Post-harvest quality of papaya coated with polivinilic alcohol and maize starch

Qualidade pós-colheita de mamão revestido com álcool polivinílico e amido de milho

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ABSTRACT
Climacteric fruits have short postharvest shelf life. Coating is an alternative to minimize fruit ripening and post-harvest losses. Maize starch (S) and polivinilic alcohol – PVOH (P), isolated or blended, can be used in the formulation of coatings. However, little is known about the potential of PVOH-containing coatings in postharvest conservation of fruits. Papaya were aftercoated with 5 coating formulations: 3% starch (S), 3% PVOH (P), 2.25% S + 0.75% P, 1.5% S + 1.5% P and 0.75% S + 2.25% P. The fruits were kept at room temperature (20 ± 5 °C and 70 ± 10% RH) and physicochemical characteristics were evaluated for up to eight days. Uncoated fruits were used as control. In general, maize starch and PVOH coatings reduced the weight loss and did not affect total soluble solids concentration. 3% PVOH coating increased the acidity and decreased the pH of the fruits, and excessively inhibited gas exchange between fruit and the environment. In this study, 3% maize starch coating was more efficient in prolonging the postharvest life of papaya.

Index terms: Carica papaya L.; storage; respiratory rate; fermentation; firmness.

INTRODUCTION
Papaya (Carica papaya L.) is widely grown in tropical and subtropical regions. World production was 13,169,443 tons in 2017, with Brazil being the world’s second largest fruit producer (Food and Agriculture Organization of The United Nations - FAOSTAT, 2019). Papaya is a climacteric fruit, so it rapidly ripens after harvesting due to ethylene production and increased respiratory rate. This rapid ripening leads to softening of fruit tissues. As a result, fruit shelf life is shortened (Cunha et al., 2018; Jiang et al., 2019; Zou et al., 2014).

Coating is an alternative method to increase fruit shelf life (Cunha et al., 2018; Ding et al., 2019). The coatings are applied or formed directly on the fruit surface, forming thin membranes. When immersing a fruit in a film-forming dispersion, the cover is formed by the deposition of polymeric species dispersed in the medium, establishing weak and strong interactions, with the surface of the fruit. Several models have been proposed for the deposition of polymeric structures and the subsequent formation of films on solid surfaces. In these models, the characteristics of the absorbent (in our case, the peel) and the absorbate (compounds diluted in the film-forming dispersion) are how
they define that the type of mechanism will be predominant in the formation of the cover. In general, five interactions may occur when dipping a fruit in dispersed polymers formulations: Hydrogen bond; Hydrophobic interaction; Interaction by dispersive frames; Polarization of π electrons and Electrostatic interaction. In practice, all types of interactions can occur simultaneously and in varying intensities, although, depending on the characteristics of the coating-forming formulation and the fruit surface, there may be a predominance of a mechanism. (Assis; Britto, 2014). After drying, protective coating is formed, which acts as a semipermeable barrier to water vapor and gases, inhibiting the migration of oxygen, carbon dioxide, flavorings, lipids and other solutes. Senescence is then retarded, increasing fruit conservation and shelf life (Ali et al., 2013; Azarakhsh et al., 2014).

Natural or synthetic substances can be used as coatings. These coatings do not replace completely inedible synthetic packaging, but can act as adjuvants, reducing the use of non-biodegradable disposable packaging (Assis; Britto, 2014). Various biodegradable and non-toxic polymers can be used as fruit coatings (Pilon et al., 2013; Azarakhsh et al., 2014; Cunha et al., 2018; Mendy et al., 2019), including starch and polivinilic alcohol – PVOH (Coutinho et al, 2015; Ding et al., 2019; Lo’ay; Taha; El-Khateeb, 2019). Starch is a low-cost and highly available natural polymer, and easy to store and handle (Mali; Grossmann; Yamashita, 2010; Alcázar-Alay; Meireles, 2015). It is a polysaccharide produced by higher plants as energy storage and consists basically of amylose and amylopectin polymers. Gels are formed when starch is dispersed in water and heated, with gel-forming temperature varying, depending on pH, source and starch concentration (Mali; Grossmann; Yamashita, 2010; Alcázar-Alay; Meireles, 2015).

Starch coatings have been used neat or blended with others polymers to coat fruits, including avocado (Coutinho et al., 2015), papaya (Castricini; Coneglian; Deliza, 2012), and guava (Coelho et al., 2017). Starch-based coatings are flexible, non-toxic to human health, biodegradable, flavorless, odorless and colorless, and virtually water-impermeable (Rodrigues et al., 2020). Additionally, other polymers such as PVOH, can be blended with starch to form polymeric blends and thereby making films and coating with desirable mechanical and barrier properties (Silva et al., 2016).

PVOH is an inert, stable, non-toxic, water-soluble synthetic petroleum-derived polymer. PVOH-based films form moisture and oxygen barriers and have high tensile and abrasion resistance (Bellelli et al., 2018; Ding et al., 2019; Muppalaneni; Omidian, 2013). Polymeric blends containing PVOH and natural polymers, such as chitosan and carboxymethyl cellulose, increase fruit shelf life of strawberries (Ding et al., 2019), grapes (Lo’ay; Taha; El-Khateeb, 2019), and bananas (Senna; Al-Shamrani; Al-Arifi, 2014; Lo’ay; Dawood, 2017).

However, little is known about the potential of polymeric blends based on starch and PVOH as a coating of papaya. Assuming that coatings containing starch and PVOH can increase fruit shelf life, the objective of this work was to evaluate whether these polymers individually or in blends enhance physicochemical characteristics and conservation of papaya for up to eight days after harvesting.

**MATERIAL AND METHODS**

Freshly harvested papaya fruits (*Carica papaya* L. variety Solo) selected considering uniformity, color and degree of ripeness, based on skin color with 15-25% of the yellow peel surface area, were previously washed in running water and superficially disinfected with 200 μL L⁻¹ sodium hypochlorite solution for 10 min. After cleaning, they were submitted to treatments (containing maize starch and, or PVOH and, or control). Maize starch and PVOH were dispersed in distilled water, gradually heated to 70 °C and kept under constant stirring until maize starch gelatinization or PVOH completely dispersion. Glycerol was added to the maize starch dispersion at a rate of 30% (30 g of glycerol per 100 g of maize starch). Then, maize starch and PVOH dispersions were mixed to prepare coating-forming formulations dispersions with a final polymers concentration of 3%, taking into account the total of maize starch and PVOH summed, according to experimental design of simplex-centroid for binary mixture: 3% corn maize starch (S) solution; 3% PVOH (P) solution; 2.25% S and 0.75% P solution; 1.5% S and 1.5% P solution; 0.75% S and 2.25% P solution. These concentrations were determined based on studies with starch coatings (Oliveira; Cruz; Alves; 2016; Castricini; Coneglian; Deliza, 2012) and other biodegradable compounds (Ali et. al, 2011; Ali; Cheong; Zahid, 2014), besides in positive results with climacterics fruits (Pigozzi et al., 2020), there are few studies with coatings using PVOH. After mixing and dispersing coating-forming constituents, they were kept under slow stirring until cooling to room temperature.

Lastly, the fruits were immersed for 5 s in the coating-forming formulations sand maintained for 5 min in a horizontal position on a sieve to drain the excess of liquid. Uncoated fruits were used as control. The fruits were kept at room temperature (20 ± 5 °C and 70 ± 10% RH), most common way of marketing papaya in Brazil, for 8 days.
The analysis of the weight loss rate was performed in a completely randomized design, with six post-harvest treatments and four replications. Fruits were weighted every 2 days in a semi-analytical electronic scale (BL-320H model; Splabor - Presidente Prudente, Brazil). Weight loss rate was calculated by the angular coefficient of the curve of weight x time (days).

The respiratory rate was determined indirectly by the adapted method of Alef and Nannipieri (1995). Fruits and flasks containing CO$_2$ capture solution (NaOH) were placed in hermetically sealed containers (respirometers) and incubated for one hour. The CO$_2$ released by the fruits during respiration reacts with the capture solution. After incubation, 1 mL BaCl$_2$ was added to the capture solution for precipitation of carbonate and phenolphthalein ions as an indicator for HCl titration of the remaining NaOH in the capture solution. The same procedure was done without the fruit in the containers (control). The amount of CO$_2$ emitted, and the respiratory rate were calculated according to Equations 1 and 2, respectively.

$$CO_2 = (B - A) \times [HCl] \times F \times 22 \times \frac{v_1}{v_2}$$

$$(B - A):$ mean HCl volume spent on control titration - volume spent on sample titration (in mL)

$[HCl]:$ HCl concentration (in mol L$^{-1}$)

$F:$ HCl concentration correction factor

$22: CO_2$ molar mass $\div 2$ (since each CO$_2$ molecule reacts with 2 of NaOH)

$(v_1/v_2):$ ratio between capture NaOH volume and titrated NaOH volume (in mL)

$$RR = \frac{CO_2}{W \times T}$$

$RR:$ Respiratory rate (mg kg$^{-1}$ h$^{-1}$)

$W:$ Fruit weight (kg)

$T:$ time (h)

Fruit firmness was determined using a digital penetrometer (PTR-300 model; Instrutherm - Brazil), coupled with a 5 mm diameter conical probe. Firmness was measured at two opposite points, on the equatorial belt of the fruit, after peeling with a sharp blade. The results were expressed in Newtons (N). Soluble solids (SS) were directly measured with analog refractometer (model ATC 103; Biobrix- Brazil). Results were given in percentage. The titratable acidity (TA) was determined using the titration method. Pulp tissues (5.0 g) were homogenized with 50 mL of distilled water, added with two to four drops of phenolphthalein 1% (indicator) and then titrated using 0.01 mol L$^{-1}$ NaOH until it reached an pink endpoint (pH 8.1). The results were expressed as the percentage of citric acid, the predominant acid in papaya.

RESULTS AND DISCUSSION

Postharvest coatings and storage time influenced fruit mass loss ($p<0.05$), with no interaction between factors. Mass loss was lower in coated fruits compared to control, regardless of coating type (Figure 1). Besides, there was a gradual increase in mass loss in all postharvest treatments during the storage period, being less pronounced on the coated fruits. Fruit coating is not intended to replace the use of conventional packaging materials or even permanently eliminate the use of cooling, but rather to present a functional and supporting role, contributing to the preservation of texture and nutritional properties, by reducing surface gases exchange and excessive water loss (Assis; Britto, 2014), increasing the post-harvest period.
Peel is an important factor for fruit mass loss. During fruit ripening, latex rupture occurs, and the integrity of the peel is reduced (Chitarra; Chitarra, 2005). Fruits that lose 10% of their initial weight are considered unfit for human consumption (Kader, 2002). In this study, we observed this condition in uncoated fruits stored for 8 days (Figure 1). On the other hand, coated fruits would present this 10% mass loss after 10 days. This shows that the coating provided an increase of 25% in the storage time of papayas.

Coating with 3% maize starch did not reduce mass loss compared to the others coatings (Figure 1), although it reduced the respiratory rate of the fruits (Table 1). This demonstrates that moisture loss from fruits through perspiration or evaporation is more significant than respiration for final mass loss over storage time (Hazarika; Lalthanpuii; Mandal, 2017).

The respiratory rate of papaya fruits was influenced only by the postharvest coatings, regardless of fruit storage time (Table 1). The 3% maize starch treatment reduced the respiration of papaya fruits, with average values of 67% compared to the control (Table 1).

The coating of papaya with 3% maize starch reduced gas exchange between fruit and environment. The reduction of gas exchange creates a modified atmosphere in fruit cells, increasing CO₂ and reducing O₂ concentrations on the fruit cell surface, which leads to lower respiration rate and consequently reduces the release of CO₂ by the fruit (Chitarra; Chitarra, 2005). Since respiratory processes are of a degradative nature, the higher the respiratory rate, the shorter the storage time (Vieites; Daiuto; Fumes, 2012). PVOH films were not efficient in reducing CO₂ production.

Fruit acidity was influenced by the interaction between coating formulation and storage time (Table 2). From the sixth day of storage higher concentrations of PVOH (3%) resulted in higher fruit acidity at the end of the storage period while opposite behavior was observed for maize starch coating or uncoated fruits.

The increase in acidity due to the increase of PVOH concentration and storage time may be due to fruit fermentation. Probably, at higher concentrations, PVOH chains interactions are stronger, creating more compact molecular structure which difficults gas exchange between fruit and environment. Under low concentrations or absence of oxygen, anaerobic respiration occurs. In this situation, pyruvate is converted to CO₂ and acetaldehyde, which is converted to ethanol (Nelson; Cox, 2014). Even in anaerobiosis, part of the tricarboxylic acid cycle happens, generating accumulation of succinic acid, increasing fruit acidity (Coulter; Godden; Pretorius 2004; Zamora, 2009). Moreover, fermentation produces less energy per mol of glucose, requiring more molecules to produce energy (Nelson; Cox, 2014). For these reasons, an increase in fruit acidity was observed (Table 2), even with no reduction in CO₂ production (Table 1).

### Table 1: Treatment and Mass Loss (% of initial mass)

| Treatment | Control (●) | 3% S - 0% P (■) | 2.25% S - 0.75% P (×) | 1.5% S - 1.5% P (●) | 0.75% S - 2.25% P (●●) | 0% S - 3% P (▲) |
|-----------|-------------|-----------------|------------------------|---------------------|-------------------------|-----------------|
| Mass loss rate (% mass loss / day) | 1.225 A | 0.938 B | 0.985 B | 0.890 B | 0.902 B | 0.916 B |

Means followed by the same capital letter do not differ by SNK test (p < 0.05). Coefficient of variation (%) = 9.96. Loss limit (--).
Fruit pH was altered due to the interaction between storage time and coating formulation. pH decreases during storage, and on the sixth day there were changes in pH by fruits coated with PVOH. At 8 days of storage, the pH of the fruits was lower with increasing concentration of PVOH (Table 3).

Papaya pulp present low levels of organic acids, which are weak acids with low dissociation constants. For this reason, the pH of this fruit is usually higher than 5 (Fagundes; Yamanishi, 2001; Almeida et al., 2006). In this study, the pH values of the fruits ranged from 4.12 to 5.90 (Table 3), similar to those found in the literature (Mendy et al., 2019). The decrease in pH over the storage time of PVOH coated fruits was possibly due to acid production during fermentation, as observed in Table 2. The data showed a negative correlation between pH and acidity ($r = -0.85$), showing that the pH reduction is related to the increase in the acid content.

Table 1: Respiratory rate of papaya fruits (mg CO$_2$ Kg$^{-1}$ h$^{-1}$) coated with solutions containing maize starch (S) and polivinilic alcohol – PVOH (P) at 0, 2, 4, 6 and 8 days under room conditions (20 ± 5 °C and 70 ± 10% RH).

| Treatment | 0 day | 2 days | 4 days | 6 days | 8 days | Mean |
|-----------|-------|--------|--------|--------|--------|------|
| Control   | 27.79 | 35.26  | 45.71  | 46.46  | 23.40  | 37.71 A |
| 3% S - 0% P | 31.62 | 27.80  | 22.54  | 19.52  | 25.37 B |
| 2.25% S - 0.75% P | 38.25 | 39.32  | 37.90  | 31.80  | 36.82 A |
| 1.5% S - 1.5% P | 31.80 | 31.69  | 33.71  | 32.72  | 32.48 A |
| 0.75% S - 2.25% P | 31.38 | 33.51  | 34.15  | 40.26  | 34.83 A |
| 0% S - 3% P | 34.82 | 35.39  | 36.57  | 29.93  | 34.18 A |

Means followed by the same capital letter in the column do not differ by SNK test ($p < 0.05$). Coefficient of variation (%) = 29.21.

Table 2: Papaya acidity (g citric acid 100 g$^{-1}$ pulp) coated with solutions containing maize starch (S) and polivinilic alcohol – PVOH (P) at 0, 2, 4, 6 and 8 days under room conditions (20 ± 5 °C and 70 ± 10% RH).

| Treatment | 0 day | 2 days | 4 days | 6 days | 8 days | Adjusted model |
|-----------|-------|--------|--------|--------|--------|----------------|
| Control   | 0.06  | 0.05 A | 0.05 A | 0.04 B | 0.03 C | No significant |
| 3% S - 0% P | 0.05 A | 0.05 A | 0.05 A | 0.05 AB | 0.04 C | No significant |
| 2.25% S - 0.75% P | 0.05 A | 0.07 A | 0.07 A | 0.08 B | No significant |
| 1.5% S - 1.5% P | 0.06 A | 0.06 A | 0.07 A | 0.08 B | No significant |
| 0.75% S - 2.25% P | 0.06 A | 0.06 A | 0.06 AB | 0.09 B | No significant |
| 0% S - 3% P | 0.05 A | 0.08 A | 0.08 A | 0.12 A | 0.2337 + 0.012x ; $R^2 = 0.7182$ |

Means followed by the same capital letter in the column do not differ by SNK test ($p < 0.05$). Coefficient of variation (%) = 13.76.

Table 3: pH of papaya fruits coated with solutions containing maize starch (S) and polivinilic alcohol – PVOH (P) at 0, 2, 4, 6 and 8 days under room conditions (20 ± 5 °C and 70 ± 10% RH).

| Treatment | 0 day | 2 days | 4 days | 6 days | 8 days | Adjusted model | $R^2$ |
|-----------|-------|--------|--------|--------|--------|---------------|-------|
| Control   | 5.60  | 5.55 A | 5.69 A | 5.77 A | 5.75 A | No significant | -     |
| 3% S - 0% P | 5.81 A | 5.76 A | 5.75 A | 5.62 A | No significant | -     |
| 2.25% S - 0.75% P | 5.76 A | 5.78 A | 5.18 B | 4.81 B | $\hat{y} = 5.618 + 0.1329x -0.03018x^2$ | 0.9462 |
| 1.5% S - 1.5% P | 5.59 A | 5.57 A | 5.18 B | 4.80 B | $\hat{y} = 5.75 -0.1003x$ | 0.8057 |
| 0.75% S - 2.25% P | 5.89 A | 5.90 A | 5.21 B | 4.28 C | $\hat{y} = 5.591 + 0.2844x -0.05638x^2$ | 0.9939 |
| 0% S - 3% P | 5.79 A | 5.39 A | 4.82 B | 4.12 C | $\hat{y} = 5.652 + 0.0835x -0.035x^2$ | 0.9874 |

Means followed by the same capital letter in the column do not differ by SNK test ($p < 0.05$). Coefficient of variation (%) = 4.76.
Fruit firmness was reduced as the storage time increased, regardless of coating formulation (Table 4). Hazarika, Lalthanpuii and Mandal (2017) also reported reduced firmness of coated papaya fruits with increased shelf life. Escamilla-García et al. (2018) reported that uncoated papaya fruits had a firmness loss of 92% during storage, while those coated with chitosan and oxidized starch had a firmness reduction of only 47%. The value similar values to the present work, where at the end of 8 days the fruits presented 43% less firmness.

Chitarra and Chitarra (2005) and Vieites, Russian and Daiuto, (2014) cite that the fruit’s firmness is due to the action of hydrolytic enzymes, including pectinamethylesterase (PME) and polygalacturonase (PG), which degrade structural carbohydrates. PG contributes to the softening of fruit pulp, as its activity is greater in the early stage of fruit ripening (Bonnin; Garnier; Ralet, 2014). The expressive initial activity of PME would provide substrate for PG’s performance (Pinto et al., 2011). PME promotes the partial demethylation of methyl esters of pectin polygalacturonic acids, facilitating the access of PG, which determines the depolymerization and solubilization of pectic substances (Bonnin; Garnier; Ralet, 2014).

Fruit coating and storage time did not influence the concentration of total soluble solids (Table 5). The Papaya Technical Regulation establishes a minimum value of 11 °Brix for papaya harvesting (Brazil, 2010). In this study, the total soluble solids values observed were below this value, indicating that the fruits were harvested before the correct time.

The absence of variation in total soluble solids concentration during the papaya ripening period is possibly justified by the low starch accumulation (less than 1%) during fruit development, which did not allow significant variation in the soluble sugar content during maturation (Gómez; Lajolo; Cordenunsi, 2002). Soluble sugars are mostly accumulated when the fruit is still connected to the plant, mainly due to photosynthesis (Chitarra; Chitarra, 2005). At the beginning of papaya fruit development, glucose is the predominant sugar. In later stages, sucrose becomes the sugar found in higher concentration, reaching higher levels than fructose and glucose (Kader, 2002).

**Table 4:** Firmness of papaya fruits coated with solutions containing maize starch (S) and polivinilic alcohol – PVOH (P) at 0, 2, 4, 6 and 8 days under room conditions (20 ± 5 °C and 70 ± 10% RH).

| Treatment | 0 day | 2 days | 4 days | 6 days | 8 days | Mean |
|-----------|-------|--------|--------|--------|--------|------|
| Control   | 10.56 | 6.12   | 5.21   | 4.88   | 2.87   | 4.77 A |
| 3% S - 0% P | 6.34 | 7.29   | 5.32   | 4.43   |        | 5.84 A |
| 2.25% S - 0.75% P | 7.84 | 6.29   | 4.78   | 3.45   |        | 5.59 A |
| 1.5% S - 1.5% P | 6.94 | 5.62   | 4.70   | 4.30   |        | 5.39 A |
| 0.75% S - 2.25% P | 7.29 | 6.39   | 4.59   | 4.27   |        | 5.64 A |
| 0% S - 3% P | 7.65 | 6.29   | 3.72   | 4.23   |        | 5.47 A |
| Mean      | 7.03  | 6.18   | 4.67   | 3.93   |        | Model*: Log (y)= 0.9763 -0.05202x; R^2: 0.9782 |

Means followed by the same capital letter in the column do not differ by SNK test (p < 0.05). Coefficient of variation (%) = 6.23.

**Table 5:** Total soluble solids (° BRIX) of papaya fruits coated with solutions containing maize starch (S) and polivinilic alcohol – PVOH (P) at 2, 4, 6 and 8 days under room conditions (20 ± 5 °C and 70 ± 10% RH).

| Treatment | 0 day | 2 days | 4 days | 6 days | 8 days | Mean |
|-----------|-------|--------|--------|--------|--------|------|
| Control   | 8.37  | 10.00  | 7.43   | 8.65   | 9.40   | 8.87 A |
| 3% S - 0% P | 8.55 | 7.43   | 7.95   | 8.03   | 7.99 A |
| 2.25% S - 0.75% P | 8.85 | 8.58   | 9.45   | 8.53   | 8.53 A |
| 1.5% S - 1.5% P | 8.45 | 7.40   | 8.30   | 7.95   | 8.03 A |
| 0.75% S - 2.25% P | 9.00 | 8.98   | 7.95   | 7.38   | 8.33 A |
| 0% S - 3% P | 8.45 | 8.10   | 9.20   | 8.55   | 8.58 A |

Means followed by the same capital letter in the column do not differ by SNK test (p < 0.05). Coefficient of variation (%) = 6.23.
CONCLUSIONS

Coating papaya fruits with maize starch and polivinilic alcohol, neat or in blends, reduces mass loss after eight days of storage. Fruits coated with 3% starch reduces gas exchange between papaya fruits and environment. 3% PVOH formulation coating increases the acidity and decreases the pH of the fruit, and excessively inhibited gas exchange between the fruit and the environment, leading to fruit fermentation. It probably occurs due to the strong PVOH chains interactions at this concentration. Thus, it is suggested to perform a new experiment reducing the concentration of PVOH in the coatings, in order to observe whether there will be a reduction in the fermentation of the fruits. In this study, the coating with 3% maize starch was more efficient in prolonging the postharvest life of papaya.

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