



**COMPARATIVE STUDY OF THE MECHANICAL PROPERTIES OF EDIBLE FILMS MADE FROM SINGLE AND BLENDED HYDROPHILIC BIOPOLYMER MATRICES**

**ESTUDIO COMPARATIVO DE LAS PROPIEDADES MECÁNICAS DE PELÍCULAS COMESTIBLES ELABORADAS A PARTIR DE MATRICES POLIMÉRICAS SIMPLES Y COMBINADAS**

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**Abstract**

Sodium alginate,  $\kappa$ -carrageenan, mesquite gum and/or whey protein concentrate were used alone or blended for obtaining edible films, using sorbitol as plasticizer. Film mechanical properties were determined with a TA-XT2 texture analyzer. Films with greater breaking factor, tensile strength, tensile strength at break, and tensile energy at break were obtained when sodium alginate was used alone. Low Young's modulus values were obtained with blends of sodium alginate and  $\kappa$ -carrageenan (with the latter predominating in the blend) and mesquite gum-whey protein concentrate (with the former predominating in the blend). The latter blend exhibited highest elongation. Films containing pure sodium alginate or  $\kappa$ -carrageenan or blended with the other gums (with sodium alginate predominating) could be classified as hard, strong and resistant. Films where mesquite gum or whey protein concentrates were on their or where their blend predominated over that of sodium alginate and/or  $\kappa$ -carrageenan were mostly soft and weak.

**Keywords:** hydrocolloids; edible films; mechanical properties; mesquite gum; sodium alginate;  $\kappa$ -carrageenan; whey protein concentrate.

**Resumen**

Se utilizó alginato de sodio,  $\kappa$ -carragenina, goma de mezquite y/o proteína concentrada de suero lácteo, solos o combinados para obtener películas comestibles, usando sorbitol como plastificante. Se determinaron las propiedades mecánicas de las películas por medio de un analizador de textura TA-TX2. Las películas con mayor factor de ruptura, esfuerzo tensil, esfuerzo tensil a la ruptura y energía tensil a la ruptura, fueron las elaboradas con solo alginato de sodio. Los menores valores del Módulo de Young, se obtuvieron con las mezclas de alginato de sodio y  $\kappa$ -carragenina (cuando esta última predominó en la mezcla) y con las mezclas de goma de mezquite y proteína concentrada de suero lácteo (cuando el primero predominó en la mezcla). La película de esta última mezcla fue también la que exhibió mayor elongación (%). Las películas elaboradas sólo con alginato de sodio o sólo con  $\kappa$ -carragenina o en mezcla con la otra goma (predominando el alginato de sodio), podrían clasificarse como duras, fuertes y resistentes. Las películas de goma de mezquite o de proteína concentrada de suero lácteo o las películas donde la mezcla de éstos predominaba sobre el contenido de alginato de sodio y/o  $\kappa$ -carragenina, fueron en su mayoría suaves y débiles.

**Palabras clave:** hidrocoloides, películas comestibles; goma de mezquite, alginato de sodio,  $\kappa$ -carragenina; proteína concentrada de suero lácteo.

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## 1. Introduction

An edible film is defined as a thin barrier of edible material formed on a food as a coating or placed on or between food components. Edible films can be used to inhibit migration of moisture, oxygen, carbon dioxide, aromas and lipids, among others; carry food ingredients such as antioxidants and antimicrobials; and/or improve mechanical integrity or handling of the food (Krochta and Mulder-Johnston, 1997). Interest in biodegradable edible films has increased in the last years, because they represent an environmentally friendly alternative to synthetic, non-biodegradable packaging films (Anker *et al.*, 1998), and because they can reduce packaging requirements and waste when forming effective coatings on foods by dipping, spraying or panning (Krochta and Mulder-Johnston, 1997).

Hydrocolloid based edible films can be used in applications where control of water vapor migration is not the objective. These films possess good barrier properties to oxygen, carbon dioxide, and lipids. A primary mode of deterioration in many food products involves the oxidation of lipids, vitamins, flavor compounds, or pigments. Enrobing of particularly susceptible foodstuffs such as nutmeats, an oxygen impermeable edible film is one way of extending shelf life and potentially reducing the cost of the external, non-edible packaging material. Impermeability to fats and oils is a desirable functional attribute when enrobed foodstuffs are fried in oil. The film or coating may retard the absorption of oil into the food, thereby yielding improved or nutritional and sensory qualities. In addition the structural integrity of a food product can be reinforced by enrobing the food with an edible coating. This can result in markedly improved durability during processing, storage, and distribution of products such as extruded or molded foods (Kester and Fennema, 1989).

The functional properties of edible films and coatings, and also their mechanical properties, are greatly influenced by the molecular structure and charge of the biopolymers used as structural matrices, their solubility and the overall formulation composition. More often than not, the use of hydrocolloids is for developing edible films and coatings is done on an empirical basis, with the result that they do not comply with the functionality that was expected from them. From a theoretical point of view, the use of hydrocolloids blends might promote favorable synergistic interactions that could result in enhanced mechanical and barrier properties leading to improvements in product quality and often significant savings in manufacturing costs (Williams and Phillips, 1995; Tharanathan, 2003).

The mechanism by which hydrocolloids form films results from a balance between water-gum interactions and intermolecular forces (i.e. hydrogen, hydrophobic and electrostatic bonds; Sánchez *et al.*, 1995). Most water soluble polysaccharides are

known to be high molecular weight polymers with a limited number of repeating monomers composing the polymer, low hydrophobicity and limited flexibility (Garti and Reichman, 1993) such as alginates and carrageenans. These polysaccharides possess the ability to form films via viscosity modification or gelation in the aqueous phase at very low polymer concentrations (Dickinson, 2003). Some other polysaccharides, such as gum Arabic (Dickinson, 2003) and mesquite gum (Vernon-Carter *et al.*, 2000; Loeza-Corte *et al.*, 2007) which are highly water-soluble (up to 50% weight) possess well-known film-forming ability. To obtain films with these polysaccharides, as is the case with many proteins such as whey protein concentrate or isolate (Anker *et al.*, 1998; Pérez-Gago *et al.*, 1999; Sabato *et al.*, 2001), high concentrations of these polymers are required for formation of aggregates or three dimensional matrix structures to take place (Sánchez *et al.*, 1995). Even under these circumstances, more often than not, the incorporation of crosslinking additives is necessary in order to increase the cohesion of the films (Fang *et al.*, 2002) or plasticizers for making the films less brittle (McHugh and Krochta, 1994; Anker *et al.*, 1998, 2000).

The objective of this work was to establish a methodology that would allow to predict the: (a) mechanical properties of edible films made from single and blended hydrophilic biopolymer matrices, describing which biopolymers contribute most to enhance a specific mechanical property, and (b) in which proportion should these biopolymers be blended to optimize a given mechanical property, using surface response methodology. We hope that by doing this we may contribute to set up the stage for designing in a controllable fashion edible films and coatings for specific applications.

## 2. Materials and methods

### 2.1 Materials

The following hydrocolloids were used: Whey protein concentrate (WPC, 81.5% protein, 4.5% moisture, 2.7% ashes, 4.7% lactose, 6.0% fat) provided by Land O'Lakes Inc. (Minnesota); sodium alginate (SA) and  $\kappa$ -carrageenan (KC) supplied by Gardhal, S.A. (México City, México); and mesquite gum (MG) purchased from Natural Products (México D. F., México). Sorbitol (S) was used as plasticizer and was obtained from Sigma-Aldrich Química, S.A. de C.V. (Toluca, State of México, México).

### 2.2 Film formation

Aqueous solutions of 2.5 % (w/w) of the hydrocolloids were prepared according to the experimental design shown in Table 1. Based on

preliminary experiments, this concentration was selected in order to ensure that the hydrocolloids solutions had manageable flow-ability and that they did not undergo liquid phase separation. It is known that phase separation of proteins and polysaccharides can occur at specific pH values and ionic strengths when total macromolecular concentration exceeds 4 % (Tolstoguzov, 1986).

The hydrocolloids SA, KC, WPC and MG were solubilized by separate in distilled water with the help of an Ultra Turrax Polytron (Model PT MR 2100, Kinematica A.G, Switzerland) homogeniser at a speed of 19 000 rpm and 90°C during 30 min. When a specific blend of the hydrocolloids was required, the prerequisite amount of each individual hydrocolloid solution was mixed to obtain it. Afterwards sorbitol was added so that in the final aqueous solution the hydrocolloid to sorbitol ratio was 2.3. Final film forming biopolymer solutions (FFBS) were degassed under vacuum to remove any dissolved air and their pH determined at 40 °C. The FFBS were held at 40 °C and 20 mL of each solution was pipetted onto an 11 cm internal diameter, rimmed, smooth, leveled surface Teflon casting

plate. Films were allowed to dry at room temperature and ambient relative humidity and peeled off after 24 h.

### 2.3. Mechanical properties

Mechanical properties of films were measured with a texture analyzer (TA, XT2, Texture Technologies Corp., Scarsdale, NY). Sample handling for the analyses was carried out according to ASTM standard method D 882-97 (ASTM, 1997). Films were conditioned at ambient temperature and 50 % relative humidity for 48 h prior to mechanical analysis (Aguilar-Mendez *et al.*, 2008; Park *et al.*, 2001). Initial grip separation and crosshead speed were set at 50 mm and 24 mm/min, respectively. The tested film strips were 80 mm long and 25 mm wide. Force and elongation were recorded during extension, and percent elongation (E), breaking factor (BF), tensile strength (TS), tensile strength at break (TSB), Young's modulus (YM), and tensile energy to break (TEB) were calculated (ASTM, 1997). Five replicates were run for each treatment.

Table 1. Proportions of biopolymers in film forming solutions in accordance to experimental design and pH of solutions.

Film forming solution or edible film code	MG	WPC	SA	KC	pH
MG <sub>1.0</sub>	1.000	0.000	0.000	0.000	4.78
MG <sub>0.7</sub> WPC <sub>0.3</sub>	0.665	0.335	0.000	0.000	5.10
MG <sub>0.7</sub> SA <sub>0.3</sub>	0.665	0.000	0.335	0.000	5.40
MG <sub>0.7</sub> KC <sub>0.3</sub>	0.665	0.000	0.000	0.335	5.38
MG <sub>0.3</sub> WPC <sub>0.7</sub>	0.335	0.665	0.000	0.000	6.55
MG <sub>0.3</sub> WPC <sub>0.3</sub> SA <sub>0.3</sub>	0.333	0.333	0.333	0.000	6.43
MG <sub>0.3</sub> WPC <sub>0.3</sub> KC <sub>0.3</sub>	0.333	0.333	0.000	0.333	6.21
MG <sub>0.3</sub> SA <sub>0.7</sub>	0.335	0.000	0.665	0.000	5.66
MG <sub>0.3</sub> SA <sub>0.3</sub> KC <sub>0.3</sub>	0.333	0.000	0.333	0.333	5.61
MG <sub>0.3</sub> KC <sub>0.7</sub>	0.335	0.000	0.000	0.665	6.76
WPC <sub>1.0</sub>	0.000	1.000	0.000	0.000	6.73
WPC <sub>0.7</sub> SA <sub>0.3</sub>	0.000	0.665	0.335	0.000	6.70
WPC <sub>0.7</sub> KC <sub>0.3</sub>	0.000	0.665	0.000	0.335	6.86
WPC <sub>0.3</sub> SA <sub>0.7</sub>	0.000	0.335	0.665	0.000	6.74
WPC <sub>0.3</sub> SA <sub>0.3</sub> KC <sub>0.3</sub>	0.000	0.333	0.333	0.333	6.81
WPC <sub>0.3</sub> KC <sub>0.7</sub>	0.000	0.335	0.000	0.665	6.69
SA <sub>1.0</sub>	0.000	0.000	1.000	0.000	6.63
SA <sub>0.7</sub> KC <sub>0.3</sub>	0.000	0.000	0.665	0.335	6.57
SA <sub>0.3</sub> KC <sub>0.7</sub>	0.000	0.000	0.335	0.665	8.24
KC <sub>1.0</sub>	0.000	0.000	0.000	1.000	8.61
MG <sub>0.25</sub> WPC <sub>0.25</sub> SA <sub>0.25</sub> KC <sub>0.25</sub>	0.250	0.250	0.250	0.250	6.58
MG <sub>0.625</sub> WPC <sub>0.125</sub> SA <sub>0.125</sub> KC <sub>0.125</sub>	0.625	0.125	0.125	0.125	5.90
MG <sub>0.125</sub> WPC <sub>0.625</sub> SA <sub>0.125</sub> KC <sub>0.125</sub>	0.125	0.625	0.125	0.125	6.83
MG <sub>0.125</sub> WPC <sub>0.125</sub> SA <sub>0.625</sub> KC <sub>0.125</sub>	0.125	0.125	0.625	0.125	6.43
MG <sub>0.25</sub> WPC <sub>0.125</sub> SA <sub>0.125</sub> KC <sub>0.625</sub>	0.125	0.125	0.125	0.625	7.16

MG: Mesquite gum; WPC: Whey Protein Concentrate; SA: Sodium Alginate; KC: κ-Carrageenan

2.4. Stress-strain curves.

Depending on the shape of the stress-strain curves films can be classified into one of the following five categories (Briston, 1990): (1) Soft and weak. They exhibit low Young's modulus values, low tensile strength, and moderate elongation (%); (2) Soft and tough. They have moderate tensile strength, low Young's modulus, and high elongation (%); (3) Hard and brittle, they show high tensile strength and Young' modulus and low elongation (%). (4) Hard and tough, High tensile strength, Young's modulus and elongation (%), which combine to produce a large area under the curve; and (5) Hard and strong. Such films have an intermediate character between that of hard and brittle and hard and resistant film. However elongation (%) and tensile strength are higher than that of hard and brittle films.

2.5. Film thickness measurements

Film thickness was measured using a Digimatic Indicator (Mitutoyo, Tokyo, Japan) at five random positions around the film, by slowly reducing the micrometer gap until the first indication of contact. The mechanical properties were calculated using the average thickness for each film replicate.

2.6. Experimental design

A Simplex Lattice experimental design (Hare, 1974) with four components (WPC, SA, KC and MG) was

applied. The response surface methodology of the mean mechanical properties results yielded polynomial models that measure the influence of each hydrocolloid singly and in combination with the rest on the value of each mechanical property. All the treatments were made randomly and the data was analysed using the statistical program Design-Expert 7.0.3 (Stat-Ease Inc. Minneapolis, MN). The probability of the models was tested by variance analysis (test F) and the determination coefficient R<sup>2</sup>. The experimental design, the independent variables and their levels of variation are shown in Table 1.

3. Results and discussion

3.1. Tensile strength (TS)

The TS of the different films have a great variation, from a low value of 1.24 MPa for WPC<sub>1.0</sub> to a high value of 58.05 MPa for SA<sub>1.0</sub>. The experimental data are adjusted significantly through a quadratic model [Eq. (1)] (p<0.05, R<sup>2</sup>=0.8370, Table 2), for what can be used with trust the built response surfaces through the model (Fig. 1), explaining the behavior of TS as a function of film biopolymer composition.

$$\begin{aligned}
 TS = & 10.58(MG) + 2.98(WPC) + 56.02(SA) \\
 & + 30.24(KC) + 6.44(MG \times WPC) \\
 & + 0.17(MG \times SA) + 5.52(MG \times KC) \\
 & - 48.90(WPC \times KC) - 99.64(SA \times KC)
 \end{aligned}
 \tag{1}$$

Table 2. Statistical analysis of the polynomial models applied to films mechanical properties.

Independent variable	TS (MPa)		E(%)		TSB (MPa)		1/YM (1/MPa)		TEB (MJm <sup>-3</sup> )		BF (Nm <sup>-1</sup> )	
	S.E.	P value	S.E.	P value	S.E.	P value	S.E.	P value	S.E.	P value	S.E.	P value
MG	4.67	<0.0001	0.61	0.0012	4.50	<0.0001	9.5E-4	0.0805	2.04	<0.0001	0.12	<0.0001
WPC	4.67	<0.0001	0.61	0.0012	4.50	<0.0001	9.5E-4	0.0805	2.04	<0.0001	0.12	<0.0001
SA	4.67	<0.0001	0.61	0.0012	4.50	<0.0001	1.0E-3	0.0805	2.04	<0.0001	0.12	<0.0001
KC	4.67	<0.0001	0.59	0.0012	4.50	<0.0001	1.0E-3	0.0805	2.04	<0.0001	0.12	<0.0001
MG WPC	23.89	0.790	3.03	0.005	23.02	0.769	-	0.0805	10.45	0.9369	0.63	0.311
MG SA	23.89	0.994	3.03	0.738	23.02	0.994	5.3E-3	0.456	10.45	0.0057	0.63	0.405
MG KC	23.89	0.819	3.03	0.033	23.02	0.665	5.3E-3	0.079	10.45	0.4114	0.63	0.544
WPC SA	23.89	0.054	3.25	0.797	23.02	0.049	5.3E-3	0.098	10.45	0.0005	0.63	0.025
WPC KC	23.89	0.770	3.24	0.477	23.02	0.606	5.3E-3	0.112	10.45	0.7932	-	0.632
SA KC	23.89	0.000	3.24	0.041	23.02	0.0004	5.3E-3	0.045	10.45	0.0001	-	0.013
WPC SA	-	-	26.41	0.135	-	-	-	-	-	-	-	-
KC	-	-	-	-	-	-	-	-	-	-	-	-
MG	-	-	7.88	0.000	-	-	-	-	-	-	-	-
WPC(MG-WPC)	-	-	-	-	-	-	-	-	-	-	-	-
MG	-	-	7.88	0.062	-	-	-	-	-	-	-	-
SA(MG-SA)	-	-	-	-	-	-	-	-	-	-	-	-
R <sup>2</sup>	0.8370		0.8294		0.8538		0.5342		0.8496		0.9010	
P	<0.0001		0.0004		<0.0001		0.0267		<0.0001		<0.0001	

MG: Mesquite gum; WPC: Whey Protein Concentrate; SA: Sodium Alginate; KC: κ-Carrageenan  
 S.E.: Standard Error; P: Probability value (Significance level); n.s: non-significant

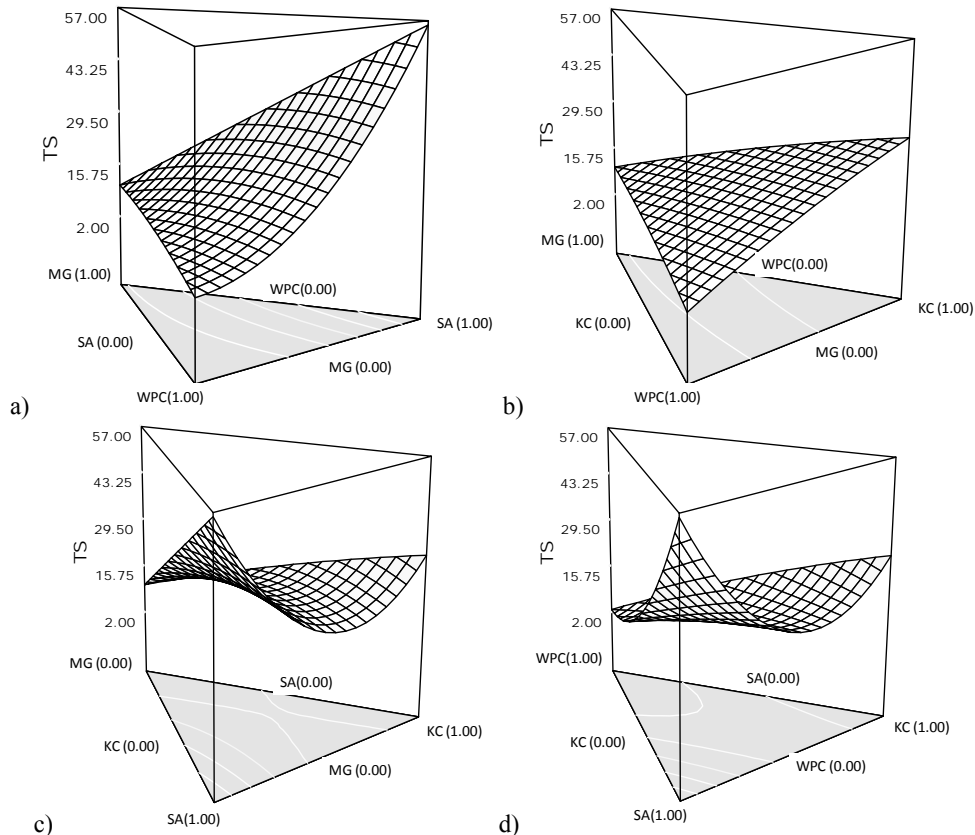


Fig 1. Tensile strength as a function of biopolymer composition.

Eq. (1) indicates that SA, followed by KC, is the individual biopolymer that contributed more markedly to film resistance, however, the interaction of KC with WPC and with SA it contributes to diminish the answer, being this last one, the most important contribution. The influence of SA and KC can be best observed in the response surfaces of TS (Fig. 1a, b, c, d). These results indicate that TS of films was probably related to the “structural” nature of SA and KC, whose gelation is accompanied by a reversible disorder-order transition. The higher TS properties imparted by SA could be probably attributed to the lesser chemical modifications that it suffered, compared to KC under the experimental conditions, developing a more ordered “helical” structure that enhanced the formation of junction zones within the gel (Morris, 1986), that forms under solvent evaporation. However binary combinations of SA and KC, decreased the film resistance (Fig. 1a and b). In binary gel systems, where both biopolymers are “active” (that form part of the molecular network), their mutual incompatibility is likely to produce a phase separated network (a composite), that tends to exhibit abrupt changes in properties (Morris, 1986). If a film was obtained using the four biopolymers, methodology response surface (MRS) pinpoints that the maximum

achievable TS would be 52.18 MPa with a theoretical film composition of 97.7% SA, 1% KC, 1% MG y 0.3% WPC, which illustrates the overwhelming importance of SA to film resistance.

### 3.2. Tensile strength at break (TSB)

The values of TSB ranged from a minimum value of 1.29 MPa for WPC<sub>1,0</sub> film to 59.78 MPa for SA<sub>1,0</sub> film, respectively. As in the case of TS, SA was the biopolymer that contributed most to TSB and another time the interaction between SA and KC is the biggest contribution to the answer, but in a negative way as can be observed in the mathematical model ( $p < 0.05$ ,  $R^2 = 0.85$ , Table 2) for this variable

$$\begin{aligned}
 TSB = & 10.97(MG) + 3.01(WPC) + 57.79(SA) \\
 & + 31.45(KC) + 6.86(MG \times WPC) \\
 & + 0.17(MG \times SA) + 10.12(MG \times KC) \quad (2) \\
 & - 48.25(WPC \times SA) + 12.05(WPC \times KC) \\
 & - 98.83(SA \times KC)
 \end{aligned}$$

The coefficients of Eq. (2) are almost the same as those of Eq. (1), so that from a mathematical point of view it is difficult to differentiate the significance between TS and TSB. TS is the force required to take the film to the point where its elastic limit is arrived at, and if further force is applied permanent

deformation of the film occurs, whereas TSB is the force required to reach the point of maximum extensibility of the film before rupture occurs. These results suggest that once that the elastic limit of the films is marginally surpassed, the external force applied to films exceeds that of biopolymer(s) interactions, that combined with their inherent stiffness, limits their inelastic deformation capacity and leads to an almost immediate film breakage.

### 3.3. Percent elongation (E)

Statistical analysis yield a significant ( $p < 0.05$ ,  $R^2 = 0.8294$ , Table 2) cubic model [Eq. (3)] that could satisfactorily explain the effect of film composition on E

$$\begin{aligned}
 E = & 2.69(MG) + 1.12(WPC) + 5.71(SA) \\
 & + 4.10(KC) + 9.71(MG \times WPC) \\
 & + 1.03(MG \times SA) - 7.07(MG \times KC) \\
 & + 0.85(WPC \times SA) + 2.36(WPC \times KC) \\
 & - 7.18(SA \times KC) + 33.67[MG \times WPC \\
 & (MG - WPC)] + 15.76[MG \times SA(MG - SA)]
 \end{aligned}
 \quad (3)$$

The film that experienced the largest elongation in relation to original length before failure was  $MG_{0.7}WPC_{0.3}$  which exhibited a 6.66 E. Both, MG and WPC, are biopolymers that exhibit very low

viscosity at high concentrations, so that the mechanism by which this biopolymer blend enhances film E is probably due to the formation of an electrostatic complex occurring between the anionic polysaccharide (MG) and the protein (WPC) below its isoelectric point (IEP), which is around pH 5.2 (Anker *et al.*, 1998). Film forming solution from which  $MG_{0.7}WPC_{0.3}$  film was obtained had a pH of 5.1. At this pH, WPC carries a slight net positive charge that leads to the mutual neutralization of chains bearing opposite charges. The neutralization of charges in the anionic MG can reduce the rigidity (i.e. increase in flexibility) of backbone chains due to a decrease in repulsive interactions of like-charged groups (Tolstoguzov, 2003), so that film can achieve a greater E, which is a measure of the extensibility of films (Fang *et al.*, 2002). Interesting enough, the  $MG_{0.3}WPC_{0.7}$  film exhibited a substantially lower value of E (1.014) compared to that of  $MG_{0.7}WPC_{0.3}$  film. Furthermore, values of E of  $MG_{1.0}$  and  $WPC_{1.0}$  films were 2.39 and 0.66, respectively. These data suggest that MG gum is the biopolymer contributing to E, so that only when it is present in a higher proportion in the biopolymer blend than WPC, but that WPC is in a sufficiently high proportion so as to neutralize anionic charges in MG, giving rise to a chemical structure that boosts E.

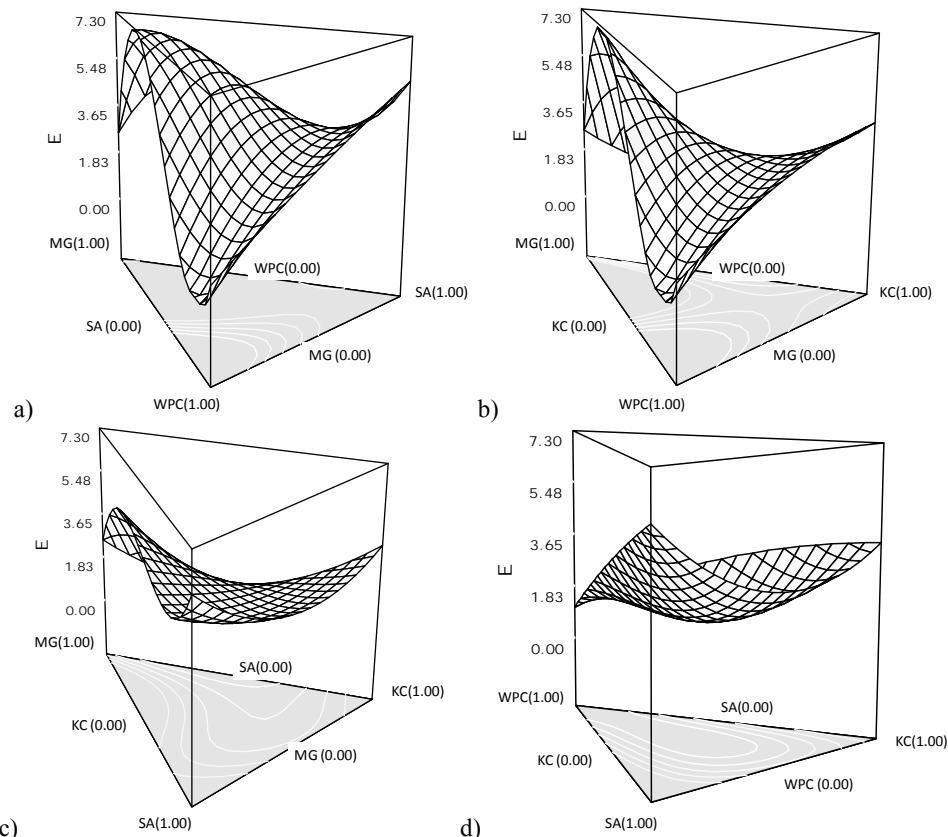


Fig 2. % Elongation as a function of biopolymer composition.

The next film showing highest E was SA<sub>1.0</sub> showing a value of 6.08 for this parameter. SA is a material that can swell largely in water and maintain its three dimensional network structure in the swollen state (Bu *et al.*, 2004). Because of its high molecular weight and molecular rigidity, SA usually forms solutions of unusually high apparent viscosity, even at low concentrations. SA exhibits a practically constant low apparent viscosity value in the pH range between 5 to 11, showing a sharp apparent viscosity increase at pH values below 5, and decreasing apparent viscosity at pH values above 11. SA film forming solution had a pH of 6.63, so that it may be considered that intra- and intermolecular repulsive interactions between like-charged moieties were minimized due to Na<sup>+</sup> counterions shielding COO<sup>-</sup> macro-ion charges, so that a less stiff conformation was adopted by SA in solution. Besides, the addition of sorbitol, decreases the intermolecular forces along SA chains, imparting increased film flexibility (McHugh and Krochta, 1994), resulting in high E values. The effect of the biopolymers on E can be best observed in the surface plots of Fig. 2. A maximum theoretical E value of 4.32% could be achievable using the four biopolymers in a proportion of 0.4 SA: 0.4 MG: 0.1 WPC: 0.1 KC.

### 3.4. Young's modulus (YM)

YM or elastic modulus is the fundamental measure of film stiffness (McHugh and Krochta, 1994), i.e. the higher the value of YM the less elastic and flexible is the film. Parris and Coffin (1997) stated that initial elastic modulus of films was of critical importance in applications where the degree of resistance to stretching is an important factor. The response of YM as a function of biopolymers composition is given in Fig. 3, and the inverse transformation of the experimental data was adjusted significantly ( $p < 0.05$ , Table 2) to the model that is described in the Eq. (4), although with a correlation coefficient ( $R^2 = 0.5342$ ) that it indicates that it is only explained around 50% of the response.

$$\begin{aligned}
 1/YM = & 2.64 \times 10^{-3} (MG) + 4.9 \times 10^{-3} (WPC) \\
 & + 4 \times 10^{-4} (SA) + 1.79 \times 10^{-3} (KC) \\
 & - 4.05 \times 10^{-3} (MG \times SA) \\
 & - 9.84 \times 10^{-3} (MG \times KC) \\
 & - 9.23 \times 10^{-3} (WPC \times SA) \\
 & - 8.83 \times 10^{-3} (WPC \times KC) \\
 & + 0.011 (SA \times KC)
 \end{aligned} \tag{4}$$

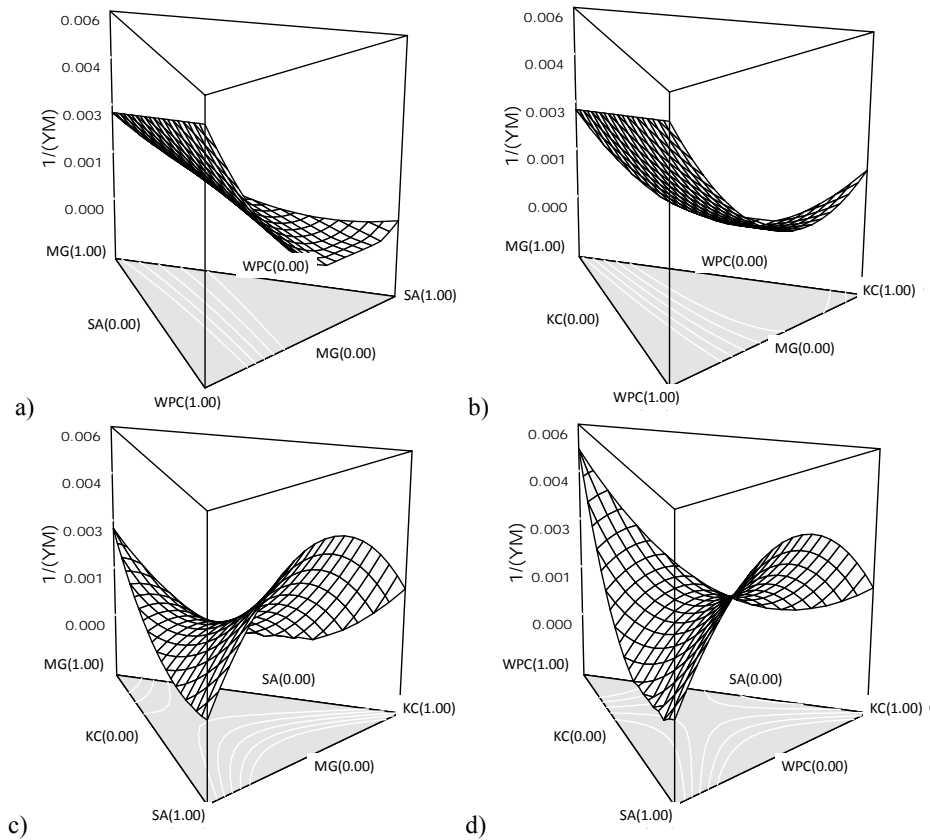


Fig 3. Young modulus as a function of biopolymer composition.

The SA<sub>0.3</sub> KC<sub>0.7</sub> film showed the lowest YM value (135.45 MPa). This suggests that miscibility between the two biopolymers occurred at this specific relative proportion between them, despite that both SA and KC are anionic macroions, and one would expect that like-negative charges would lead to repulsion of neighboring molecules and to incompatibility. However, complete miscibility may occur when biopolymers are charged. This arises from the fact that counterions associated with the charged polymers backbones greatly increase the entropy of mixing, and consequently a great entropy loss would occur if the biopolymers (and their counterions) were confined to a smaller volume, as would be the case of phase separation (Williams and Phillips, 1995). Likewise, hydrophilicity of KC afforded by the presence of sulphate groups is higher than that of SA, so that when KC is predominant in the mixture, larger amount of water is entrapped in the swollen three dimensional hydrated structures providing greater flexibility to film.

The MG<sub>0.7</sub>WPC<sub>0.3</sub> film exhibited the next lowest YM value (155.6 MPa), and as discussed above in % E, this seems to be due to a weak electrostatic interaction between MG and WPC plus the shielding of the MG negatively charged by positively charged WPC, giving as overall result a greater flexibility to the complex formed than either biopolymer on its own. De Kruif and Tuinier (2001) reported that gum Arabic and β-lactoglobulin when

mixed at neutral pH solution is stable and completely mixed, and only when mixed at pH below 4.6 did a complex coacervate formed. Given the structural similarity of MG to gum Arabic (Orozco-Villafuerte *et al.*, 2003; Román- Guerrero *et al.*, 2009) and that β-lactoglobulin is a main component of WPC, it is likely that at pH 5.1, besides polymer-polymer interactions taking place also polymer-solvent interactions are favored so that a good degree of hydration of the complex occurs, further contributing to YM decrease.

The minimum theoretical YM value achievable using the four biopolymers was 400.03 MPa when used in a proportion of 0.46 WPC: 0.33 SA: 0.20 MG: 0.01 KC.

### 3.5. Tensile energy to break (TEB)

TEB was best described by the following quadratic model ( $p < 0.05$ ,  $R^2 = 0.85$ , Table 2):

$$TEB = 1.41(MG) + 0.33(WPC) + 22.71(SA) + 6.71(KC) + 0.84(MG \times WPC) - 32.53(MG \times SA) - 49.36(WPC \times SA) - 8.88(MG \times KC) - 2.78(WPC \times KC) + 57.76(SA \times KC) \quad (5)$$

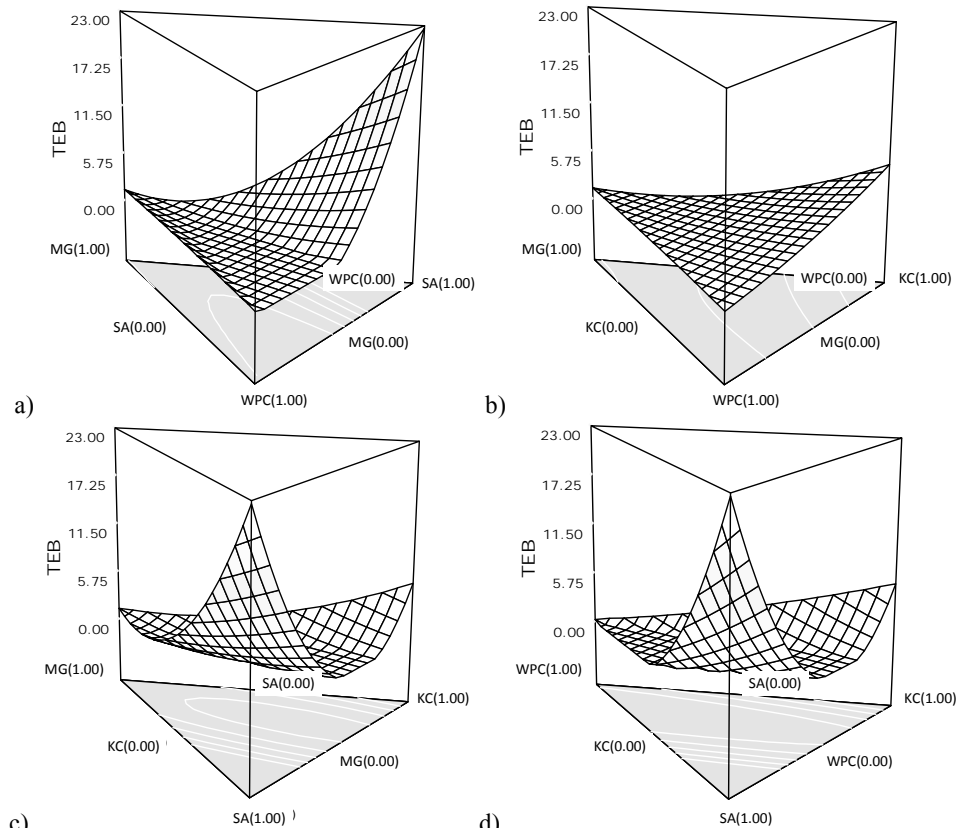


Fig 4. Tensile energy to break as a function of biopolymer composition.



TEB is a measure of the toughness that a film can endure when subjected to heavy abuse. The highest value of TEB was exhibited by SA<sub>1,0</sub> film with a value of 22.66 MJm<sup>-3</sup>, followed by GM<sub>0,3</sub>SA<sub>0,7</sub> film with a value of 4.96 MJm<sup>-3</sup>, while the lowest value was exhibited by WPC<sub>1,0</sub> film with a value of zero. The model indicates that the four biopolymers in their own contributed to TEB, but that all binary interactions between biopolymers decreased TEB. This fact pinpoints that single biopolymers tend to occupy a smaller hydrodynamic volume than biopolymer blends in solution, and that upon solvent evaporation these films tend to show a more compact structure that results in a film smaller unit volume. For films absorbing an equivalent total energy to the point of rupture, those having compact structure will tend to exhibit higher TEB, and be tougher against external heavy abuse. The influence of SA can be best observed in the surface plots of TEB response in Fig. 4.

The maximum theoretical achievable TEB was 3.40 MJm<sup>-3</sup> using a blend of the four biopolymers in proportions of 0.972 SA: 0.018 KG: 0.005 MG: 0.005 WPC, which tends to confirm that the addition of even very slight amounts of other biopolymers to a pure biopolymer tends to increase the hydrodynamic volume of the latter.

### 3.6. Breaking factor (BF)

The mathematical model ( $p < 0.05$ ,  $R^2 = 0.90$ , Table 2) describing the BF behavior was:

$$BF = 0.12(MG) + 0.18(WPC) + 1.77(SA) + 1.36(KC) + 0.66(MG \times WPC) + 0.54(MG \times SA) + 0.39(MG \times KC) - 1.53(WPC \times SA) + 0.31(WPC \times KC) - 1.73(SA \times KC) \quad (6)$$

This equation indicates that both SA and KC are the individual biopolymers that contributed more to the maximum load supported by the film per unit original film width. The influence of SA and KC and of the interactions among the used biopolymers can be best observed in the surface plots of BF response in Fig. 5. Values for BF varied from a low value of 0.155 Nm<sup>-1</sup> for MG<sub>1,0</sub> film, to high values 1.44 for SA<sub>0,3</sub>KC<sub>0,7</sub> film and 1.82 for SA<sub>1,0</sub> film. BF is a parameter that acquires relevance when films are thin (~0.13 mm) for which breaking load may not be proportional to cross-sectional area and whose thickness may be difficult to determine with precision. In this work film thickness averaged 0.0338 mm, and in general terms films thickness was considerably lower when proportion of WPC or MG predominated than when SA or KC predominated in the film blend.

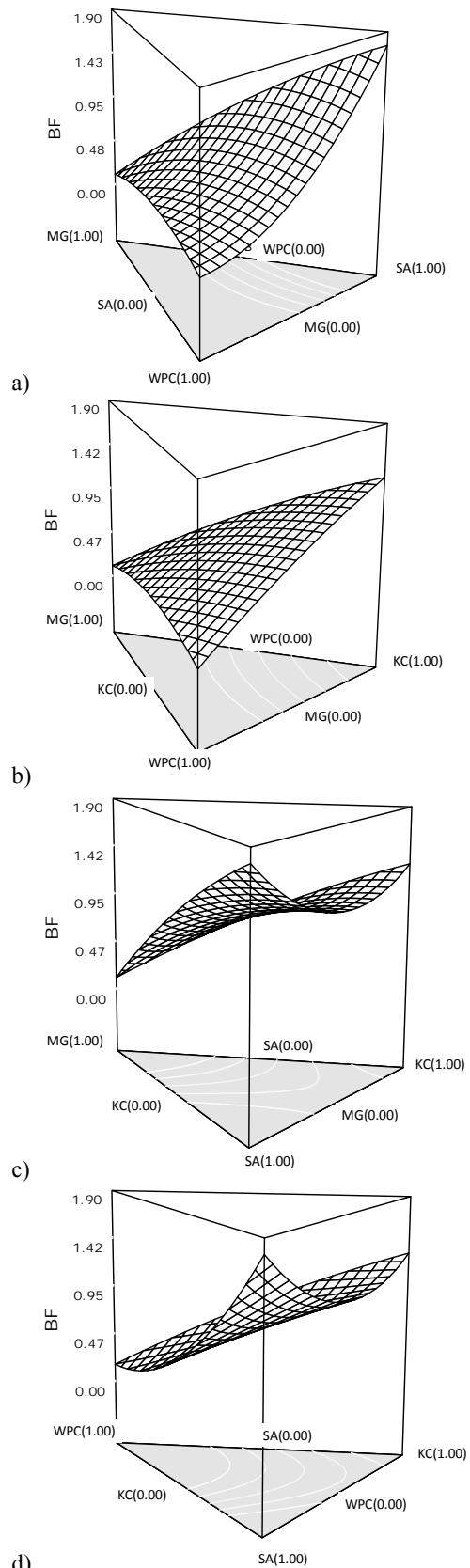


Fig 5. Breaking factor as a function of biopolymer composition.

### 3.7. Classification of films

Edible films were classified into the categories defined by the stress-strain curve shape (Table 3). Hard and tough films could only be obtained when using pure SA or KC. Hard and strong films could only be obtained in binary combinations where SA predominated with MG or KC. Hard and brittle films in general terms were characterized by being made up by mainly binary combinations of either SA or KC with MG or WPC, where presumably SA and/or KC conferred the hardness character and MG and/or WPC the brittleness to the films. Soft and hard films occurred mostly when KC or when the combination of KC and SA predominated in blends containing WPC or MG. Soft and weak films happened when WPC and MG were used alone or combined, and in blends where the proportion of MG and /or WPC predominated over that of SA and /or KC. The findings from these results can be used as a basis for obtaining further data and for design films, which can be used in future food-applications (Aguilar-Mendez et al., 2008).

Table 3. Classification of edible films based on shape of stress/strain curves.

Film category	Edible film code
Soft and weak	MG <sub>1.0</sub>
	MG <sub>0.7</sub> WPC <sub>0.3</sub>
	MG <sub>0.3</sub> WPC <sub>0.3</sub> SA <sub>0.3</sub>
	WPC <sub>1.0</sub>
	WPC <sub>0.7</sub> SA <sub>0.3</sub>
	WPC <sub>0.3</sub> SA <sub>0.3</sub> KC <sub>0.3</sub>
	MG <sub>0.625</sub> WPC <sub>0.125</sub> SA <sub>0.125</sub> KC <sub>0.125</sub>
Soft and hard	MG <sub>0.125</sub> WPC <sub>0.625</sub> SA <sub>0.125</sub> KC <sub>0.125</sub>
	WPC <sub>0.7</sub> KC <sub>0.3</sub>
	WPC <sub>0.3</sub> KC <sub>0.7</sub>
	SA <sub>0.3</sub> KC <sub>0.7</sub>
	MG <sub>0.25</sub> WPC <sub>0.25</sub> SA <sub>0.25</sub> KC <sub>0.25</sub>
	MG <sub>0.125</sub> WPC <sub>0.125</sub> SA <sub>0.625</sub> KC <sub>0.125</sub>
	MG <sub>0.25</sub> WPC <sub>0.125</sub> SA <sub>0.125</sub> KC <sub>0.625</sub>
Hard and brittle	MG <sub>0.7</sub> SA <sub>0.3</sub>
	MG <sub>0.7</sub> KC <sub>0.3</sub>
	MG <sub>0.3</sub> WPC <sub>0.7</sub>
	MG <sub>0.3</sub> WPC <sub>0.3</sub> KC <sub>0.3</sub>
	MG <sub>0.3</sub> SA <sub>0.3</sub> KC <sub>0.3</sub>
	MG <sub>0.3</sub> KC <sub>0.7</sub>
	WPC <sub>0.3</sub> SA <sub>0.7</sub>
Hard and resistant	SA <sub>1.0</sub>
	KC <sub>1.0</sub>
Hard and strong	MG <sub>0.3</sub> SA <sub>0.7</sub>
	SA <sub>0.7</sub> KC <sub>0.3</sub>

MG: Mesquite gum; WPC: Whey Protein Concentrate; SA: Sodium Alginate; KC: κ-Carrageenan

The sub index of each component in the mixture indicates the proportion in the blend

### Conclusions

In this work a successful methodology for predicting the mechanical properties of films obtained from combining biopolymers, and the proportions in which they should be combined for achieving the expected mechanical properties for a specific application was established. Thus, it was found in general terms that in order to obtain hard, resistant, strong films it was best to formulate them with high viscosity sodium alginate or kappa carrageenan biopolymer as the sole component, or in blends where sodium alginate predominated. On the other hand for obtaining soft, weak, brittle films it was best to use low viscosity mesquite gum or whey protein concentrate as the sole component or in blends where the combination of these two biopolymers predominated over that of sodium alginate and/or kappa carrageenan. In the last instance, final selection of biopolymers making up the formulation must be based on the functional properties expected from films for potencial applications.

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### References

- Aguilar-Mendez, M. A., San Martin-Martinez, E., Tomas, S. A., Cruz-Orea, A., Jaime-Fonseca, M. R., (2008) Gelatine-starch films: physicochemical properties and their application in extending the postharvest shelf life of avocado (*Persea americana*), *Journal of the Science of Food and Agriculture* 88, 185-193.
- Anker, M., Stading, M. and Hermansson, A. M. (1998). Mechanical properties, water vapour permeability, and moisture contents of β-lactoglobulin and whey protein films using multivariate analysis. *Journal of Agricultural and Food Chemistry* 46, 1820-1829.
- Anker, M., Stading, M. and Hermansson, A.M. (2000). Relationship between the microstructure and the mechanical and barrier properties of whey protein films. *Journal of Agricultural and Food Chemistry* 48, 3806-3816.
- ASTM (1997). In: *Annual book of American standard testing methods*, ASTM, Philadelphia, Pp. 165-173.
- Briston, J.H. (1990). *Plastic films*. Pp. 93-112. Longman Scientific & Technical, England.
- Bu, H., Kjøniksen, A.L., Knudsen, K.D. and Nyström, B. (2004). Rheological and

- structural properties of aqueous alginate during gelation via de Ugi multicomponent reaction. *Biomacromolecules* 5, 1470-1479.
- De Kruif, C.G. and Tuinier, R. (2001). Polysaccharide protein interactions. *Food Hydrocolloids* 15, 555-563.
- Dickinson, E. (2003). Hydrocolloids at interfaces and the influence on the properties of dispersed systems. *Food Hydrocolloids* 17, 25-39.
- Fang, Y., Tung, M.A., Britt, I.J., Yada, S. and Dalgleish, D.G. (2002). Tensile and barrier properties of edible films made from whey proteins. *Journal of Food Science* 67,188-193.
- Garti, N. and Reichman, D. (1993). Hydrocolloids as food emulsifiers and stabilizers. *Food Structure* 12, 411-426.
- Hare, L.B. (1974). Mixture designs applied to food formulation. *Food Technology* 28(3), 50-62.
- Kester, J.J. and Fennema, O. (1989). Edible films and coatings: A review. *Journal of Food Science* 40, 47-59.
- Krochta, J.M. and Mulder-Johnston, C. (1997). Edible and biodegradable polymer films: Challenges and opportunities. *Food Technology* 51(2), 61-74.
- Loeza-Corte, J.M., Verde-Calvo, J.R., Cruz-Sosa, F., Vernon-Carter, E.J. and Huerta-Ochoa. (2007). S. L-arabinose production by hydrolysis of mesquite gum by a crude extract with  $\alpha$ -L-arabinofuranosidase activity from *Aspergillus niger*. *Revista Mexicana de Ingeniería Química* 6, 259-265.
- McHugh, T.H. and Krochta, J.M. (1994). Sorbitol- vs-glycerol-plasticized whey protein edible films: Integrated oxygen permeability and tensile property evaluation. *Journal of Agricultural and Food Chemistry* 42 (2), 841-845.
- Morris, V.J. (1986). Multicomponent gels. In: *Gums and stabilisers for the food industry 3* (G.O. Phillips, D.J. Wedlock and P.A. Williams, eds), Pp. 87-100. Elsevier Applied Science Publishers, New York.
- Orozco-Villafuerte, J., Cruz-Sosa, F., Ponce-Alquicira, E. and Vernon-Carter, E.J. (2003). Mesquite gum: Fractionation and characterization of the gum exuded from *Prosopis laevigata* obtained from plant tissue culture from wild trees. *Carbohydrate Polymers* 54, 327-333.
- Park, H.J., Rhee, C.O., Bae, D.H. and Hettiarachchy, N.S. (2001). Mechanical and water-vapor permeability of soy-protein films affected by calcium salts and glucono- $\delta$ -lactone. *Journal of Agricultural and Food Chemistry* 59, 2308-2312.
- Parris, N., Coffin, D.R. (1997). Composition factors affecting the water vapour permeability and tensile properties of hydrophilic zein films. *Journal of Agricultural and Food Chemistry* 45, 1568-1599.
- Pérez-Gago, M.B., Nadaud, P. and Krochta, J.M. (1999). Water vapor permeability, solubility, and tensile properties of heat denatured versus native whey protein films. *Journal of Food Science* 64, 1034-1037.
- Román-Guerrero, A., Orozco-Villafuerte, J., Pérez-Orozco, J.P., Cruz-Sosa, F., Jiménez-Alvarado, R. and Vernon-Carter, E.J. (2009). Application and evaluation of mesquite gum and its fractions as interfacial film formers and emulsifiers of orange peel oil. *Food Hydrocolloids* 23, 708-713.
- Sábato, S.F., Outtara, B., Yu, H., D'Apramo, G., Le Tien, C., Mateescu, M.A. and Lacroix, M. (2001). Mechanical and barrier properties of cross-linked soy and whey protein based films. *Journal of Agricultural and Food Chemistry* 49, 1397-1403.
- Sánchez, V.E., Bartholomai, G.B. and Pilosof, A.M.R. (1995). Rheological properties of food gums as related to their water binding capacity and to soy protein interaction. *Lebensmittel Wissenschaft und Technology* 28, 380-385.
- Tolstoguzov, V. (1986). Functional properties of protein-polysaccharides mixtures. In: *Functional properties of food macromolecules*, (J.R. Mitchell and D.A. Ledward, eds), Pp. 385-415. Elsevier, London.
- Tolstoguzov, V. (2003). Some thermodynamic considerations in food formulation. *Food Hydrocolloids* 17, 1-23.
- Tharanathan, R. N. (2003). Biodegradable films and composite coatings: past, present and future. *Trends Food Technology*, 14, 71-78.
- Vernon-Carter, E.J., Beristain, C.I. and Pedroza-Islas, R. (2000). Mesquite gum (*Prosopis* gum). In: *Novel macromolecules in food systems*, (G. Doxastakis and V. Kiosseoglou, eds), Pp. 217-238. Elsevier, Amsterdam.
- Williams, P.A. and Phillips, G.O. (1995). Interactions in mixed polysaccharide systems. In: *Food polysaccharides and their applications* (A.M. Stephen, ed), Pp. 463-500. Marcel Dekker, New York.