Chitosan coating and films: evaluation of surface, permeation, mechanical and thermal propertiess

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Abstract

The potentialities of chitosan (from lobster of the cuban coasts) coating to extend the shelf life of vegetables were evaluated. To do so, the surface properties of tomato and carrot were characterized and the wettability properties of chitosan coatings were studied. In such coatings, chitosan concentration and effects of type and concentration of plasticizer or surfactant on wettability of chitosan coatings were evaluated, as well as the respective barrier and mechanical properties. Additionally, a blend of chitosan and clay microparticles was performed and the films obtained were characterized in terms of barrier, mechanical and thermal properties.

The values of the polar and dispersive components of the superficial tension for the tomato and the carrot were determined, being the superficial tensions of the tomato and carrot 28.55 and 26.40 mN/m, respectively. The results of wettability determinations allowed the construction of one factorial model. 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 gas permeability coefficients and chitosan concentration (while keeping Tween concentrations constant).

The water vapour barrier property of the chitosan films was significantly improved by incorporation of clay, the tensile strength increased significantly with increasing chitosan and clay concentrations, while the values of elongation decreased slightly for high values of chitosan concentration. The obtained models are meant to predict the properties of chitosan/clay films to be prepared.

Resumen

Las potencialidades del empleo de coberturas de quitosana (obtenida a partir de langosta) para extender la vida de anaquel de los vegetales fueron evaluadas. En este sentido fueron determinadas las propiedades de superficie del tomate y la zanahoria y el efecto de la concentración de polímero, tipo y concentración de plastificante, así como la concentración de agente surfactante sobre la humectabi-lidad de las coberturas de quitosana. Las coberturas que mostraron mejor humectabilidad fueron ca-racterizadas en relación a sus propiedades de barrera y mecánicas. Adicionalmente fueron obtenidas películas de quitosana/arcilla y caracterizadas sus propiedades de barrera, mecánicas y térmicas

Los valores de las componentes polar y dispersiva de la tensión superficial del tomate y la zanahoria fueron determinados, siendo la tensión superficial de los mismos 28.55 y 26.40 mN/m, respectivamente. Los resultados de las determinaciones de humectabilidad se ajustaron a un modelo factorial. Los mejores valores en términos de humectabilidad correspondieron a la cobertura con una composición de: quitosana 1.5% (m/v) y 0.1 % (m/v) de Tween 80.

Una incidencia de la concentración de quitosana (concentración de Tween constante) sobre las propiedades mecánicas y de barreras de las coberturas fue encontrada.

La permeabilidad al vapor de agua de las películas de quitosana fue significativamente mejorada con la adición de arcilla en su composición. El esfuerzo tensil aumentó significativamente con el aumento de la concentración de quitosana y arcilla, mientras que la elongación disminuyó ligeramente. Los modelos obtenidos permiten predecir las propiedades de las películas de quitosana/arcilla que se quie-ran preparar.

Keywords: Chitosan, edible coating, surface properties, clay, nanocomposite, gases permeability, mechanical properties, thermal properties, modeling.

Introduction

Edible films and coatings 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 antio-xidants or antimicrobials, and improving appearance, structure and handling.

The characterization of chitosan films obtained from chitosan derived from crab and shrimp has been extensively performed [1-5], however Cuban coasts are very rich in lobsters, and the recycling of their exoskeletons produced by the fishing industry is an important goal, even more important if some value is added to that sub-product. For this reason the objectives of this work were to determine the effects of presence of type and concentration of hydrophilic plasticizer, surfactant and polymer concentration on the wettability of Cuban chitosan based coatings in view of their application on vegetables and to develop a model allowing to optimize coating composition. Besides, the transport, mechanical and thermal properties of chitosan coatings, showing the best wettability, were characterized. The effects of chitosan and clay concentrations on the transport, mechanical, and thermal properties of chitosan/clay films were also evaluated.

Materials and Methods

The materials used to prepare the edible coating solutions or chitosan/clay films were: chitosan (obtained in the Pharmaceutical Laboratories Mario Muñoz, Cuba) with a degree of deacetylation of 90 %, glycerol 87% (Panreac, Spain), sorbitol 97% or polyethylene glycol MW 400 (Acros Organics, Belgium) as plasticizers, Tween 80 (Acros Organics, Belgium) as surfactant, lactic acid (Merck, Germany), clay (courtesy of Instituto Politécnico de Viana do Castelo, Portugal) with a mean particle size distribution of 2 ì and distilled water.

The coating solutions were prepared dissolving chitosan (1.0, 1.5 or 2.0 % w/v) in a 1% (v/v) lactic acid solution; 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/v). 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 constant.

Nanoclay solutions (1 and 3 % w/w chitosan) were prepared according with the methods reported by Xu and others, (2005) [5] by dispersing appropriate amounts of clay into 5 mL of 1% lactic acid solution and vigorously stirring for 24 h. Afterwards, 100 mL of chitosan solution (1.0 to 2.0 % (w/v)) was added slowly into pretreated clay solutions. The mixtures were stirred continuously for 4 h and then cast onto a glass plate.

The films were dried in an oven at 35 ° C. Dried films were peeled from the plate and cut in circles with approximately 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

Both contact angle (è) and surface tension (γ_L) were determined with a face contact anglemeter (OCA 20, Dataphysics, Germany). The (γ_L) of the coating solution was measured by the pendent drop method and Laplace-Young approximation (Song, 1996) [6]. The (è) was measured by the sessile drop method. Ten replicates of contact angle and surface tension measurements were analyzed at 20 (± 1) ºC.
Oxygen permeability (OP) and Carbon dioxide permeability (CO2 P) were determined based on the ASTM (2002) method [7] while water vapor permeability (WVP) of the films was determined gravimetrically based on ASTM E96-92 method [8].
Tensile strength (TS) and elongation-at-break (E) were measured with an Instron Universal Testing Machine (Model 4500, Instron Corporation) following the guidelines of ASTM Standard Method D 882-91[9].
Differential scanning calorimetry and Thermogravimetric analyses (TGA) measurements were performed with a Shimadzu DSC-50 (Shimadzu Corporation, Kyoto, Japan). About 10 mg of the samples were placed in stainless steel DSC pans and were heated from 25 to 350 °C at a heating rate of 10 °C/min in a helium atmosphere, while for the TGA measurement the samples were placed in the balance system and heated from 25 °C to 600 °C at a heating rate of 10 °C/min in a helium atmosphere.

Results and Discussion

BThe 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) [10,11]. It is therefore necessary to determine the surface energy of tomato and carrot in order to verify the applicability of that method.
The contact angle determinations of at least three pure compounds (water, formamide and bromonaphthalene) on the surface of tomato or carrot combined with their surface tension values [12, 13], allowed the adjustment of the experimental data to a plot and produces the following equations for tomato (Eq.1) and carrot (Eq.2).

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

[Equation 1]

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

[Equation 2]

The polar and dispersive components of the surface tension 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 [14].The Zisman method can therefore be applied to estimate the critical surface tension. In the present work it has been found that the critical surface tension has values of 17.8 and 24.5 mN/m.

Table 1: Model equations adjusting to W_a, W_s and W_c as functions of chitosan (q) and Tween 80 (t) 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 $RE = \left|\left(\frac{OE - OM}{OE}\right)\right| \times 100$, where OE is the Optimal Experimental and OM is the Optimal Model.

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 ($p < 0.05$) were found between the values of adhesion coefficient (W_a) and W_s for tomato and carrot. The influence of plasticizers in the surface properties of the chitosan coating was studied and a tendency can be observed that W_a and W_s decreased and cohesion coefficient (W_c) 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 in this order Also in this case remarkable differences were found between the behavior of tomato and that of the carrot ($p<0.05$).

The influence of chitosan and Tween 80 concentrations on the W_a, W_c and W_s were described by a polynomial model (Table 1) for both vegetables. 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 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.

The transport properties of chitosan coatings, showing the best wettability, were characterized. 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} similar to those results reported by others authors [1], while that the OP and CO_2P values increase with increasing chitosan concentration. Similar results were obtained with respect to WVP. The chitosan films exhibited WVP of 3.02 to 3.31 10^{-1} g m^{-1} day^{-1} atm^{-1} values lowest that 9.42 x 10^{-1} g m^{-1} day^{-1} atm^{-1} reported [1]. 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 [5].

Results also show that increases in chitosan concentration while keeping Tween 80 concentration constants increased the values of TS while E decreased significantly ($p < 0.05$). This behaviour may be due to the fact that chitosan forms hydrogen bonds between hydroxyl groups and amino groups in chitosan film, during the film formation and hydrogen bonding in the chitosan films increased with the increasing amount of amino and hydroxyl groups, due to the increased in concentration of chitosan [2].

The chitosan/clay films showed an improvement of the water vapour barrier property by incorporation of clay in the film matrix ($p = 0.05$) (Table 2). The greatest values of WVP were obtained for those films with the lowest concentration of chitosan and significant influence of both chitosan and clay concentration ($p = 0.05$) was found. The WVP value of the chitosan films were between 2.38 x 10^{-12} kg m/m^2 s Pa and 2.49 x 10^{-12} kg m/m^2 s Pa, higher values than to those reported [4], for chitosan films 2% (w/v) in solution of acetic acid 1% (w/v) (1.31 x 10^{-12} kg/m^{2}sPa), this difference could be due by the acid used to dissolve the chitosan and because we used chitosan obtained from lobster instead of chitosan from another source. The WVP of the nanocomposite films decreased significantly ($p = 0.05$) by 9-32% depending on the chitosan and clay concentration. The decrease in WVP of nanocomposite films is believed to be due to the presence of ordered dispersed nanoparticle layers with large aspect ratios in the polymer matrix [15]. This forces water vapor traveling through the film to follow a tortuous path through the polymer matrix surrounding the particles, thereby increasing the effective path length for diffusion [4]

The influence of chitosan and clay concentration (q and c) on the WVP was described by a polynomial model that suggested that chitosan concentration is the variable of higher influence.

$$WVP = 3.05 \times 10^{-12}\, q - 8.32 \times 10^{-13}\, c + 2.46 \times 10^{-13}\, c^{2;}\ p = 0.05 \qquad R^2 = 0.75 \qquad \text{[Equation 3]}$$

Table 2: Chitosan and clay concentration: effects on barrier and mechanical properties of chitosan/clay films. (Standard Deviations given in parentheses)^a

Film		**WVP x 10^{-12} (Kg m^{-1} s^{-1} Pa^{-1})**	**OP ($cm^3 m^{-1} day^{-1}$ atm^{-1})**	**CO_2P ($cm^3 m^{-1} dia^{-1}$ atm^{-1})**	**TS (MPa)**	**E (%)**
Chitosan (%w/v)	**Clay (% w/w chitosan)**					
1.0	0	2.41 (0.19) b	0.012 (0.0007) c	23.15 (0.98) a	11,69 (1.98) a	14,33 (3.36) c
1.0	1	1.75 (0.19) a	0,013 (0.0001) c	23.46 (1.54) a	17,05 (3.68) a	6,79 (1.18) b
1.0	3	1.96 (0.12) a	0.013 (0.0006) c	24.89 (2.95 a	21,54 (3.52) a	6,14 (1.37) ab
1.5	0	2.48 (0.10) b	0.012 (0.0003) bc	23.24 (1.70) a	47,46 (7.6) bc	4,77 (1.26) ab
1.5	1	2.49 (0.02) b	0.008 (0.0005) ab	26.40 (1.86) a	44,97 (0.04) b	6,86 (1.18) b
1.5	3	2.36 (0.13) b	0.010 (0.0008) a	22.34 (1.46) a	45,21 (4.99) b	6,41 (1.12) ab
2.0	0	2.94 (0.08) c	0.012 (0.0008) ab	23.19 (0.49) a	58,85 (7.25) cd	3,56 (1.25) ab
2.0	1	1,97 (0.07) a	0.007 (0.0009) a	22.84 (0.68) a	61,26 (5.44) d	3,32 (0.32) a
2.0	3	2.38 (0.24) b	0.007 (0.0008) a	21.40 (1.26) a	76,67 (8.21) e	5,54 (0.52) ab

$^{a-d}$ Means with different letters within a column indicate significant differences (p= 0.05).

The values of OP of these films oscillated in a range of 7.4 to 13.1 x 10^{-3} cm^3 O_2 m^{-1} day^{-1} atm^{-1} similar to those results reported [1]. The chitosan concentration has a significant incidence to $p = 0.05$ and as tendency a decrease it can be observed with the clay presence in chitosan films. On the other hand the chitosan and clay concentration don't influence significantly on the CO_2 permeability to $p = 0.05$ (see Table 2)

The OP of the films can be described by the following polynomial equations:

$OP = 0.029 - 0.022\ q - 0.061\ q^2$ $p = 0.05$ $R^2 = 0.75$ [Equation 4]

The TS of chitosan/nanoclay films increased significantly ($p<0.05$) with increasing chitosan and clay concentration, while the values of E decreased slightly for high values of chitosan concentration (Table 2). These values were in good agreement with previously reported values for chitosan film [4]. The main reason for the increase in tensile strength in polymer/layered silicate clay nanocomposites in the strong interaction between polymer matrix and silicate layers via the formation of hydrogen bonds [16]. The extent of the increase in TS depends directly upon the average length of the dispersed clay particles and, hence, the aspect ratio [4].The TS and E of the films can be described by the following polynomial equations:

$TS = -133.0 + 193.4\ q - 48.77\ q^2$ $p = 0.05$ $R^2 = 0.92$ [Equation 5]

$E = 31.166 - 22.765\ q - 6.805\ c + 3.154\ qc.$ $p = 0.05$ $R^2 = 0.70$ [Equation 6]

DSC plots of chitosan films showed two endothermic peaks for all products. The first endothermic peak that occur over a temperature range (78 ^{0}C – 94^{0}C) was attributed to solvent evaporation [5, 17], while the peaks in the range of 179–190°C showed that crystallization of the chitosan was not inhibited by the nanoclays. The T_m (melting point) increased with the increase of chitosan concentration, the changes in T_m, with addition of clay, were not significant to films, similar results were report [5]. The onset temperatures of thermal degradation did not show significant variations among the chitosan and chitosan/clay films. All chitosan films were degraded at 286 ^{0}C to 297 ^{0}C which agrees well with the results reported [5, 17].

Conclusions

Tomato and carrot have low energy surfaces; their critical surface tensions were determined. The increase of the concentration of chitosan and plasticizers decreased the values of W_s and W_a. The optimum values of the spreading coefficients were experimentally obtained. The results of wettability determinations allowed adjusting a polynomial model, thus creating the basis for a future choice of the composition of the films.
The oxygen, carbon dioxide and water vapor permeability of chitosan films depend on chitosan concentrations while keeping Tween 80 concentration constant.
The chitosan-based nanocomposite films showed an improvement of the water vapour barrier property by incorporation of clay in the film matrix. The chitosan and clay concentration had incidence on the properties evaluated.

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