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Effect of glycerol concentration on edible film production from cress seed carbohydrate gum

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ABSTRACT

In this study an edible film plasticized with glycerol was successfully prepared from cress seed gum (CSG). The physical, optical, water vapor permeability (WVP) and mechanical properties of CSG films incorporated with three levels of glycerol (25%, 35%, and 50% w/w) as plasticizer were determined. Dynamic mechanical thermal analysis was used to determine the glass transition temperature. WVP of the films was found to increase as the glycerol content increased from 25% to 50% w/w in the formulation, resulted in improvement of films flexibility and significantly lower tensile strength and higher elongation at break. The color measurement values showed that increasing the glycerol concentration in polymer matrix caused the b and L values increased while ΔE value decreased. The electron scanning micrograph indicated smooth and uniform surface morphology without signs of phase separation between the film components. The results of the present study demonstrated that CSG can promisingly be used in producing edible films with improved quality characteristics.

1. Introduction

The use of plastic for packaging has increased extensively in recent years. One of the current trends in the food industry is the substitution of petro-based plastic materials with those which are natural and compostable. The use of biodegradable or edible films as a substitute for petrochemical polymers is an interesting perspective, since it provides an alternative to nondegradable products. Recently there is a growing interest in edible films and coatings due to the concerns of environmental threats, as well as the costs and supply of petroleum (Janjarasskul & Krochta, 2010).

Materials available for forming films and coating generally fall into the categories of polysaccharides, proteins and lipids. Various polysaccharides have been used for the preparation of edible films including starch (Osés, Niza, Ziani, & Maté, 2009), psyllium seed gum (Ahmadi, Kalbasi-Ashtari, Oromiehie, Yarmand, & Jahandideh, 2012), tapioca (Vásconez, Flores, Campos, Alvarado, & Gerschenson, 2009), corn starch (Psomiadou, Arvanitoyannis, & Yamamoto, 1996), cellulose and cellulose derivatives such as HPMC (hydroxypropyl-methylcellulose), CMC (carboxymethylcellulose), and MC (methylcellulose) (Pérez, Flores, Marangoni, Gerschenson, & Rojas, 2009; Sánchez-González, Vargas, González-Martínez, Chiralt, & Cháfer, 2009). However, over the past few years, there has been a renewed interest to investigate other new resources for the production of edible and biodegradable films.

Lepidium sativum is an annual herb, belonging to the Cruciferae family, which grows widely in the Middle East, Europe and USA. It is commonly named as Garden Cress, Pepper Grass, Garden Pepper Cress, Water Cress, and Pepper Wort (Duke, Bogenschutz-Godwin, Ducelliar, & Duke, 2002). The *L. sativum* seeds are brown, of length about 300 μm, width about 100 μm, and oval shaped. They can adsorb water quickly when soaked in water and produce a sticky and tasteless liquid. The seeds contain a large amount of mucilaginous substances and have been shown to contain gum of high molecular weight (Karazhiyan, Razavi, Phillips, Fang et al., 2011). It has a great potential to utilize as a thickening and stabilizing ingredient in the food systems. Furthermore, the potential of cress seed gum (CSG) as antibacterial, anti-asthmatic, diuretic, aphrodisiac, and abortifacient has been reported in some publications (Duke et al., 2002; Sahraiyan, Naghipour, Karimi, & Davoodi, 2013). Recently, Karazhiyan, Razavi, and Phillips (2011) have shown that the majority of the CSG is carbohydrate and the major sugars were mannose (38.9%), arabinose (19.4%), galacturonic acid (8%), fructose (6.8%), glucuronic acid (6.7%), galactose (4.7%), rhamnose (1.9%) and glucose (1.0%). They also reported in another work that the optimum extraction parameters of CSG were temperature of 35 °C, water to seed ratio of 30:1 and an extraction time of 15 min (Karazhiyan et al., 2009).

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Therefore, owing to its rheological and also various functional properties, CSG appears to be a very interesting raw material for the preparation of edible films and coatings. The observations in our preliminary studies showed that CSG can produce films with good appearance and satisfactory mechanical properties. The low production cost (in comparison with most biopolymers), hydrophilic, biocompatible and biodegradable characteristic as well as good rheological properties make CSG an excellent alternative to common synthetic plastic materials. However, to the best of our knowledge, there is no information on its film physiochemical properties in the literatures.

In order to increase the workability and flexibility of edible films, various plasticizers, usually polyols, have been widely used, glycerol being one of the most preferred and most studied (Araujo-Farro, Podadera, Sobral, & Menegalli, 2010). Glycerol is a hydrophilic plasticizer, and when added at the correct level with respect to the biopolymer content can reduce intermolecular forces and increase the mobility of polymer chains; a process generally used to improve the mechanical properties of edible films (Ghasemlou, Khodaiyan, Oromiehie, & Yarmand, 2011). The aim of this work was to develop a new edible film based on CSG, with potential applications as an edible film and a biodegradable food packaging material, and to examine the physical, optical, mechanical, barrier, thermal and microstructural properties of the resulting films as a function of varying concentrations of glycerol as plasticizer.

2. Materials and methods

2.1. Materials

The cress seeds were obtained from the local market in Tehran, Iran. The seeds were manually cleaned to remove all foreign matter such as dust, dirt, stones, chaff, immature and broken seeds. The cleaned seeds were then packed in plastic bags, sealed and preserved in a dry and cool place until they were tested. Ethanol 96% was purchased from Razi Corporation (Tehran, Iran). Magnesium nitrate and sodium chloride (used to equilibrate films at 50% RH and 75% RH, respectively) together with glycerol were purchased from Sigma Chemical Co. (St. Louis, MO, USA). All other reagents used were of analytical grade.

2.2. Extraction of CSG and preparation of edible film solution

The CSG based films were prepared by the method of Karazhiyan, Razavi, and Phillips (2011) with some modifications. About 10 g cress seeds were first sieved to remove immature and damaged seeds and then washed with its triple weight of ethanol for 15 min under constant stirring. After removing ethanol and drying the seeds in an oven at 70 °C, the seeds were soaked in distilled water (distilled water:seed of 30:1) at 35 °C for 8 h. The seed–water slurry was slowly mixed throughout the soaking period. To extract the CSG from whole seed, a rod paddle blender (Rondo-2500, KA702, France) was used to disperse seeds in 100 mL distilled water at 35 °C for 15 min under constant stirring (1500 rpm). Separation of the gum from the swollen seeds was achieved by filtration with cheese cloth. The insoluble non-carbohydrate fractions of cress seed were removed and the dry matter of filtrate (or dry hydrocolloid) was determined (13.2%).

For preparing film-forming solution, mixtures containing 1.2% (w/v) hydrocolloid concentration and glycerol (15%, 25%, and 35% (w/w)) were prepared under magnet stirring (750 rpm) at 55 ± 3 °C for 15 min. Preliminary experiments and literature data showed that this range of plasticizer results in the best mechanical properties of CSG based films (Abdorreza, Cheng, & Karim, 2011; Ahmadi et al., 2012). The film-forming solutions were degassed under vacuum for 5 min to remove air bubbles formed during heating. CSG based films were cast by pouring the mixture onto a Teflon plate placed on a leveled granite surface for approximately 18 h at room temperature (25 °C) and room relative humidity (30%). Dried films were peeled off the casting surface and stored inside desiccators at 25 °C until evaluation. Saturated magnesium nitrate solution was used to meet the required relative humidity.

2.3. Determination of physical properties of films

2.3.1. Film thickness and density measurements

The film thickness was measured using manual digital micrometer (Mitutoyo No. 293-766, Tokyo, Japan) to the nearest 0.001 mm. Measurements were made in at least ten random locations for each film, and an average value was calculated. The average value was used in calculations for tensile properties and WVP tests. For determining film density, samples of 2 cm × 2 cm were maintained in a desiccator with phosphorus pentoxide (0% RH) for 20 days and weighed. Thus, dry matter densities were calculated by Eq. (1).

$$\rho_s = \frac{m}{A \times \delta} \quad (1)$$

where A is the film area (4 cm^2), δ the film thickness (cm), m the film dry mass (g) and ρ_s the dry matter density of the film (g/cm^3) (Larotonda, Matsui, Sobral, & Laurindo, 2005). The film density was expressed as the average of ten determinations.

2.3.2. Moisture content

Film's moisture content was determined through the weight loss undergone by the film after a 24 h oven drying at 90 °C. Preliminary experiments showed that 24 h was sufficient to dry the samples. The temperature was chosen to avoid loss of plasticizer.

2.3.3. Film solubility in water

Solubility of CSG films in water was measured following the method of Shojaee-Aliabadi et al. (2013). Film samples were dried at 90 °C for 24 h in a laboratory oven and then weighted to determine initial solid content. Pre-weighed film samples (1 cm × 3 cm) were immersed under constant agitation in 50 ml of distilled water for 6 h at 25 °C. After that period, the remaining pieces of films were filtered and dried at 90 °C to constant weight (final dry weight). The water solubility (%) of the film was calculated according to Eq. (2):

$$\mathrm{WS}(\%) = \frac{W_0 - W_f}{W_0} \times 100 \quad (2)$$

where W_0 is the initial weight of the film expressed as dry matter and W_f is the weight of the desiccated undissolved film.

2.3.4. Contact angle measurements

The contact angle is defined as the angle between the baseline of the drop and the tangent line at the point of contact of the water droplet with the surface (Ojagh, Rezaei, Razavi, & Hosseini, 2010). Contact angles were measured using a goniometer (Krüss G10, Hamburg, Germany) with the sessile drop technique, by depositing a drop of a liquid onto the film surface. 5 μL distilled water was carefully dropped on films and contact angles were quickly measured before the swelling started. The contact angle measurements were carried out in open air at a relative humidity of 30% RH and at a room temperature of 25 °C. The angle of the tangent to the basis of the droplet (contact angle) was measured and expressed in degrees. To obtain a reliable contact angle for each film sample, this test repeated at least six times and the mean values were calculated.

2.4. Water vapor permeability

The water vapor transmission of the films was determined gravimetrically according to ASTM E-96 method (ASTM, 1995) with a 75% RH gradient at 25 °C. A permeation cells containing anhydrous calcium chloride (0% RH) were sealed by the test film (0.00263 m^2 film area) using melted paraffin. To maintain a 75% RH gradient across the film, a sodium-chloride-saturated solution (75% RH) was used in the desiccators. The RH inside the cell was always lower than outside, and water-vapor transport was determined from the weight gain of the cell at a steady state of transfer. Changes in the weight of the cell were plotted as a function of time at 12 h intervals over a 7 days period to the nearest 0.0001 g. The slope of each line was calculated by linear regression ($r^2 > 0.99$), and the water-vapor transmission rate was calculated from the slope of the straight line (g/s) divided by the test area (m^2). All values for water-vapor transmission rate (WVTR) were corrected for air–gap distance between the calcium chloride and the film surface according to Eq. (3) (Gennadios, Weller, & Gooding, 1994).

$$\mathrm{WVTR} = \frac{\text{slope}}{\text{film area}} = \frac{\Delta m}{A\,\Delta t} \tag{3}$$

After the permeation tests, the film thickness was measured and water-vapor permeability (WVP) ($g\,Pa^{-1}\,s^{-1}\,m^{-1}$) was calculated using Eq. (4):

$$\mathrm{WVP} = \frac{\Delta m}{A\ \Delta t}\frac{X}{\Delta p} \tag{4}$$

where $\Delta m/\Delta t$ is the weight of moisture gain per unit of time (g/s), X is the average film thickness (mm), A is the area of the exposed film surface (m^2), and Δp is the water vapor pressure difference between the two sides of the film (Pa). WVP was measured in triplicates for each type of film.

2.5. Color measurement

The color of the films was determined using a colorimeter (Minolta CR300 Series, Minolta Camera Co. Ltd., Osaka, Japan). Film specimens were placed on a white standard plate ($L^* = 93.49$, $a^* = 0.25$, $b^* = 0.09$) and the lightness (L) and chromaticity parameters a (red-green) and b (yellow-blue) were measured. Three readings on different sites of each film were recorded. The total color difference (ΔE) and whiteness (WI) indexes of samples were calculated using Eqs. (5) and (6), respectively (Bolin & Huxsoll, 1991).

$$\Delta E = \sqrt{(L^* - L)^2 + (a^* - a)^2 + (b^* - b)^2} \tag{5}$$

$$\mathrm{WI} = 100 - \sqrt{(100 - L)^2 + a^2 + b^2} \tag{6}$$

where L^*, a^*, and b^* are the color parameter values of the standard and L, a, and b are the color parameter values of the sample.

2.6. Mechanical properties

Film's mechanical properties were determined from tension tests, using a Testometric Machine M350-10CT (Testometric Co. Ltd., Rochdale, Lancashire, England) according to the ASTM D-882 standard method (ASTM, 2001). First, films were cut in rectangular strips of 15.4 mm width × 100 mm length and preconditioned for 48 h at 25 °C and 50% RH inside desiccators containing saturated solutions of calcium nitrate. The CSG films were clamped between grips (initial distance, 50 mm) and then force and deformation were recorded during extension at 50 mm/min. Tensile strength (TS), elongation at break (EB) and Young's modulus (EM) were calculated as outlined in ASTM D882 (2000). At least 4 replicates of each test sample were run to achieve dependable data.

2.7. Dynamic mechanical thermal analysis (DMTA)

DMTA is a thermo-analytical technique used to study and characterize materials. It is the most useful instrument for observing the viscoelastic nature of polymers. The glass-transition temperatures (T_g) of CSG films were determined using a dynamic mechanical thermal analyzer (DMTA, Triton Technology, Nottinghamshire, UK), working with liquid nitrogen and film grip clamps that allows possible uniaxial traction tests. All the necessary thermal and mechanical calibrations of the instrument were performed before the experiments according to its operation manual. Film samples were clamped in the instrument with the initial grip separation of 5.5 mm. The films were subjected to a sinusoidal strain on top of a static deformation. The test was conducted at a constant frequency of 1 Hz and a strain of 0.02% over a temperature range of −50 to 150 °C, at a heating ramp rate of 5 °C/min. To prevent water loss during the experiment, the exposed surface of each sample was partially wrapped with aluminum foil, leaving the bottom and top in direct contact with the clamp holders. The storage modulus (E') and loss tangent ($\tan\delta$) of each film sample were obtained as a function of temperature. The transition temperature was determined at the point of inflection of the curve of loss tangent ($\tan\delta$) as a function of temperature. All the measurements were conducted at least in duplicate.

2.8. Film microstructure

The surface and internal structure of the films were evaluated using a Scanning Electron Microscopy (EM-3200, KYKY, China). The CSG films containing 35% glycerol were fractured in liquid nitrogen, mounted on specimen holder using an aluminum tape, and sputtered with a thin layer of gold using a BAL-TEC SCD 005 sputter coater (BALTEC AG, Balzers, Liechtenstein). All samples were examined under high vacuum condition and at an accelerating voltage of 25.0 kV. Samples were photographed at tilt angles of 60–90° to the electron beam for the views in the cross section.

2.9. Statistical analysis

Microsoft Windows Excel 2007 and SAS software (Version 9.1, Statistical Analysis System Institute Inc., Cary, NC, USA) were used to analyze the resulting data. Data were initially evaluated by analysis of variance (ANOVA), and significant results were further analyzed using Duncan's multiple range tests ($p < 0.05$) to compare the mean values of films' properties.

3. Results and discussion

3.1. Film formulation

Preliminary experiments were carried out to determine the plasticizer concentration range for film formulation. The maximum compatible concentration of glycerol in the formulations was 50% (w/w) with respect to CSG content. When this limit was exceeded, phase separation occurred leading to a physical exclusion of the plasticizer from the film. Films formulated without plasticizer were brittle and thus it was necessary to handle them carefully. However, it was not possible to evaluate their mechanical and barrier properties. The CSG films containing 25% (w/w) glycerol were found to be weak, and difficult to handle and peel from the plates. As glycerol concentration increased, films became more flexible, homogeneous with smooth surface without pores or cracks, and slightly yellow but still transparent.

Table 1
Physical properties of cress seed gum (CSG) films incorporated with various glycerol concentrations as plasticizer.[a,b]

Glycerol conc. % (w/w) (based on CSG content)	Moisture content (%)	Density (g/cm^3)	Thickness (mm)	Solubility in water (%)	Water contact angle (degree)
0	15.45 ± 0.22d	1.30 ± 0.01a	0.067 ± 0.002c	48.30 ± 0.58c	79.80 ± 3.08a
25	16.37 ± 0.23c	1.26 ± 0.02b	0.070 ± 0.002bc	50.49 ± 0.65c	70.74 ± 2.53b
35	17.54 ± 0.17b	1.25 ± 0.01b	0.073 ± 0.003b	52.66 ± 0.50b	58.59 ± 2.43c
50	18.78 ± 0.21a	1.22 ± 0.01c	0.079 ± 0.002a	54.12 ± 0.31a	43.76 ± 3.15d

[a] Means within each column with same letters are not significantly different ($p < 0.05$).
[b] Data are means ± SD.

3.2. Physical properties of films

Table 1 shows the impact of incorporating glycerol on the physical properties of CSG films. There was significant difference in the film thicknesses among treatments, which varied from 0.067 mm to 0.079 mm. The film density decreased upon glycerol addition and showed very small variations. On the other hand, when glycerol concentration increased from 25 to 35 and then to 50% (w/w) the moisture content of CSG based films increased significantly ($p < 0.05$) due to the water holding capacity of glycerol (Cerqueira, Souza, Teixeira, & Vicente, 2012).

Ghasemlou, Khodaiyan, Oromiehie, and Yarmand (2011) found similar results in kefiran films when glycerol concentration increased more than 15%. These authors suggested that in the absence of glycerol, the hydroxyl groups of kefiran polymers are surrounded by water molecules through hydrogen bonds. The addition of small amounts of glycerol causes an interaction with the kefiran–water system without changing the moisture content. When glycerol concentration reaches to 15% and higher, the film properties can change due to forming glycerol–kefiran and glycerol–water interactions.

The solubility of edible films is an important characteristic when choosing a film for specific applications (Arvanitoyannis, Nakayama, & Aiba, 1998). The solubility of the CSG films plasticized with various concentrations of glycerol increased significantly ($p < 0.05$) from 48.30% to 54.12%. In glycerol plasticized CSG films, glycerol can reduce interactions between biopolymer molecules and increase solubility due to its hydrophilic nature giving the polymer molecules higher affinity to bind water (Ghasemlou, Khodaiyan, & Oromiehie, 2011). The highest solubility was achieved when the highest concentration of glycerol (50% w/w) was used in the formulation.

3.3. Water contact angle

Surface hydrophobicity was evaluated by means of contact angle determination. In theory, the contact angle may be from 0° (complete spreading of the liquid onto the solid surface) up to 180° (the unrealistic limit of absolutely no wetting) (Ghanbarzadeh et al., 2007). Practically, a large contact angle shows a hydrophobic surface, whereas a small contact angle implies a hydrophilic surface. The contact angles for each film sample are shown in Table 1. Increasing the glycerol concentration significantly ($p < 0.05$) diminished initial water contact angle of films from 79.80° to 43.86°. It has been shown that the addition of plasticizers diminished the films' water contact angle, which in turn, decreased hydrophobicity of the films. The higher hydrophilicity of the samples is attributable to the hygroscopicity (water-binding capacity) of the plasticizer (Ghasemlou, Khodaiyan, Oromiehie, & Yarmand, 2011). It can be concluded from our results that water contact angles of CSG films were between 30° and 90° showing these films were less readily wetted and had similar behavior to most polysaccharide-based edible films (Ghanbarzadeh et al., 2007).

3.4. Surface color measurement

Table 2 shows the *L*, *a*, and *b* Hunter Lab color values, total color difference (ΔE), and whiteness index (WI) of the CSG films.

From our results, it can be seen that all of the color parameters of the CSG films were significantly ($p < 0.05$) changed when glycerol concentration increased (except *a* value). The overall color of the films was lightened with incorporation of glycerol. Therefore, addition of plasticizer to CSG films, can improve their optical properties. The color changes due to incorporation of plasticizer can be elucidated better using other color functions (Ghanbarzadeh, Almasi, & Entezami, 2010), such as ΔE, which indicates the degree of total color difference from the standard color plate, and WI, which indicates degree of whiteness. ΔE value was significantly ($p < 0.05$) lower than that of unplasticized films conversely, WI increased with increasing glycerol content. Similar effects on the color parameters for the glycerol addition to the film matrix have been previously reported by Ghasemlou, Khodaiyan, Oromiehie, and Yarmand (2011) and Ahmadi et al. (2012).

3.5. Water vapor permeability

Table 3 shows the water vapor permeability (WVP) values of the CSG films with different glycerol concentrations.

There was a significant difference between the WVTR and WVP values of films made with different glycerol concentrations ($p < 0.05$). The WVP of the films increased with increasing the glycerol concentration. The same behaviors were shown in the work of Ghanbarzadeh et al. (2006), who found that increasing the glycerol concentration increased the WVP of zein films. The authors explained this behavior by the fact that glycerol reduces intermolecular forces between polymer chains and increased free volume and segmental motions. The increased mobility results in greater free volume in the matrix, which facilitates the migration

Table 2
L, *a*, and *b*, total color difference (ΔE) and whiteness index (WI) of the cress seed gum (CSG) films.[a,b]

Glycerol conc. % (w/w) (based on CSG content)	*L*	*a*	*b*	ΔE	WI
0	63.44 ± 0.62d	−0.89 ± 0.02b	3.89 ± 0.35d	35.89 ± 0.61a	60.41 ± 0.76c
25	66.51 ± 0.39c	−0.93 ± 0.04a	4.38 ± 0.16c	28.88 ± 0.54b	66.37 ± 0.60c
35	68.62 ± 0.48b	−0.92 ± 0.02a	4.93 ± 0.15b	23.65 ± 0.67c	72.55 ± 0.74b
50	73.53 ± 0.36a	−0.93 ± 0.03a	5.29 ± 0.21a	19.45 ± 0.43d	74.34 ± 1.06a

[a] Means within each column with same letters are not significantly different ($p < 0.05$).
[b] Data are means ± SD.

Table 3
Water vapor transmission rate, water vapor permeability of cress seed gum (CSG) films incorporated with various glycerol concentrations as plasticizer.[a,b]

Glycerol conc. % (w/w) (based on CSG content)	Water vapor transmission rate (WVTR) ($\times 10^{-3}$ g H_2O s^{-1} m^{-2})	Water vapor permeability (WVP) ($\times 10^{-10}$ g H_2O m^{-2} s^{-1} MPa^{-1})	R^2
25	4.97 ± 0.06c	2.10 ± 0.05c	0.9945
35	5.20 ± 0.09b	2.27 ± 0.06b	0.9967
50	5.45 ± 0.06a	2.43 ± 0.06a	0.9943

[a] Means within each column with same letters are not significantly different ($p < 0.05$).
[b] Data are means ± SD.

of water vapor molecules through the film (Sothornvit & Krochta, 2001). The high hydrophilicity of glycerol molecules which is favorable to the adsorption of water molecules could also contribute to the increase in the film WVP (Gontard, Duchez, Cuq, & Guilbert, 1994). WVP of films is a characteristic which depend on solubility coefficient and diffusion rate of water in film (partial pressure of water vapor (Pearoval, Debeaufort, Desprea, & Voille, 2002). Thus, lower WVP of the plasticized films as compared to those of films without plasticizer could be resulted from coincident effects of both solubility coefficient and diffusion rate. Similar results have been reported for wheat gluten (Gontard et al., 1994), sodium caseinate and soluble starch (Arvanitoyannis & Biliaderis, 1998) and whey protein (McHugh & Krochta, 1994). The films produced in this work showed to be more permeable to water vapor than those of psyllium seed gum elaborated by Ahmadi et al. (2012), who determined the WVP in the range of 1.16 and 1.88 $\times 10^{-10}$ g H_2O m^{-2} s^{-1} MPa^{-1}.

3.6. Mechanical properties

Results of the mechanical tests are shown in Fig. 1.

The presence of glycerol in films caused significant differences in TS, EB and EM. The glycerol plasticized films had significantly ($p < 0.05$) higher TS and lower EB. When 50% (w/w) glycerol was added to the CSG films, the TS decreased up to 42% of the original values, while the EB increased significantly ($p < 0.05$) up to 115% in comparison with the original value. Based on these results, it can be concluded that increasing of glycerol concentration in the CSG films improved film extensibility and reduced its resistance. The effect of plasticizer concentration increment on the film's mechanical properties has been broadly discussed in the literature (Averous & Boquillon, 2004; Cuq, Gontard, Aymard, & Guilbert, 1997; McHugh & Krochta, 1994). Ghasemlou, Khodaiyan, Oromiehie, and Yarmand (2011) have discussed that a small quantity of plasticizer could be easily inserted between polymer chains, producing a "cross-linker"

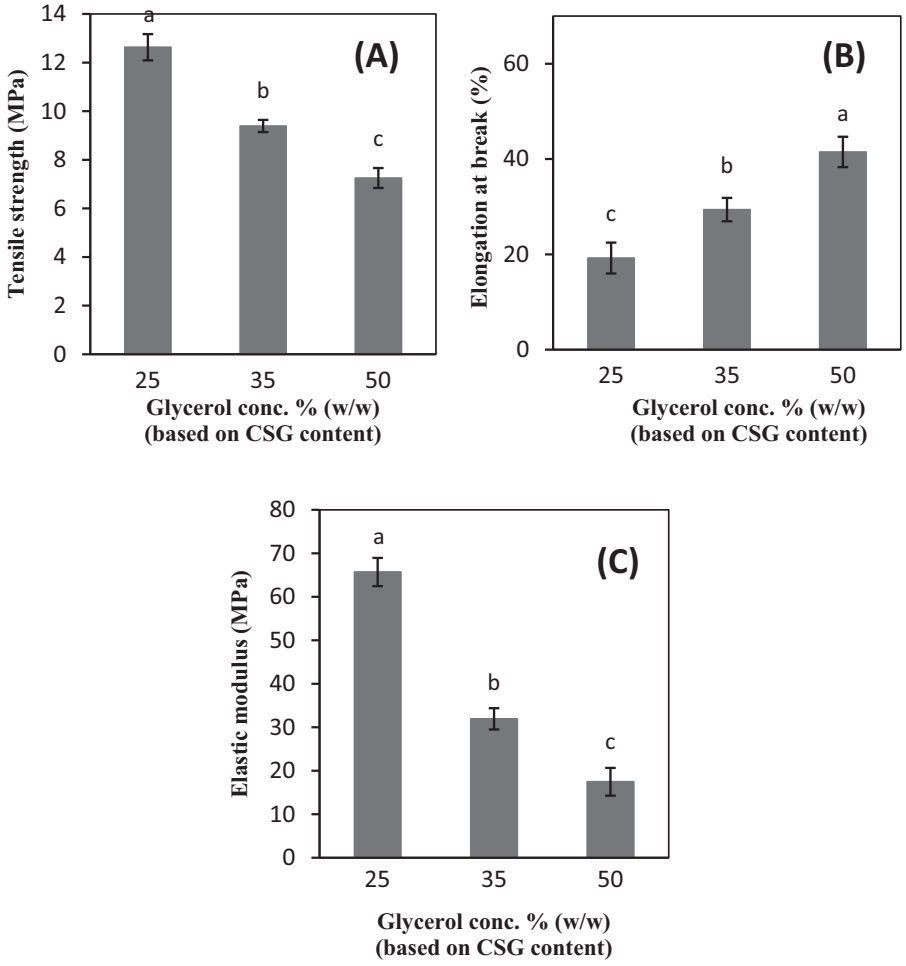

Fig. 1. Tensile strength (A), elongation at break (B) and elastic modulus (C), of the cress seed gum (CSG) films incorporated with various glycerol concentrations as a plasticizer. Note: a, b and c are different letters represent significant differences ($p < 0.05$) between the means obtained in Duncan's test.

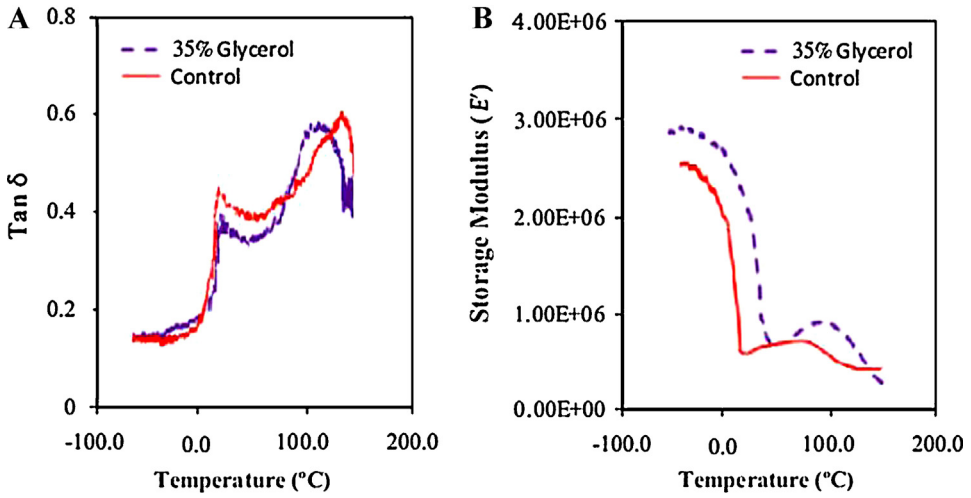

Fig. 2. The effect of glycerol concentration on loss factor and storage modulus of the cress seed gum (CSG) films in DMTA.

effect that decreases the free volume of the polymer, causing the extensibility of resulting films to be improved and the mechanical strength to be diminished. Cuq et al. (1997) also verified that the films based on myofibrillar fish proteins plasticized with glycerol showed lower TS and higher EB than the unplasticized films. The TS of the CSG films were almost equal to that reported for psyllium seed gum with glycerol as plasticizer (Ahmadi et al., 2012), Whereas, EB of CSG films was two times higher than the EB of psyllium seed gum based films. This difference in the mechanical property is due to the different method of film preparation, or the effect of plasticizer used.

3.7. Dynamic mechanical thermal analysis (DMTA)

A dynamic mechanical thermal analysis (DMTA) instrument used to investigate the glass transition of CSG films. The results of loss tangent ($\tan\delta$) and storage modulus (E') of the CSG films with 35% w/w glycerol are shown in Fig. 2A and B, respectively. Because the values for glass transition temperature (T_g) were very close for all plasticized CSG films, the figure shows only the T_g of the 35% concentration level. The value of the T_g of a polymer mixture is often claimed to be a criterion to establish its miscibility (Ghanbarzadeh & Oromiehi, 2009). Many researchers also claimed

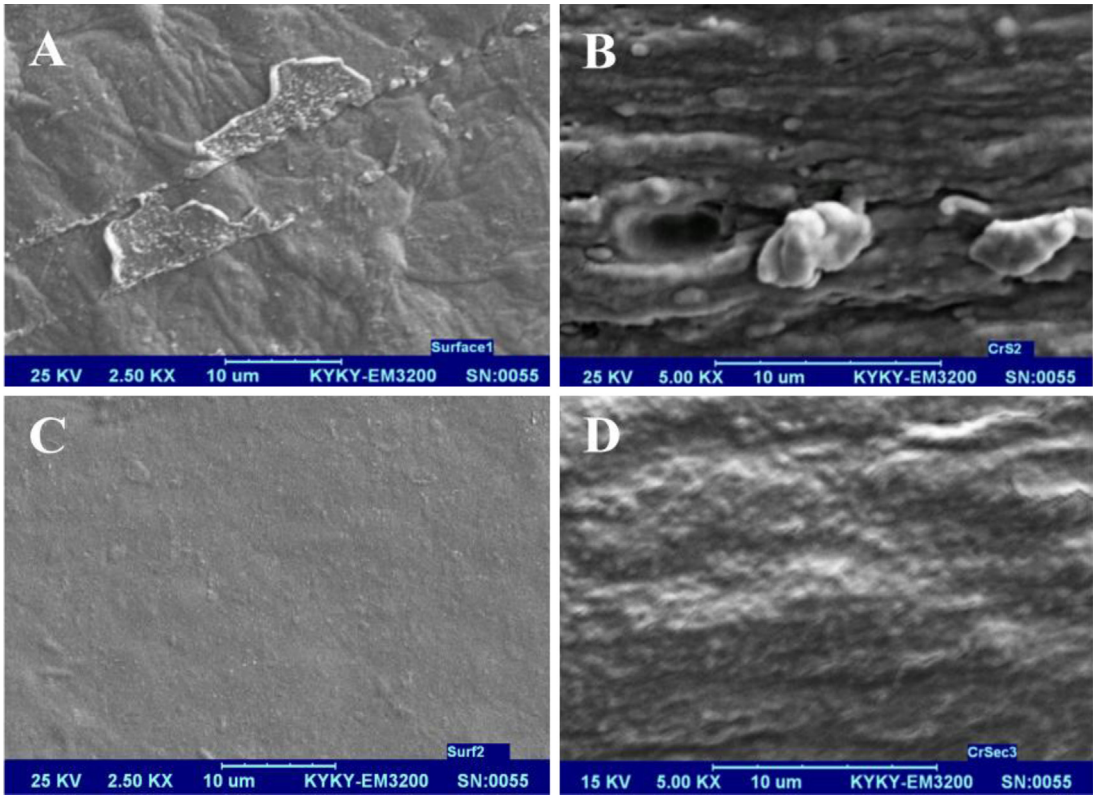

Fig. 3. Scanning electron microscopic images of the CSG-based films; (A, B) unplasticized, (C, D) plasticized with 35% w/w glycerol, surfaces (left) viewed at a magnification of 2500× and cross-section (right) viewed at a magnification of 5000×, respectively.

that there is no phase separation between the polymer and the plasticizer in the films if there is no evidence for two individual α-relaxations occurring in tan δ curve. In our findings, a one-step drop in elastic modulus (E') as well as a single peak in tan δ was observed in the DMTA curves. Within the temperature range from 120 °C to 150 °C, there was an unexpected inflection point. A possible reason could be the evaporation of the residual moisture in the film even though it was covered with aluminum foil. Glycerol appeared to be miscible with the CSG at the composition used because only one transition was observed. It was found that glycerol significantly affected the T_g of the films. For all films, those without plasticizer had the highest T_g; moreover, the T_g decreased with increased glycerol concentration due to the plasticization process.

The depression of T_g with the addition of plasticizer may be explained by a number of theoretical approaches such as free volume or classical thermo-dynamic theories proposed by Couchman and Karaz (1978). The T_g of the glycerol plasticized films were higher than pure glycerol at −93 °C. This effect was probably due to miscibility of dominant phase of CSG with glycerol that resulted in higher glass transition temperature because of increasing in the average molecular weight. The similar observation was also reported by Ahmadi et al. (2012) who investigated psyllium seed based films. In another study, Ghasemlou, Khodaiyan, and Oromiehie (2011) compared plasticization effect of glycerol and sorbitol. They suggested that larger sorbitol molecules compared to glycerol molecules, had more limitation to access the high-density junction zones of the polymer matrix.

3.8. Film microstructure

Scanning electron microscopy (SEM) can provide a better understanding of the relationships of water vapor transmission, mechanical and optical properties with the films' structural characteristics.

Fig. 3 shows the SEM micrographs of surface (left) and cross-section (right) for both the control and glycerol containing CSG films. No marked differences were detected between the surface microstructures of the control and glycerol-plasticized films. The cross section images revealed that the control films had rough and uneven surfaces while the glycerol-plasticized films indicated smooth and uniform surface morphology without noticeable cracks, breaks, or openings on the surfaces. The appearance of all glycerol added films were generally smooth and homogeneous and no marked differences in structure among different glycerol concentrations were detected.

4. Conclusion

This is the first report on the feasibility of CSG to form biodegradable edible film. The results of the present study show that CSG could be a very promising raw material for the preparation of edible films and coatings. The physical, mechanical, optical and barrier properties, which are important in food packaging applications, were examined as a function of glycerol concentration. Glycerol is a plasticizer which in this study, was proved to be compatible with CSG, improving film flexibility, facilitating its handling and preventing cracks. Hydrophilicity of glycerol was found to be the most important factor in determining WVP value of CSG films. Overall, this study demonstrated that CSG had a good potential to make new edible films with required specifications. Further studies should be performed to modify CSG films properties, e.g. improvement of WVP by lipid addition, can be used.

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