



## Physical properties of edible coatings and films made with a polysaccharide from *Anacardium occidentale* L.

Maria G. Carneiro-da-Cunha<sup>a,\*</sup>, Miguel A. Cerqueira<sup>b</sup>, Bartolomeu W.S. Souza<sup>b</sup>, Marthyna P. Souza<sup>a</sup>, José A. Teixeira<sup>b</sup>, António A. Vicente<sup>b</sup>

<sup>a</sup> Departamento de Bioquímica/Laboratório de Imunopatologia Keizo Asami, Universidade Federal de Pernambuco, Campus Universitário, s/n, Cidade Universitária – CEP, 50.670-420 – Recife, PE, Brazil

<sup>b</sup> IBB – Institute for Biotechnology and Bioengineering, Centre of Biological Engineering, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal

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### ABSTRACT

The effect of the concentrations of the polysaccharide from *Anacardium occidentale* L. (Policaaju) and a surfactant (Tween 80) on relevant properties of edible coatings/films, in view of their application on apples (cv. Golden) was evaluated. The influence of the interactions between those two constituents on apples' surface properties and on the coating/film's wettability, water vapor permeability, opacity and mechanical properties was evaluated. The effects of the studied variables (polysaccharide and surfactant concentrations) were analyzed according to a 2<sup>2</sup> factorial design. Pareto bar charts were used to understand the most significant factors on the studied properties. The addition of surfactant reduced the cohesion forces, therefore reducing the surface tension and increasing the wettability; this resulted in an improved compatibility between the solution and the fruit skin surface. The opacity was also reduced. The results of each of the analyzed properties were adjusted to a polynomial, multifactor model, which provided a good fitting accuracy. This model is important once it will reduce the characterization work needed in subsequent applications of these coatings/films on foods.

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### 1. Introduction

In the most recent years, food and packaging industries have been joining efforts to reduce the amount of food packaging materials. This attitude is closely connected with the growing importance of the environmental issues at the consumer level, which are being translated to increasingly restrictive policies by the governments of many countries worldwide. As an answer to these issues, the commercial use of bio-based primary food packaging materials is being implemented, based on the research efforts which are being made by many groups all over the world. Related with the concerns for a safer and healthier environment, consumers also demand for high quality food, without chemical preservatives, and with an extended shelf life, leading to additional efforts to get new natural preservatives and antimicrobials.

The modified atmosphere created by edible coatings protects the food from the moment it is applied until it reaches the final consumer (Durango et al., 2006; Ribeiro et al., 2007). Several researchers have studied the application of coatings on fruits such as apples (Rojas-Grau et al., 2007), strawberries (Mali and Grossmann, 2003; Tanada-Palmu and Grosso, 2005; Ribeiro et al., 2007), mangoes

(Chien et al., 2007; Dang et al., 2008), tomato (Casariego et al., 2008) and kiwi (Xu et al., 2001). Polysaccharide-based coatings are colorless, have an oily-free appearance and a low caloric content and can be used to increase the shelf life of fruits, vegetables, shellfish or meat products avoiding or significantly reducing dehydration, oxidative rancidity and darkening of the surface. Other characteristics that make them attractive are their transport properties (permeability to water vapor), through which they can reduce e.g., the weight loss and the microbial spoilage of the fruits (Dang et al., 2008). The knowledge of the wettability of the coatings is also of particular importance, as it is a parameter that defines the ability of a coating to be uniformly distributed on the surface of the fruit (Lin and Zhao, 2007), thus directly affecting its performance as a preservation agent.

Policaaju gum is a bark exudate from *Anacardium occidentale* L., a tree that grows in tropical and subtropical countries. This gum is a complex polysaccharide, has a highly branched galactan framework consisting of chains of (1 → 3)-linked β-D-galactopyranosyl units with interspersed β(1 → 6) linkages. The main aldobiouronic acid present is 6-O-(β-D-glucopyranosyluronic acid)-D galactose (Zakaria and Rahman, 1996).

The easy access to this inexpensive, non-toxic, hydrophilic, biocompatible and biodegradable polysaccharide from *A. occidentale* L. (cashew tree) gum, presenting interesting biological activity and

\* Corresponding author. Tel.: +55 81 21268547; fax: +55 81 21268576.  
E-mail address: [mgcc@ufpe.br](mailto:mgcc@ufpe.br) (M.G. Carneiro-da-Cunha).

good rheological properties are factors that also make viable its potential use as immobilization matrix in other applications such as, e.g., cutaneous dressing (Monteiro et al., 2007).

The development of applications from natural products and their use at production sites to increase the fruits' shelf life might be an important contribution for the economy of countries like Brazil.

The objective of this work was to evaluate the effect of Policaju and Tween 80 concentrations on relevant properties of edible coatings/films, in view of their application on apple fruit. In view of this, the influence of the interactions between those constituents on the coatings'/films' wettability, work of adhesion and cohesion, water vapor permeability, opacity, tensile strength and on elongation at break was evaluated. A polynomial model was used to describe the results obtained for each of these properties.

## 2. Materials and methods

### 2.1. Materials

The polysaccharide from *A. occidentale* L. tree gum (collected in the South coast of Pernambuco, Brazil) was obtained according to Menestrina et al. (1998) and termed Policaju. Sorbitol 97% and Tween 80 were obtained from Acros Organics (Belgium). Apples (cv. Golden) were purchased from a local supermarket (Braga, Portugal).

### 2.2. Coatings and films preparation

Edible coatings/films were prepared using water, Policaju, sorbitol and Tween 80. Coatings/films solutions were based on a two level factorial design with Policaju concentrations of 1.5% and 3.0% (w/v) and Tween 80 concentrations of 0.0% and 0.1% (w/v), together with sorbitol, always present at the concentration of 0.4% (w/w). Policaju was dissolved in distilled water under agitation, using a magnetic stirrer at 200 rpm for 24 h at room temperature (20 °C), sorbitol (and, eventually, Tween 80) was subsequently dissolved in this solution. A constant amount (13 mL) of each of the solutions obtained was cast onto a 5.7 cm diameter glass plate. The films were then dried in an oven at 35 °C for 16 h and maintained at 20 °C and 50% relative humidity (RH) until characterization. Although the raw materials and the production methods are the same, the designation coatings/films is used throughout the text once the form under which they are characterized varies depending on the test being performed (e.g., mechanical tests and permeabilities need to be made on films, while the tests on wettability need to be performed on the coated fruits).

### 2.3. Film thickness

Film thickness was measured with a digital micrometer (No. 293–561, Mitutoyo, Japan). The measurements were performed as follows: each film obtained as described in the previous section was divided into five pieces; on each piece, five different, randomly chosen points were measured, thus totaling 25 measurements for each film. The mean values were used to calculate films properties.

### 2.4. Fruit and their preparation for contact angle measurements

The apples were selected for their uniformity, size, color (paying particular attention at their ripeness state) and absence of physical damages and fungal infection. Before testing, the fruits were left at room temperature (20 °C) and their surface was cleaned with distilled water. Thin portions of the outer surface (skin) of the fruits were cut with a knife and placed on a glass plate for contact angle measurements.

### 2.5. Critical surface tension

According to Zisman (1964), in systems having a surface tension lower than 100 mN m<sup>-1</sup> (low-energy surfaces), the contact angle formed by a drop of liquid on a solid surface will be a linear function of the surface tension of the liquid,  $\gamma_{LV}$ , (were phase V is air saturated with the vapor of the liquid, L). Zisman's method is applicable only for low-energy surfaces; therefore it is necessary to determine the surface energy of the apple.

For a pure liquid, if polar ( $\gamma_L^p$ ) and dispersive ( $\gamma_L^d$ ) interactions are known, and if  $\theta$  is the contact angle between that liquid and a solid, the interaction can be described in terms of the reversible work of adhesion,  $W_a$ , as:

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

where  $\gamma_S^p$  and  $\gamma_S^d$  are the polar and dispersive contributions of the surface of the studied solid. Rearranging Eq. (1), yields:

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

The contact angle determinations of at least three pure compounds: bromonaphthalene (Merck, Germany), formamide (Merck, Germany) and ultra pure water, on the surface (skin) of the apple combined with the respective dispersive and polar component values, will allow the calculation of both the independent variable,  $\left( \sqrt{\frac{\gamma_L^p}{\gamma_L^d}} \right)$ , and the dependent variable,  $\left( \frac{1 + \cos \theta}{2} \cdot \frac{\gamma_L}{\sqrt{\gamma_L^d}} \right)$ , from Eq. (2).

The surface tension, the dispersive and the polar component are, respectively, 72.10, 19.90 and 52.20 mN m<sup>-1</sup> for water, 44.40, 44.40 and 0.00 mN m<sup>-1</sup> for bromonaphthalene and 56.90, 23.50 and 33.40 mN m<sup>-1</sup> for formamide (Busscher et al., 1984).

The estimation of the critical surface tension ( $\gamma_C$ ) was performed by extrapolation from Zisman plots (Zisman, 1964). The critical surface tension ( $\gamma_C$ ) is defined as:

$$\gamma_C = \lim_{\theta \rightarrow 0} \gamma_{LV} \quad (3)$$

### 2.6. Wettability

The wettability was obtained by determining the values of the spreading coefficient ( $W_s$ ) and the works of adhesion ( $W_a$ ) and cohesion ( $W_c$ ). The surface tension of the coating solution was measured by the pendant drop method using the Laplace–Young approximation (Song and Springer, 1996).

The contact angle ( $\theta$ ) of a liquid drop on a solid surface is defined by the mechanical equilibrium of the drop under the action of three interfacial tensions: solid–vapor ( $\gamma_{SV}$ ), solid–liquid ( $\gamma_{SL}$ ), and liquid–vapor ( $\gamma_{LV}$ ). The equilibrium spreading coefficient ( $W_s$ ) is defined by Eq. (4) (Rulon and Robert, 1993) and can only be negative or zero.

$$W_s = W_a - W_c = \gamma_{SV} - \gamma_{LV} - \gamma_{SL} \quad (4)$$

where  $W_a$  and  $W_c$  are the works of adhesion and cohesion, defined by Eqs. (5) and (6), respectively.

$$W_a = \gamma_{LV} + \gamma_{SV} - \gamma_{SL} \quad (5)$$

$$W_c = 2 \cdot \gamma_{LV} \quad (6)$$

Contact angle ( $\theta$ ) and liquid–vapor surface tension ( $\gamma_{LV}$ ) were measured in a face contact angle meter (OCA 20, Dataphysics, Germany). The samples of the coatings were taken with a 500  $\mu$ L syringe (Hamilton, Switzerland), with a needle of 0.75 mm of diameter. The contact angle at the fruit surfaces was measured

by the sessile drop method (Newman and Kwok, 1999). Measurements were made in less than 30 s. Twenty replicates of contact angle and surface tension measurements were obtained at 21.1 ( $\pm 0.4$ ) °C.

### 2.7. Water vapor permeability (WVP) measurement

Water vapor permeability (WVP) was determined gravimetrically based on ASTM E96-92 method (Guillard et al., 2003). The film was sealed on the top of a permeation cell containing distilled water (100% RH; 2337 Pa vapor pressure at 20 °C), placed in a desiccator at 20 °C and 0% RH (0 Pa water vapor pressure) containing silica. The cells were weighted at intervals of 2 h during 10 h. Steady-state and uniform water pressure conditions were assumed by keeping the air circulation constant outside the test cell by using a miniature fan inside the desiccator. The slope of the weight loss versus time was obtained by linear regression. The thicknesses values used in WVP calculus were presented in Table 1. Three replicates were obtained for each film.

### 2.8. Opacity

The films were whitish and not completely opaque. Their opacity was determined using a Minolta color meter (CR 400; Minolta, Japan) and according to the Hunterlab color scale. Following this method the opacity ( $Y$ ) was calculated as the ratio between the opacity of each sample on the black standard ( $Y_b$ ) and the opacity of each sample on the white standard ( $Y_w$ ). From three replicates of each film sample were determined at random three  $Y_b$  and  $Y_w$  and an average of them were used for calculations. The results were expressed as a percentage:  $Y (\%) = 100 (Y_b/Y_w)$ .

### 2.9. Tensile strength (TS) and elongation at break (EB)

TS and EB were measured with an Instron Universal Testing Machine (Model 4500, Instron Corporation) following the guidelines of ASTM Standard Method D 882-91. The initial grip separation was set at 30 mm and the crosshead speed was set at 5 mm min<sup>-1</sup>. TS was expressed in MPa and calculated by dividing the maximum load ( $N$ ) by the initial cross-sectional area (m<sup>2</sup>) of the specimen. EB was calculated as the ratio of the final length at the point of sample rupture to the initial length of a specimen (30 mm) and expressed as a percentage. According to the ASTM standard, film strips with a length of 45 mm and a width of 20 mm were used. TS and EB tests were replicated at least five times for each type of film.

### 2.10. Statistical analysis

#### 2.10.1. Design of experiments

A design of 2-levels was applied, giving a total of four non-center-points runs. The independent variables were Policaju concen-

tration (1.5% and 3.0% (w/v)) and Tween 80 concentration (0.0% and 0.1% (w/v)).

#### 2.10.2. Data and graphical analysis

All data and graphical analyses were performed using Microsoft Windows Excel 2003 and Statistica software (release 7, edition 2004, Statsoft, Tulsa, OK, USA). Pareto charts were used to evaluate the statistical significance of each factor and the interactions between the factors.

#### 2.10.3. Modelling

The experimental data were fitted to a multifactor model, represented by Eq. (7):

$$Y = a + bX_1 + cX_2 + e \cdot X_1X_2 \quad (7)$$

where  $Y$  represents the dependent variables:  $W_s$ ,  $W_a$ ,  $W_c$ , WVP, Opacity, TS and EB; and  $X_1$ ,  $X_2$  are the independent variables, Policaju and Tween 80 concentrations, respectively.

The fitting accuracy of the models was evaluated by the determination of the following coefficients: coefficient of determination ( $R^2$ ), mean relative deviation modulus ( $E$ ) and by the accuracy factor ( $A_f$ ). The goodness of fit was quantified by the  $R^2$  which gives the percentage of the variance of the data that is explained by the model:

$$R^2 = 1 - \frac{SSR}{SSD} \quad (8)$$

where SSD is the variance times the degrees of freedom:

$$SSD = \sum_{i=1}^n (y_e - \hat{y}_e)^2 \quad (9)$$

with  $\hat{y}_e$  being the average of all experimental data points:

$$\hat{y}_e = \frac{\sum_{i=1}^n y_e}{n} \quad (10)$$

The higher the  $R^2$  value, the better the model fits the experimental data (Neter et al., 1996).

The mean relative percentage deviation modulus,  $E$ , in Eq. (11), indicates the goodness of fit between the observed and predicted values of the analyzed parameters for the independent variables used, being  $N$  the number of data points,  $R_{obs}$  the observed values of each parameter, and  $R_{pre}$  the values predicted by the model. Values below 10% are indicative of a good fit (McLaughlin and O'Beirne, 1999).

$$E = \frac{100}{N} \cdot \sum_{i=1}^N \frac{|(R_{obs} - R_{pre})|}{R_{obs}} \quad (11)$$

**Table 1**

Values of wettability, adhesion and cohesion coefficients, water vapor permeability, opacity, tensile strength, elongation at break and thickness obtained for Policaju coating/film.

| Properties   | 1.5% Policaju + 0.0% Tween 80 | 1.5% Policaju + 0.1% Tween 80 | 3.0% Policaju + 0.0% Tween 80 | 3.0% Policaju + 0.1% Tween 80 |
|--|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| $W_s$ (mN m <sup>-1</sup> )  | −53.85 ± 1.41 <sup>a</sup>    | −29.01 ± 0.51 <sup>b</sup>    | −52.98 ± 0.81 <sup>a</sup>    | −26.16 ± 0.48 <sup>c</sup>    |
| $W_a$ (mN m <sup>-1</sup> )  | 38.55 ± 1.14 <sup>a</sup>     | 36.09 ± 0.63 <sup>b</sup>     | 42.69 ± 0.91 <sup>c</sup>     | 35.40 ± 0.83 <sup>b</sup>     |
| $W_c$ (mN m <sup>-1</sup> )  | 93.21 ± 0.10 <sup>a</sup>     | 65.47 ± 0.14 <sup>b</sup>     | 95.97 ± 0.17 <sup>c</sup>     | 61.61 ± 0.33 <sup>d</sup>     |
| WVP × 10 <sup>-11</sup> g m <sup>-1</sup> s <sup>-1</sup> Pa <sup>-1</sup> | 7.83 ± 0.63 <sup>a</sup>      | 10.83 ± 0.22 <sup>b</sup>     | 8.84 ± 0.31 <sup>c</sup>      | 13.56 ± 0.67 <sup>d</sup>     |
| Opacity (%)  | 8.81 ± 0.56 <sup>a</sup>      | 4.16 ± 0.28 <sup>b</sup>      | 8.64 ± 1.21 <sup>a</sup>      | 4.89 ± 0.66 <sup>b</sup>      |
| TS (MPa)   | 4.61 ± 0.33 <sup>a</sup>      | 8.67 ± 0.41 <sup>b</sup>      | 3.50 ± 0.31 <sup>c</sup>      | 5.40 ± 0.37 <sup>d</sup>      |
| EB (%)   | 15.01 ± 1.12 <sup>a</sup>     | 15.24 ± 1.54 <sup>b</sup>     | 9.08 ± 1.94 <sup>c</sup>      | 5.93 ± 0.27 <sup>d</sup>      |
| Thickness × 10 <sup>-4</sup> (m)   | 0.083 ± 0.006 <sup>a</sup>    | 0.109 ± 0.002 <sup>b</sup>    | 0.122 ± 0.006 <sup>c</sup>    | 0.164 ± 0.019 <sup>a</sup>    |

<sup>a-d</sup>Different superscript letters in the same line indicate a statistically significant difference (Turkey test  $p < 0.05$ ). Data are averages ± standard deviation:  $W_s$ ,  $W_a$  and  $W_c$ ,  $n = 20$ ; WVP,  $n = 3$ ; opacity and mechanical properties,  $n = 5$ .

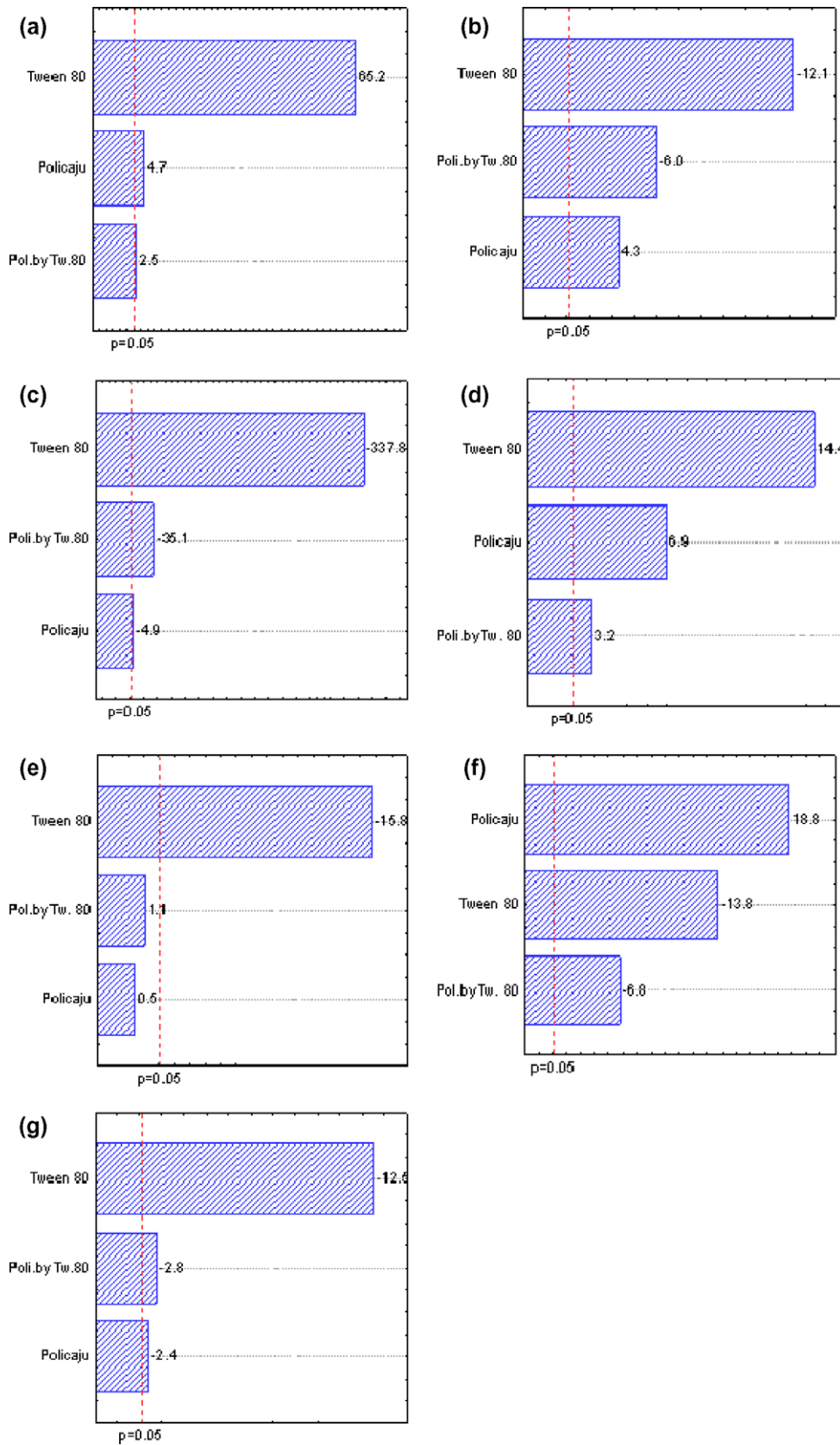


Fig. 1. Pareto charts for the analyzed properties:  $W_s$  (a),  $W_a$  (b),  $W_c$  (c), water vapor permeability (d), opacity (e), tensile strength (f) and elongation at break (g).

Also the accuracy factor ( $A_f$ ) gives us information of the fitting accuracy. The closer the  $A_f$  value is to 1, the better the accuracy (Ross, 1996):

$$A_f = 10^{-\left(\frac{\sum_{j=1}^J \log\left(\frac{R_{pred}}{R_{obs}}\right)}{J}\right)} \quad j = 1, 2, 3, \dots, J \quad (12)$$



### 3. Results and discussion

Preliminary experiments (data not shown) have shown that a Policaju content lower than 1.5% (w/v) would render the film too brittle, therefore only polysaccharide concentrations of 1.5% or above were used here. Different plasticizers such as glycerol, polyethylene glycol and sorbitol were also subjected to a preliminary evaluation, being sorbitol the one that provided a better flexibility to the film, at a concentration of 0.4 g/g of Policaju. It is known that the plasticizer decreases the interaction forces between adjacent polymeric chains and increases the chain mobility, becoming the coating/film more flexible. The addition of sorbitol therefore improves the mechanical properties of the coating/film once it is formed, and made it possible to form stand-alone films with good flexibility and easily removable from the Petri dishes where they were cast, making them easier to handle. Tween 80 was added to the solution due to its surface active properties, aiming at improving the wettability of the coatings/films.

#### 3.1. Surface tension and critical surface tension

As described in the Materials and Methods, the determination of the surface tension and of the critical surface tension allows the characterization of the surface properties of the apples' skin. The critical surface tension values that are reported in the literature are generally lower than the surface tension values. In our work, the apple surface presents values of the critical surface tension and of the surface tension of  $25.4 \text{ mN m}^{-1}$  and  $27.81 \text{ mN m}^{-1}$ , respectively. The apple surface is therefore a low-energy surface (values well below  $100 \text{ mN m}^{-1}$ ). Being so, its surface interacts with liquids primarily through dispersion forces as reported by [Rulon and Robert \(1993\)](#). Under this circumstance, Zisman's method was used to determine the wettability of the apples' surface, which presented a high dispersive component ( $27.13 \text{ mN m}^{-1}$ ), and a low polar component ( $0.68 \text{ mN m}^{-1}$ ), demonstrating the ability of the apple's surface to participate in non-polar interactions.

#### 3.2. Wettability ( $W_s$ ), work of adhesion ( $W_a$ ) and work of cohesion ( $W_c$ )

Wettability ( $W_s$ ) is one of the most important properties when evaluating the capacity of a solution to coat a surface of interest, where higher values of  $W_s$  (closer to zero) are considered the most suitable to coat the surface. The obtained results are reported in [Table 1](#). Summarizing, the best  $W_s$  values were found with the addition of 0.1% (w/v) Tween 80 as follows:  $-29.01 \pm 0.51$  and  $-26.16 \pm 0.48$ , for 1.5% and 3.0% (w/v) Policaju, respectively. The addition of Tween 80 to the solution reduced the surface tension of the liquid through a reduction of the cohesion forces; this provoked an increase of  $W_s$  thus improving the compatibility between the solution and the fruit's skin surface.

This behavior has already been found by [Zhang and Quantick \(1997\)](#) when working with chitosan coatings. They have added, as reported, 0.1% (v/v) Tween 80 to improve the wettability. [Choi](#)

et al. (2002) have also reported that the addition of 0.1% (w/v) of Tween 80 improved the compatibility of the chitosan coating solution and the apple skin.

The Pareto bar charts of standardized effect estimates (absolute values) showed the magnitude of the positive effect of Tween 80 concentration on  $W_s$  ([Fig. 1a](#)). Pareto charts also showed that the Policaju concentration and the interaction between Tween 80 and Policaju influences the  $W_s$  values.

The influence of the addition of Tween 80 on  $W_a$  was relatively poor ([Table 1](#)). The Pareto bar chart of effects showed a negative effect of Tween 80, thus reinforcing the idea that this factor does not have a favorable influence on that variable ([Fig. 1b](#)). Also in this case the interaction between Tween 80 and Policaju concentration influences the  $W_a$  values. The best  $W_a$  values, compatible with the best  $W_s$  values, were found to be  $36.09 \pm 0.63$  and  $35.40 \pm 0.83$  for the films containing 1.5% and 3.0% (w/v) Policaju, respectively.

The influence of Tween 80 concentration on  $W_c$  was considerable ([Table 1](#)). The Pareto bar chart of effects ([Fig. 1c](#)) showed that Tween 80 was by far the most important factor influencing the values of  $W_c$ , with a negative effect, followed by the interaction of Tween 80 and Policaju, also showing a negative effect. Policaju concentration, in turn, has only a marginal effect when compared with the other two. The addition of Tween 80 decreased substantially the cohesion forces, thus increasing the spreading coefficient.

[Table 2](#) shows the parameters of the model presented in [Eq. \(7\)](#) that provided the better fit to the obtained results. The quality of the fitting for  $W_s$ ,  $W_a$  and  $W_c$  is also displayed, being the values of  $R^2$  always above 0.93, those of  $E$  always below 10% and those of  $A_f$  very close to 1 at all times, showing that the models provide a very good fit to the data. [Casariego et al. \(2008\)](#) used a similar model to adjust the values of  $W_s$ ,  $W_a$  and  $W_c$  in tomato and carrot, with values of  $R^2$  higher than 0.85.

#### 3.3. Water vapor permeability (WVP)

The water vapor permeability is the most extensively studied property of edible films, mainly because of the importance of the water in deteriorative reactions. The Pareto bar chart ([Fig. 1d](#)) shows that Tween 80, followed by Policaju and by the interaction of both (in a lesser extent), are important factors influencing the value of WVP. The addition of surfactant provoked an increase of WVP ([Table 1](#)), this was somewhat unexpected since the surfactant has a hydrophobic component.

Similar behaviors were reported by [Rodriguez et al. \(2006\)](#) and [Ziani et al. \(2008\)](#). These authors also reported the considerable synergetic effect between the plasticizer and the surfactant both under low and high levels of surfactant. However [Chen et al. \(2009\)](#) found a decrease of WVP in starch/decolorized hsian-tsao gum (dHg) composite films in the presence of sucrose ester surfactant. According to these authors the effect of surfactant on the WVP of edible films would be strongly dependent on the types and concentrations of surfactants as well as the material properties of the film-forming materials.

**Table 2**  
Model equations and the corresponding quality of the fit evaluation parameters.

| Model equations   | $R^2$ | $E$    | $A_f$ |
|---|-------|--------|-------|
| $W_s = -54.7252 + 0.5811 \times \text{Policaju} + 228.5957 \times \text{Tween80} + 13.2069 \times \text{Policaju} \times \text{Tween80}$        | 0.99  | 0.0001 | 1.00  |
| $W_a = 34.4107 + 2.7596 \times \text{Policaju} + 23.7146 \times \text{Tween80} - 32.1912 \times \text{Policaju} \times \text{Tween80}$          | 0.93  | 0.0002 | 0.99  |
| $W_c = 90.4440 + 1.843 \times \text{Policaju} - 213.1600 \times \text{Tween80} - 42.8770 \times \text{Policaju} \times \text{Tween80}$          | 0.99  | 0.0407 | 0.99  |
| $WVP = 6.8229 + 0.6745 \times \text{Policaju} + 12.9829 \times \text{Tween80} + 11.3770 \times \text{Policaju} \times \text{Tween80}$           | 0.97  | 0.5957 | 0.99  |
| $\text{Opacity} = 8.9868 - 0.1155 \times \text{Policaju} - 52.2887 \times \text{Tween80} + 4.0130 \times \text{Policaju} \times \text{Tween80}$ | 0.94  | 0.0013 | 1.00  |
| $TS = 0.5438 + 2.7079 \times \text{Policaju} + 9.1820 \times \text{Tween80} - 13.5107 \times \text{Policaju} \times \text{Tween80}$             | 0.97  | 0.0015 | 0.99  |
| $EB = 14.7800 + 0.1547 \times \text{Policaju} - 25.5340 \times \text{Tween80} - 22.5347 \times \text{Policaju} \times \text{Tween80}$           | 0.91  | 0.0008 | 0.99  |

The WVP of edible films depends on many factors including, the integrity of the films, the polymeric chain mobility and the hydrophilic–hydrophobic ratio. The properties of the surfactant molecules are differently affected by the hydrophilic head group and hydrophobic tail. Their total effect is known as the Hydrophilic–Lipophilic Balance (HLB). This Balance is defined by a number that ranges from 0 to 40. Generally, an HLB number <10 indicates that a surfactant has low solubility in water while an HLB number between 10 and 20 indicates that the surfactant is readily soluble in water. The HLB of the Tween 80 surfactant is 15 and the WVP increase on Policaju film suggests that the hydrophilic part of the surfactant was probably the responsible for permeability increase as discussed in the section on mechanical properties, below.

Also the thickness of the films can influence the values of WVP. With the increase of Policaju concentration, the solid content in the films increased and the films presented higher values of thickness (Table 1). Other works were performed to better understand the influence of film thickness in the WVP values (Morillon et al., 2002). Further work has to be done to understand how the thickness of Policaju films can influence their WVP values, and if a correlation exists between the obtained WVP values and the increase of thickness.

The WVP values obtained in the present work are in agreement with other polysaccharide based films. Cerqueira et al. (2009) presented values of WVP for galactomannan and glycerol films, ranging between  $4.89$  and  $6.05 \times 10^{-11} \text{ g m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$ ; in the same work. Souza et al. (2009) obtained values of WVP for chitosan films with Tween 80 of  $3.69 \times 10^{-11} \text{ g m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$ .

When the model equation (Eq. (7)) was fitted to the WVP experimental data a good fit, with  $R^2$  above 0.97,  $E$  below 10% and  $A_f$  very close to 1, was obtained (Table 2), thus satisfactorily describing the behavior of WVP under the influence of the factors under consideration.

#### 3.4. Opacity

The average values of opacity of Policaju and sorbitol films in the presence and in the absence of the surfactant Tween 80, were reported in Table 1. The presence of Tween 80 in the solution reduced the opacity (or increased the transparency). The higher reduction of opacity was found with 1.5% (w/v) Policaju and 0.1% (w/v) of Tween 80, reaching an expressive 47% reduction.

The opacity is an important element to control the light incidence on a food (apple, in this case), being a relevant property since it has a direct impact on the appearance of the coated product. The opacity of starch/dHG films in the presence of different sucrose ester surfactants was evaluated by Chen et al. (2009) and they did not find a significant opacity change; however, the opacity values of those films were lower when compared with other biodegradable films without addition of surfactants. These authors also found that the concentration increase of S-1170 surfactant from 0% to 25% led to an increase of opacity of about 43%.

The decrease of the opacity with the addition of Tween 80 can be related with the influence of the surfactant on the film plasticization. The presence of surfactants could reduce the interactions between polymer molecules, which resulted in a microstructure with apparent cracks (Chen et al., 2009), increasing the light that passes through the film, thus decreasing the overall opacity. This does not mean that opacity would be the same all over the film; in fact, it may increase locally in the area between the cracks. However, once these are micro-cracks our equipment does not allow determining the opacity values for such small areas in order to avoid crack presence.

The Pareto bar chart (Fig. 1e) showed that Tween 80 concentration was the most important factor influencing the value of opacity (with a negative effect, meaning that the surfactant decreased the

opacity). The effect of the concentration of Tween 80 in opacity is evident, however it is also evident that Policaju concentration (or its interaction with Tween 80) do not significantly influence that property (Fig. 1e).

The fitting of the model equation (Eq. (7)) to the experimental values of opacity shows very good results (Table 2), with values of  $R^2$  above 0.94,  $A_f$  very close to 1 and  $E$  always above 10%.

#### 3.5. Mechanical properties

The tensile strength ( $TS$ ) is the ability of a material to resist breaking under tensile stress. The Pareto bar chart (Fig. 1f) shows that Policaju concentration is the most important factor influencing this property, with a positive effect. Tween 80 concentration also has an influence on  $TS$  but with a negative effect (an increase of Tween 80 concentration decreases the value of  $TS$ ).

The fitting of the model equation (Eq. (7)) to the experimental values of  $TS$  shows a very good quality of the fit, with values of  $R^2$  above 0.97 and  $A_f$  very close to 1;  $E$  presented values above 10% in both cases (Table 2).

The elongation at break ( $EB$ ) of an engineering material is the length increase, expressed as a percentage, which occurs before it breaks under tension. The Pareto analysis (Fig. 1g) demonstrates that Tween 80 concentration is by far the most important factor, showing a negative effect on the values of  $EB$ .

The fitting of the model equation (Eq. (7)) to the experimental values of  $EB$  shows quite good results, with values of  $R^2$  above 0.91,  $E$  below 10% and  $A_f$  very close to 1 in both cases (Table 2).

A reduction on  $TS$  values from  $4.61 \pm 0.33$  to  $3.50 \pm 0.31$  MPa and from  $8.67 \pm 0.41$  to  $5.40 \pm 0.37$ , was observed when Policaju concentration was increased from 1.5% to 3.0% in films without and with Tween 80, respectively (Table 1). Equally, a corresponding reduction was also found on  $EB$ , from  $15.01 \pm 1.12\%$  to  $9.08 \pm 1.94\%$  and from  $15.24 \pm 1.54\%$  to  $5.93 \pm 0.27\%$ , respectively.

Similar behaviors were reported by Rodriguez et al. (2006), Ziani et al. (2008) and Chen et al. (2009). Both  $TS$  and  $EB$  decreased by incorporation of a surfactant. The loss of mechanical strength may be a significant disadvantage for films in some applications but its importance is relatively lower if the material is used for coatings on a supporting material. The surfactants hold hydrophilicity and hydrophobicity simultaneously and one possible explanation for the behavior observed in our work is that the hydrophilic part of the surfactant established interactions with the solvent (water) or with the hydrophilic parts of the polysaccharide (e.g., through Hydrogen bonding), a further possibility is that the establishment of these interactions caused a disruption of the structure as it was prior to their occurrence that affected the mechanical properties of the material. The values obtained for mechanical properties are in agreement with those of other polysaccharide based films. Cerqueira et al. (2009) presented values of for  $TS$  values that ranged between 2.56 and 3.96 MPa and  $EB$  values ranging from 28.26% to 46.36%. Casariego et al. (2009) obtained values, for films of 1% of chitosan, of approximately 10 MPa and 14% for  $TS$  and  $EB$ , respectively.

## 4. Conclusion

This work shows how Policaju-based coating/films properties can be affected by the concentration of Policaju and the presence of Tween 80 in coating/film. Tween 80 was found to be the most significant factor in these coating/films properties.

The obtained values of the measured properties were: the spreading coefficient ranged from  $-26.16$  to  $-53.85 \text{ mN m}^{-1}$ ; the adhesion work ranged from  $35.40$  to  $42.69 \text{ mN m}^{-1}$ ; the cohesion work ranged from  $61.61$  to  $95.97 \text{ mN m}^{-1}$ ; the water vapor perme-

ability ranged from  $7.83 \times 10^{-11}$  to  $13.56 \times 10^{-11} \text{ g m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$ ; the opacity ranged from 4.16% to 8.81%; the tensile strength ranged from 3.50 to 8.67 MPa; and the elongation at break ranged from 5.93% to 15.24%. The multifactor model gave good fitting accuracy with coefficient of determination above 0.91, a mean relative deviation modulus below 0.60 and an accuracy factor with values between 0.99 and 1.00, allowing the further optimization of this kind of coating/films, depending on the desired optimum value. This model is important once it will reduce the characterization work needed in subsequent applications of these coatings/films on foods.

These findings provided important information on properties of Policaju-based coating/films in view of their use by the food industry e.g., as coatings and films for the improvement of fruits storage conditions.

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