the glycerol create strong bonding between the polymer chains. This limits the mobility of polymer chains and therefore requires higher temperatures for the movement of chains.

Table 3: Differential scanning calorimetry (DSC) measurement results of CPG films with different glycerol concentration

Glycerol Concentration (%w/w)	T_G (°C)	ΔH_f ($J\ g^{-1}$)
0	11.7	52.83
5	19.67	77.48
10	24.36	89.35
15	29.98	92.01
20	36.5	95.48

Conclusion

The properties of CPG-based films were enhanced by the addition of nanoclay. This research results showed that the CPG films incorporated with 20% glycerol have a great potential for application as a natural film to preserve food.

Water solubility, gas permeability, mechanical and thermal properties of CPG based films varied depending on the glycerol concentrations. Addition of glycerol at a level of 20% w/w reduced the water solubility from 20.24% to 14.11%. Hydrophilic natural glycerol showed suitable interaction with the CPG matrix. Films incorporated with 20% glycerol showed in significant increased tensile strength and elongation of the films.

Moreover, the film prepared with the 20% w/w glycerol was found to be the best as it had the lowest water vapor and oxygen permeability. WVP and oxygen permeability of the composite film containing 20% glycerol decreased to $1.42*10^{-7}$g/m.h.Pa and 20.56 ml .day/m^2. Moreover the tensile strength and elongation at break rose to 14.76 MPa and 5.82%, respectively in films with 20% glycerol. Furthermore, glass transition temperatures of CPG film containing 20% glycerol increased to 36.5°C compare to control films.

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