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Influence of Processing Additives on the Quality and Stability of Dried Papaya Obtained by Osmotic Dehydration and Conventional Air Drying

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The combination of osmotic dehydration and hot air drying (OD/HA) is an industrial alternative to papaya production, but tissue softening and color loss are technological problems. The objective of this work was to study, during OD/HA processing of papaya (Formosa cultivar), the influence of organic acids (citric and lactic), calcium salts (lactate and chloride), and the enzyme pectinmethylesterase (PME) on the texture, color, and sensory characteristics of the product. The stability of the products treated with lactic acid/calcium chloride, PME/calcium chloride, and the standard sample (without additives) was evaluated at 25 and 35°C for up to 100 days, analyzing vitamin C and color degradation. Light microscopy analysis performed at the beginning of stability study showed that the additives better preserved the cell structure. The use of lactic acid/calcium chloride maintained the color of the dried papaya, but the additives did not have an effect on vitamin C degradation. The variations in the chromaticity parameters (b^* and a^*) were adjusted to zero- and first-order kinetic models, respectively, with Q_{10} values ranging between 0.88 and 2.30 and $R^2 \sim 0.90$. The combination of lactic acid/calcium chloride resulted in higher sensory acceptance and color stability of dried papaya during storage.

Keywords Calcium; Color; Kinetics; Pectinmethylesterase; Vitamin C

INTRODUCTION

Brazil is the world's greatest producer of papaya (*Carica papaya* L.), with 1.8 million tons per year, and the second largest exporter of the fresh fruit.[1,2] Three different cultivars are grown: Comum, Solo, and Formosa. The production of Formosa cultivar is directed to the internal market, resulting in larger fruits with greater transportation resistance and containing higher sugar contents.[3] The fruit has a high nutritive value; it is rich in vitamins C (30–130 mg/100 g), vitamin B1 (40–45 mg/100 g), B2 (40–50 mg/100 g), and A (1,200–1,650 units/100 g), as well as minerals such as potassium (222 mg/100 g) and magnesium (17 mg/100 g).[3,4] Papaya, principally the red pulp ones such as Formosa cultivar, is also an important source of lycopene (21 to 29.6 μg/g), a bioactive compound with preventative action against heart diseases and some types of cancer.[5,6]

The production of dried fruits could be an alternative to exploit any excess fruit production, offering the opportunity to add value to the product and generate jobs and income. Dried fruit products are also healthy and convenient.[7]

The production of dried fruit using the combined method of osmotic dehydration (OD) and complementary hot air drying (HA) is a technological alternative with some advantages compared to conventional processes, improving the nutritional and sensory properties of air-dried products.[8] OD has been studied as a preliminary step in the drying of fruits, and consists of immersing them in a hypertonic solution of one or more solutes, such that the partial removal of water occurs mainly due to the chemical potential established.[9,10] The combination of both techniques has been employed in several fruits, such as cherry tomato,[11] mulberry,[12] seabuckthorn fruits,[13] strawberry,[14] and chayote,[15] resulting in products with good quality.

Some studies have reported the potential for the application of OD in papaya processing.[3,9,16–19] However, the technique presents some technological problems that complicate the industrial-scale process, notably softening of the vegetable tissue during OD and loss of color.[17] The cell tissues of papaya are highly fragile, tending to collapse during the process as a function of the ripening stage and time–temperature conditions, making them difficult to handle, which results in losses. In addition, due to carotenoid oxidation, the color of the fruit undergoes changes during shelf life, compromising product quality.[9,16]

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The application of organic acids and calcium salts during OD of papaya has been reported in the literature with the aim of minimizing these problems. Weak acids such as lactic and citric acids prevent color change due to inhibition of enzymatic browning, and calcium salts (calcium lactate and chloride) are applied as texture agents.[16–18,20–22] According to Suttirak and Manurakchinakorn,[23] weak acids retard browning by lowering the pH of the product, minimizing the activity of poliphenol oxydase (PPO). Some acids like citric acid also delay discoloration by chelating the copper at the PPO active site. According to Chiumarelli et al.,[20] the use of weak acids, such as citric acid, can avoid enzymatic browning of plant tissue, thereby reducing changes in product appearance. The calcium ion is supposed to form a complex with pectin in the cell wall and middle lamella of vegetable tissue, resulting in a firmer structure.[17]

The use of the enzyme pectinmethylesterase (PME) associated with calcium salts has also been evaluated as a texture agent in fruit processing. PME is produced by fungi and catalyzes the hydrolysis of methyl esters on the pectin molecule, resulting in pectin free of carboxyl groups, whose negative charges bind to Ca^{2+} ions, forming a tridimensional matrix and promoting greater resistance of the cell wall middle lamella. The use of PME associated with calcium chloride was reported in the combined OD/freezing and heat processing/high-pressure processes of strawberries.[24,25] However, the application of PME/calcium chloride in the combined OD/HA drying process has not been reported yet.

In this context, the objective of the present study was to analyze the effect of some organic acids (citric and lactic) associated with calcium salts (lactate and chloride) on the combined OD/HA processing of papaya. The use of PME with calcium chloride was also evaluated as an alternative, because its application is completely unknown. Technological aspects such as texture, color, and stability of the final products during storage were determined.

MATERIALS AND METHODS

Raw Material

Papayas of Formosa cultivar (~2.5 kg) were obtained from a local market in Campinas, Brazil, and stored at room temperature for maturation. The fruits were used in the mature state known as three quarters, when 50 to 75% of the skin is yellow.[26] Table 1 shows the physicochemical characteristics of the raw material.

Refined União brand sugar (Coopersucar, Piracicaba, Brazil) was used to prepare the osmotic solution. The acids and organic salts were obtained from Labsynth (Brazil). The enzyme E.C 3.1.1.11 (10 pectin esterase units/mL; NovoShape, Novozyme, Denmark), obtained from fermentation with *Aspergillus aculeatus*, was used.

TABLE 1
Physicochemical properties of fresh papaya[a]

Analysis	Mean value	Methods
Moisture content	87.58 ± 1.43	AOAC[27]
Titratable acidity (g citric acid/100 g)	0.076 ± 0.001	AOAC[27]
pH	5.49 ± 0.08	pH meter
Total sugar content (g/100 g)	10.15 ± 2.04	AOAC[27]
Reducing sugar content (g/100 g)	8.94 ± 1.66	AOAC[27]
Soluble solids content (°Brix)	12.00 ± 0.17	Refractometer
Vitamin C content (mg ascorbic acid/100 g)	53.65 ± 2.63	Oliveira et al.[28]

[a]All data are the mean of triplicate measurements ± standard deviation.

Methodology

The study was carried out in two steps: study of the (1) effect of the additives on the combined OD/HA process and (2) stability during storage.

Study of the Effect of the Additives on the Combined OD/HA Process

Experimental OD/HA trials. The fruits were selected, washed with tap water, peeled, and cut into slices of approximately $6 \times 2 \times 0.5$ cm.

According to some preliminary tests, the trials were carried out with the following combinations of additives: 0.1 M citric acid with calcium lactate (0.5 g/100 g syrup; CA/CL); 0.1 M lactic acid with calcium lactate (0.5 g/100 g syrup; LA/CL); 0.1 M citric acid with calcium chloride (0.5 g/100 g syrup; CA/CC); 0.1 M lactic acid with calcium chloride (0.5 g/100 g syrup; LA/CC); and PME (1 mL/kg fruit) with calcium chloride (1 g/kg fruit; PME/CC). The last trial, considered as the standard, was carried out without additives (P).

OD was carried out in an 8-L heat-controlled bath with circulation (10 L/min; model 1266-02, Cole-Parmer, USA). The concentration of the sucrose syrup was 65 °Brix and the mass ratio of syrup to fruit was 4:1 (syrup: fruit). The additives were added to the syrup at the beginning of each trial. The manufacturer's instructions were followed in the trial with PME, using 1 mL of enzyme (10 pectin esterase units/mL) per kilogram of fruit, corresponding to 0.03 g/100 g of syrup, plus 1 g calcium chloride per kilogram of fruit, corresponding to 0.03 g/100 g of syrup. The process was performed for 2 h at 50°C, according to some preliminary tests. At the end of OD, the slices were removed from the bath, drained, rinsed with water, and carefully drained with absorbent paper. The mass of the fruit was weighed

at the beginning and end of OD using a mechanical balance (BPS-15, Filizola, São Paulo, Brazil), separating samples for the analyses.

The osmodehydrated fruits were dried in a tray dryer (K13964, Proctor & Schwartz, USA) with air circulation (velocity of 1.5 m/s) at 60°C, for a time sufficient to obtain a final moisture content of around 16%.

Mass transfer parameters. During the OD process, water loss (WL) and solids incorporation (SI) were calculated using the following equations:

$$WL = (UiMi - UfMf)/ Mi \times 100\,(\text{g of water}/100\text{ g of initial mass}) \quad (1)$$

$$SI = (STfMf - STiMi)/ Mi \times 100\,(\text{g of solute}/100\text{ g of initial mass}). \quad (2)$$

Analyses

The raw material used in the trials was subjected to the following analyses: moisture content, vitamin C content, and instrumental color. After OD, the osmodehydrated fruits were analyzed with respect to moisture content and vitamin C content. The final product after HA (dried fruits) was analyzed in terms of moisture content, water activity, color, and texture. These samples were also subjected to sensory analysis.

The moisture content was determined in a vacuum oven at 70°C to constant weight, according to the Association of Official Analytical Chemists (AOAC),[27] and the water activity was determined using a hygrometer (Aqualab-3TE, Decagon Devices Inc., Pullman, WA, USA) at 25°C. A colorimeter (CR400, Minolta, Osaka, Japan) was used for the color analyses, taking a direct reading of the sample with the d/0 configuration and D65 illuminant and employing the CIELAB system: chromaticity parameters a^* (green [−] to red [+]) and b^* (blue [−] to yellow [+]). Lightness L^* ($L^* = 0$ for black and $L^* = 100$ for white) was also measured. The texture (cutting force) was evaluated using a universal testing machine (TA.XT2i Texture Analyzer, Stable Micro Systems, Godalming, England), with a blade set probe (HDP/BSK) and the HDP/90 platform. The parameters used in the test were as follows: (1) pretest velocity = 2.0 mm/s; (2) test velocity = 1.0 mm/s; (3) post test velocity = 10.0 mm/s; (4) distance 99% of the sample, with a compression force of 100 gram-force (gf), time of 5 s, trigger of 5 *g*, and load cell of 50 kg. The vitamin C content was determined according to the titration method of Oliveira et al.,[28] and the percentage retention of vitamin C in relation to the raw material calculated according to Murphy et al.[29]

The physicochemical analyses were carried out in triplicate. Fifteen samples were used per treatment for the texture determination (cutting force). Color analysis was performed with 10 measurements taken from five samples per treatment. The results for these analyses are presented as the mean value plus the standard deviation. The means were statistically evaluated by analysis of variance using the Statistica 7.0 program (StatSoft, Inc., Tulsa, OK, USA), and the separation of the means was determined employing Tukey's test at $p \leq 0.05$.

Sensory analysis. A sensory evaluation of the final products obtained from the trials with additives was carried out with a panel of 16 trained judges using horizontal structured scales with four adjectives for each attribute and 12 corresponding numerical points: appearance (poor, 1–3; regular, 4–6; good, 7–9; optimum, 10–12); orange color (weak, 1–3; regular, 4–6; moderate, 7–9; intense, 10–12); texture/elasticity (low, 1–3; regular, 4–6; medium, 7–9; high, 10–12); flavor (poor, (1–3; regular, 4–6; good, 7–9; optimum, 10–12), and overall quality (poor, 1–3; regular, 4–6; good, 7–9; optimum, 10–12).[30] Standard treatments (without additives) were not subjected to sensory analysis, because the main goal of this work was to compare the treatments with the additives. Therefore, the use of standard samples in sensory tests could have interfered with the results, confusing the judges. The results were analyzed by the analysis of variance, F test and Tukey's test using the Statistical Analysis System (SAS Institute Inc., USA).

Stability Study of the Dried Papaya Slices During Storage

This study was carried out with the products obtained from two treatments chosen in the first step and with the product treated without additives (standard). To obtain the samples, three new experimental OD/HA trials were carried out under the same conditions described previously. The products were packed into double-film packages of low-density polyethylene (1.5 mm thickness) and aluminum foil and stored in a BOD incubator (LS370, Logen Scientific, Diadema, Brazil) at 25 or 35°C and relative humidity of 65% for 70 to 100 days.

At the beginning of the study, the dried fruits were subjected to light microscopy analysis and instrumental color, vitamin C content, and moisture content analyses. The vitamin C and instrumental color were periodically evaluated during storage according to the methods previously described. Due to the low water activity values of the final products and some previous results, microbiological stability and pH analyses were not performed. Water activity and moisture content were also not evaluated, due to the very good vapor barrier properties of the package employed. However, for a complete shelf life study these analyses should be considered.

Light microscopy. Samples of fresh papaya and dried fruit were submitted to a cell structure analysis by light microscopy at time zero of the stability study. The samples

were prepared according to the methodology described by Ferrari et al.[31] and the light microscope used was an Olympus BX51 (Olympus Optical Co., Tokyo, Japan).

Analysis of the reaction order and determination of kinetic parameters. Changes in the vitamin C content and color parameters were evaluated using the zero- and first-order kinetic models, Eqs. (3) and (4), respectively, according to Teixeira Neto et al.[32]:

$$C_t = C_0 - kt \tag{3}$$

$$\ln \frac{C_t}{C_0} = -kt. \tag{4}$$

The reaction order was determined with the model that best fitted the experimental data (best coefficient of determination, R^2). The kinetic parameter k (reaction velocity) was obtained from the best-fitted models, and Q_{10} calculated using this parameter according to Eq. (5). The half life, $t_{1/2\text{life}}$, was calculated using Eqs. (6) and (7) for the zero- and first-order models, respectively, according to Teixeira Neto et al.[32]:

$$Q_{10} = \frac{k_T}{k_{T-10}} \tag{5}$$

$$t_{\frac{1}{2}life} = \frac{0.693}{k} \tag{6}$$

$$t_{\frac{1}{2}life} = \frac{C_0}{2k}. \tag{7}$$

RESULTS AND DISCUSSION

Study of the Effect of Processing Additives on the Combined OD/HA Process

Osmotic Dehydration Parameters

The values obtained for WL and SI in the standard trial (Table 2) were similar to those reported by Jain et al.[19] for the OD of papaya carried out under similar conditions (50°C/60 °Brix/4 h): WL of 40 g/100 g; SI of 7.0 g/100 g. On the other hand, the results obtained for WL in the trials with additives (Table 2) were higher than the values obtained in the standard trial (P). The use of CA/CL resulted in an increase in WL of approximately 50%. Calcium lactate had a slightly greater effect on this parameter than calcium chloride for the same acids. According to Ferrari et al.,[31] who studied the use of calcium lactate in the OD of melon, the increase in WL is due to a more open cell structure with the formation of calcium pectates and bridges in the cell wall. However, Table 2 shows that the values for SI were slightly lower in the trials with additives compared to the standard trial, with the exception of the treatment with PME/CC. Heng et al.[16] observed the same behavior in the OD of papaya with calcium chloride. The authors stated that the association of calcium with the low methoxy pectin in the cell wall causes an increase in the tortuosity of the intercellular spaces and also in the local viscosity, decreasing the diffusion of sugar. In agreement with this result, Silva et al.,[33] studying the OD of pineapple, reported that the presence of calcium in the solution decreased the diffusivity of sucrose within the samples. Nevertheless, in the trial with PME/CC, there was an increase in the value for SI compared to the standard treatment (P). This was also observed by Van Buggenhout et al.[24] in the OD of strawberry with sucrose and the addition of the same additives, who reported a higher increase in dry matter content (44%) in the treatment with additives.

The moisture contents of the final products ranged from 14.2 to 18.5%. These differences may be due to small operational variations and to natural variations in the biological tissue. The values for water activity of the resulting products showed significant differences ($p \leq 0.05$) and were in the range from 0.60 to 0.65. However, it was not possible to verify the influence of the different additives on this property.

Texture

With respect to the texture (cutting force) of the final product, Table 2 shows that, with the exception of PME/CC, all treatments resulted in higher values that were significantly different from that of the standard treatment ($p \leq 0.05$). The highest mean was obtained for the treatment with CA/CL, although this result could also be related to the lower moisture content of the final product for this trial. Ferrari et al.[31] also reported an important increase in the stress of failure of melons pretreated with calcium lactate, and Rodrigues et al.[17] showed a significant increase in the fracture stress with the use of calcium chloride in the OD of papaya. On the other hand, the texture after treatment with PME/CC showed no significant difference from the value obtained for the standard treatment ($p > 0.05$).

Independent of the results obtained for instrumental texture, all treatments with additives, including PME/CC, resulted in more integral slices at the end of the OD, which were also easier to handle when compared to the standard treatment. The osmodried fruit treated with PME/CC showed an excellent appearance in terms of volume and form, similar to that reported by Van Buggenhout et al.[24] for the freezing/thawing of strawberries pretreated with an aqueous solution of PME/CC.

Instrumental Color

According to Table 3, the color parameters of fresh papaya were located in the first quadrant of CIELAB color diagram (a^* and $b^* > 0$), corresponding to the region of red and yellow. In additon, a slight predominance of chromaticity parameter b^* was observed. According to Sentanin

TABLE 2
Processing additives used, OD/HA parameters, and physical properties of the dried papaya subjected to different treatments[a]

		OD parameters (%)		Dried product		
Trial	Processing additives	WL	SI	Moisture content %	aw	Cutting force (N)
CA/CL	Citric acid (0.1 M) Calcium lactate (0.5 g/100 g syrup)	63.48 ± 5.08^{c}	5.07 ± 0.51^{a}	14.21 ± 0.01^{a}	0.596 ± 0.001^{a}	35.98 ± 3.65^{c}
LA/CL	Lactic acid (0.1 M) Calcium lactate (0.5 g/100 g syrup)	61.68 ± 6.17^{c}	4.47 ± 0.45^{a}	15.62 ± 0.16^{b}	0.645 ± 0.002^{e}	24.38 ± 4.67^{b}
CA/CC	Citnc acid 0.1M Calcium chloride (0.5 g/100 g syrup)	52.00 ± 4.16^{ca}	4.61 ± 0.37^{a}	16.97 ± 0.03^{d}	0.630 ± 0.002^{c}	28.16 ± 5.47^{b}
LA/CC	lactic acid (0.1 M) Calcium chloride (0.5 g/100 g syrup)	60.25 ± 5.42^{c}	4.29 ± 0.51^{a}	18.50 ± 0.63^{e}	0.634 ± 0.001^{d}	24.47 ± 3.98^{b}
PME/CC	PME (1 ml/kg fruit) Calcium chloride (1 g/Kg fruit)	51.37 ± 5.4^{bc}	9.94 ± 1.10^{b}	$16.64 \pm 0.02^{*}$	0.650 ± 0.000^{f}	17.64 ± 5.37^{a}
P	Standard - no processing additives	40.65 ± 4.3^{ab}	6.20 ± 0.93^{a}	15.78 ± 0.10^{bc}	0.624 ± 0.001^{b}	17.77 ± 3.43^{a}

[a]Means in the same column followed by different letters indicate significant differences at $p \leq 0.05$.

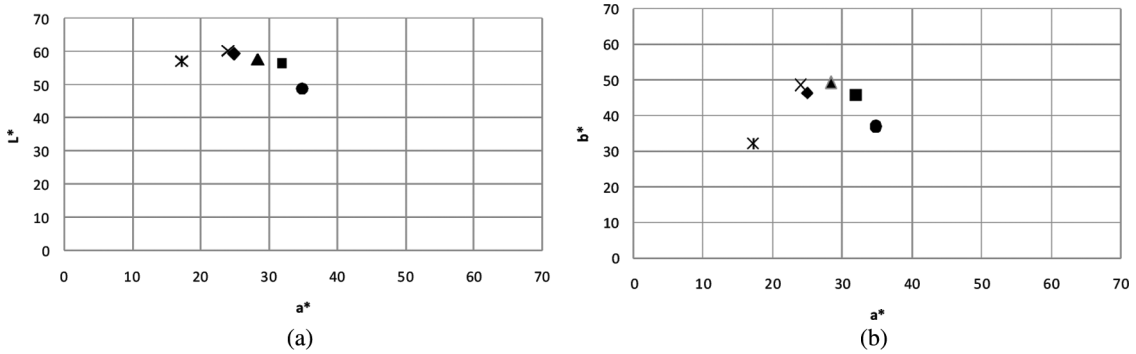
and Rodriguez-Amaya,[6] the main pigments of papaya of Formosa cultivar are lycopene, β-carotene, and β-cryptoxanthine. Lycopene, responsible for the red coloration, is the majority pigment, representing 65% of the total pigments, whereas β-cryptoxanthine and β-carotene, responsible for the yellow color, are present as 30 and 4%, respectively. Due to the variability in the raw material, a dimensionless analysis of the color parameters was carried out (Table 3). A comparison of the color of dried products is shown in Fig. 1. The processes with additives, with the exception of the treatment with PME/CC, resulted in a lighter product compared to the fresh sample, as indicated by the values for L^{*}_{dim} greater than 1 (Table 3). On the other hand, all of the processed fruits with additives are lighter than the standard product (Fig. 1a). This could be partially explained by the action of the employed organic acids in avoiding enzymatic browning. Germer[34] reported similar results in a study with peaches and related the lightening to a slight crystallization of sugars on the surface. Rodrigues et al.[17] also observed an increase in lightness in their study on the OD of papaya with calcium salts and organic acids and associated the result to the incorporation of calcium in the vegetable tissue.

With respect to the other color components, Table 3 shows a slight increase in the values for the parameter b^{*} in the process ($b^{*}_{\mathrm{dim}} > 1$), indicating an intensification of the yellow color, with the exception of the treatments PME/CC and P. However, Fig. 1b shows that, with the exception of the treatment with PME/CC, the products obtained with additives are more yellow than those obtained from the standard process. This could be explained by the action of the employed organic acids in avoiding enzymatic browning. A slight increase in a^{*} was also observed during the process ($a^{*}_{\mathrm{dim}} > 1$), indicating an intensification of the red color for CA/CL, LA/CL, and CA/CC treatments (Table 3). The redder product obtained by P treatment could be attributed to the differences in the raw material, because the fresh sample showed the highest a^{*} values. In general, in a drying process, the removal of water provides an increase in the color parameter values as a function of the concentration of the pigments in the raw material. However, pigments losses to the syrup during OD may occur, as well as their degradation, resulting in a decrease in the color parameters.[34] Rodrigues et al.[17] reported higher a^{*} and b^{*} values during OD of papaya with additives, and Germer[34] found an increase in yellowness (higher b^{*} values) in the osmotic solution employed during OD of peaches, relating this fact to a leaching of pigments from the fruit to the syrup. Similar behavior was pointed out by García-Martínez et al.[35] Variations in b^{*} occurred with the reuse of syrup in the OD of kiwi due to leaching of pigments such as β-carotenes, chlorophylls, and xanthophylls from fruit to

TABLE 3
Color parameters of the fresh papaya and dried papaya subjected to different treatments[a]

	Color parameters								
		Fresh papaya			Dried papaya			Dimensionless*	
Trial	L*	a*	b*	L*	a*	b*	L*adm	a*adm	b'adm
CA/CL	55.47 ± 3.46^{cb}	24.58 ± 1.99^{a}	38.17 ± 2.25^{a}	59.23 ± 1.51^{bc}	24.86 ± 1.93^{b}	46.44 ± 1.18^{c}	$1.07 + 0.07^{a}$	1.01 ± 0.11^{ba}	1.22 ± 0.08^{b}
LA/CL	54.08 ± 2.97^{b}	25.70 ± 1.34^{ba}	40.85 ± 2.12^{b}	56.39 ± 2.45^{b}	31.90 ± 1.45^{d}	45.6 ± 1.69^{c}	1.04 ± 0.07^{a}	1.24 ± 0.09^{b}	1.12 ± 0.07^{bc}
CA/CC	52.61 ± 2.98^{ba}	24.70 ± 1.97^{a}	39.92 ± 2.47^{abc}	57.69 ± 3.50^{bc}	28.32 ± 2.38^{c}	49.16 ± 3.79^{c}	1.10 ± 0.09^{a}	1.15 ± 0.13^{bc}	1.23 ± 0.12^{b}
LA/CC	52.40 ± 1.63^{ba}	28.03 ± 1.71^{b}	40.75 ± 2.13^{abc}	60.09 ± 2.80^{c}	24.02 ± 2.00^{b}	48.55 ± 3.28^{c}	1.15 ± 0.06^{a}	0.86 ± 0.09^{ac}	1.19 ± 0.10^{b}
PME/CC	8.79 ± 4.55^{c}	23.91 ± 3.02^{a}	39.94 ± 1.30^{bc}	56.99 ± 2.24^{b}	17.26 ± 2.49^{a}	32.09 ± 4.74^{a}	0.97 ± 0.08^{a}	0.72 ± 0.14^{a}	0.80 ± 0.12^{a}
P	49.76 ± 2.14^{a}	$30.38 + 1.79^{c}$	40.76 ± 2.77^{bc}	48.67 ± 1.81^{a}	34.8 ± 2.20^{e}	36.84 ± 1.60^{b}	0.98 ± 0.05^{a}	1.15 ± 0.10^{bc}	0.90 ± 0.07^{ac}

[a]Parameter $(L^*, a^*, b^*)_{dim}$ = parameter of the dried papaya (L^*, a^*, b^*)/parameter of the fresh papaya (L^*, a^*, b^*). Means in the same column followed by different letters indicate significant differences at $p \leq 0.05$.



(a) (b)

FIG. 1. Comparison of color of dried papaya subjected to different treatments: (a) L^* (lightness) and chromaticity parameter a^* (redness); (b) chromaticity parameter a^* (redness) and b^* (yellowness): (◆) CA/CL; (■) LA/CL; (▲) CA/CC; (×) LA/CC; (*) PME/CC; (●) P.

syrup. Furthermore, according to Heng et al.,[16] at the beginning of processing, hydrophobic carotenoids may concentrate in intracellular spaces during parallel dehydration of papaya (OD process). This leads to a relative increase in their content in the dehydrated fruit. When the dehydration time is long enough, the syrup becomes tinted, meaning that a part of the pigments is lost by diffusion.

Based on the results observed, the use of processing additives, in general, helped to preserve the instrumental color of the product, but the combination of PME and CC was less effective in maintaining this quality characteristic.

Vitamin C Content

The mean vitamin C content of the raw material used in the trials was 60.12 mg/100 g (Table 4). This value was between those reported by Garcia[36] and El-Aouar[37] for papaya of Formosa cultivar (44.30 and 71.31 mg/100 g, respectively). The differences are due to variability in the raw material, principally in the state of maturity. The mean loss of vitamin C during OD for the different treatments was approximately 55%, and the trial performed with PME/CC resulted in the greatest retention (Table 4). This result is almost within the range of 30 to 60% for vitamin C retention reported by Heng et al.[16] in the OD of papaya under similar process conditions. According to Santos and Silva,[38] vitamin C losses occurring during OD are related to both chemical deterioration and diffusion of ascorbic acid from the fruit to the solution. The vitamin C content of the dried products is not presented in Table 4, because its determination was compromised due to the monitoring of the product weight during hot air drying for the adjustment of the final moisture content, necessary for the other analyses (mainly texture and sensory tests).

TABLE 4
Vitamin C content of the fresh and osmodehydrated fruits and the retention values (%) observed in the different treatments[a]

Trial	Vitamin C content (mg/100 g)		Vitamin C retention in OD (%)
	Fresh	Osmodehydrated	
CA/CL	76.56 ± 0.26^f	52.84 ± 2.81^b	33.10 ± 3.78^a
LA/CL	45.47 ± 0.95^a	41.18 ± 0.01^a	33.51 ± 2.09^a
CA/CC	64.61 ± 0.19^d	57.25 ± 0.44^c	46.62 ± 0.72^b
LA/CC	69.01 ± 0.15^e	53.36 ± 0.23^b	34.05 ± 0.37^a
PME/CC	55.18 ± 0.65^c	59.17 ± 0.90^c	62.81 ± 2.06^d
P	49.90 ± 0.57^b	43.23 ± 0.33^a	56.78 ± 1.17^c

[a]Means in the same column followed by different letters indicate significant differences at $p \leq 0.05$.

In a similar work, An et al.[11] studied the influence of OD and pulsed vacuum osmotic dehydration (PVOD) with sucrose solutions (50 and 70 °Brix) in combination with air drying on the vitamin C retention of cherry tomatoes. Air drying led to a great loss of vitamin C, showing a retention rate of only 24.79%. Dried samples pretreated in sucrose solution had higher vitamin C retention rates (about 41–49%), indicating that osmotic dehydration can aid in the retention of vitamin C, due to the protective effect of the sugar. The PVOD process had a more favorable effect in vitamin C retention due to a greater infusion of sugar solute and shorter hot air drying time. Dried samples pretreated with 50 °Brix solution under PVOD had the maximum vitamin C retention of about 55%.

Sensory Analysis

Concerning the attributes appearance and orange color, the best scores were obtained for the fruits treated with CA/CC and LA/CC (see Table 5), with no significant difference ($p > 0.05$). This can be partially related to the instrumental color results, because these treatments showed similar behavior for the dimensionless variations in L^* and b^* (Table 3). On the other hand, from Fig. 1b, it is also possible to see that these treatments resulted in products with a slightly yellower color. As previously discussed, PME/CC treatment presented lower L^* and b^* values, but the mean scores for color attribute did not differ from CA/CC and LA/CC

TABLE 5
Mean sensory acceptance scores of the dried papaya subjected to different treatments[a]

Attributes	Trials				
	CA/CL	LA/CL	CA/CC	LA/CC	PME/CC
Appearance	7.31 ± 1.82^{b}	2.62 ± 1.20^{a}	9.18 ± 1.97^{c}	8.62 ± 1.71^{bc}	7.75 ± 2.21^{b}
Orange color	7.43 ± 1.90^{b}	2.68 ± 1.49^{a}	9.25 ± 2.02^{c}	8.81 ± 2.46^{bc}	8.37 ± 1.86^{bc}
Flavor	5.68 ± 2.55^{a}	6.75 ± 2.38^{ab}	6.43 ± 2.19^{ab}	6.62 ± 2.00^{ab}	7.87 ± 2.63^{b}
Texture/elasticity	7.00 ± 2.18^{a}	6.31 ± 2.73^{a}	6.18 ± 2.56^{a}	6.87 ± 1.89^{a}	5.56 ± 2.99^{a}
Overall quality	5.93 ± 1.57^{ab}	5.43 ± 2.06^{a}	7.00 ± 1.97^{bc}	7.81 ± 1.64^{cd}	8.50 ± 2.13^{d}

[a]Means in the same row followed by different letters indicate significant differences at $p \leq 0.05$.

treatments at $p \leq 0.05$, as seen in Table 5. For the flavor, no significant differences ($p > 0.05$) were observed between LA/CL, LA/CC, CA/CC, and PME/CC treatments, but samples produced with PME/CC showed the best mean scores, followed by LA/CL and LA/CC treatments. As mentioned before, the highest SI in OD was observed in the PME/CC trial (Table 2), which can explain the flavor results in the sensory analysis, because the product of this trial was sweeter. Concerning the texture/elasticity, there was no significant difference ($p > 0.05$) between the means (Table 5), implying that the panelists did not notice the differences pointed out in the previous analysis of instrumental texture (Table 2). With respect to overall quality, PME/CC treatment was the most acceptable, with mean scores around 8.50, showing significant differences ($p \leq 0.05$) from CA/CL, LA/CL and CA/CC treatments (Table 5). LA/CC sample also presented high scores for this attribute and did not differ significantly from PME/CC treatment ($p > 0.05$).

The treatments with LA/CC and PME/CC were selected for the next step of this work (stability study), based mainly on the results of the sensory evaluation. For this choice, it was taken into account the observation that all the treatments resulted in osmodehydrated products with better aspect and greater handling facility as compared to the standard treatment, independent of the instrumental texture results. Despite the lower efficiency in preserving the instrumental color, the treatment PME/CC was chosen for the stability study, mostly due to the sensory acceptance scores for flavor and overall quality attributes (Table 5) and to its innovative character. The choice of the treatment with LA/CC was also based in the sensory analysis results (flavor and overall quality attributes), though it showed a greater loss of vitamin C in comparison to the trial with CA/CC, as seen in Table 4.

Stability Study

Microscopy

The images obtained in the light microscopy analysis for fresh papaya and dried papaya (OD/HA) at time zero of the stability study are presented in Fig. 2.

Figure 2a shows that the fresh papaya presented turgid, round cells with a well-defined, consistent cell wall. The presence of pectic substances was evidenced by the toluidine blue (purple color), and they were concentrated in the cell wall and intercellular spaces. Garcia-Noguera et al.,[14] working with osmotic dehydration and ultrasound processes prior to convective drying, reported that the cells of fresh strawberry were evenly distributed, showing a consistent semicircular shape with little distortion of the cells. Pectin-laced walls were intact and the tissue presented several interlamellar spaces. In the present work, the combined OD/HA process without additives resulted in important alterations in cell format and turgor (Fig. 2b). The cell wall was destructured as evidenced by the loss in adhesion between adjacent walls, and intense plasmolysis was observed in the cytoplasm (see arrows).

According to Figs. 2c and 2d, the OD process carried out with the addition of additives resulted in better maintenance of the cell structure. In the trial with LA/CC, the cell walls of the samples were thicker due to the formation of calcium pectate (see arrows), which could explain the higher cutting force values observed in the previous part of the work (Table 2). Similar results were reported by Ferrari et al.[31] in melon predried with a sucrose solution containing calcium lactate. However, Pereira et al.[39] found no differences in cell structure between guava predried with calcium lactate and the fresh fruit in a microscopic analysis, even though differences in texture had been found. Figure 2d, which refers to the treatment with PME/CC, shows less thickening of the cell wall, with an apparent spreading out of the pectic substances throughout the tissue. This could explain the lower cutting force obtained for the papaya subjected to treatment with PME/CC in the previous part of the work (Table 2). Van Buggenhout et al.[24] reported an intense coloration of the cell wall and of the intercellular spaces in the microscopic analysis of osmodehydrated strawberry obtained with the addition of PME/CC during OD with sucrose. However, the authors used greater amounts of enzyme (0.12% v/v) and calcium chloride (0.5% w/w) than employed in the present study. Fraeye et al.,[25] studying the infusion of strawberries in a PME/CC solution, observed

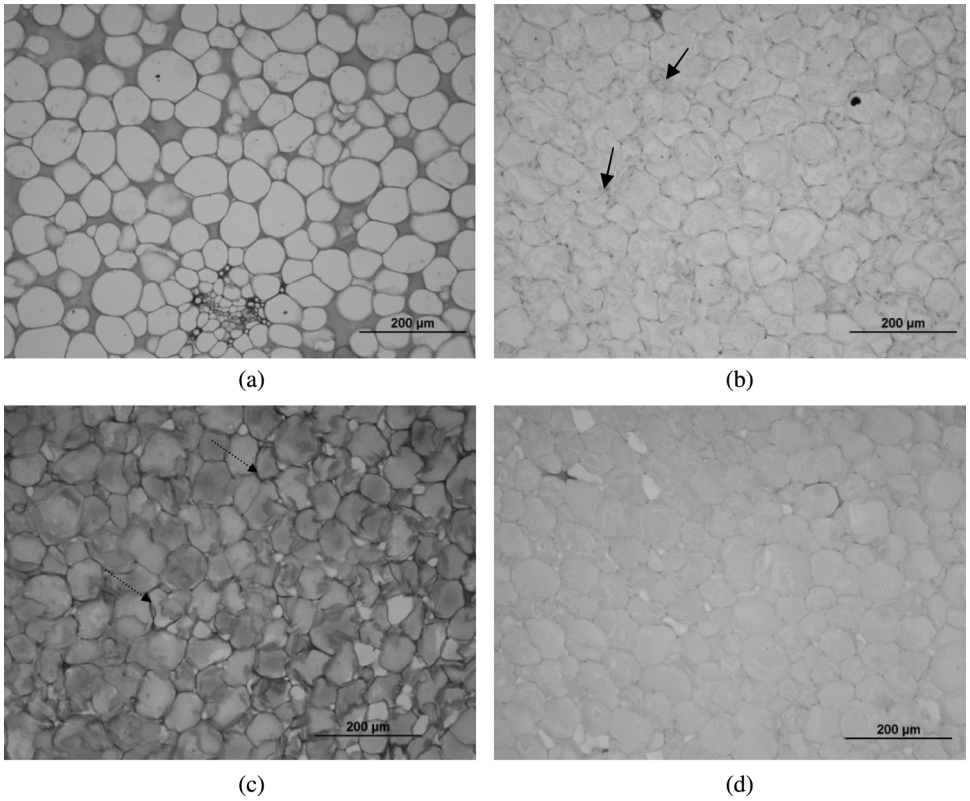


FIG. 2. Light microscopy images of fresh papaya and dried papaya (OD/HA) at time zero of the stability study: (a) fresh papaya, (b) OD with no processing additives (P); (c) OD with LA/CC; (d) OD with PME/CC. Scale bar = 200 µm.

that the cell walls were more brightly colored and related this to the formation of a pectin–calcium network. However, OD pretreatment was followed by high-pressure heat treatment, and the results showed that prolonging the heat treatment (70°C for more than 10 min) caused a loss in the firmness obtained in the osmotic pretreatment. Considering this observation, it is possible that in the present study the hot air drying performed at 60°C could have damaged the pectin–calcium network established during the OD step, causing a decrease in texture values (cutting force).

Color Degradation Kinetics

According to Fig. 3, there was a decrease in the parameter b^* of the dried papaya with time under the different storage conditions, indicating a loss of yellow color. The zero-order kinetic model fitted the experimental data better (R^2 between 0.83 and 0.92), as seen in Table 6. Koca et al.[40] also reported a decrease in the parameter b^* during storage of dehydrated carrot, using zero-order kinetic models. In this study, the authors correlated the decay in the chromaticity parameters with degradation of β-carotene. Table 7 shows that b^* values for samples treated with LA/CC and stored at 25°C were not fitted to kinetic models. No significant difference ($p > 0.05$) was observed throughout storage, meaning that the yellow color of the product was maintained. Considering this observation and the values obtained for $t_{1/2\text{life}}$ at 35°C in Table 6, the treatment with LA/CC resulted in greater stability of the yellow color, followed by PME/CC and P treatments. On the other hand, the results for Q_{10} (Table 6) indicated that the degradation reaction of b^* for the samples subjected to PME/CC treatment was less dependent on temperature than that observed for P treatment.

As shown in Fig. 4, there was also a decrease in the parameter a^* for the different treatments throughout the study, indicating degradation of the red color of dried papaya. The variations in a^* followed first-order models (R^2 between 0.80 and 1.0) for P and LA/CC treatments, with identical equations, as can be seen in Table 6, resulting in equal values for $t_{1/2\text{life}}$ at the respective temperatures. The degradation of parameter a^* in light guava jam was reported by Moura et al.,[41] who also obtained a first-order model and Q_{10} value of 2 for the total color difference (ΔE). Similar values for Q_{10} were also reported by Moura et al.[42] for the total color difference (ΔE) of traditional blackberry jam. The treatment with PME/CC also resulted in first-order kinetics for parameter a^*, with k values (reaction velocity) much higher than the corresponding values in the other treatments and lower $t_{1/2\text{life}}$ values, indicating less stability of the red color (Table 6). However, the lower value for

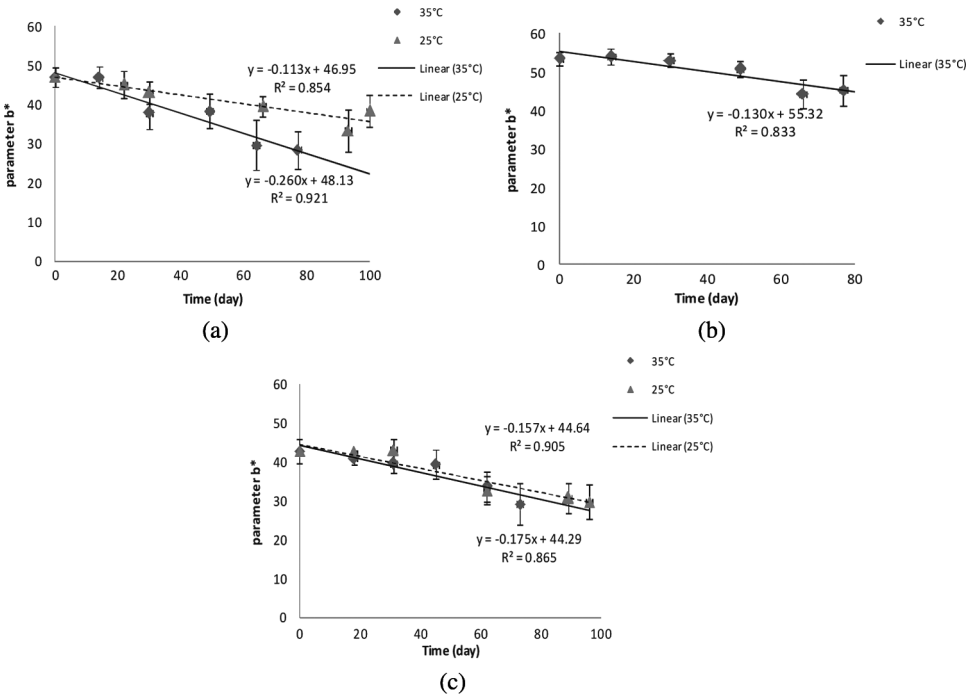


FIG. 3. Kinetics of the variation in parameter b^* (blue–yellow) of the dried papaya subjected to different treatments throughout storage: (a) standard (P); (b) LA/CC; and (c) PME/CC.

Q_{10} obtained for the treatment with PME/CC indicated less dependence of the degradation reaction on temperature.

Parameter L^* (lightness) remained practically unchanged throughout storage for samples subjected to treatment with LA/CC and stored at 25°C, indicating that the fruits did not become darker (Table 7). On the other hand, for the other treatments performed at this temperature a slight increase in L^* can be seen after 90 days, which means that the papaya pieces became lighter. This could have occurred due to crystallization of sugar on the surface. An increase in L^* was also reported by Torreggiani et al.[43] during storage of osmodehydrated cherries for 6 months at 25°C. At 35°C, no significant variation in the parameter L^* ($p > 0.05$) was observed for the samples treated with PME/CC (Table 7). However, lightness values significantly decreased ($p \leq 0.05$) at the end of storage time for LA/CC (around 8%) and P

TABLE 6
Kinetic parameters for the variations in a^* and b^* of the dried papaya subjected to different treatments throughout storage[a]

Parameter	Treatment	Reaction order	T (°C)	k (day^{-1})	R^2	Q_{10}	$t_{1/2}$ life (day)
b^*	P	0	25	0.113 (−)	0.854	2.30	207.7
		0	35	0.26 (−)	0.922		92.6
	LA/CC	0	25	nf	nf	nf	nf
		0	35	0.13 (−)	0.833		212.8
	PME	0	25	0.157 (−)	0.905	1.11	142.2
		0	35	0.175 (−)	0.865		126.5
a^*	P	1	25	0.002 (−)	1.000	1.50	346.5
		1	35	0.003 (−)	0.848		231.0
	LA/CC	1	25	0.002 (−)	0.935	1.50	346.5
		1	35	0.003 (−)	0.803		231.0
	PME	1	25	0.008 (−)	0.986	0.88	86.6
		1	35	0.007 (−)	0.978		99.0

[a]nf = not fitted.

TABLE 7
Color parameters values (not fitted to kinetic models) of the dried papaya subjected to different treatments throughout storage[a]

		P	LA/CC		PME/CC
Temperature (°C)	Time (days)	L*	L*	b*	L*
25	0	58.76 ± 3.72^{a}	63.45 ± 2.34^{b}	53.49 ± 1.88^{a}	54.94 ± 2.95^{a}
	15	55.63 ± 2.91^{a}	61.67 ± 5.58^{ba}	51.97 ± 4.96^{a}	54.85 ± 3.32^{a}
	30	57.02 ± 3.61^{a}	62.29 ± 4.74^{b}	53.21 ± 4.39^{a}	55.13 ± 4.29^{a}
	60	54.84 ± 2.44^{a}	56.83 ± 5.51^{a}	48.04 ± 4.27^{a}	56.39 ± 4.20^{ba}
	90	55.12 ± 3.97^{a}	61.66 ± 3.15^{ba}	48.87 ± 8.83^{a}	60.10 ± 3.06^{b}
	100	61.53 ± 3.07^{b}	64.06 ± 1.92^{b}	53.73 ± 1.50^{a}	62.78 ± 3.69^{b}
35	0	58.76 ± 3.72^{b}	63.45 ± 2.34^{c}	md	54.94 ± 2.95^{a}
	15	58.56 ± 4.05^{b}	63.22 ± 2.03^{c}	md	54.40 ± 2.27^{a}
	30	50.49 ± 4.31^{a}	63.92 ± 2.89^{c}	md	53.01 ± 2.94^{a}
	45	49.39 ± 4.23^{a}	61.53 ± 2.79^{cb}	md	53.51 ± 3.78^{a}
	60	48.32 ± 3.43^{a}	55.75 ± 3.97^{a}	md	56.27 ± 3.44^{a}
	75	$46.16 \pm 5\ 48^{a}$	58.07 ± 4.17^{ba}	md	55.06 ± 5.76^{a}

[a]md = modeled data. Means in the same column followed by different letters indicate significant differences at $p \leq 0.05$.

(around 21%) treatments, which is related to possible browning.

Based on the above, the addition of lactic acid with calcium chloride to the sucrose syrup used in the OD of papaya presented an effective contribution to color stability of the product during a storage period of 75 to 100 days. This may be related to the action of weak acids previously mentioned in avoiding enzymatic browning during the process, the effect of which is prolonged during storage. The same behavior was not verified for the use of PME with calcium chloride, because the red color component of the dried papaya obtained in this treatment showed an important degradation over time.

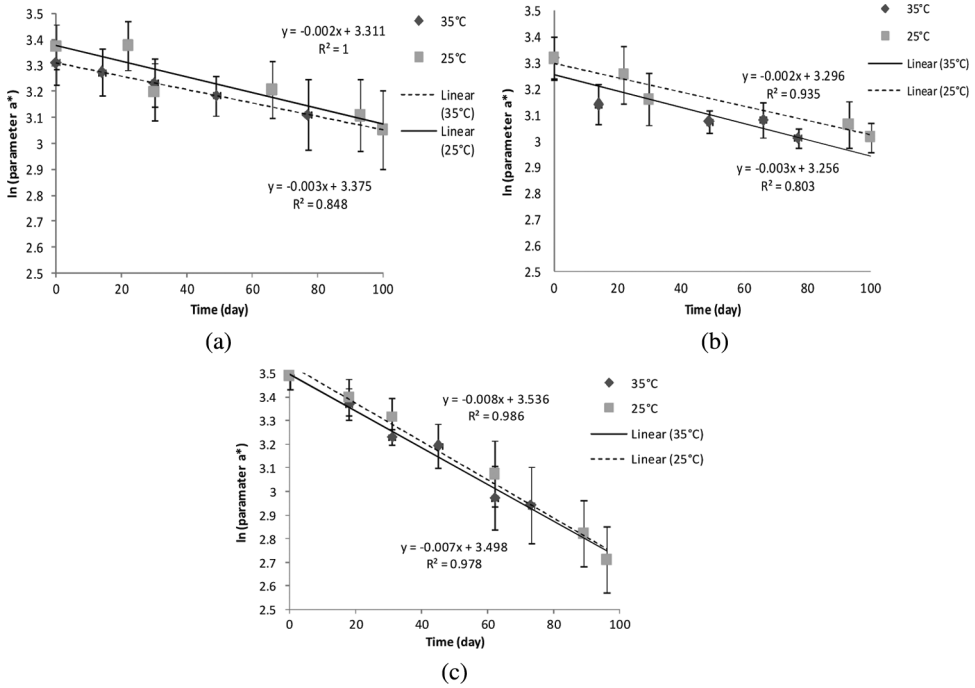


FIG. 4. Kinetics of the variation in parameter a^* (green–red) of the dried papaya subjected to different treatments throughout storage: (a) standard (P); (b) LA/CC; and (c) PME/CC.

TABLE 8
Kinetic parameters for vitamin C degradation of the dried papaya subjected to different treatments throughout storage

Treatment	Reaction order	T (°C)	k (day^{-1})	R^2	Q_{10}	$t_{1/2}$ life
P	1	25	0.012 (−)	0.982	3.08	57.8
	1	35	0.037 (−)	0.991		18.7
LA/CC	1	25	0.013 (−)	0.969	3.08	53.3
	1	35	0.040 (−)	0.980		17.3
PME/CC	1	25	0.010 (−)	0.910	3.90	69.3
	1	35	0.039 (−)	0.967		17.8

Vitamin C Degradation Kinetics

The samples (dried fruit) produced for the stability study presented initial vitamin C contents of 152.28 ± 1.43 mg/100 g (P treatment), 115.59 ± 0.77 mg/100 g (LA/CC treatment), and 144.54 ± 0.42 mg/100 g (PME/CC treatment), corresponding to retentions of 63, 37, and 62%, respectively, with respect to the raw material. These contents are relatively high, independent of the observed losses. Thus, the dried papaya obtained by these different processes can be considered an important source of the nutrient.

The first-order kinetic model showed good fit (R^2 from 0.91 to 0.99) with the experimental values of vitamin C content throughout the stability study at 25 or 35°C, as can be seen in Table 8 and Fig. 5. Similarly, Dermesonlouoglou et al.[44] reported first-order kinetic models for the degradation of vitamin C in osmodehydrated tomatoes. In another work, Chottamon et al.[12] studied the osmotic treatment (using sucrose, sorbitol, and maltose solutions) in combination with air drying of mulberries and evaluated the influence of different osmotic solutions on drying kinetics, reaction kinetics, and anthocyanins and phenolics content. Air drying caused degradation of anthoyanins and phenolics, which followed a zero-order reaction with R^2 values ranging from 0.866 to 0.996. Osmotic treatment with maltose was found to be a good treatment for mulberry drying and preserved the phenolic and anthocyanin contents and provide high antioxidant capacity.

Table 8 shows that the parameters obtained were very close, indicating that the velocity of vitamin C degradation throughout the time was practically the same for the three treatments. This means that the use of lactic acid, calcium chloride, or PME/CC did not contribute to the retention of vitamin C during storage in comparison to the standard treatment. The half life of the different products at 25°C was approximately 60 days (Table 8). Uddin et al.[45] reported a $t_{1/2life}$ value of just 5 days for freeze-dried guava stored at 30°C. In a similar work, Roopa et al.[46] showed that the vitamin C content in dried star fruit, obtained by a combined OD/HA process, did not reduce to half the original value in

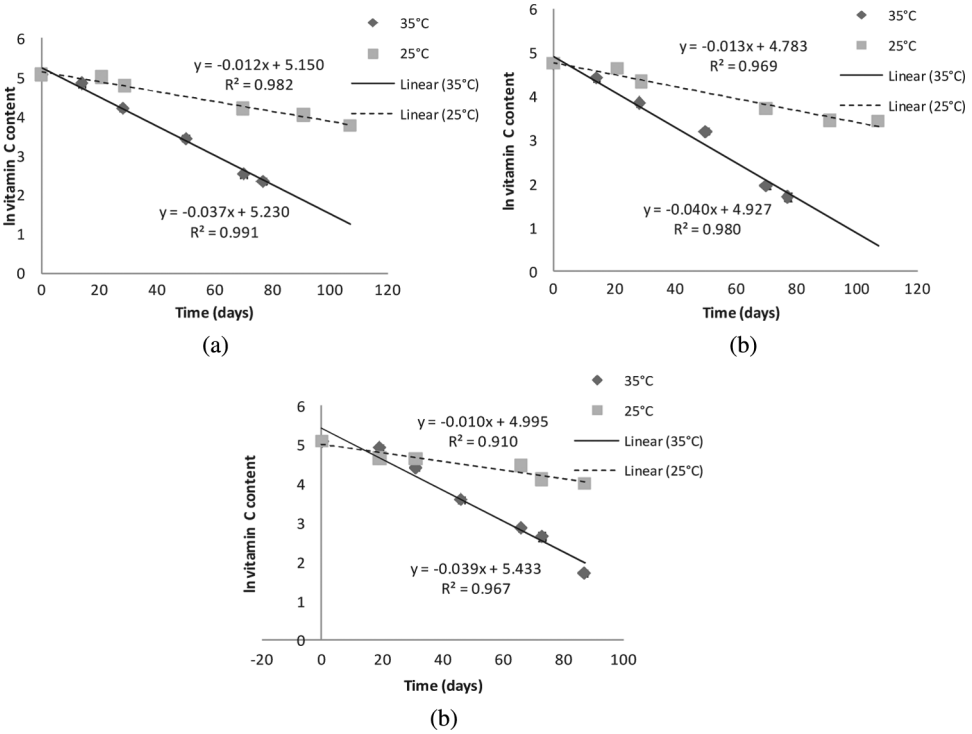


FIG. 5. Kinetics of vitamin C degradation in dried papaya subjected to different treatments throughout storage: (a) standard (P); (b) LA/CC; and (c) PME/CC.

10 months of storage at 25°C. In the present work, the relatively high Q_{10} values indicated great sensitivity of the vitamin C degradation reaction in relation to the storage temperature, especially in the treatment with PME/CC (Table 8). The values for Q_{10} were within the range reported by Labuza[47] for the degradation of vitamin C in dehydrated vegetables (from 1.5 to 4).

CONCLUSIONS

The addition of the investigated additives in the osmotic dehydration of papaya resulted in easier handling of samples compared to the standard trial. The instrumental color of the papaya was better preserved during the OD/HA process with the additives, despite the higher color losses verified in the treatments performed with PME/CC. Samples treated with PME/CC and LA/CC showed higher acceptance scores for overall quality and flavor attributes. With respect to the morphology, the use of the additives resulted in better maintenance of the fruit cellular structure. The combination of LA/CC maintained the yellow color (b^*) of the dried papaya during storage at 25°C for 100 days, but the additives did not help preserve the vitamin C content. The variations in color parameters throughout storage were fitted to first-order kinetic models with Q_{10} values in the range from 1 to 2. First-order kinetic models were obtained for the degradation of vitamin C, with Q_{10} values ranging from 3 to 4. In general, papaya pieces treated with LA/CC presented the best results, especially regarding sensory attributes and color stability throughout storage. The application of PME/CC was less effective for color stability during storage, but this enzyme contributed to the maintenance of the fruit texture, avoiding excessive tissue hardening, and also resulted in good sensory acceptance for dried papaya. Therefore, the use of PME deserves to be investigated with others raw materials, calcium salts, and processing conditions.

NOMENCLATURE

a^*	Chromaticity parameters (green [−] to red [+])
a^*_{dim}	Dimensionless parameter a^* (a^* of dried papaya/a^* of fresh papaya)
b^*	Chromaticity parameters (blue [−] to yellow [+])
b^*_{dim}	Dimensionless parameter b^* (b^* of dried papaya/b^* of fresh papaya)
C_o	Concentration of the quality component or parameter at time zero
C_t	Concentration of the quality component or parameter at time t
k_T	Reaction rate constant at temperature T
$k_{T\text{-}10}$	Reaction rate constant at a temperature 10°C lower
L^*	Lightness ($L^* = 0$ for black and $L^* = 100$ for white)
L^*_{dim}	Dimensionless parameter L^* ($L^*$of dried papaya/L^* of fresh papaya)
M_f	Mass at the end of the process
M_i	Initial mass
Q_{10}	Temperature coefficient/quotient
ST_f	Total solids content at the end of the process
ST_i	Initial solids content
T	Temperature
t	Time (day)
$t_{1/2\text{life}}$	Half life time (day)
U_f	Moisture content at the end of the process
U_i	Initial moisture content

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