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Chitosan coating surface properties as affected by plasticizer, surfactant and polymer concentrations in relation to the surface properties of tomato and carrot

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Abstract

The objectives of this work were to determine the effects of the concentrations of glycerol and sorbitol (as hydrophilic plasticizers), Tween 80 (as surfactant) and chitosan on the wettability of Cuban chitosan-based edible coatings in view of their application on tomato and carrot and to develop a model allowing the optimization of coating composition.

The values of the polar and dispersive components of the superficial tension of the foods were determined to be 3.04 and 25.67 mN/m, respectively, for tomato, and 0.34 and 26.13 mN/m, respectively, for carrot, the sum of the two components being the superficial tensions of tomato and carrot (28.71 and 26.48 mN/m, respectively). The skins of both foods are therefore low-energy surfaces, meaning that the Zisman method for the determination of wettability could be applied.

The best experimental values of wettability were obtained for the following coating composition: 1.5% (w/v) of chitosan and 0.1% (w/w) of Tween 80.

The increase in the concentration of chitosan and glycerol or sorbitol as plasticizers decreased the values of wettability and adhesion coefficients.

The results of wettability were adjusted to a polynomial model that describes the dependence of the adhesion coefficient (W_a), cohesion coefficient (W_c) and spreading coefficient (W_s) on chitosan and Tween 80 concentrations. The optima calculated by the model equations were in excellent agreement (relative error below 3%) with the experimental values.

Keywords: Chitosan; Edible coating; Surface properties; Modeling; Coating composition

1. Introduction

Edible films and coatings can be used to help in the preservation of fruit and vegetables because they provide a partial barrier to moisture, O_2 and CO_2, also improving mechanical handling properties, carrying additives, avoiding volatiles loss and even contributing to the production of aroma volatiles (Olivas & Barbosa-Cánovas, 2005).

Nevertheless, the effectiveness of edible coatings for fruits and vegetables depends primarily on the control of the wettability of the coating solutions, which affects the coating thickness of the film (Park, 1999), thereby affecting its permeability and mechanical resistance.

The surface energy or surface tension is a controlling factor in the processes involving wetting and coating of surfaces (Hong, Han, & Krochta, 2004).

The coating process involves wetting of the produce to be coated by the coating solution, possible penetration of the solution into the skin (Hershko, Klein, & Nussinovitch, 1996), followed by a possible adhesion between these two

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Nomenclature

θ	contact angle between liquid and solid, deg
γ_L	superficial tension of liquid, mN/m
γ_c	critical surface tension of wettability process, mN/m
$\gamma_L{}^p$	superficial tension of liquid (polar component), mN/m
$\gamma_L{}^d$	superficial tension of liquid (dispersive component), mN/m
$\gamma_S{}^p$	superficial tension of solid (polar component), mN/m
$\gamma_S{}^d$	superficial tension of solid (dispersive component), mN/m
γ_{SV}	interfacial tension solid vapor
γ_{LV}	interfacial tension liquid–vapor
γ_{SL}	interfacial tension solid vapor
W_a	adhesion coefficient, mN/m
W_c	cohesion coefficient, mN/m
W_s	spreading coefficient, mN/m
q	chitosan concentration, % w/v
t	Tween 80 concentration, % w/v

commodities. The wetting stage (spreadability) is very important, because if the suitability of the coating for the object to be coated is ideal, the time interval necessary for such an operation is minimal, or, in others words, spreadability is virtually spontaneous (Mittal, 1977).

The determination of the surface tension usually involves the measurement of the contact angles that several standard liquids make with that surface. The surface energy of the solid surface is then related to the surface tensions of the liquids and the contact angles. This method invokes an estimation of the critical surface tension of the surface of the solids studied, by extrapolation from the Zisman plot (Zisman, 1964).

Chitosan is the *N*-deacetylated derivative of chitin; although this *N*-deacetylation is almost never complete, this could be defined as chitin sufficiently deacetylated to form soluble amine salts. The required degree of deacetylation to obtain a soluble product must be 80–85% or higher. Chitosan products are highly viscous, resembling natural gums (Peniston & Johnson, 1980).

The physico-chemical and biological properties of chitosan justify its introduction in food formulations once it could improve nutritional, hygienic and/or sensory properties, because of its emulsifying, antimicrobial, antioxidant and gelling properties, while also acting as a functional fiber. Chitosan's safety can be evaluated by its remarkably high lethal doses (1.6 g/kg of body weight in rats), being comparable to those of sugar and even less toxic than salt. For all these reasons, chitosan has been accepted as a dietary supplement or a food additive in many countries (e.g. Italy, France, Norway, Poland, United States of America, Argentine, Japan and Korea (Argulló, Albertengo, Pastor, Rodríguez, & Valenzuela, 2004; Park, Marsh, & Rhim, 2002)).

Chitosan is not water soluble, but it forms viscous solutions in various organic acids (Park et al., 2002). Acetic acid often has been used as a solvent for the production of chitosan films (Caner, Vergano, & Wiles, 1998), but it imparts a strong acidic flavor and aroma to the foods in which it is used. Lactic acid has been used instead of acetic acid because it has a weaker acidic flavor and aroma, which was found using a trained sensory panel that compared chitosan films produced with both acids (Forero, 2001).

Most of the naturally occurring polysaccharides, e.g. cellulose, dextran, pectin, alginic acid, agar, agarose and carragenans, are neutral or acidic in nature, whereas chitin and chitosan are examples of highly basic polysaccharides. By this unique property many potential products using chitosan have been developed, including flocculating agents for water and waste treatment, chelating agents for removal of traces of heavy metals from aqueous solutions, coatings to improve dyeing characteristics of glass fibers, wet strength additives for paper, adhesives, photographic and printing applications, thickeners and fibers and films (Hench, 1998).

Cuban coasts are very rich in crustaceous, namely lobsters and therefore the fishing industry is a very important sector of activity. Furthermore, most of the lobster is locally processed and exported, their carapaces being a left over that can be used to obtain chitosan. In fact, a local project has been running for several years aiming at producing chitosan with a high degree of deacetylation. Given its economical relevance for the country, the project is now at the industrial level and the chitosan has been used successfully in the medical industry as well as for some applications in the food industry.

The objectives of this study are to characterize the surface properties of the food to be coated, to study the wetting properties of the Cuban chitosan coatings and to determine the effects of type and concentration of hydrophilic plasticizer, surfactant concentration and polymer concentration on the wettability of chitosan coatings.

This characterization is made in order to evaluate the possibility of using the material as an edible coating for fruits and vegetables, while developing a methodology to optimize the composition of chitosan-based coatings.

2. Materials and methods

2.1. Coating materials

The materials used to prepare the edible coating solutions were chitosan (from lobster of the cuban coasts) obtained in the Pharmaceutical Laboratories Mario Muñoz, Cuba, with a degree of deacetylation of 90% (approximately), glycerol 87% (Panreac, Spain) or sorbitol 97% (Acros Organics, Belgium) as plasticizers, Tween 80 (Acros Organics, Belgium) as surfactant, lactic acid 90% (Merck, Germany) and distilled water. The addition of a surfactant agent to the coating-forming solution reduces the interfacial tension and improves the adhesion on the surface to be covered. Taking into account the nature of the solution, a value of HLB (the hydrophilic–lipophilic balance) >13 is required to obtain a clear solution, so that both Tween 20 and Tween 80 could have been used. Choi, Park, Anh, Lee, and Lee (2002) reported that the addition of 1% Tween 80 to a solution of 1.5% chitosan improved the compatibility of the chitosan coating solution and the apple skin. Further in previous works of the group (see e.g. Ribeiro, Vicente, Teixeira, & Miranda, 2007), Tween 80 has also been used and that use has been maintained here for comparison purposes.

2.2. Coatings preparation

The coating solutions were prepared dissolving the 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 h at room temperature (20 °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 at concentrations between 0.02% and 0.10% (w/v).

2.3. Preparation of specimens for contact angle measurements

The tomatoes (*Lycopersicon lycopersicum*) and carrots (*Daucus carota*) used in the experiment were purchased from the local supermarket, and they were kept at 6 °C until use. Both were selected for their uniformity, size, color and absence of damage and fungal infection. Before testing, tomatoes and carrots were left at room temperature and cleaned with distilled water. Thin portions of the outer surface (skin) of tomato or carrot were cut with a sharp knife and adhered to a glass plate (8 cm diameter).

2.4. 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, 1996a, 1996b). Samples of the coating solution were taken with a 500 μL syringe (Hamilton, Switzerland) in order to determine the drop shape, using computer-aided image processing. The diameter of the needle (0.72 ± 0.01 mm), necessary for γ_{LV} determination, was obtained with a digital micrometer (Mitutoyo, Japan). The contact angle at the tomato and carrot surface was measured by the sessile drop method (Newman & Kwok, 1999), in which a droplet of the tested liquid was placed on a horizontal surface and observed with a face contact angle meter. To avoid changes on the tomato and carrot surfaces, measurements were made in less than 60 s. Ten replicates of contact angle and surface tension measurements were obtained at 20 (± 1) °C.

The estimation of the critical surface tension (γ_C) of the tomato and carrot surfaces was obtained by extrapolation from the Zisman plot (Zisman, 1964), which was built using water, formamide and bromonaphthalene (Merck, Germany) as reference liquids.

2.5. Modeling

Specifically, the data related to the influence of Tween 80 and chitosan concentration on the wettability of the chitosan coating were adjusted with polynomial models (Eq. (1)) and independent variables were codified according to a multifactor design

$$Y = b_0 + b_1 A + b_2 B + b_3 A^2 + b_4 B^2 + b_5 (AB), \tag{1}$$

where Y is the dependent variable (W_a, W_c or W_s), A is chitosan concentration (1.0, 1.5 and 2.0% w/v) and B is Tween 80 concentration (0.02, 0.04, 0.06, 0.08 and 0.1% w/v). The values of b_0–b_5 are model coefficients.

2.6. Statistical analysis

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

3. Results and discussion

3.1. Surface tension and critical surface tension of tomato and carrot skin

The Zisman method (described below) is based on the fact that a straight line is obtained when the cosine of the contact angle is plotted versus the superficial tension (liquid–vapor) on a given solid and this method is applicable only for systems with a surface tension below 100 nN/m (low energy surfaces) (Owens & Wendt, 1969; Zisman, 1964). thus it is 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 liquid–vapor interfacial tension is the sum of contributions from the different intermolecular forces (Kaelble, 1970; Owens & Wendt, 1969; 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

$$W_a = W_a^d + W_a^p \Leftrightarrow W_a = 2\left(\sqrt{\gamma_S^d \gamma_L^d} + \sqrt{\gamma_S^p \gamma_L^p}\right) = \gamma_L(1+\cos\theta), \quad (2)$$

where $\gamma_l(1+\cos\theta)$ can be found from

$$\frac{1+\cos\theta}{2}\frac{\gamma_L}{\sqrt{\gamma_L^d}} = \sqrt{\gamma_S^p}\sqrt{\frac{\gamma_L^p}{\gamma_L^d}} + \sqrt{\gamma_S^d}. \quad (3)$$

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

$$W_c = 2\gamma_{LV} \quad (4)$$

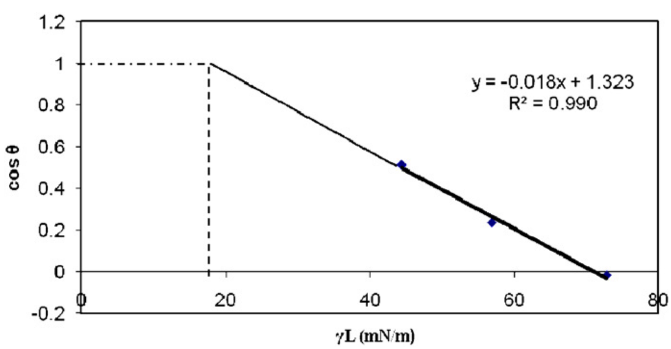

Fig. 1. Zisman plot of tomato surface.

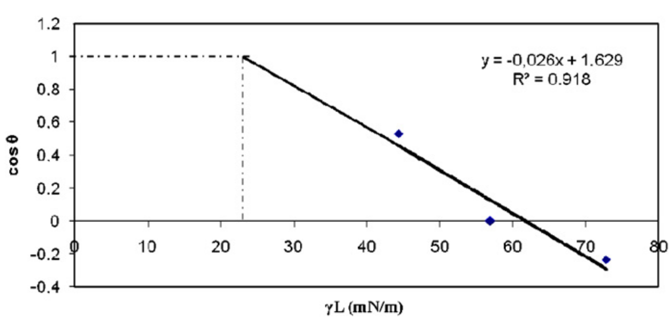

Fig. 2. Zisman plot of carrot surface.

and the spreading coefficient

$$W_s = W_a - W_c = \gamma_{SV} - \gamma_{LV} - \gamma_{SL}. \quad (5)$$

The contact angle determinations of at least three pure compounds on the surface of tomato or carrot, combined with the surface tension values reported by Dann (1970) and Hershko and Nussinovitch (1998), will allow the calculation of both the independent variable $\left(\sqrt{\gamma_L^p/\gamma_L^d}\right)$ and the dependent variable

$$\left(\frac{1+\cos\theta}{2}\frac{\gamma_L}{\sqrt{\gamma_L^d}}\right)$$

from Eq. (3).

The adjustment of the experimental data to a straight line produced the following equations for tomato (Eq. (6)) and carrot (Eq. (7)):

$$\frac{1+\cos\theta}{2}\frac{\gamma_L}{\sqrt{\gamma_L^d}} = 1.7438\sqrt{\frac{\gamma_L^p}{\gamma_L^d}} + 5.0670; \quad r^2 = 0.9960, \quad (6)$$

$$\frac{1+\cos\theta}{2}\cdots\frac{\gamma_L}{\sqrt{\gamma_L^d}} = 0.5901\sqrt{\frac{\gamma_L^p}{\gamma_L^d}} + 5.1122; r^2 = 0.9876. \quad (7)$$

Eqs. (6) and (7) were used to calculate the values of the polar and dispersive components of the surface tension, which were determined to be 3.04 and 25.67 mN/m, respectively, for tomato and 0.34 and 26.13 mN/m, respectively, for carrot, the surface tensions of tomato and carrot being the sum of the two components (28.71 and 26.48 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 and Robert (1993).

The Zisman method can therefore be applied to estimate the critical surface tension. This empirical quantity is defined as the value of the superficial tension (liquid/vapor) at the intercept of the Zisman plot (Figs. 1 and 2) for $\cos\theta = 1$.

Table 1
Effect of chitosan and glycerol concentration on W_a, W_s and W_c for the different chitosan coatings (mean values for chitosan and glycerol concentration)

Factors	Mean values (tomato)			Mean values (carrot)		
	W_a (mN/m)	W_s(mN/m)	W_c (mN/m)	W_a (mN/m)	W_s (mN/m)	W_c (mN/m)
Chitosan concentration (% w/v)						
1.00	33.046a	−48.971a	82.017c	25.596a	−56.421a	82.017c
1.50	33.196a	−50.853b	84.048b	25.638a	−58.411b	84.048b
2.00	32.612a	−53.207c	85.820a	25.192a	−60.628c	85.820a
Glycerol concentration (mL/g chitosan)						
0.000	35.392a	−53.010c	88.402a	26.449a	−61.953c	88.402a
0.250	32.212b	−49.525a	81.738c	25.358ab	−56.379a	81.738c
0.375	32.328b	−49.943a	82.271c	25.376ab	−56.895a	82.271c
0.500	31.872b	−51.563b	83.435b	24.716b	−58.718b	83.435b

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

Table 2
Effect of chitosan and sorbitol concentration on W_a, W_s and W_c for the different chitosan coating (mean values for chitosan and sorbitol concentration)

Factors	Mean values (tomato)			Mean values (carrot)		
	W_a (mN/m)	W_s (mN/m)	W_c (mN/m)	W_a (mN/m)	W_s (mN/m)	W_c (mN/m)
Chitosan concentration (% w/v)						
1.00	30.856c	−50.952a	82.017c	25.324a	−56.487a	81.810c
1.50	31.918b	−54.957b	84.048b	26.878b	−59.983b	86.861b
2.00	33.239a	−57.647c	85.820a	26.291ab	−64.596c	90.886a
Sorbitol concentration (mL/g chitosan)						
0.000	35.392a	−53.010a	88.402a	26.449a	−61.953c	88.402a
0.250	31.562b	−53.296a	84.868d	25.881a	−58.987a	84.868d
0.375	30.733c	−55.325b	86.004c	26.106a	−59.898ab	86.004c
0.500	30.332c	−56.444c	86.803b	26.220a	−60.583bc	86.803b

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

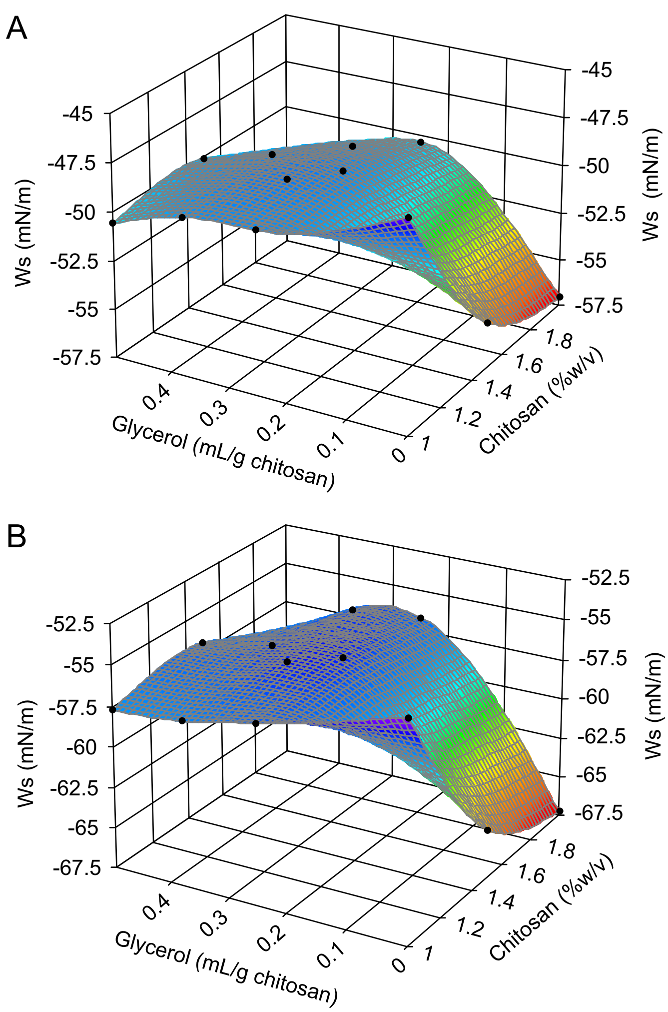

Fig. 3. Spreading coefficient versus chitosan and glycerol concentrations in tomato (A) and carrot (B).

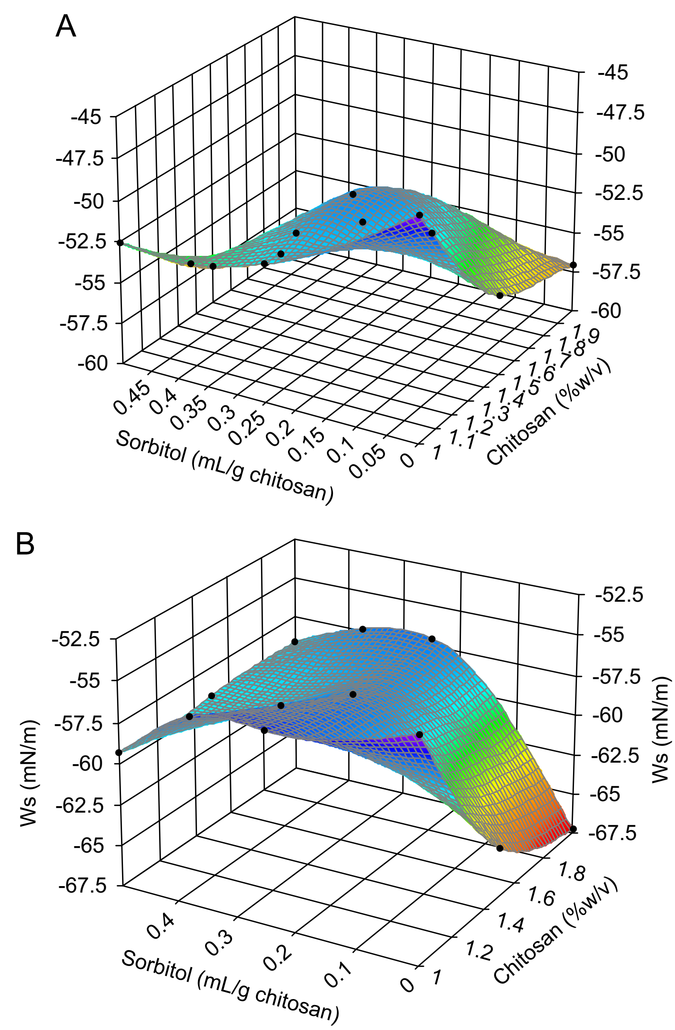

Fig. 4. Spreading coefficient versus chitosan and sorbitol concentrations in tomato (A) and carrot (B).

It should be noted that critical surface tension values have been reported to be lower than the surface tension values of the same tested surfaces (Dann, 1970). The critical surface tension values found in the present work were 17.4 and 24.1 mN/m, which are well below the respective surface tension values; similar results were obtained by Ribeiro et al. (2007) when working with strawberry (23.0 mN/m), Choi et al. (2002) with apple

(18.7 mN/m), Hagenmaier and Baker (1993) with orange and grapefruit (23.0 mN/m) and Hershko and Nussinovitch (1998) with garlic (18.3 mN/m).

It is noteworthy to emphasize the differences between the values obtained for tomato and carrot. Such differences are presumably due to the differences in texture and composition between the skin of tomato, which is covered by a wax layer and is very uniform, and that of the carrot which is a root with a ligneous, rough texture and irregular surface.

3.2. Wettability of the coating solutions

The polycationic properties of chitosan provide this polymer with the possibility of forming films by the breakage of polymer segments and subsequent reforming of the polymer chain into a film matrix or gel; this can be achieved by evaporating a solvent thus creating hydrophilic and hydrogen bonding and/or electrolytic and ionic cross-linking (Butler, Vergano, Testin, Bunn, & Wiles, 1996). These films are an excellent oxygen barrier and their mechanical properties are comparable to many medium-strength commercial polymer films (Butler et al., 1996; Caner et al., 1998; Park et al., 2002). However, this does not guarantee that chitosan coatings will have the same properties of the films, once the former must be tailored to ensure the appropriate affinity between the coating and the food to be coated.

Common plasticizers used for edible films preparation are water, glycerol, sorbitol and other low-molecular-weight polyhydroxy compounds. Glycerol and sorbitol are widely used as plasticizers because of their stability and edibility (Bangyekan, Aht-Ong, & Srikulkit, 2006; Rindlav-Westling, Stading, Hermanson, & Gatenholm, 1998). Several authors have studied the effects of type and concentration of a few hydrophilic plasticizers on the properties of various hydrocolloid-based films (Caner et al., 1998; Cuq, Gontard, Cuq, & Guilbert, 1997; Donhowe & Fennema, 1993; Gennadios, Weller, & Testin, 1993; Gontard, Guilbert, & Cuq, 1993).

The results in Tables 1 and 2 show that the spreading coefficient (W_s) decreased as the chitosan concentration increased for the food studied, independent of plasticizer concentration and a statistically significant difference has been found ($p<0.05$) between the different chitosan coatings. 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 glycerol and chitosan concentration in the surface properties of the coatings was studied and a tendency can be observed that the adhesion and the spreading coefficient decreased and the cohesion coefficient

Table 3
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	RE^{a} (%)
Tomato	$W_a = 29.8998 + 1.7635q - 0.2728t + 2.6633q^2 - 0.3226qt + 0.5885t^2$	66.5027	37.00	37.87	2.35
Carrot	$W_a = 22.2664 + 2.1876q + 0.8803t + 2.0082q^2 + 0.4620qt + 0.3300t^2$	55.1187	30.82	30.47	1.13
Tomato	$W_s = -25.9038 - 3.6992q + 1.0132t - 8.0450q^2 - 1.2957qt$	90.3553	−22.67	−22.17	2.20
Carrot	$W_s = -33.5581 - 3.2493q + 2.1710t - 8.6743q^2 - 0.5041qt$	85.0101	−30.20	−29.27	3.07
Tomato	$W_c = 55.8036 + 5.4627q - 1.2861t + 10.7084q^2 + 0.9731qt + 0.4686t^2$	95.9525	74.04	74.01	0.04
Carrot	$W_c = 55.8246 + 5.4370q - 1.2906t + 10.6826q^2 + 0.9662qt + 0.4768t^2$	95.976	74.07	74.50	0.58

[a] Relative error defined as

$$RE = \left| \left(\frac{OE - OM}{OE} \right) \right| \times 100,$$

where OE is the optimal experimental value and OM is the optimal model value.

increased as the glycerol or chitosan concentration increased (Fig. 3); such differences were statistically significant for the chitosan and glycerol concentration ($p<0.05$) (Table 1). Similar results are obtained with the application of sorbitol to the coatings (Fig. 4); that is, there is an inverse relation between the chitosan and sorbitol concentration and the adhesion and the spreading coefficients. 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 these foods. The two-way ANOVA showed an influence of chitosan concentration on the adhesion coefficient of tomato and of both chitosan and sorbitol concentration on the spreading coefficient of tomato and carrot ($p<0.05$) (Table 2).

As previously demonstrated, the tomato and carrot skins are low-energy surfaces, so their surface interacts with liquids primarily through dispersion forces. This explains why chitosan solutions (polar liquids) are characterized by low values of work of adhesion on tomato and carrot skins,

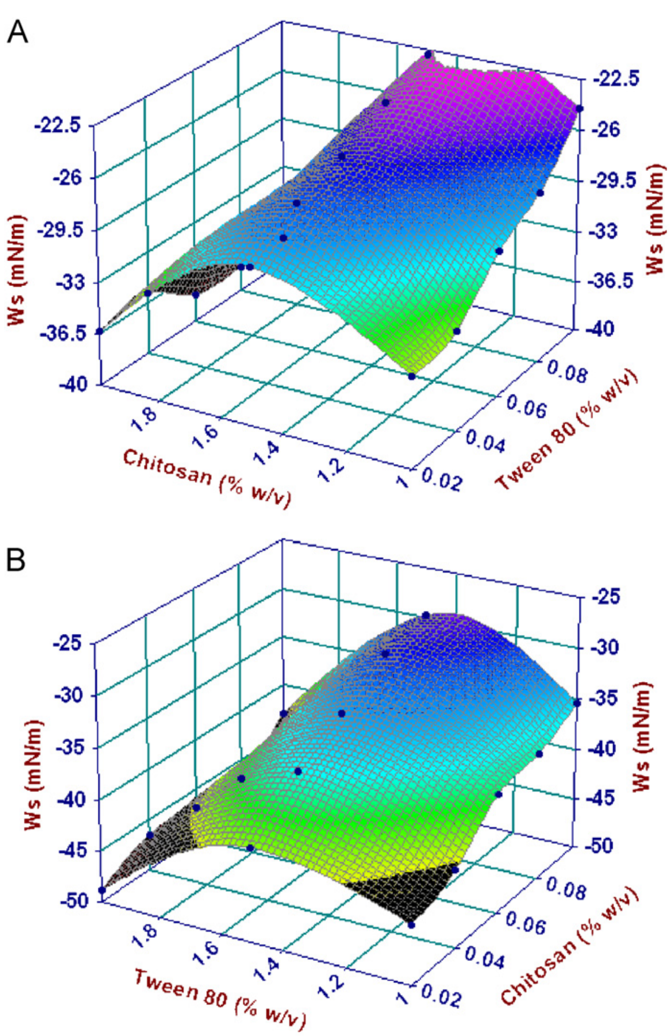

Fig. 5. Spreading coefficient versus chitosan and Tween 80 concentrations in tomato (A) and carrot (B).

even when plasticizers such as glycerol or sorbitol are added. The objective of the addition of such plasticizers is to improve the mechanical properties of the chitosan coating once it is formed; this is because the plasticizer decreases the attractive intermolecular forces in the molecular tridimensional organization, and increases the chain mobility, thus rendering the films more flexible (Banker, Gore & Swabrick, 1966).

3.3. Modeling

The influence of chitosan and Tween 80 concentrations on the adhesion, cohesion and spreading coefficients were described by a polynomial model (Table 3) for both tomato and carrot 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 W_a, W_c and W_s, reaching its higher effect when the concentration is 1.5% (w/v); 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 W_a, W_c and W_s independently, in equations of Table 3. 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 foods (Fig. 5). 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 necessarily the result of the combination of the optima for W_a and W_c. The optimum values obtained with the model for W_a, W_c and W_s are in very close agreement with those obtained experimentally (relative error below 3%).

4. Conclusions

Tomato and carrot skins are low-energy surfaces, with a surface tension of 28.71 and 26.48 mN/m, respectively, and with polar and dispersive components of 3.04 and 25.67 mN/m for tomato and 0.34 and 26.13 mN/m for carrot, respectively. The critical surface tensions for tomato and carrot are 17.4 and 24.1 mN/m, respectively.

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.

A polynomial model has been obtained, allowing the optimization of chitosan-based edible coatings for foods such as carrot and tomato. Such a model suggests a stronger effect of chitosan concentration and a weaker effect of Tween concentration on the wettability of the studied solutions.

The results previously presented point at the fact that chitosan obtained from lobster of the Cuban coasts can be recommended as an edible coating to be applied on fruits and vegetables, possibly contributing to extend their shelf life.

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