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Physico-chemical properties of tragacanth gum-based films

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ABSTRACT

Emulsion coatings were formulated and films were developed using tragacanth gum as the basic structural component. Preliminary experiments were carried out to determine the proper concentration of tragacanth gum, lipid and plasticizers in the film. The effects of tragacanth gum, oil and glycerol concentration on water vapor permeability (WVP), mechanical properties and opacity (OP) of the films were evaluated using the response surface methodology. WVP increased by tragacanth and glycerol concentration and was decreased by oil concentration. Increasing the amount of tragacanth gum and decreasing the glycerol and oil concentration increased tensile strength (TS) while elongation at break (EB) increased by increasing both tragacanth and glycerol concentration and decreased by increasing oil concentration. Oil was the most influential factor that affected opacity, which increased with increasing oil concentration. Models developed for WVP, EB, TS and OP had high coefficient of multiple determination (R^2) values (0.983, 0.952, 0.824, 0.94) respectively.

KEYWORDS

Tragacanth;
Barrier - mechanical properties;
Opacity;
Response surface methodology.

INTRODUCTION

Edible films and coatings, which are defined as thin layers of edible material applied to the surface of a food as a coating, or placed (preformed) between food components. The types of materials used to elaborate edible coatings and films include lipids, resins, polysaccharides and proteins[16]. Each group of material has certain advantages and disadvantages and for this reason, many coatings are actually formulations of any or all of the above. Edible coatings can function as barriers to water vapor, gases, and other solutes and also as carriers of many functional ingredients, such as antimicrobial and antioxidant agents thus enhancing quality and extending the shelf life of fresh and minimally processed foods[18]. Among the various edible films, a composite hydrocolloid-lipid film is particularly desirable because it has acceptable structural integrity (imparted by the hydrocolloid) and good barrier properties to water vapor, contributed by the lipid. Films made from natural products are of increasing scientific and commercial interest. These materials are not only inherently biodegradable but also are potentially recyclable. The variety of uses, the possibility of multiple methods of

reuse and disposal, and the replacement of fossil-based raw materials with renewable ones suggest that these materials are excellent candidates for commercial development[6].

Tragacanth gum the exudates of the plant genus Astragalus, particularly *Astragalus gummifera* is one of the oldest known drugs. This gum is native to Asia Minor and to the semi-desert and mountainous regions of Iran, Syria, and Turkey. The structure of Tragacanth gum is highly complex and it is a mixture of polysaccharides consisting of three main components, namely: tragantic acid, a neutral polysaccharide, and a third component which appears to be a glycoside. This gum gives the highest viscosity of all plant hydrocolloids and produces viscous colloidal sols which have a texture similar to that of a soft gel[28].

Aside from being a major source of calories in typical diets, lipids, as adjuncts in food coating, have been used to add gloss to confectionery products, to retard respiration of fruits and vegetables, and to lessen moisture loss from foods to the environment. Recently, some studies have taken advantage of the hydrophobic nature of lipids and combined them with hydrocolloids, for structural support, to form edible films that are good barriers to moisture.A plasticizer is defined as "a substantially non-volatile, high boiling, non-separating substance, which when added to another material changes the physical and/or mechanical properties of that material"[2]. Polyols, such as sorbitol and glycerol, effectively plasticize because of their ability to reduce internal hydrogen bonding while increasing intermolecular spacing. Molecular size, configuration and total number of functional hydroxyl groups of the plasticizer, as well as its compatibility with the polymer, could affect the interactions between the plasticizer and the polymer. The best concentration of plasticizer and lipid for forming film was 40-50% (w/w based on film based material)[19]. Some studies have been carried out on preparation of films and their functional property, films made from a blend of pectin and starch[6,8], caseinate mechanical and barrier properties[25], combination of pectin, glycerol, orange albedo and starch[9], films based on agar, cassava starch and arabinoxylan blends[22], Tapioca starch based film[5] and whey protein films[21]. No detailed study has been carried out to improve barrier, mechanical and optical properties of Tragacanth gum-based coatings for food products.

The objectives of this study were to gain a better understanding of relationships between film-forming constituents and film properties, and to analyze the effects of Tragacanth gum, glycerol and oil concentration on barrier, mechanical and optical properties of the films using response surface methodology.

EXPERIMENTAL

Materials

Different concentrations of Tragacanth gum (Eghlid, Fars, Iran) were used to determine the best concentration of Tragacanth gum solution as a film forming agent. Oil (Aftab, Behshahr, Iran) was used as lipid and glycerol (kimia Drug, Tehran, Iran), while sorbitol and polyethylene glycol (Sigma, MO, USA) were also used as plasticizers in preliminary works to determine the best plasticizer compatible with tragacanth gum.

Preparation of tragacanth gum films

After rehydrating tragacanth gum in distilled water for 18 h at 20°C, glycerol (kimia drug, Tehran, Iran) was added to the tragacanth solution and thoroughly mixed with magnetic stirring. Then, oil and 30% (lipid dry weight basis) lecithin (Serva, New York, USA) were added and emulsified using a homogenizer (PowerGen 700, Fisher Scientific, Pittsburg, PA) in 14,000 rpm for 4 min. Films were cast by spreading emulsions on smooth poly ethylene plates. Emulsions were spread evenly with a bent glass rod and allowed to dry for approximately 18 h at 25°C and 40% relative humidity (RH). Air bubbles in the solutions were removed by placing the plates under vacuum. All films used for the experiments were equilibrated at 53% RH, using a saturated solution of magnesium nitrate (Merck, Darmstadt, Germany) at 25°C for 72 h before being tested. Film thickness was measured and verified at several positions with a digital micrometer (Mitutoyo Corp., Morton Grove, IL) before the experiments. Film thickness was 0.05 mm after drying.

Water vapor permeability

The ASTM Standard Method E 96-80[1] was used to determine water vapor transmission by sealing a known open area of an impermeable container with the

film. Glass cups were filled with saturated solution of magnesium nitrate to maintain an RH of 53% beneath the films. Films were sealed with grease onto the dish lids over circular holes. The cups were stored in desiccators maintained at 0% RH using anhydrous calcium chloride at 25°C. Covered cups were periodically weighed and the time was recorded. A linear regression analysis was carried out with weight loss as the dependent variable and elapsed time as the independent variable. The slope of the regression curve divided by the area of the opening was defined as the water vapor transmission rate (WVTR). WVTR divided by the vapor pressure difference across the film is the permeance of the film. Permeance multiplied by the thickness of the film is the WVP.

Mechanical properties

Tensile test measurements were evaluated on samples of films using a Dynamic Mechanical Analyser (TA X2i Instruments, Surey, UK) with a film testing fixture. Experiments were carried out within 72 h of the sample preparation. During this period, samples were stored in desiccators at 25°C and 53% RH. Test samples were cut from the film with a razor blade. The gap between the jaws at the beginning of each test was 12.79 mm. Tensile properties were determined from the curves of stress versus strain. TS was calculated by dividing the peak load by the initial cross-sectional area of the specimen. Elongation at break (EB) was expressed as the percentage change of the original length of the specimen between the grips at break (Figure 1).

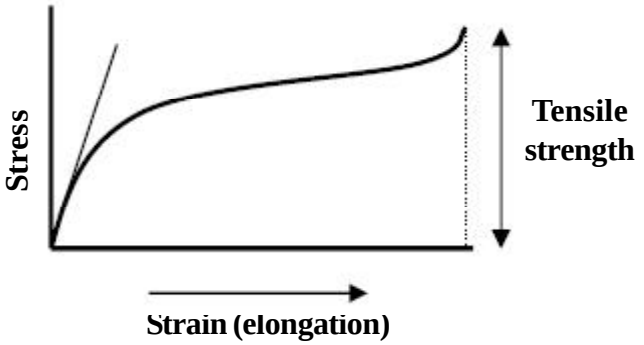

Figure 1 : Stress-strain curve

Film opacity

Film opacity (OP) was determined using a modified standard procedure[3]. The film sample was cut into a rectangular shape and placed on the internal side of a spectrophotometer cell. The absorbance spectrum (400–800 nm) was recorded for each sample using a spectrophotometer (Novaspec II, Biochrom Ltd, Cambridge, England). OP was defined as the area under the recorded curve determined by an integration procedure. The opacity was expressed as absorbance units in nanometers (AU.nm)[12].

Experimental design

A reduced, three-level, response surface factorial design was used to evaluate each main effect, as well as the interaction effects. The experimental design adopted was a modification of Box's central composite design for three variables at five levels each. The three independent variables (factors) were tragacanth gum concentration (T), glycerol concentration (G) and oil concentration (O) of film-forming emulsion. The in-

TABLE 1 : Experimental design of 3-variable 5-level central composite rotatable design and responses of dependent variables to the film-forming constituents

Run Number	Independent Variables[a] (real and coded values)			Dependent Variables[b]			
	X_1	X_2	X_3	Y_1	Y_2	Y_3	Y_4
1	1 (-1)	40 (-1)	30 (-1)	9.55	2.13	2.99	185
2	1 (-1)	60 (1)	30 (-1)	8.45	1.45	2.74	301
3	1 (-1)	40 (-1)	50 (1)	23.2	2.43	4.85	190
4	1 (-1)	60 (1)	50 (1)	19.5	1.32	4.69	303
5	2 (1)	40 (-1)	30 (-1)	16.2	5.49	3.35	196
6	2 (1)	60 (1)	30 (-1)	12.5	3.62	3.19	301
7	2 (1)	40 (-1)	50 (1)	32.7	5.31	6.05	195
8	2 (1)	60 (1)	50 (1)	28.3	4.4	5.95	303
9	1.5 (0)	33 (-1.68)	40 (0)	23.5	3.09	4.71	185
10	1.5 (0)	67 (1.68)	40 (0)	2.05	2.82	3.33	320
11	0.65 (-1.68)	50 (0)	40 (0)	14.3	1.47	2.35	280
12	0.65 (-1.68)	60 (1)	40 (0)	14.3	2.47	2.13	302
13	1.5 (0)	40 (-1)	58 (1.68)	36	0.672	7.8	280
14	1.5 (0)	60 (1)	58 (1.68)	33	0.65	5.07	302
15	2.35 (1.68)	50 (0)	40 (0)	22.3	7.15	4.91	281
16	2.35 (1.68)	60 (1)	40 (0)	21.3	5.52	4.61	303
17	1.5 (0)	50 (0)	23 (-1.68)	8.08	4.39	2.03	280
18	1.5 (0)	60 (1)	23 (-1.68)	6.62	1.97	1.99	300
19 (6X)	1.5 (0)	50 (0)	40 (0)	15	2.94	4.34	285

[a]X1, Tragacanth concentration (g Tragacanth /g distilled water); X2, glycerol concentration (%Tragacanth dry wt.) and X3, oil concentration (%Tragacanth dry weight).

[b]Y1, water vapor permeability (g m-1 s-1 Pa-1) x 10^{-11} ; Y2, tensile strength (MPa), Y3,elongation at break (%) and Y4, opacity (AU.nm).

dependent variable coded values were -1.68 (lowest level), -1, 0 (middle level), 1 and 1.68 (highest level). The actual values and the corresponding coded values of the three independent variables and responses of dependent variables to film-forming constituents are shown in TABLE 1. The correspondence between the coded and actual values can be obtained using the following formula (for variable X):

$$Z = (X - X^0)/\Delta X \quad (1)$$

Where Z is the coded value for the variable, X is the corresponding actual value, X^0 is the actual value in the center of the domain, and ΔX is the increment of X corresponding to 1 unit of Z. The complete design consisted of 24 experimental points which included six replications of the center point to estimate the pure error of the analysis and to predict the lack of fit of the models. Each of the four dependent variables (Y) (responses) was assumed to be affected by the three independent variables. Responses under observations were: water vapor permeability (*WVP*), tensile strength (*TS*), elongation at break (*EB*) and opacity (*OP*).

Statistical analyses

Data were analysed to fit the following equation to each dependant variable (*Y)*:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{123}X_1X_2X_3 \quad (2)$$

where b_n are constant regression coefficients and X_1, X_2, and X_3 are coded independent variables.

The analyses of variance and regression coefficient calculation were carried out using Microsoft Excel. SAS software[24] was used to perform stepwise procedure to simplify the models. Three dimensional surface plots were generated from obtained models by Sigma Plot[26].

RESULTS AND DISCUSSION

To determine the best concentration, different solutions of tragacanth gum (0.1-2.5 w/w) prepared and film making properties were investigated. Results showed that 0.5-2% (w/w) gum can produce proper films, more than 2% (w/w) resulted in very thick solution that plating technique was too difficult, and less than 0.5% w/w gum produced very thin and brittle films. Hence, the concentration of tragacanth gum solution was selected over the range of 0.5-2 %. For the next step, three types of plasticizers (sorbitol, polyethylene glycol and glycerol) were used in combination with tragacanth gum to formulate film emulsions. The best plasticizer for the tragacanth gum film-forming solution was glycerol. With the equipment available, prime consideration was given to the films which could be easily removed from Poly ethylene plates on which they were formed, and to durability, that it could be removed without tearing the film and not to be brittle.

Model development

Equation (2) was fitted to the experimental data (TABLE 1). Four equations were obtained and tested for adequacy and fitness by ANOVA. TABLE 2 summarizes the results of the ANOVA for each dependent variable with its corresponding coefficient of multiple determination (R^2). The models developed for WVP, EB, TS and OP yielded high R^2 values and significant F values.

$$WVP = 14.38*10\text{-}11 + 2.8*T + 7.68*G - 1.45*O + 0.988*T^2 + 1.99*G^2 + 2.19*O^2 \quad (3)$$

$$TS = 2.64 + 1.35*T - 0.399*G - 0.481*O + 0.624*T^2 \quad (4)$$

$$EB = 4.13 + 0.610*T + 1.42G - 0.237*O + 0.176*T^2 + 0.255G^2 \quad (5)$$

$$OP = 286 + 49.46T - 6.44G - 6.80O - 16.6T^2 \quad (6)$$

WVP

One of the primary functions of an edible film or coating is to restrict the moisture transfer between the food and the surrounding atmosphere, or between two components of a heterogeneous food product. Hence, the WVP should be as low as possible[12]. The WVP of tragacanth-based films was influenced by linear effects of tragacanth, glycerol and oil concentration, and quadratic effects of tragacanth, glycerol and oil (TABLE 2).

As can be seen from TABLE 1, the lowest experimental WVP can be seen with the film corresponding to design point #10, and the highest was observed at #13; tragacanth films exhibited higher WVP with an increase in tragacanth concentration (Figure 2). It could be attributed to the higher number of free hydroxyl groups, enhancing interaction with water and favoring water vapor transmission through the films. According to Higushi and Aguiar[14], the WVP of the films is dependent on the number of polar groups the polymer contains. This is caused by the sorption of migrating water molecules to polar groups, thereby facilitating

water transport. TABLE 2 shows that tragacanth concentration was a significant factor affecting WVP.

TABLE 2 : Regression coefficient and analysis of variance for five response variables

Coefficient	Water vapor permeability	Tensile strength	Elongation at break	Opacity
b0	14.4[a]	0.288[a]	4.17[a]	286[a]
Linear				
b1	2.99[a]	1.44[a]	0.588[a]	1.49
b2	7.74[a]	-0.412[b]	1.41[a]	0.588
b3	-1.45[a]	-0.434[b]	-0.233[b]	49.3[a]
Interactions				
b12	0.985[b]	0.054	0.206	-0.75
b 13	-0.611	-0.293	0.079	-1.67
b 23	-0.190	0.047	0.051	0.002
Quadratic				
b 11	0.989[a]	0.543[a]	-0.178[a]	-6.44
b 22	2.19[a]	-0.248	0.253[b]	-6.80[b]
b 33	0.237[a]	-0.005	-2.048	-16.6[b]
B 123	0.237	0.174	-0.003	0.75[a]
% Variability explained (R^2)	0.983			0.940
F-value		0.824	0.952	
	81.0			74.4
Probability of F		22.1	72.03	
Regression	N. S.[c]			N. S.
Lack of fit		N. S.	N. S.	

[a]**Highly significant ($P < 0.01$)**
[b]**Significant ($P < 0.05$)**
[c]**Non significant**

Figure 2a shows that the WVP increased with tragacanth and glycerol contents. This is in agreement with the experiments performed by Gontard et al.[13] with wheat gluten films; Yang and Paulson[27] with gellan film; Mali et al.[20] with yam starch films and Maftoonazad et al.[19] with pectin films, all indicating an increase in WVP with an increasing plasticizer concentration. Generally, water vapor transmission through a hydrophilic film depends on both diffusivity and solubility of water molecules in the film matrix[11]. Inclusion of glycerol molecules between the polymer chains causes an increase in the inter chain spacing, promoting water vapor diffusivity through the film and hence enhancing the water vapor transmission. The high hydrophilicity of glycerol molecules, which favors the adsorption of water molecules, could also contribute to the increase in the film's WVP. Additionally, at high glycerol concentration, glycerol could cluster itself to open the polymer structure, thereby enhancing the permeability of the film to moisture[17].

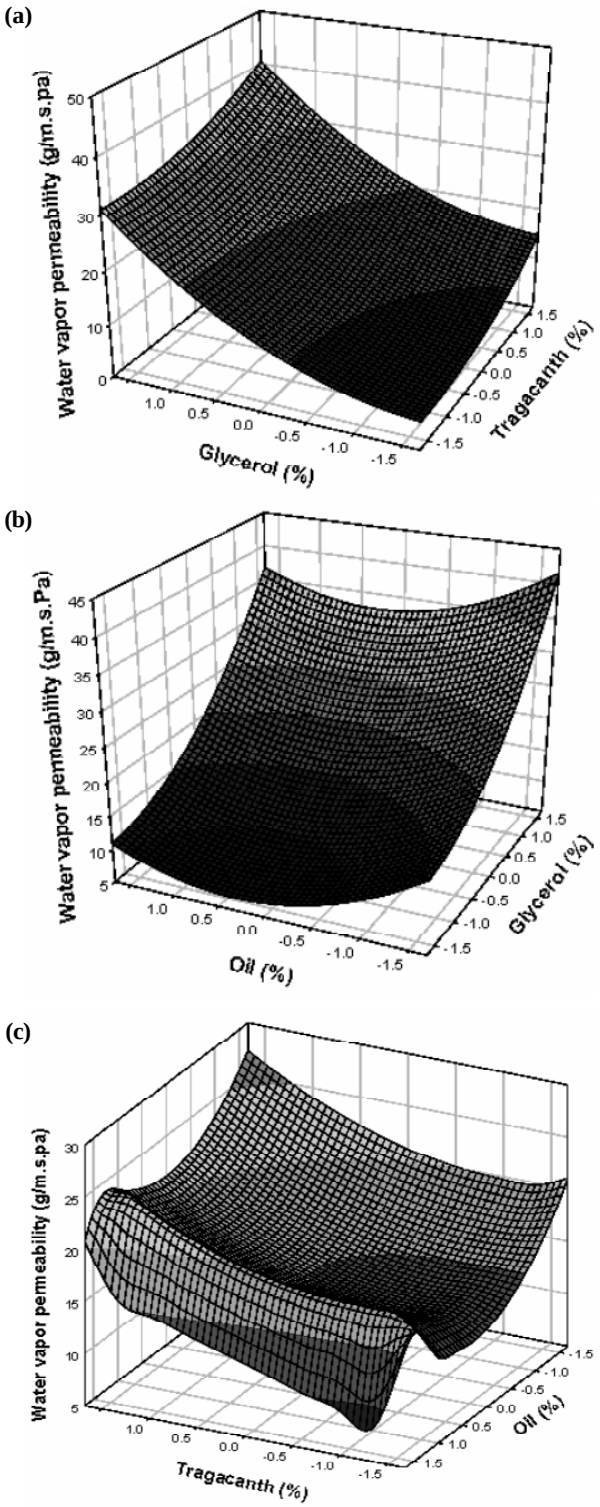

Figure 2 : Water vapor permeability: (a) effects of glycerol and tragacanth gum concentration; (b) effects of oil and glycerol concentration and (c) effects of oil and tragacanth gum concentration

The concentration of oil in the formulation also influenced the WVP of the film. As shown in Figure 2b, increasing the oil concentration up to 35% (tragacanth gum dry weight basis) decreased the WVP; however, by increasing the amount of lipid more than 35% (tragacanth gum weight basis), WVP was positively influenced. At the very high concentration of lipid the WVP again decreased. It is probable that at lower concentrations, the added lipid increases the hydrophobicity and hence decreases the film permeability. At higher concentrations, the lipids could result in larger globules during the drying stage of film making and contribute to disruption of the continuous structure of films, and consequently contributing to higher WVP[15]. Moreover, Sapru and Labuza[23] explained that the increase of the permeability for concentrations of stearic acid higher than the critical value is due to the formation of large fat crystals allowing interstitial zones free of lipids that favor moisture migration. Although the presence of an emulsifier stabilized film emulsions in the experimental conditions, increasing permeability in tragacanth – based films as a function of higher lipid concentration was maybe due to a more heterogeneous lipid globule distribution (number of populations) within the pectin matrix. At the very high concentration of lipid WVP decreased (Figure 2c). It seems that the film has changed to a bilayer film. It means that one layer of lipid is formed on the surface of the film.

Mechanical properties

The desired property of a food packaging material depends on the applications. In general, an edible film must withstand the normal stresses encountered during its application, subsequent shipping and handling of the food, to maintain its integrity and also barrier properties[12]. A three-dimensional matrix, constructed by the interaction of polysaccharide molecule, is presumably the supporting structure that dictates the mechanical properties of the films. Interactions between polysaccharide and small molecules including water, plasticizers, lipids and other additives dispersed in the space of the matrix, also contribute to the mechanical behavior of the films. Adequate mechanical strength ensures the integrity of a film and its freedom from minor defects, such as a pinhole, which can damage the barrier property. Coating can also alleviate damages to food during handling and transportation. Sometimes, edible coatings and films may be used to change handling properties of materials[4]. TS is a measure of integrity and heavy-duty use potential of films, and EB is a quantitative representative of the film's ability to stretch[10]. Depending upon the film-forming conditions, mechanical properties (TABLE 1) demonstrated a wide range of magnitude: TS ranged from 0.65 to 7.15 MPa and EB between 1.99 to 7.8%. The TS of tragacanth-based films was influenced by the linear effects of tragacanth ($P<0.01$), glycerol and oil concentration ($P<0.05$), and quadratic effects of tragacanth (TABLE 2). Tragacanth films exhibited an increase in TS by increasing tragacanth concentration (Figure 3a and 3b). The response surface tends to indicate that high tragacanth concentration induces the formation of a resistant film with a high TS. During drying of the film emulsion, moisture evaporates, allowing the formation of a polysaccharide network, and during this stage, the proximity of tragacanth chains is favored by higher tragacanth content, thus facilitating the formation of a denser matrix. The most resistant films could be expected to be formed at high tragacanth concentration (2g/100 mL). As seen in Figure 3a, this point is at the most upper part of the surface plot. In fact by increasing the amount of glycerol, the TS of the film decreased. The weakest films came at the lower amounts of tragacanth (0.63 g/100 mL) and higher amounts of glycerol (67% tragacanth dry weight basis). A large number of hydroxyl groups along tragacanth molecules could be responsible for the numerous hydrogen bonds between the tragacanth molecular chains. These extensive interchain interactions may contribute to the high mechanical strength. Incorporation of glycerol molecules into tragacanth films probably established glycerol – tragacanth hydrogen bonds replacing some of the tragacanth – tragacanth hydrogen bonds. As a result, direct interactions between the molecular chains are reduced, and the chain segmental mobility is increased, causing the mechanical strength of the films to decrease[27]. The same results were observed by Yang and Paulson[27] for gellan films plasticized by glycerol, Gontard et al.[13] for wheat gluten films and Maftoonazad et al.[19] for pectin films plasticized by sorbitol.

Figure 3b shows the effect of oil concentration on the film's TS. Increasing the amount of lipid in the film structure decreases the film's TS. This is probably due

to a lower continuity of film as a result of dispersion of lipid globules throughout the film matrix. This was supported by the interactive effect of tragacanth, glycerol and oil. Debeaufort and Voilley[7] showed that the smaller the lipid globule diameters and that the higher their homogeneous distribution within the methylcellulose ma-

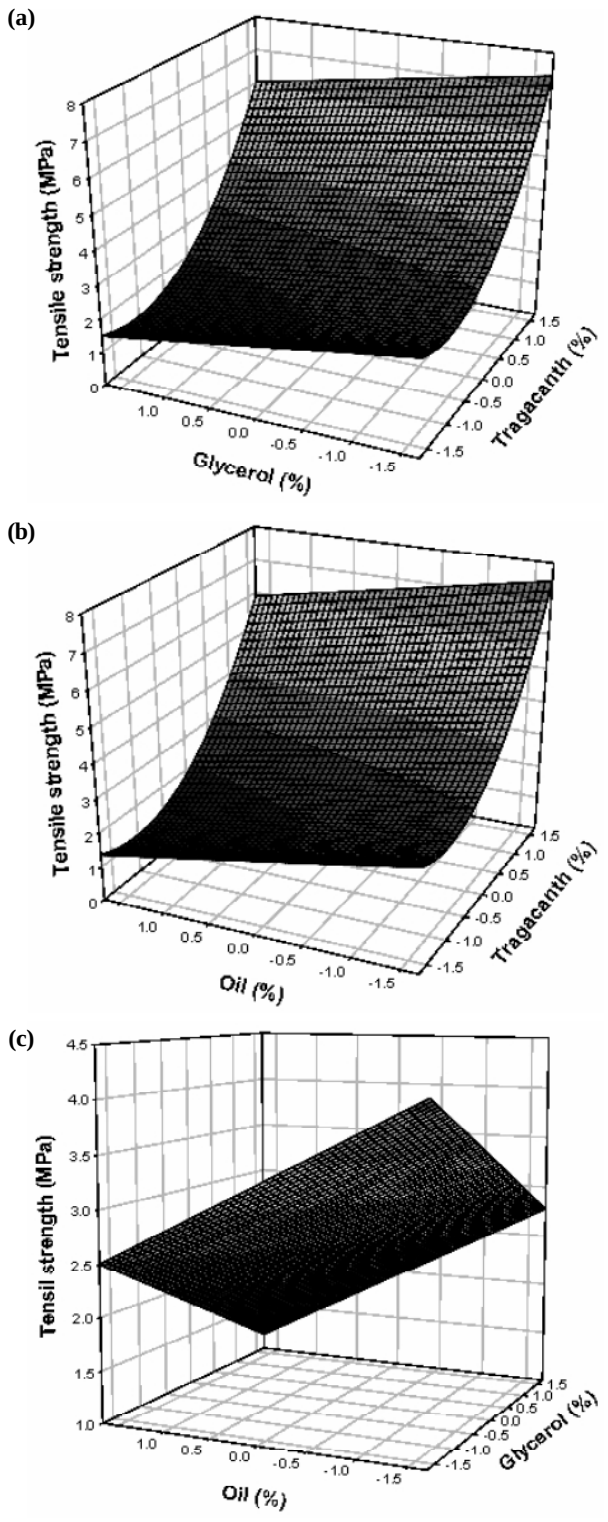

Figure 3 : Tensile strength: (a) effect of glycerol and tragacanth gum concentration; (b) effect of oil and tragacanth gum concentration and (c) effect of oil and glycerol concentration

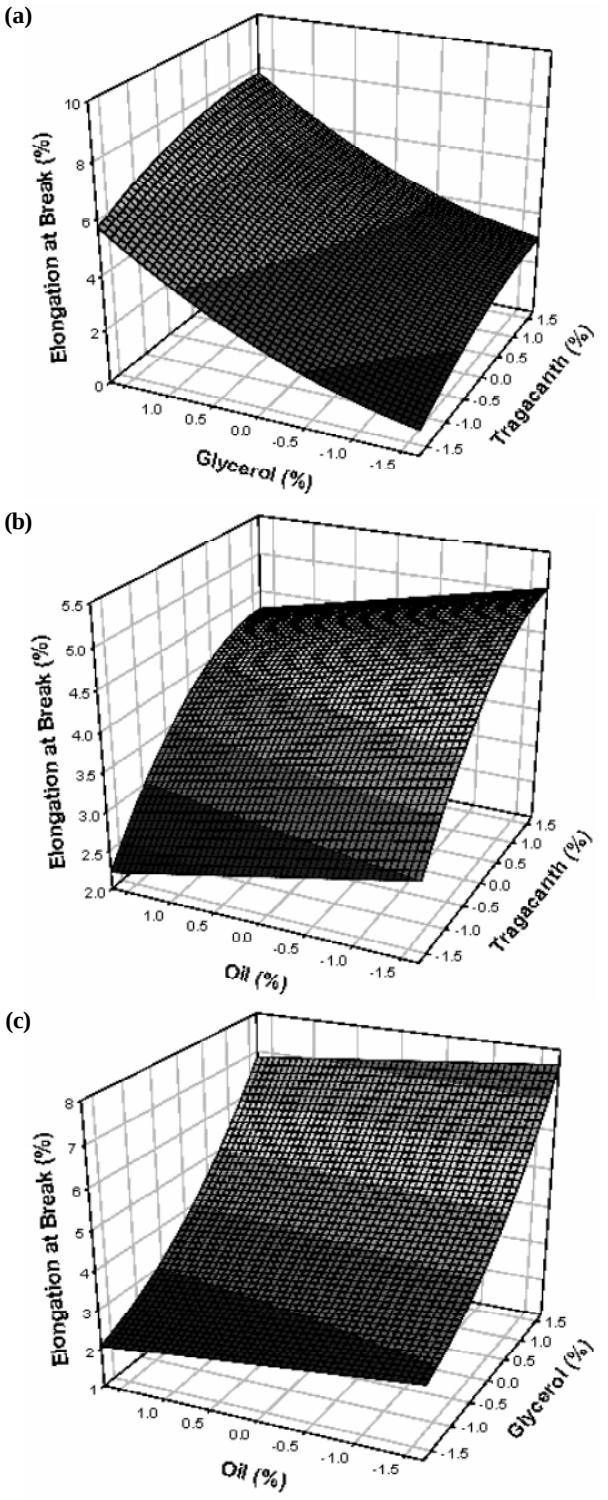

Figure 4 : Elongation at Break: (a) effect of glycerol and tragacanth gum concentration; (b) effect of oil and tragacanth gum concentration and (c) effect of oil and glycerol concentration

trix were, the higher the TS and percentage of elongation were. Hence, decreasing the mechanical strength by increasing the amount of beeswax in tragacanth films may be attributed to the increase in the nonhomogeneity of the film as a result of the formation of larger lipid globules during drying.

High film extensibility, always a desirable characteristic, is indicated by a high EB. The EB of tragacanth-based films was influenced by the linear effects of tragacanth ($P<0.01$), glycerol ($P<0.01$) and oil ($P<0.05$) concentration and the quadratic effects of tragacanth and glycerol (TABLE 2).

Tragacanth films exhibited an increase in EB with increasing tragacanth concentration (Figure 4a and 4b). Increasing the amount of glycerol molecule also increased the EB (Figure 4c). Again, it can be attributed to the replacement of the tragacanth - tragacanth hydrogen bond with the tragacanth – glycerol hydrogen bond, which results in reduction in the direct interaction between polymer chains, and hence results in an increased chain segmental mobility and enhanced extensibility of the film. It could thus be expected the most stretchable films to be formed at the largest concentration of glycerol (67% based on tragacanth dry weight basis). The lowest EB was observed at the lowest concentration of glycerol used (23% based on tragacanth dry weight basis). In addition, as mentioned before, increasing the amount of plasticizer decreases the film resistance.

Opacity

A more complete comprehension of the film structure can be obtained by including the optical properties. When the film is to be used as a superficial coating, opacity values would be of primary importance. Transparent films are required when films are used as coatings to preserve the original appearance of wrapped or coated food. To have a transparent film, the opacity of the film should be low in relative value. Alternately, in order to modify the appearance characteristics, films with different color shades and opacity could be employed. TABLE 2 shows the factors influencing film opacity. The most important factor with respect to film opacity is the oil concentration. The linear effect of oil, the quadratic effect of glycerol and oil and the interaction of tragacanth, glycerol and oil were found to be significant. It could be expected that the most transparent film to be formed is at the lowest oil concentration (23% based on tragacanth gum dry weight basis).

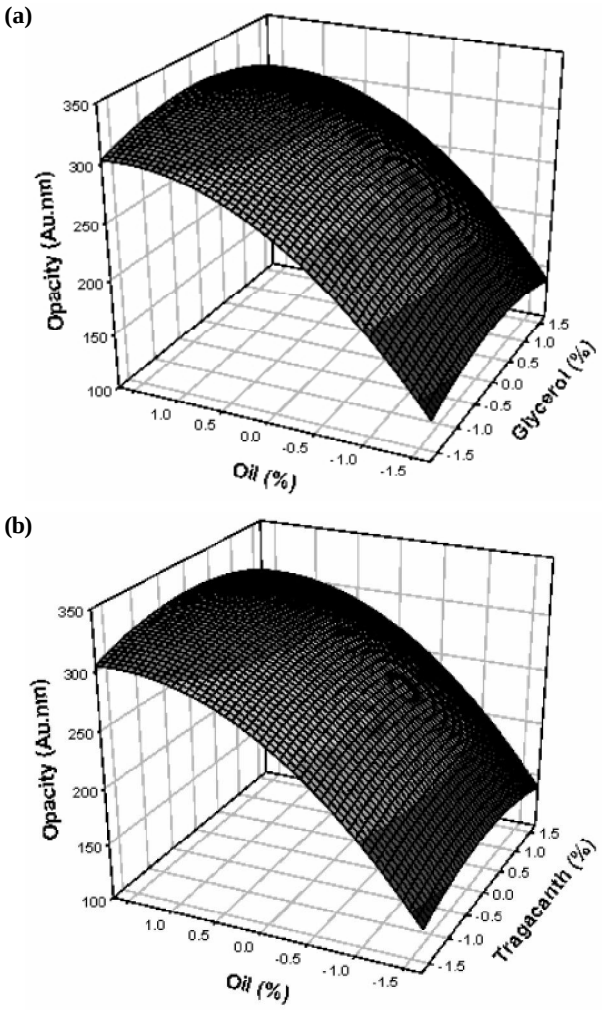

Figure 5 : Opacity: (a) effect of glycerol and tragacanth gum concentration and (b) effect of oil and tragacanth gum concentration

CONCLUSION

Film components had a marked influence on film properties. Tragacanth gum and glycerol concentration had significant effects on WVP and mechanical properties. Oil concentration influenced WVP, mechanical properties and opacity significantly. The use of response surface methodology was effective for the study of complex film-forming conditions and the effect of different variables. To optimize film-forming conditions, other factors such as the use of the film and application techniques should also be considered. The use of traga-

canth gum as a film-forming component has good potential because of its functional role and economic value.

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