Chitosan coating surface and permeation properties as affected by plasticizer, surfactant and polymer concentration-application to vegetables

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Abstract. *Edible coatings can act as moisture, lipid, and gas barriers and can improve the textural properties of foods or serve as carriers of functional agents such as colors, flavors, antioxidants, nutrients and antimicrobials. The objectives of this work were to study the potentialities of chitosan (obtained from lobster of the cuban coasts) coating to extend the shelf life of fruits. To do so, the surface properties of tomato and carrot were characterized and the wettability properties of chitosan edible coatings were studied. In such coatings, parameters such as chitosan concentration and effects of type and concentration of hydrophilic plasticizer or surfactant on wettability of chitosan coatings were evaluated, as well as the respective barriers properties to gases.*

It was possible to determine the values of the polar and dispersive components of the superficial tension, that are 3.32 and 25.24 mN/m, respectively, for the tomato and 0.48 and 25.62 mN/m, respectively, for the carrot; being the superficial tensions of the tomato and carrot the sum of the two components (28.55 and 26.40 mN/m) respectively. Both are therefore, low energy surfaces.

The results of wettability determinations allowed to adjust one factorial model that suggests an increase of the spreading coefficient as the chitosan concentration decreases and Tween concentration increases. The best values of wettability correspond to the following coating composition: 1.5 % (w/v) of chitosan and 0.1 % (w/w) of Tween 80.

A correlation has been found between the water vapor, oxygen and carbon dioxide permeability coefficients, and glycerol concentration (while keeping Tween and chitosan concentrations constant). In the absence of glycerol, a decreased permeability to the gases was observed.
An increase of the chitosan concentration decreases a lightness and increase yellow color of coatings. The chitosan coatings with glycerol showed high values lightness and were more transparent and yellowier than those without glycerol.

Keywords. Chitosan, edible coating, surface properties, gas permeability.

Introduction

Edible films have potential in a number of different areas, they can coat food surfaces, separate different components, or act as casings, pouches or wraps. They can preserve product quality by forming oxygen, aroma, oil or moisture barriers; carrying functional ingredients, such as antioxidants or antimicrobials; and improving appearance, structure and handling.

The objectives of this work were to determine the effects of type and concentration of hydrophilic plasticizer (glycerol, sorbitol and polyethylene glycol), Tween 80 as surfactant and polymer concentration on the wettability of Cuban chitosan based coatings in view of their application on vegetables (tomato and carrot) and to develop a model allowing to optimize coating composition. Furthermore, the barrier, and optical properties of chitosan coatings, showing the best wettability, were characterized.

Materials and Methods

Materials.

The materials used to prepare the edible coating solutions were: chitosan (obtained in the Pharmaceutical Laboratories Mario Muñoz, Cuba) with a degree of deacetylation of 90 % approximately, glycerol 87% (Panreac, Spain), sorbitol 97% or polyethylene glycol MW 200 (Acros Organics, Belgium) as plasticizers, Tween 80 (Acros Organics, Belgium) as surfactant, and lactic acid (Merck, Germany).

Coating and film preparation.

The coating solutions were prepared dissolving chitosan (1.0, 1.5 or 2.0 % w/v) in a 1% (v/v) lactic acid solution with agitation using a magnetic stirrer during 2 hours at room temperature (20 ^{o}C). The plasticizers were added in concentrations between 0.25 and 0.50 mL plasticizer/g of chitosan. Tween 80 was added as a surfactant with concentrations between 0.02 and 0.10 % (w/w). The chitosan films were prepared pouring a constant amount (28 mL) of chitosan solution onto an 8 cm diameter glass plate in order to maintain the film thickness. The films were dried an oven at 35 ° C. Dried films were peeled from the plate and cut in circles about 80 mm of diameter, for property testing. All chitosan films for permeability test were conditioned in desiccators, and maintained at 20 °C and 25 % RH.

Analysis

Wettability

Both contact angle (θ) and surface tension (γ_L) were determined with a face contact anglemeter (OCA 20, Dataphysics, Germany). The surface tension of the coating solution was measured by the pendent drop method and Laplace-Young approximation (Song & Springer. 1996). The contact angle was measured by the sessile drop method. Ten replicates of contact angle and surface tension measurements were analyzed at 20 (± 1) ºC. The estimation of the critical surface tension (γ_c), of the vegetables surface was obtained by extrapolation from the Zisman

plot (Zisman, 1964), which was built using water, formamide and bromonaphthalene (Merck, Germany) as reference liquids.

Thickness

The film thickness was measured with a hand-held digital micrometer (Mitutoyo, Japan) having a sensitivity of 0.001 mm. Ten thickness measurements were taken on each testing sample in different points and the mean values were used in permeability calculations.

Gases Permeability

Oxygen permeability (OP) and Carbon dioxide permeability (CO_2 P) were determined based on the ASTM (2002) method. A chitosan film was sealed between two chambers; having each one two channels. In the lower chamber O_2 or CO_2 are supplied at a controlled flow rate to keep its pressure constant in that compartment. The other chamber was purged by a stream of nitrogen, also at a controlled flow. This nitrogen acted as a carrier for the O_2 or CO_2 and the flow leaving this chamber was connected to an O_2 sensor. The flows of the two chambers were connected to a manometer to ensure the equality of pressures between both compartments.As the O_2 or CO_2 were carried continuously by nitrogen flow, it was considered that O_2 or CO_2 partial pressure in the upper compartments is null, therefore ΔP is equal a 1 atm. Carbon dioxide permeability (CO_2 P) was determined measure CO_2 concentration in a gas chromatograph (Chrompack 9001, Middelburg, Netherlands) with a column Porapak Q 80/ 100 mesh- 2 m x 1/8 "x 2 mm SS.

Water vapor permeability (WVP) of the films was determined gravimetrically based on ASTM E96-92 method (McHugh, Avena-Bustillos & Krochta, 1993; Guillard, Broyart, Bonazzi, Guilbert, & Gontard, 2003). The test film was sealed on the top of a permeation cell containing distilled water (100 % RH; $2,337 \times 10^3$ Pa vapor pressure at 20 °C), placed in a desiccator which was maintained at 20 °C and 0 % RH (0 Pa water vapor pressure) with silica gel. The water transferred through the film and adsorbed by the desiccant was determined from weight loss of the permeation cell. The cups were weighed at intervals of 2 hours during 10 hours. Steady-state and uniform water pressure conditions were assumed by keeping the air circulation constant outside the test cup by using a fan inside the desiccator (McHugh, Avena-Bustillos & Krochta, 1993). The slope of weight loss versus time was obtained by linear regression. The measured (WVP) of the films was determined as follows:

WVP = (WVTR. L) / ΔP

where *WVTR* in the measured water vapor transmission rate ($g /m^{-2}.s^{-1}$) through a film, *L* is the mean film thickness (m), and *ΔP* is the partial water vapor pressure difference (Pa) across the two sides of the film. For each type of film, *WVP* measurements were replicated three times.

Optical Properties

The color of chitosan films was determined with a Minolta colorimeter (Cr 300; Minolta, Japan). A white standard color plate (*Y*=93.5, *x*=0.3114, *y*=0.3190) for the instruments' calibration was used as a background for color measurements of the coated films, and the CIE *L* a*b** values of each films were evaluated by reflectance measurement. The opacity of a material is an

indication of how much light passes through it. The higher the opacity, the lower the amount of light that can pass through the material. Generally, opacity is calculated from reflectance measurements. The opacity of the samples was determined according to Hunter lab method, as the relationship between the opacity of each sample on the black standard (Y_b) and the opacity of each sample on the white standard (Y_w).

Statistical analysis

All data were analyzed and compared by using ANOVA and Duncan Multiples range (α = 0.05) to determine the significance of differences, on Statgraphics Plus version 5.1 software (Statistical Graphics Corp. 2000. USA).

Results and Discussion

Surface tension and critical surface tension of tomato and carrot skin

The Zisman method is based on that a plot of the cosine of the contact angle vs. the superficial tension (liquid-vapor) on a given solid is generally a straight line and is applicable only for systems with a surface tension below 100 nN/m (low energy surfaces) (Zisman, 1964; Owen & Wendt, 1969). It is therefore necessary to determine the surface energy of tomato and carrot in order to verify the applicability of that method.

When considering the attractive forces at a given interface, it has been suggested that the interfacial tension liquid vapor is the sum of contributions from the different intermolecular forces, (Owens & Wendt, 1969; Kaelble, 1970 & Rabel, 1971). For a pure liquid, if polar and dispersive interactions are known, and if the contact angle between that liquid and a solid is obtained, the interaction can be described by the adhesion coefficient (work of adhesion per unit area), given by:

$$W_a = W_a^d + W_a^p \Leftrightarrow W_a = 2 \cdot \left(\sqrt{\gamma_s^d \gamma_l^d} + \sqrt{\gamma_s^p \gamma_l^p} \right) = \gamma_1 \left(1 + \cos \theta \right) \quad \text{Equation 1}$$

where $\gamma_1 \left(1 + \cos\theta \right)$ can be found from:

$$\frac{1 + \cos \theta}{2} \cdot \frac{\gamma_L}{\sqrt{\gamma_L^d}} = \sqrt{\gamma_S^p} \cdot \sqrt{\frac{\gamma_L^p}{\gamma_L^d}} + \sqrt{\gamma_S^d} \quad \text{Equation 2}$$

It is also possible to define the cohesion coefficient (work of cohesion for unit area):

$$W_c = 2 \gamma_{lv} \quad \text{Equation 3}$$

and the spreading coefficient:

$$W_s = W_a - W_c = \gamma_{sv} - \gamma_{lv} - \gamma_{sl} \quad \text{Equation 4}$$

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The contact angle determinations of at least three pure compounds on the surface of tomato or carrot combined with the values of Table 1 will allow the calculation of both the independent variable, $\left(\sqrt{\dfrac{\gamma_L^p}{\gamma_L^d}}\right)$, and the dependent variable, $\left(\dfrac{1+\cos\theta}{2}\cdot\dfrac{\gamma_L}{\sqrt{\gamma_L^d}}\right)$, from equation 2.

Table 1. Surface tension from the tested liquids and their respective components, at 20 °C.

Compound	γ_L (mN/m)	γ^d (mN/m)	γ^p (mN/m)
Water	72.10	19.90	52.20
Bromonaphthalene	44.40	44.40	0.00
Formamide	56.90	23.50	33.40

Adapted from Busscher *et al*., 1984

The adjustment of the experimental data to a plot produces the following equations for tomato (Eq.5) and carrot (Eq.6).

$$\frac{1+\cos\theta}{2}\cdot\frac{\gamma_L}{\sqrt{\gamma_L^d}}=1.8490\sqrt{\frac{\gamma_L^p}{\gamma_L^d}}+5.0231\,;\quad r^2=0.9995\quad\text{Equation 5}$$

$$\frac{1+\cos\theta}{2}\cdot\frac{\gamma_L}{\sqrt{\gamma_L^d}}=0.6672\sqrt{\frac{\gamma_L^p}{\gamma_L^d}}+5.095\,;\quad r^2=0,9997\quad\text{Equation 6}$$

Equations 5 and 6 were used to calculate the values of the polar and dispersive components of the surface tension, which were determined to be 3.32 and 25.24 mN/m. respectively for the tomato and 0.48 and 25.62 mN/m, respectively for the carrot, being the surface tensions of the tomato and carrot the sum of the two components (28.56 and 26.10 mN/m. respectively). These results clearly show that both tomato and carrot are low energy surfaces and that their surface interacts with liquids primarily through dispersion forces, as reported by Rulon & Robert (1993).

The Zisman method can therefore be applied to estimate the critical surface tension. This empirical quantity is defined as the value the superficial tension (liquid / vapor) at the intercept of the Zisman plot for cos θ = 1.It should be noted that critical surface tension values had been reported to be lower than the surface tension values of the same tested surfaces (Dann. 1970). In the present work it has been found that the critical surface tension has values of 17.8 and 24.5 mN/m, which are well below the respective surface tension values. It is noteworthy to emphasize the differences between the values obtained for both vegetables. Such differences are presumably due to the differences in texture and composition between the skin of tomato,

that is covered by a wax layer and is very uniform, and that of the carrot that is a root with a ligneous, rough texture and irregular surface.

Wettability of the coating solutions

The Figure 1 showed that the spreading coefficient (W_s) decreased as the chitosan concentration increased for the vegetables studied, independently of plasticizer concentration, and a statistically significant difference has been found ($p<0.05$) between the different chitosan coating ($p<0.05$). Statistically significant differences ($p<0.05$) can also be observed between the values of W_a and W_s for tomato and carrot, probably due to the type of surface interaction with the liquids that happens mainly through the dispersion forces and explains the fact that the drops of polar liquids are not absorbed in a short period of time (Rulon & Robert. 1993).

The influence of plasticizers in the surface properties of the chitosan coating was studied and a tendency can be observed that the work of adhesion and the spreading coefficient decreased and cohesion coefficient increased as the plasticizer concentration increased, such differences were statistically significant. The best results, in term of wettability, were obtained with glycerol, polyethyleneglycol and sorbitol for this order (Table 2 and 3). Also in this case remarkable differences were found between the behavior of tomato and that of the carrot ($p<0.05$), possibly due to the factors previously mentioned in relation to the texture and the surface properties of those foods.
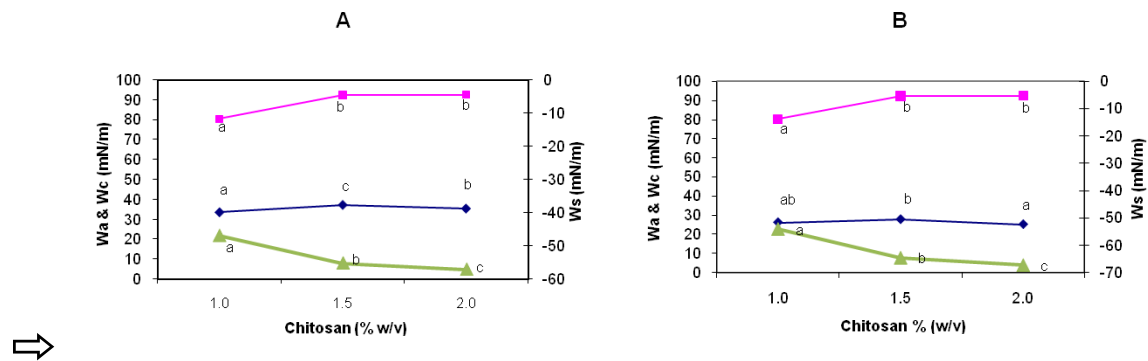

Figure 1: Adhesion (♦), cohesion (■) and spreading (▲) coefficient versus chitosan concentration in tomato (A) and carrot (B).

Table 2: Effect of chitosan and plasticizer concentration on Ws for the different chitosan coating (mean values) in tomato.

Plasticizer (mL/g chitosan)		Chitosan		
		Ws (mN/m) Tomato		
		1.0	1.5	2.0
without		-46.80 ± 1.65 a	-55.17 ± 1.52 ij	-57.06 ± 1.23 jk
glycerol	0.25	-49.15 ± 0.72 b	-49.07 ± .80 bc	-50.34 ± 0.67 cde
	0.37	-49.38 ± 0.99 bc	-49.08 ± 0.86 b	-51.37 ± 1.16 de
	0.50	-50.55 ± 0.88 cde	-50.08 ± 1.21 bcd	-54.06 ± 0.94 hi
Sorbitol	0.25	-51.69 ± 0.57 e	-51.14 ± 0.52 de	-57.06 ± 1.08 jk
	0.37	-52.78 ± 0.89 efgh	-55.84 ± 0.83 j	- 57.35 ± 0.99 k
	0.50	-52.53 ± 0.87 efg	-57.68 ± 1.10 k	-59.12 ± 0.87 l
polyethylene glycol	0.25	-51.38 ± 0.94 de	-52.44 ± 0.95 efg	-51.79 ± 1.11 ef
	0.37	-53.64 ± 0.94 gh	-53.11 ± 0.89 fgh	-52.91 ± 0.97 efgh
	0.50	-53.75 ± 0.98 gh	-53.31 ± 1.19 gh	-53.21 ± 1.32 fgh

*Different letters in the same column correspond to statistically different samples for 95% level of confidence.

Table 3: Effect of chitosan and plasticizer concentration on Ws for the different chitosan coating (mean values) in carrot.

Plasticizer (mL/g chitosan)		Chitosan		
		Ws (mN/m) Tomato		
		1.0	1.5	2.0
without		-54.10 ± 3.19 a	-64.52 ± 3.61 g	- 67.22 ± 3.72 h
glycerol	0.25	-56.46 ± 1.94abc	-55.97 ± 1.21 ab	-56.70 ± 1.27bcd
	0.37	-57.39 ± 2.33 bcde	-56.20 ± 1.77 ab	-57.10 ± 1.15bcde
	0.50	-57.73 ± 1.48bcde	-56.94 ± 1.77 bcde	-61.49 ± 1.01 f
Sorbitol	0.25	-56.92± 1.02 bcde	-57.24± 1.79 bcde	-62.79± 1.46 fg
	0.37	-57.23± 1.13 bcde	-58.87± 1.92 cde	-63.59± 1.67 fg
	0.50	-57.69± 1.27 bcde	-59.28± 1.68 e	-64.78± 1.81g
polyethylene glycol	0.25	-56.15 ± 1.01ab	-55.88 ± 1.74 ab	-55.71 ± 1.34 ab
	0.37	-56.66 ± 0.87 bcd	-55.40 ± 1.32 ab	-57.64 ± 1.24 bcde
	0.50	-56.86 ± 0.78 bcd	-57.25 ± 2.15 bcde	-59.06 ± 1.00 de

*Different letters in the same column correspond to statistically different samples for 95% level of confidence.

The influence of chitosan and Tween 80 concentration on the adhesion, cohesion and spreading coefficient were described by a polynomial model (Table 4) for both vegetables and an equation relating each dependent variable with those independent variables was obtained. The models suggested that Chitosan concentration is the variable of higher influence in the values of $\underline{W_a}$, $\underline{W_c}$ and $\underline{W_s}$, reaching its higher effect when the concentration is 1.5 % (w/v); in term Tween 80 (in the concentration studied) shows the lowest influence. The wettability of the solution was therefore optimized by minimizing / maximizing the values of $\underline{W_a}$, $\underline{W_c}$ and $\underline{W_s}$ independently, in equations of Table 4. The optimal composition found (in terms of the wettability) was obtained for a concentration of chitosan of 1.5 % (w/v) and 0.1 % (w/w) of Tween 80 for both vegetables (Figure 2). Although the best results in terms of adhesion and cohesion coefficients were obtained with a different composition of the chitosan coating, it is necessary to emphasize that the wettability of a solid by a liquid is determined by the balance between adhesive forces (represented by the adhesion coefficient) of the liquid in the solid and cohesive forces (represented by the cohesion coefficient) of the liquid. This means that the optimum value of wettability is not necessarilly the result of the combination of the optima for $\underline{W_a}$ and $\underline{W_c}$. The optimum value obtained with the model for $\underline{W_a}$, $\underline{W_c}$, and $\underline{W_s}$ are very close agreement with those obtained experimentally (relative error below 3%)

Table 4: Model equations adjusting to W_a, W_s and W_c as functions of chitosan and Tween 80 concentrations.

Vegetable	Model Equations	R^2	Optimal Experimental.	Optimal Model	*R.E (%)
Tomato	$Wa = 29.8998 + 1.7635\,q - 0.2728\,t + 2.6633\,q^2 - 0.3226\,q\,t + 0.5885\,t^2$	66.5027	37.00	37.87	2.35
Carrot	$Wa = 22.2664 + 2.1876\,q + 0.8803\,t + 2.0082\,q^2 + 0.4620\,q\,t + 0.3300\,t^2$	55.1187	30.82	30.47	1.13
Tomato	$Ws = -25.9038 - 3.6992\,q + 1.0132\,t - 8.0450\,q^2 - 1.2957\,q\,t$	90.3553	-22.67	-22.17	2.20
Carrot	$Ws = -33.5581 - 3.2493\,q + 2.1710\,t - 8.6743\,q^2 - 0.5041\,q\,t$	85.0101	-30.20	-29.27	3.07
Tomato	$Wc = 55.8036 + 5.4627\,q - 1.2861\,t + 10.7084\,q^2 + 0.9731\,q\,t + 0.4686\,t^2$	95,9525	74.04	74.01	0.04
Carrot	$Wc = 55.8246 + 5.4370\,q - 1.2906\,t + 10.6826\,q^2 + 0.9662\,q\,t + 0.4768\,t^2$	95.976	74.07	74.50	0.58

*Relative error defined as $RE = \left| \left(\dfrac{OE - OM}{OE} \right) \right| \times 100$, where OE is the Optimal Experimental and OM is the Optimal Model.
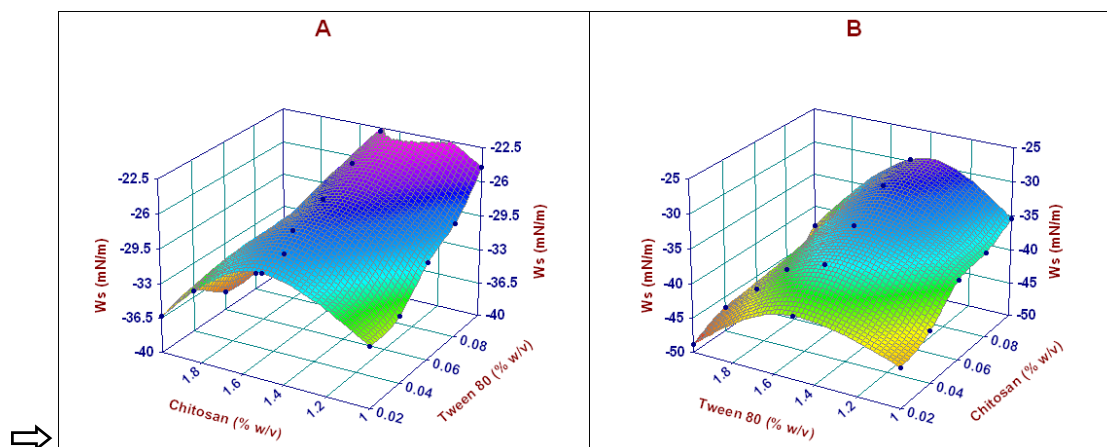
Figure 2**:** Spreading coefficient versus chitosan and Tween 80 concentrations in tomato (A) and carrot (B).

O_2, CO_2 and water permeability

The values of OP of chitosan films are comparable with commercial polyvinylidene choride (PVDC) or ethylene vinyl alcohol copolymer films (Butler, Vergano, Testin, Bunn & Wiles, 1996). Many previous studies of chitosan films with acetic acid reported their lower OP (Muzzarrelli, Isolati & Ferrero, 1974; Butler et al, 1996). However, chitosan films with lactic acid have equal or lowers values of OP. this could be concluded from this present study, where the values of OP oscillated in a range of 2.87 to 15.03 x 10^{-3} cm^3 O_2 m^{-1} day^{-1} atm^{-1} (Figures 3 and 4) similar to those results reported by Caner, Vergano & Wiles (1998), who obtained OP values of 4.42 and 0.19 x 10^{-3} cm^3 O_2 m^{-1} day^{-1} atm^{-1} for films with chitosan 3% (w/w) and lactic acid 1 and 7.5%, respectively. These authors evaluated the effect of type and concentration of acid on the OP and found that lactic acid produced the lowest values, followed by acetic, propionic, and formic.
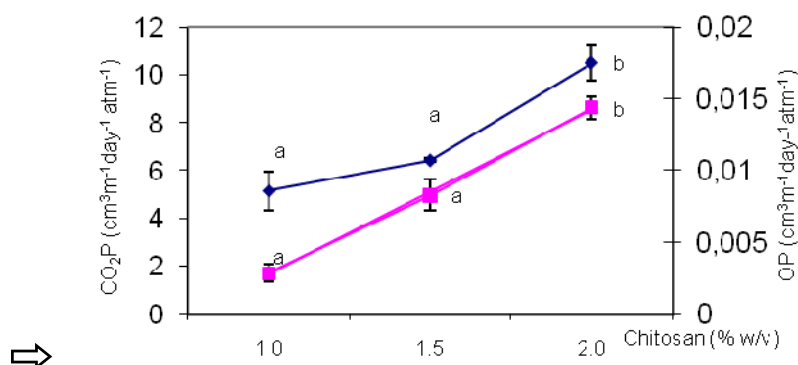

Figure 3: OP (♦) and CO_2P (■) as function of chitosan concentration on films produced with 1% (v/v) lactic acid and 0.1 % (w/v) Tween 80.

It should be noted that the additions of Tween 80 in the compositions of chitosan films did not affect their OP and CO_2P. This increased the possibilities of use of chitosan films, once he use of Tween 80 will influence others important properties such as superficial properties.

From Figure 3 is it possible to conclude that permeability (both OP and CO_2P) values increase with increasing chitosan concentration (while keeping Tween 80 concentration constant). However, it is necessary to consider also the effect of the thickness of the films, because it also increases when increasing the chitosan concentration and this lead to an increased resistance to mass transfers across the films. The ANOVA suggests that all samples are significantly different to 95% level of confidence.

The effects of plasticizer concentration were significant. Increasing plasticizer concentration contributed to the increase OP and CO_2P values. This can due to an increased mobility of polymer chains caused by the plasticizers resulting in a reduction of both the attraction forces between the chains and the activation energy to gas or vapor diffusion through the films (Maté & Krochta, 1996). The ANOVA suggests that all samples are significantly different to a level of confidence of 95% (Figure 4).
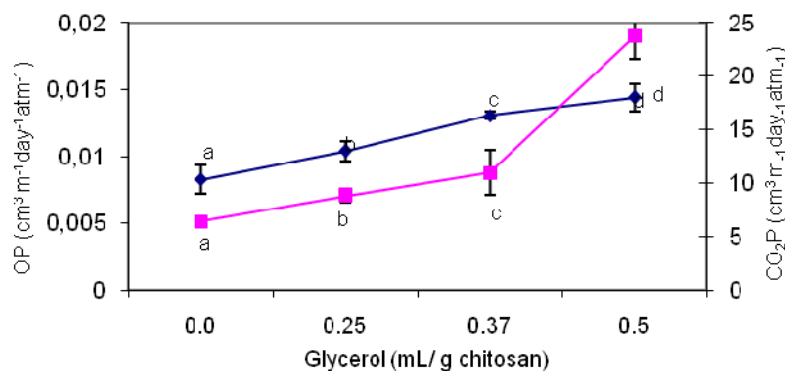

Figure 4: OP as a function of glycerol concentration on chitosan films produced with 1.0 % (v/v) lactic acid and 0.1 % (w/v)Tween 80.
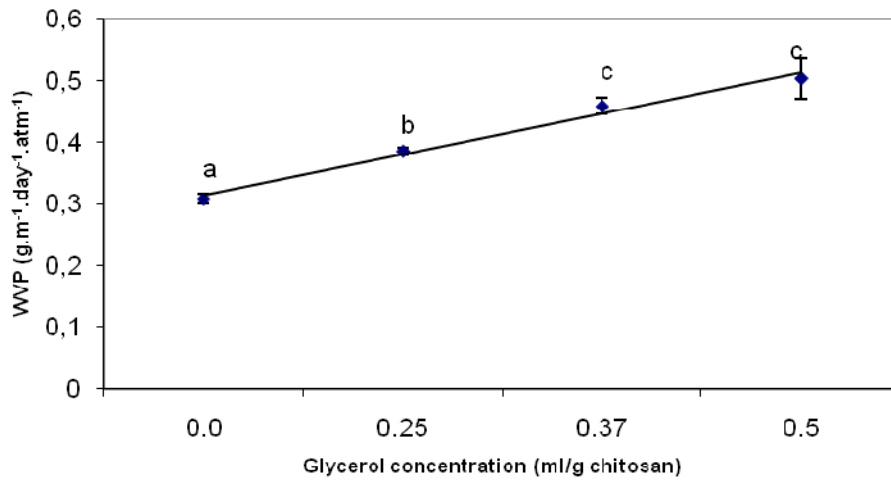
Figure 5: Water vapor permeability as a function of glycerol concentration on chitosan films produced with 1.0 % lactic acid and 0.1 % Tween 80
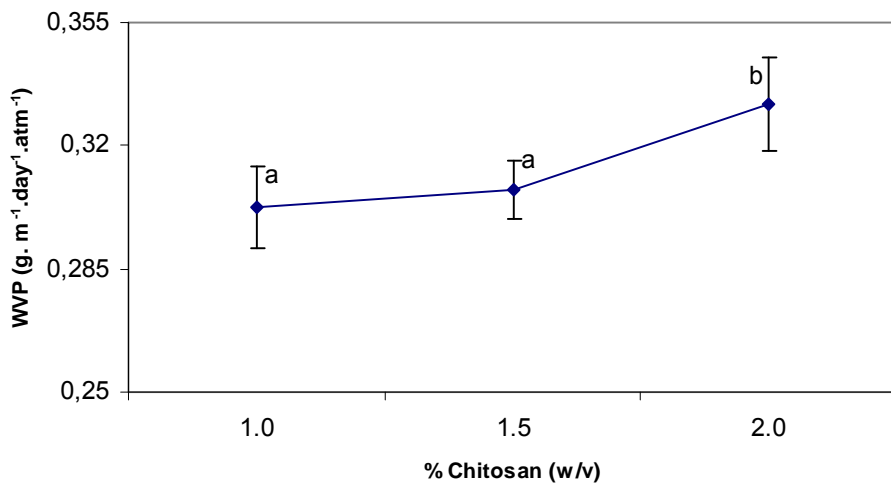

Figure 6: Water vapor permeability as a function of chitosan concentration on films produced with 1.0 % lactic acid and 0.1 % Tween 80.

Similar results were obtained with respect to WVP. However, the mechanism for the prediction of water transport through hydrophilic films such as chitosan is more complex, due to nonlinear water sorption isotherms and water content dependent diffusivities (Schwartzberg, 1994). Besides the fact that water vapor flux through hydrophilic films varies non-linearly with water vapor partial pressure gradient (Mc Hugh et al, 1993) if films are cationic and strongly hydrophilic water molecules will interact with the polymer matrix, increasing water vapor permeation (Wiles et al, 2000).

The chitosan films with glycerol (Figure 5) exhibited WVP of 3.85 to 5.02×10^{-1} g m^{-1} day^{-1} atm^{-1}, while the films without glycerol (Figure 6) presented values of WVP of 3.02 to 3.31 10^{-1} g m^{-1} day^{-1} atm^{-1} values lowest that 9.42×10^{-1} g m^{-1} day^{-1} atm^{-1} reported by Caner et al. (1998). This could be due to the presence of Tween 80 as surfactants which might improve the barrier to water vapor due to their polar side which can be bonded to the polar part of the chitosan molecule while the non polar groups can place away from the chitosan molecule thus creating an extra barrier to water vapor (Miranda, Garnica, Lara & Cárdenas, 2004).

The ANOVA of films with constant Tween 80 and chitosan concentrations and with glycerol concentration changing in the range of 0 to 0.5 ml glycerol/ g chitosan indicated that films with the lowest glycerol concentration showed significant differences from others.

On the other hand while evaluating the influence of chitosan concentration in WVP statistically significant differences were found between the film with the highest chitosan concentration and the others.

It should be noted that hydrophilic films often exhibit positive slope relationships between thickness and WVP (McHugh et al, 1993). Several explanations have been provided for thickness effects. Banker et al. (1966) attributed thickness effects to film swelling as a result of attractive forces between film and water. This effect happens on the side of the film in contact with atmosphere of high humidity, reason why this effect must be smaller when the film has greater thickness. Such film swelling could result in varying film structures. This aspect will be a cause of little difference between WVP of chitosan films without plasticizer.

A study on the influence of the solubilization and diffusion process on the barrier properties of 4 different edible films was presented by Buonocore, Conte & Del Nobile (2005). The results suggest that alginate films, which show the highest water and oxygen permeability coefficient, have both higher affinity with water and a higher macromolecular mobility than sodium alginate, zein and chitosan film. The lowest water and oxygen permeability coefficient were detected for chitosan and zein films.

Optical Properties.

The results of the measurements of color are shown in Table 12. With respect to the lightness of the chitosan films it is possible to observe that these values are little lower, but still high in comparison with those of albumen (from egg) films, for which the valor range between 95.67 and 96.20 (Gennadios, Weller, Hanna, & Fronnig, 1996). Such films were reported to be clearer and more transparent that the films based on wheat, soy isolated and corn zein, studied by this

same author. This means that it's possible to consider that the chitosan films obtained in the present work are within an acceptable range for this parameter. Further, the values of lightness for chitosan films are higher than those reported for wheat protein films, which presented values of L between 83.3 and 89.7, and values of b between 29.8 and 39.3 (Rayas, Hernandez, & Perry, 1997); our films were clearer (higher L) and less yellow (smaller b^*+). The high values of the component b^{*+} indicate the predominance of the yellow color in the chitosan films; this coincides with the reported by Butler et al. (1996) with respect to chitosan.

Table 12: Results of the measurements of color on chitosan films with 0.1 % of tween 80.

Film		L*	a*	b*	ΔL*	ΔC*	ΔE*
Chitosan (% w/v)	Glycerol (mL/g chitosan)						
1.0	_	94.24 ± 0.64 d	4.21 ± 0.16 a	7.46 ± 1.12 a	+65.65 ± 0.64 d	+7.12 ± 1.62 a	66.21 ± 0.46 c
1.5	_	92.79 ± 0.39 c	3.74± 0.20 a	11.64 ± 0.56 b	+64.20 ± 0.39 c	+11.42 ± 0.55b	65.49 ± 0.28 b
2.0	_	91.01 ± 0.99 a	3.88 ± 0.44 a	17.26 ± 2.23 c	+62.41± 1.00 a	+17.49 ± 1.20c	64.68 ± 0.41 a
1.5	0.25	91.94 ± 0.48 bc	3.94 ± 0.13 a	12.78 ± 1.41 b	+63.34 ± 0.49 bc	+12.56 ± 1.35b	64.89 ± 0.22 a
1.5	0.37	92.33 ± 0.16 c	3.82 ± 0.07 a	13.24 ± 1.00 b	+63.74 ± 0.16 c	+12.97 ± 0.98b	65.36 ± 0.21 b
1.5	0.50	91.28 ± 0.71 ab	3.86 ± 0.09 a	17.29 ± 1.47 c	+62.69 ± 0.71 ab	+16.91 ± 1.45c	65.35 ± 0.37 b

*Different letters in the same column correspond to statistically different samples for 95% confidence level.

The results indicated that an increase in the concentration of the chitosan and glycerol tends to increase the values of b^{*+}, according to the fact that some plasticizers (such as sorbitol and glycerol) increase the values of b^*+ and decrease those of a^*+ (Gennadios et al, 1996).

In this study, the difference of color was mainly due to the variation of b^*+, and therefore to the variation of $ΔC^*$ and not as much to the slight variation in $ΔL^*$, this suggest that the film presented a bright yellow color. Statistically both parameters showed differences between films

with different chitosan concentrations. However for the films with glycerol only those with higher glycerol concentration differ for the others.

Opacity

The transparency of a film is desirable property once the consumer wishes to see clearly the aspect of the product. The opacity is an established measurement of the transparency of a film. A greater value of opacity means a smaller transparency (Cuq, Gontard, Cuq, & Guilber, 1996).

Table 13: Results of the measurements of Opacity of chitosan films

Film		Opacity (%)
Chitosan (% w/v)	Glycerol (mL / g chitosan)	
1.0	-	8.53 ± 0.78 b
1.5	-	10.65 ± 0.81 c
2.0	-	11.31± 0.21 c
1.5	0.25	10.84 ± 0.89 c
1.5	0.37	4.79 ± 0.64 a
1.5	0.50	4.34 ± 0.33 a

*Different letters in the same column correspond to statistically different samples for 95% confidence level.

The opacity of the films presented an increasing tend with decreasing chitosan concentration which is related to the increase of dry matter the film.

However, it can also be observed that films with glycerol are more transparent. This can be due to the effect in the decrease of the intermolecular forces that the glycerol exerts in the polymer (Gennadios et al, 1996), meaning that a more open structure is obtained, leading to higher quantity of entrapped water due to the hydrophilic nature of this substance (Chick & Ustunol. 1998). Statistical analysis confirmed that those films with higher glycerol concentration were less opaque and more transparent statistically.

Conclusions

Tomato and carrot have low energy surfaces with a surface tension of 28.56 and 26.10 mN/m, respectively, and polar and dispersive components of 3.32 and 25.24 mN/m for the tomato and 0.48 and 25.62 mN/m to the carrot, respectively. The critical surface tensions are 17.8 and 24.3 mN/m. respectively, being tomato and carrot skin low energy surfaces. The increase of the concentration of chitosan and plasticizers decreased the values of wettability and adhesion coefficients. The optimum values of the spreading coefficients were experimentally obtained with solutions of 1.5 % (w/v) of chitosan and 0.1 % of Tween 80 (w/w) as surfactant agent *(- 22. 81 and -29.71 mN/m, respectively)* for tomato and carrot. The results of wettability determinations allowed to adjust one polynomial model that suggests an increase of the spreading coefficient as the chitosan concentration decreases and Tween concentration increases.

The oxygen, carbon dioxide and water vapor permeability of chitosan films depend of chitosan and glycerol concentrations while keeping Tween 80 concentration constant. The best values of the oxygen, carbon dioxide and water vapor permeability were obtained with films of 1.0 % (w/v) of chitosan and 0.1 % of Tween 80 (w/w).

An increase of the chitosan concentration decreases the lightness and increase the yellow color of coating. The chitosan coatings containing glycerol showed high values of lightness and were more transparent and yellowier than those without glycerol.

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