Retarding strawberry fruit senesce with edible coatings – case study

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Abstract

The objectives of this work were to study the ability of starch, carrageenan and chitosan based coatings to extend the shelf life of strawberry fruit (*Fragaria ananassa*). To do so, the surface properties of fresh strawberry and the wettability of the coatings were studied.

The superficial tension of the strawberry was 28.94 mN/m, and its polar and dispersive component was 22.99 mN/m and 5.95 mN/m, respectively. The critical superficial tension of the strawberry was 18.84 mN/m, obtained from a Zisman plot.

The wettability of the coatings (starch, carrageenan and chitosan) is optimized with compositions of, respectively: 2 % of starch and 2 % of sorbitol; 0,3 % of carrageenan, 0,75 % of glicerol and 0,02 % of Tween 80; 1 % of chitosan and 0,1 % of Tween 80.

The effect of the application of these coatings in fresh strawberry was assessed by controlling the content in soluble solids, the colour evolution, the firmness, the mass variation and the microbiological growth during a period of 6 days. No significant differences were found between the chromaticity coordinates. The minimum loss of firmness was obtained in strawberries coated with carrageenan and calcium chloride. The minimum loss of mass was obtained in fruits with chitosan and carrageenan coatings both with calcium chloride. Relatively to the content in soluble solids the coating of chitosan and calcium chloride presented the best result.

The addition of 1 % of di-hydrated calcium chloride to coatings was also studied, and this was shown to decrease the microbial growth rate of the fruit. The minimum rate of microbial growth was obtained with strawberries coated with chitosan and calcium chloride.

Keywords:

Edible coatings; strawberry shelf-life; oxygen permeability; wettability of edible coatings

1. Introduction

Research into edible coatings and films has been intense in recent years. The attempt to diminish the losses in the crops and to maintain the quality of fresh fruits for a longer period is priority for all the producers. The development of coatings from water soluble has brought a surge of new types of coatings for extending the shelf-life of fruits and vegetables because of the selective permeabilities of these polymers to O_2 and CO_2. Polysaccharide based coatings can be used to modify the internal atmosphere of the fruit and thus retarding is senesce (Nisperos- Carriedo, 1994).

Even though some edible coatings have been successfully applied to fresh produce, other applications adversely affect quality. Modification of the internal atmosphere by the use of edible coatings can increase disorders associated with high carbon dioxide or low oxygen concentration (Ben-Yehoshua, 1969), is only natural that the control of gas permeability of the films should be a priority in the development of the latest.

The effectiveness of edible coatings for fruits and vegetables depends primarily on controlling the wettability of the coating solutions, which affects the coating thickness of the film (Park, 1999). Edible coating formulations must wet and spread on the fruit's surface uniformly and upon drying form a coating that has adequate adhesion, cohesion, and durability to function properly (Krochta and Mulder-Johnston, 1997). Among other functionalities edible coatings can act like carriers for food additives such as antioxidants and antimicrobial agents onto the surface of the food.

The aim of this work was to study the ability of starch, carrageenan and chitosan based coatings to extend the shelf life of the strawberry fruit (*Fragaria ananassa*). This study was dived in two parts, in the first part wettability and gas permeability of coating solutions were determined, in the second part quality parameters of the fresh fruit were observed during the storage of the coated fruits.

2. Material and methods

2.1. Materials

All polysaccharides used in this study were food-grade. Specific material included starch Crisp Coat 868 (National Starch, Germany), κ-carrageenan DX5253 (FMC, Belgium), chitosan powder (Aqua Premier Co., Tailand), sorbitol 97%, polyethylene glycol MW 200 and Tween 80 (Acrōs Organics, Belgium), glycerol 87 % (Panreac, Spain), citric acid and calcium chloride (Merck, Germany).

2.2. Coating solutions

Solutions with 2 % (w/v) of starch were gelatinized by heating at 90 ºC; the pH value was adjusted to 5.6 with citric acid and the solutions were equilibrated during 10 minutes. Both glycerol and sorbitol were added as plasticizers, with concentrations between 1.5 and 2.5 $g_{solute}/L_{solution}$.

Carrageenan solution was prepared by dissolving 0.3 % (w/v) on distilled water, and heating at 80 ºC for 10 minutes; the pH value was adjusted with citric acid. Glycerol, sorbitol and PEG 200 were tested as plasticizers, with percentages between 0.5 and 1 % (w/v). Tween 80 was added solution as a surfactant with various concentrations (between 0.01 and 0.1 % (w/v)).

Chitosan solutions were made according to El Ghaouth *et al.* (1991).

2.3. Wettability

Both contact angle and surface tension (γ_{LV}) were determined with a face contact anglemeter (OCA 20, Dataphysics, Germany). Surface tension of the coating solution was measured by the pendent drop method and Laplace-Young approximation. Contact angle was measured by the sessile drop method. Twenty replicates of contact angle and surface tension measurements were analyzed at (19 ± 1) ºC.

Estimation of the critical surface tension (γ_C) of strawberry surface was obtained by extrapolation from the Zisman plot (Zisman, 1964), obtained using water, formamide, bromonaphthalene and toluene.

2.4. Physicochemical properties of coated fruits

Fresh strawberries (*Fragaria ananassa* cv. Camarosa) were purchased at the local market; the fruits were randomly distributed in seven equal parts. Sprays of the different coating solutions were applied and then stored at controlled temperature (0-5 ºC).

Weight loss of fresh strawberries during storage was measured by monitoring the weight changes of fruits.

Soluble solids were determined according to the AOAC 932.12 standard method.

The colour of the fruits was determined with a Minolta colorimeter (CR 300; Minolta, Japan).

The firmness was determined using a Texture Analyzer (TA-XT2, Stable Micro Systems, UK). A compression load cell of 25 kg and Ottawa cell with a holed extrusion plate were used.

2.5. Microbial assays

The total count was made according to the Portuguese standard NP 4405 (2002).

2.6. Statistical analysis

SPSS software (version 12.0, SPSS Inc., US) was used for all statistical analysis. Analysis of variance (ANOVA) and regression analysis were applied. The significance level used was 0.05.

3. Results and discussion

3.1. Critical surface tension

According to Zisman (1964), systems having a surface tension inferior to 100 mN/m (low-energy surfaces), the contact angle formed by a drop of liquid on the solid surface will be primarily a function of the surface tension of the liquid, γ_{LV}, (were phase V is air saturated with the vapour of liquid).

Given a pure liquid, for which surface tension its polar and dispersive contribution are known, if θ is the contact angle between the liquid and some solid, the interaction can be described in terms of the reversible work of adhesion, W_a, as:

$$W_a = W_a^d + W_a^p = 2 \cdot \left(\sqrt{\gamma_s^d + \gamma_l^d} + \sqrt{\gamma_s^p + \gamma_l^p} \right) = \gamma_L \left(1 + \cos\theta \right) \qquad \text{(Eq. 1)}$$

Rearranging this equation:

$$\frac{1 + \cos\ \theta}{2} \cdot \frac{\gamma_L}{\sqrt{\gamma_L^d}} = \sqrt{\gamma_S^p} \cdot \sqrt{\frac{\gamma_L^p}{\gamma_L^d}} + \sqrt{\gamma_S^d} \qquad \text{(Eq.2)}$$

The determined surface tension of the strawberry is 28.94 mN/m (therefore, it is a low-energy surface), its polar and dispersive components are 5.95 mN/m and 22.99 mN/m, respectively. These values were extrapolated from Figure 1 and based on data from Table 1.

Table 1 – Surface tension components of the liquids used for characterization of the strawberry surface

Compound	γ_L (mN/m)	γ_L^d (mN/m)	γ_L^p (mN/m)
Water[a]	72,10	19,90	52,20
Bromonaphthalene[a]	44,40	44,40	0,00
Formamide[a]	56,90	23,50	33,40
Toluene[b]	28,50	27,18	1,32

[a] Data adopted from Busscher *et al.*, 1984; [b] data adopted from Janczuk *et al.*, 1989

Being the surface of the strawberry a low-energy surface is now possible to apply the Zisman plot (Figure 2) to determine the critical surface tension. According to Rulon and Robert (1993) this kind of surfaces interacts with liquids primarily by dispersion forces and this fact explains why drops of polar liquids were not absorbed after a short period (Figure 3).

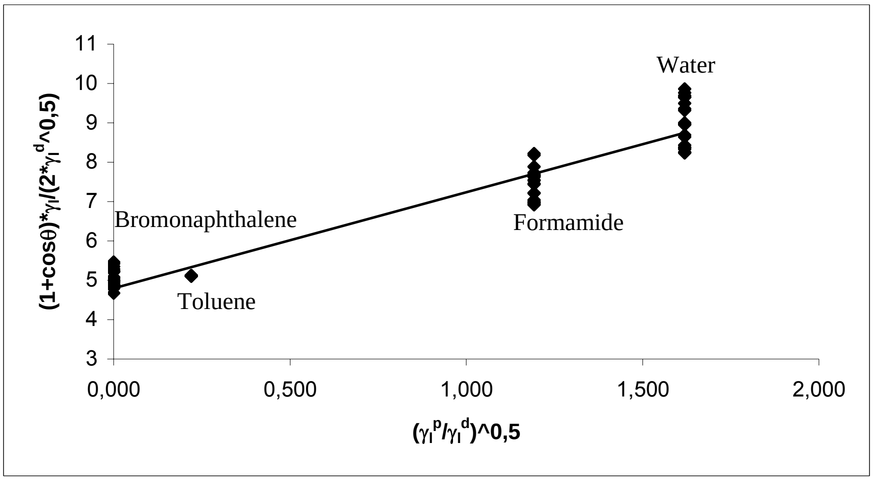

Figure 1 – Linear regression using Eq. 2 (0.05 confidence level and *n* = 80).

$$\frac{1+\cos\theta}{2}\cdot\frac{\gamma_L}{\sqrt{\gamma_L^d}}=(2.4391\pm 0.1229)\cdot\sqrt{\frac{\gamma_L^p}{\gamma_L^d}}+(4.7944\pm 0.0093); \qquad R = 0.9712 \qquad \text{(Eq. 3)}$$

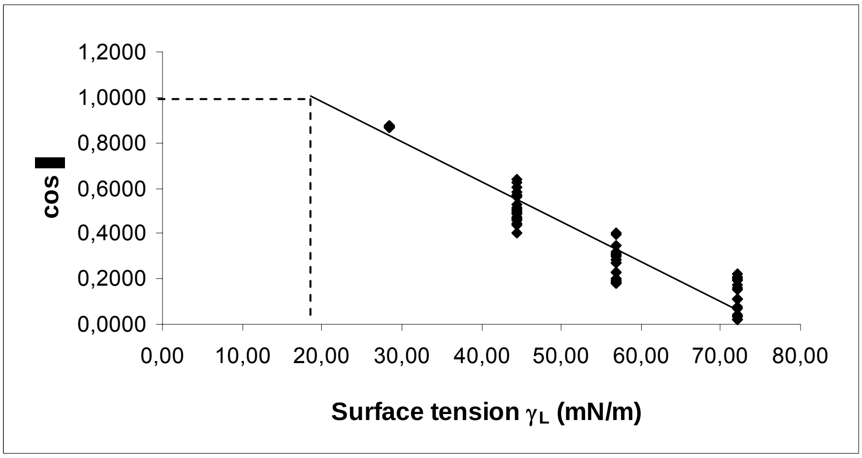

Figure 2 – Zisman plot for strawberry surface (0.05 confidence level and *n* = 80).

$$\cos\theta = (-0.0175\pm 0.0008)\cdot\gamma_L + (1.3339\pm 0.0011); \qquad R = 0.9683 \qquad \text{(Eq. 4)}$$

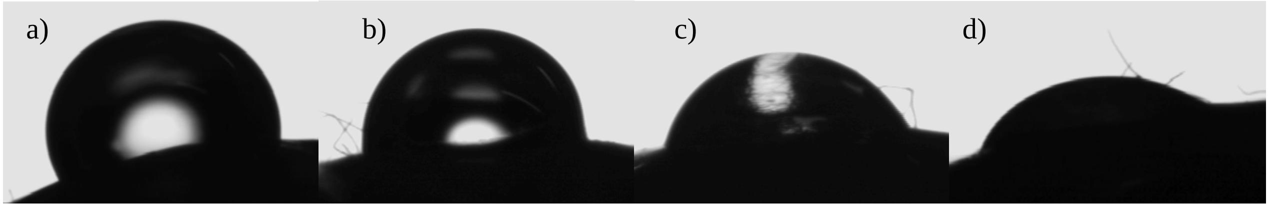

Figure 3 – Contact angle of the tested liquids on strawberry surface: a) water, b) formamide, c) bromonaphthalene, d) toluene.

The determined critical surface tension has a value of 18.84 mN/m.

3.2. Wettability of the coating solutions

The optimization of the composition of the coating solution can be made considering three parameters: the wettability, the adhesion and the cohesion coefficients. The control of the adhesion and cohesion coefficients is very important because if the former promotes the spreading of the liquid the later promotes its contraction. Table 3 presents the results for the optimized coatings.

The starch coating is optimized with the addition of 2 % of sorbitol.

Table 3 – Surface tension (γ_L), interfacial tension solid-liquid (γ_{SL}), contact angle (θ), wettability, adhesion and cohesion coefficients obtained for the different optimized coatings (average ± confidence interval, α= 0.05 and n = 20)

	Edible coating		
	Starch	Carrageenan	Chitosan
% Plasticizer	2.0 % sorbitol	0.75 % glycerol + 0.02 % Tween 80	0.10 % Tween 80
θ (º)	83.03 ± 3.46	86.07 ± 1.03	80.01 ± 3.51
γ_L (mN/m)	50.71 ± 0.27	48.62 ± 0.18	46.98 ± 0.07
γ_{SL} (mN/m)	22.83 ± 3.05	25.60 ± 0.88	20.85 ± 2.83
W_e (mN/m)	-44.61 ± 3.05	-45.28 ± 0.88	-38.89 ± 2.83
W_a (mN/m)	56.82 ± 3.04	51.96 ± 0.92	55.06 ± 2.84
W_c (mN/m)	101.43 ± 0.54	97.24 ± 0.36	93.95 ± 0.14

The high surface tension of carrageenan coatings indicate that the contact angles on the strawberry surface will be high; to minimize this problem Tween 80 was added and led to a significant reduction of γ_L; the critical concentration of this component is 0.02 % (w/v).

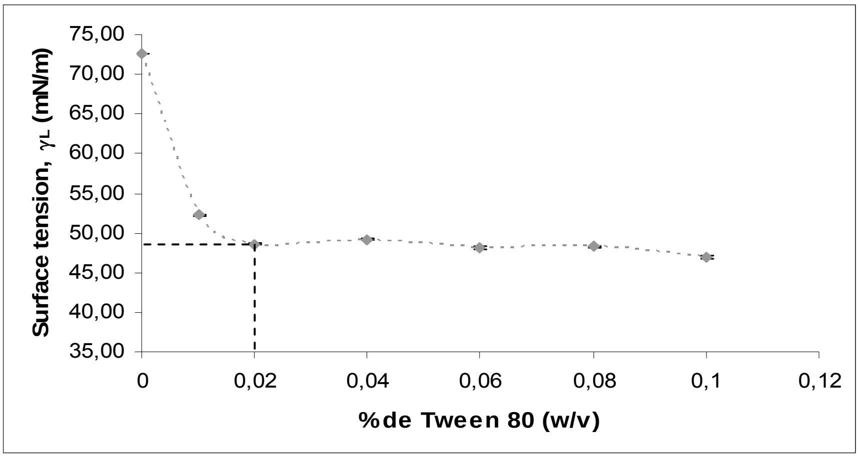

Figure 4 – variation of surface tension of the carrageenan based coating with the addition of Tween 80 (average ± confidence interval, α= 0.05 and n = 20).

Choi *et al.* (2002) related that the addition of 1 % of Tween 80 to a solution of 1.5 % (w/w) of chitosan increased the compatibility between the coating and the skin of apples, reducing the superficial tension of the liquid and thus increasing the spreading coefficient. The surface tension of the coating reported in Choi *et al.* (2002) study is similar to the one obtained in this work.

3.3. Post-harvest application

In this part the work the aim was to determine which coating is more efficient in retarding the strawberry senesce.

Loss of texture is dependent on both cell wall degradation and loss of turgidity of the tissue. Cell wall degradation during ripening is an enzymatic process and follows increase in the activity of endogenous cell wall degrading enzymes (e.g. polygalactoronase and cellulose). Loss of turgor pressure is related with loss of water or desiccation due to transpiration and respiration (Arul *et al.,* 2000).

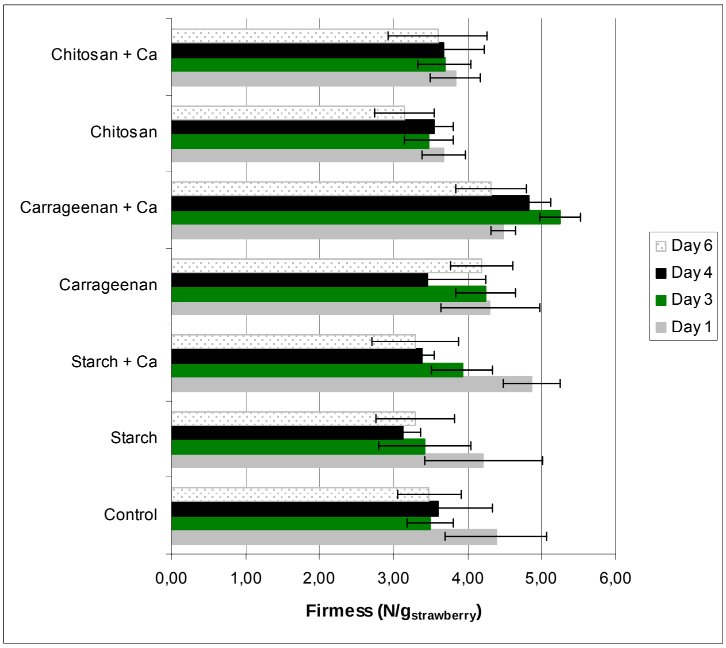

Figure 5 – Firmness changes in the strawberry fruit with and without coating during storage (average ± standard deviation, *n* = 4).

The strawberries coated with carrageenan, chitosan and chitosan and calcium presented smallest variation in firmness (Figure 5). It is interesting to notice that the calcium chloride addition seems to influence the firmness of the fruit. These results are in agreement with the ones obtained by Garcia *et al.* (1996), who reported that the presence of calcium in postharvest treatments delayed the loss of firmness of fresh strawberry.

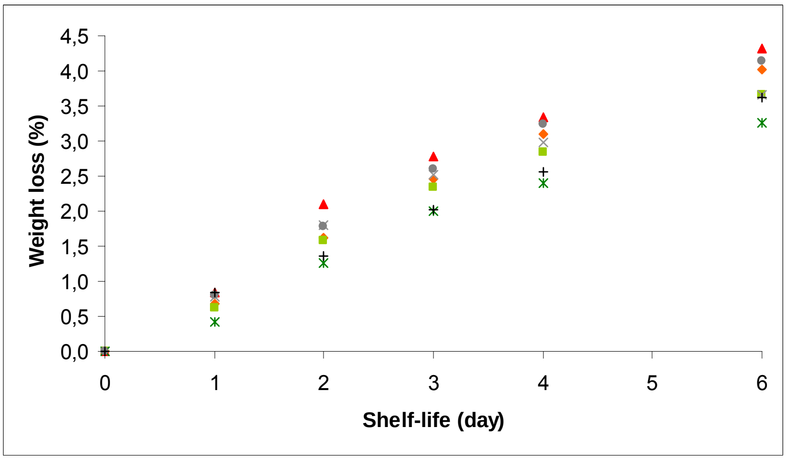

Figure 6 – Strawberry weight loss: uncoated (●), starch coating (■), starch and calcium chloride coating (▲), carrageenan coating (×), carrageenan and calcium chloride coating (✳), chitosan coating (✹), chitosan and calcium chloride coating (+), during storage (average ± standard deviation, *n* = 3).

The smallest loss of weight was obtained with chitosan and carrageenan coatings, both with calcium chloride (Figure 6). The water vapour transference occurs generally for the hydrophilic part of the film, thus the permeability to water vapour depends on the ratio of the hydrophilic/hydrophobic components (Hernandez, 1994). Even though polysaccharide films have high selectivity to oxygen and carbon dioxide, they are very permeable to water vapour; this fact explains why there were not large differences between coated and uncoated fruits. To avoid this, addition of lipids to the coatings could be considered.

The soluble solid percentage did not vary significantly during storage (Figure 7). The strawberries coated with chitosan and calcium chloride coating presented the smaller variation in the soluble solid content, however the differences between coated and uncoated fruits were statistically not significant.

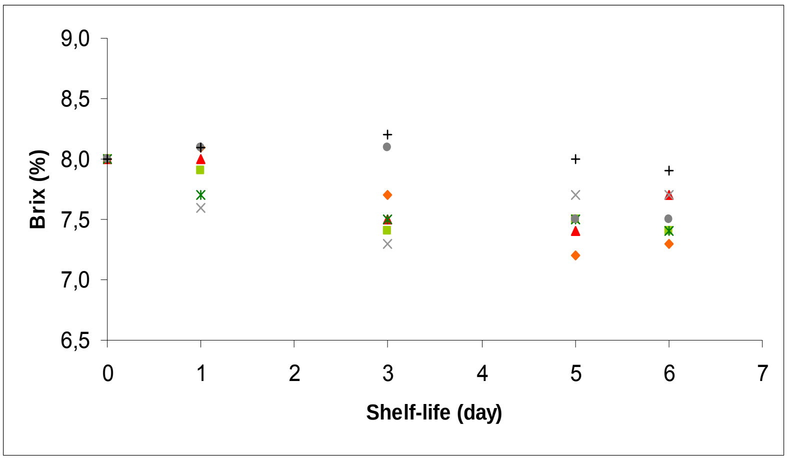

Figure 7 – Variation of the soluble solids content with storage: uncoated (●), starch coating (■), starch and calcium chloride coating (▲), carrageenan coating (×), carrageenan and calcium chloride coating (✳), chitosan coating (⬢), chitosan and calcium chloride coating (+) (average ± standard deviation, n = 3).

Colour changes in fresh fruits are a good indication of maturation. In this work no significant changes were obtained for lightness (L*).

With exception of the strawberries without covering, that had presented a considerable variation of the chromaticity coordinates, the coated fruits kept approximately the same value of a* and the b* until the fourth day of storage. At the sixth day of storage a decrease in the chromaticity coordinates was observed in the fruits coated with starch, carrageenan and calcium and chitosan solution, motivated essentially by the reduction of the coordinate a*. Coordinate b* slightly diminishes for all the studied fruits, indicating a loss of yellowness. This reduction is expressed as a typical dark red, very common in very mature fruits.

Assuming that in a given microbial culture the rate of growth in a given time t is proportional to the population density (q), at that instant:

$$\frac{1}{q}\cdot\frac{dq}{dt}=\mu_c \qquad \text{(Eq. 5)}$$

were μ_c is the growth rate.

The comparison of growth rates for the studied coatings indicates that coatings with calcium chloride have lower growth rates that the ones without this salt (Figure 8 and Table 4). Tissue maceration results in adequate supply of nutrients for pathogen’s growth. Calcium has long been used as firmness agent and therefore it may have an important role in the reduction of the growth rate.

Chitosan coatings have the lowest growth rate; this fact could be attributed to either its fungistatic property or/and the ability to induce defence enzymes and phytoalexins in plants (El Ghaouth et al., 1992).

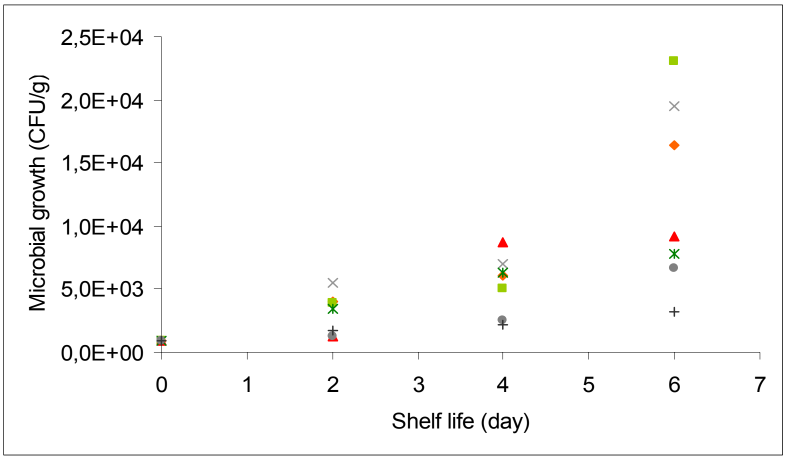

Figure 8 – Microbial growth in fresh strawberries: uncoated (●), starch coating (■), starch and calcium chloride coating (▲), carrageenan coating (×), carrageenan and calcium chloride coating (✳), chitosan coating (✸), chitosan and calcium chloride coating (+), during storage (according to NP4405).

Table 4 – Rate of microbial growth and correlation coefficient obtained for coated and uncoated strawberries stored at 0 - 5 ºC

Coating	μ_c (CFU/($g_{strawberry}$.day))	Correlation coefficient, R
Control	0.4621	0.9748
Starch	0.5060	0.9712
Starch + $CaCl_2$	0.4486	0.9339
Carrageenan	0.4795	0.9528
Carrageenan + $CaCl_2$	0.3604	0.9394
Chitosan	0.3388	0.9847
Chitosan+ $CaCl_2$	0.2037	0.9782

4. Conclusions

In this study we conclude that the strawberry surface is a low energy surface with a surface tension of 28.94 mN/m, and a polar and dispersive component of 22.99 mN/m and 5.95 mN/m, respectively. The critical surface tension of the strawberry surface is 18.84 mN/m.

The addition of calcium chloride to coatings decreases the microbial growth rate of the fruit. The minimum rate of microbial growth was obtained with strawberries coated with chitosan and calcium chloride.

No significant differences were found between the chromaticity coordinates. The minimum loss of firmness was obtained in strawberries coated with carrageenan and calcium chloride. The minimum loss of mass was obtained in fruits with chitosan and carrageenan coatings, both with calcium chloride. Relatively to the content in soluble solids the coating of chitosan and calcium chloride presented the best result.

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