



Effect of alginate-based coating charged with hydroxyapatite and quercetin on colour, firmness, sugars and volatile compounds of fresh cut papaya during cold storage

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Abstract

Active alginate-based coatings with quercetin glycoside and complexes of hydroxyapatite/quercetin-glycoside were used to study the shelf life of fresh cut papaya stored at 6 °C. Hydroxyapatite was used as a carrier for the release of the bioactive compound. The parameters considered affecting the quality of the fruit during storage were weight loss, color, texture, sugars and volatile compounds. Active coatings with hydroxyapatite and quercetin glycoside proved a higher capacity to slow down the degradation phenomena studied, showing less weight loss, a lower reduction in glucose and fructose, as well as better firmness, than the other samples after 14 days of cold storage. Benzyl isothiocyanate, the characteristic odor compound of papaya fruit, ranged from approximately 10.0 µg/kg in fresh cut fruit to approximately 7.50 µg/kg in samples coated by alginate with hydroxyapatite/quercetin and 3.6 µg/kg in the fresh cut papaya without coating after 14 days of cold storage. The trials also indicated greater effectiveness of alginate coatings alone and with quercetin-glucoside in preserving the color of freshly cut papaya.

Keywords Fresh cut papaya · Alginate coating · Quercetin-glycoside · Volatile compounds

Introduction

Papaya (*Carica papaya* L.) belongs to the Caricaceae family, which includes around 6 genera and 35 species of mainly American origin. It is a succulent herbaceous plant with a single stem that becomes fibrous and woody when mature. The fruit is a berry with deep carpel-like depressions, orange–yellow in color when ripe, fleshy mesocarp with a cavity containing numerous seeds and a shape that can be round, ovoid or pyriform ranging from 250 g to more than 2 kg. World papaya production has increased over the past 50 years from 1 to 10 million tons per year, to reach 13.7 million tons in 2019 (FAO). The main producing countries are Indonesia, Nigeria, India, Brazil and Mexico, the latter also being among the most

important exporters along with Belize and Malaysia, while the United States, Singapore, Canada, the Netherlands and Germany are the main importers. The largest number of commercial papaya orchards are located between 23° N and 23° S latitude, although cultivation has recently expanded to regions up to 32° N and S latitude. At these new latitudes, papayas must be grown in suitable areas at sea level and often in a greenhouse [1, 2]. In Europe, papayas are only produced in Spain and Italy, where in many southern areas such as Sicily, it has found climate-friendly areas [3, 4]. Italian tropical fruit production, characterized by a short supply chain within the Mediterranean Basin, will make it possible to reduce transport times and the treatments applied, bringing to the European market a product appreciated by consumers and with a limited environmental impact [5]. Papaya consumption in Europe is not yet as widespread as in most tropical countries but is rapidly increasing due to the growing demand for healthy, convenient or ready-to-eat foods. [6]. Although papayas are not easy to handle, they fit well within the development of convenience fruit fresh-cut products that are expected to become more prominent in the next years creating great marketing opportunities [6]. The main papaya cultivars on the EU

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market are 'Solo', 'Golden', 'Sunrise' and 'Formosa' [7]. The *Formosa* variety is often sold as well, due to its longer shelf life and good flavor, and is, therefore, also increasingly used by food manufacturers. Papaya is a climacteric fruit with a limited post-harvest shelf life (7–14 days), depending on the state of ripeness at harvest [8]. Fruit ripening varies according to cultivar and generally occurs within a range of 7–16 days from color-break. Fruits should be harvested when the color of the skin changes from dark green to light green and a yellow (or orange depending on the variety) stripe starts to develop from the base to the top: if harvested before this stage they will never reach full maturity, maintaining a total soluble solids value that is often less than 10%, and will have a bland taste and little aroma; if harvested after this stage they will be more susceptible to damage and bruising. Freshly cut fruit deteriorates more rapidly than whole fruit due to the different processing steps used [9]. These alterations can be reduced by applying different preservation techniques, such as modified atmospheres and edible coating. The edible coatings are an effective way to extend the shelf life of sliced papaya by forming a thin layer on the surface of the fruit that can be consumed together with it. The coating provides a partial barrier to moisture, oxygen and carbon dioxide, it is environmentally friendly, affordable and safe and therefore the food industry shows increasingly interested in its use to preserve the quality and extend the storage period of fresh-cut papaya fruit. Alginate is a natural polysaccharide suitable as a coating material, mainly derived from brown algae [10]. To increase the shelf life of sliced fruit, antioxidants can be added to the edible coatings formed from alginate, such as quercetin glucoside, phenolic compound with high antioxidant activity. Hydroxyapatite (HA), based on calcium phosphate, is a biomaterial present in human tissue, especially in bone and cartilaginous tissues. Thanks to the composition and structure of HA nanoparticles [11, 12], HA can chemically interact with different organic molecules and thus could represent a potential carrier for the delivery of bioactive compounds in the development of edible coating systems [13]. The purpose of this article was to study the effects of alginate-based edible coatings activated with quercetin glucoside and with hydroxyapatite/quercetin glucoside complexes on the shelf life of freshly cut papaya. For this purpose, the evolution of weight loss, sugars, color and volatile compounds in sliced papaya was studied during a storage period of 14 days at 6 °C.

Materials and methods

Plant material

The research was carried out in a commercial orchard in Palermo, Italy (33S 0,333,746 m.E, 4,217,131.00 m.N) on *Formosa* cultivar of hermaphrodite papaya plants. Trees were

subjected to routine orchard cultivation. The fruits were hand-picked at stage 4, measuring the color of the skin fruit as maturity index [8]. Papayas were selected according to visual color perception, elongated shape, good physical condition, and lack of any signs of anthracnose or ring spot virus. Twenty fruits were subjected to physico-chemical analysis and subsequent storage tests.

Edible coating

A colloidal dispersion of biomimetic hydroxyapatite (HA) was purchased from the Research and Development Department (Chemical Center Srl, Italy). Quercetin glucoside (Qu) was acquired by Oxford® Vitality Company (Bicester, UK). The peeled fruits were cut into cubes of about 3 cm, washed with a solution (5% v/v) of sodium hypochlorite for about 1 min and then dried with paper. Three sodium alginate solutions were prepared as follow: sodium alginate solution, sodium alginate with the addition of 500 ppm of quercetin glycosides (Qu), sodium alginate with hydroxyapatite/quercetin complexes (500 ppm) (HA/Qu) [13]. Coating was performed according to the layer-by-layer (LBL) technique. by immersing the papaya cubes in sodium alginate solutions and then in calcium chloride solution (1% w/v), both for about 2 min. The coated samples were dried at room temperature for approximately 5 min. Coated and uncoated samples were packed in polyethylene terephthalate boxes (13.5×12.5×5 cm) provided with a lid. The four samples analyzed during the shelf life had the following coding:

- fresh cut papaya without coating (C);
- fresh cut papaya covered by alginate coating (Al);
- fresh cut papaya covered by alginate coating (Al) enriched with (Qu) quercetin (AlQu);
- fresh cut papaya covered in alginate coating (Al) enriched with (Qu) quercetin and (HA) hydroxyapatite (AlQuHA).

12 packs of about 100 g were prepared for each treatment and stored at 6 °C for 14 days. Measurements of the different parameters were performed on three replicates at different intervals (when not otherwise indicated).

Physicochemical analyses

Fruit weight was determined by a digital scale (Gibertini, Italia). The weight loss of papaya samples was determined according to the following equation:

$$\text{Weight loss (\%)} = \frac{w_i - w_f}{w_i} * 100$$

where w_i is the weight of the sample at the initial storage time (0 days) and w_t is the weight of the sample at the day of analysis during the 14-day storage period [14].

Color was evaluated on basis of CIE $L^*a^*b^*$ color system: (L^*) lightness; (a^*) redness/greenness; (b^*) yellowness/blueness; (C^*) Chroma; (h°) Hue angle, measured using a digital colorimeter (CR-400 Chroma Meter, Minolta, Japan). Calibration of the colorimeter was performed against a white tile background (Illuminants C: $Y \frac{1}{4} 89.53$, $x \frac{1}{4} 0.3247$, $y \frac{1}{4} 0.3198$) prior to each measurement [15]. Total soluble solids content (TSSC— $^\circ\text{Brix}$) was measured by a digital refractometer (Atago, Tokyo, Japan) and expressed as $^\circ\text{Brix}$, and titratable acidity (TA— g L^{-1}) were measured using a pH meter-titrator (Titromatic 1S, Crison, Barcelona, Spain) and expressed as grams of citric acid per liters of crude loquat juice ($\text{g citric acid L}^{-1}$) and was determined by titration to an end point of pH 8.2 using 5 mL of juice diluted with 10 mL distilled water.

Sugars

Glucose and fructose were determined by HPLC system using an Agilent 1100 chromatograph with a refractive index detector (Agilent, Santa Clara, USA) equipped with a Knauer column (Eurokat, 300×8 mm, $10 \mu\text{m}$). The mobile phase was a water solution with a flow rate of 1 mL/min and a column temperature of $80 \text{ }^\circ\text{C}$. The results were expressed as mg glucose g^{-1} fresh papaya.

Firmness evaluation

Firmness of fresh-cut papaya samples was evaluated by Compression tests using a Texture Analyzer (Ametek Lloyd Instruments LRX plus, UK) provided with a specific software (Nexygen batch 4.1). Compression tests were carried out by a cylindrical stainless-steel probe with 1 cm diameter. The crosshead speed was 60 mm min^{-1} with a load cell of 50 N . Firmness (N) was calculated as the average of five compression tests applied on cut papaya for each treatment and each storage time.

Volatile compounds

Volatile compounds (VOCs) were isolated by headspace solid-phase microextraction (HS-SPME, $50/30 \mu\text{m}$ DVB/Car/PDMS fiber—Supelco Inc., Bellefonte, PA) and analyzed by GC/FID-MS. Before analysis, each papaya cubes sample was crushed in a mortar, 5 g of homogenate transferred into a 35 mL vial, added with 5 mL of H_2O , 0.1 ascorbic acid, 1 g of NaCl , to increase the extraction rate of VOCs, $15 \mu\text{l}$ of 1-heptanol (35 mg L^{-1} in 10% ethanol) as internal standard,

and closed with a cap with a Teflon-lined silicone rubber septum (Supelco Inc., Bellefonte, PA). Before the first extraction, the fiber was conditioned in the GC injector port at $300 \text{ }^\circ\text{C}$ for 1 h , according to the manufacturer's recommendation. Extraction temperature of the headspace was $40 \text{ }^\circ\text{C}$ for 30 min . The samples were mildly vortexed during extraction using a magnetic stirrer. Fiber exposition was prolonged for 30 min at $40 \text{ }^\circ\text{C}$. Thermal desorption in splitless mode was performed in the injector at $250 \text{ }^\circ\text{C}$ for 2 min into a Finnegan Trace MS for GC/MS (Agilent 6890 Series GC system, Agilent 5973 Net Work Mass Selective Detector; Milan, Italy) equipped with a DB-WAX capillary column (Agilent Technologies; 30 m 0.250 mm i.d. film thickness $0.25 \mu\text{m}$). The GC-MS system and the chromatographic conditions used for the analysis have been described in more detail elsewhere [16]. Individual peaks were identified as previously described [17, 18] and the concentration ($\mu\text{g kg}^{-1}$ pulp) of volatile compounds was determined as 1-heptanol equivalents.

Statistical analysis

The experiments were performed in triplicate and the results were reported as mean and standard deviation and subjected to analysis of variance (ANOVA). Principal components analysis (PCA) was realized to reduce the multidimensionality of the dataset generating new principal components that account for most of the total variation. The significance of differences ($p < 0.05$) among samples was determined by Student's t test using Analysis Lab software. Anova F-Test was used to determine the variability of volatile compounds content among papaya samples.

Results and discussion

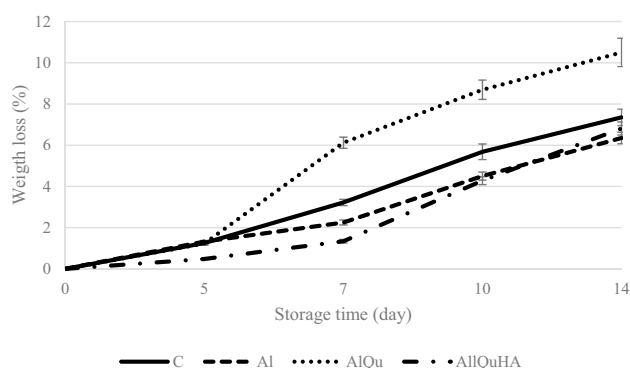
The main chemical-physical characteristics of the fresh-cut papaya fruits grown in Sicily and used in the present research are shown in Table 1.

Weight loss

Weight loss in fresh cut fruit is caused by the loss of moisture, through vapour diffusion, driven by the difference in water vapour pressure between the product and the surrounding air. Up to day 3 of cold storage, all the samples had the same weight loss level (around 1.3%) except AIQuHA sample, whose weight loss level was only about half that of the others (Fig. 1). From the 3rd day onwards, the weight loss in all samples increased gradually, with significantly greater drops in sample C than in samples AI and AIQuHA. At the end of the 14-day storage period, AI and AIQuHA samples showed the lowest weight loss, highlighting two important

Table 1 Quality of *Formosa* raw papaya fruit

Parameters	Fresh fruit
Weight (g)	658.12 ± 51.68
Longitudinal diameter (mm)	144.50 ± 9.19
Transversal diameter (mm)	78.00 ± 4.24
Skin color	
L*	55.04 ± 8.67
a*	0.70 ± 8.69
b*	30.31 ± 6.89
Firmness (kg cm ⁻¹)	11.00 ± 1.41
Total soluble solids (°Brix)	10.05 ± 1.34
Tritatable acidity (g l ⁻¹)	0.10 ± 0.001
Flesh color	
L*	56.90 ± 3.50
a*	17.48 ± 3.86
b*	26.16 ± 1.18

**Fig. 1** Weight loss (%) of fresh cut *Formosa* papaya during cold storage at 6 °C with different coatings

synergistic effects: the alginate-based coating helped prevent juice leakage and the hydroxyapatite structure gave the coating a strong water retention capacity. In contrast, significant weight loss was observed in the AlQu sample, due to the oxidation of quercetin, an antioxidant subject to both chemical and enzymatic oxidation. The oxidation products of quercetin (mainly 3,4-dihydroxybenzoic acid (approx. 53%) and 2,3,4-trihydroxybenzoic acid (approx. 33%)), as reported in the literature [19], were able to favour the degradation of alginate and thus increase water loss. In the AlQuHA samples, quercetin glucoside, being adsorbed into the HA structure, was protected from oxidative phenomena and, therefore, showed less weight loss during storage.

Color changes

Some differences in colour among the fruits were already present at the beginning of the tests, after only coating the

edible films. This was due to the colour of the film-forming solution, with the sodium alginate solution having a pale-yellow colour, like quercetin glucoside. Hydroxyapatite crystals, instead, had white colour that partially neutralized the yellowness of AlQu, bringing the colour of AlQuHA samples closer to the colour of the control. During the storage period, the lightness of control C and AlQuHA samples decreased, while the lightness in Al and AlQu samples remained almost constant (Fig. 2a). The hue angle values increased in all samples except AlQu, which had a more constant trend. In general, hue differences recorded at time 0 tended to decrease after 14 days of storage, with values ranging between 30 and 35° (Fig. 2b). The trend in chroma values was like lightness: at the beginning of storage, the control and AlQuHA samples had higher chroma values compared to Al samples and AlQu samples. During the storage period, the chroma value of C and AlQuHA samples decreased, while in Al samples and AlQu samples chroma value remained roughly the same. The reason for the increase in hue angle values could also explain the decrease in chroma values: both were due to oxidative phenomena and reactions with other compounds in papaya pigments (carotene, lycopene and anthocyanins) during storage [20, 21]. Finally, changes in colour were assessed by (ΔE) a synthetic index, which measures the overall change in colour compared to the fresh sample. On the last day of storage, the control samples and AlQuHA samples showed a strong increase in ΔE values, while the Al samples and AlQu samples had fewer changes. Therefore, the results indicated greater effectiveness of alginate coatings alone and Qu loaded coatings in preserving the colour of freshly cut papaya. The color changes in AlQuHa samples did not appear to be due to oxidative phenomena and probably resulted from pigments bonds with other compounds and with HA.

Firmness evaluation

The firmness values of all papaya samples decreased during the cold storage. The decrease in hardness in papaya can be attributed to enzymatic activity in cell wall degradation [22]. The trend of this important fruit texture parameter of the samples showed the positive effect of the AlQuHA coating in slowing down the loss of firmness during shelf life. The lower loss of firmness in the AlQuHA coated papaya could be due to a reduction of enzyme activity in the fruit. After 14.

days storage, the AlQuHA sample showed a loss of hardness of approximately 40%, compared to 83% and 71% shown in the control and AlQu samples, respectively (Table 2).

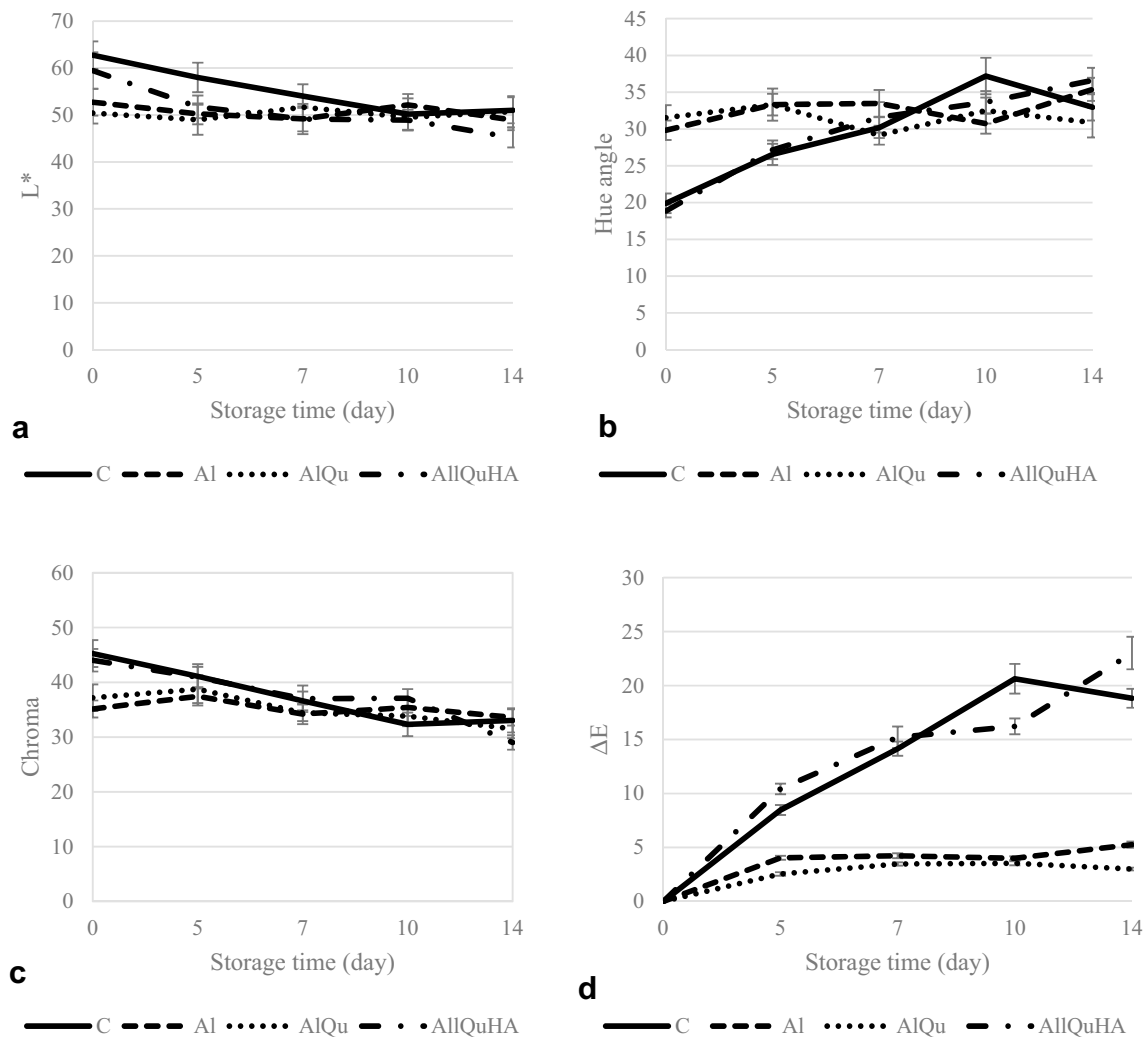


Fig. 2 Evolution of color parameters: **a** Lightness; **b** Hue angle; **c** Chroma; **d** Overall color changes (ΔE), on fresh cut Formosa papaya during cold storage at 6 °C with different coatings

Sugars

The sweet taste is an important parameter of papaya quality due to the content of soluble sugars [23], which also have a vital influence in improving stress tolerance, regulating the osmotic pressure and removing ROS [24]. Although the sugar changes in papaya fruits after harvest are not yet fully established, the sweet taste is a possible indication of quality [25]. The initial glucose and fructose content in the fresh fruit was 32.8 g kg⁻¹ and 41.9 g kg⁻¹, close to the values reached by Soto et al. [26] for *Carica* papaya, ranging from 36.0 to 41.3 g kg⁻¹ for glucose and 35.2 to 39.9 g kg⁻¹ for fructose [26]. According to the literature [27, 28] sucrose content was negligible. At time 0 the value of 100% was considered, to make the variations more understandable (Fig. 3). Up the 7 days of storage, the glucose content in control and AlQu samples remained almost constant, while

in AlQuHA sample and Al samples was lower. At 14 days of storage, the glucose content in the coated papaya samples decreased slightly to between 79 and 83% of the fresh fruit, while the glucose content in the control samples decreased dramatically to 44%. A similar trend was observed for fructose content, too. However, on the 7th day, fructose content in control samples was the lowest, while changes in glucose content in the samples with different coatings were about the same. The degradation of fructose in the control sample occurred more strongly, while the coatings protected the papaya and preserved fructose better. At the end of storage time, the fructose content in C, Al, AlQu, and AlQuHA samples were 67%, 81%, 71%, and 83%, respectively, compared to the initial content. The decreases in contents of sugars in papaya samples could be linked to reduced metabolic activity in the fruit during storage and to the active microbial growth [29]. Various microorganisms, such as LAB, yeasts

Table 2 Volatile organic compounds ($\mu\text{g kg}^{-1}$ [dry fruit]) on fresh cut *Formosa* papaya and after 14 days of cold storage with different coatings

	Odor thresh- old (ppb)	Odor quality	Reference	Fresh cut papaya	C	AI	AIQu	AIQuHA	Anova, <i>F</i> test sign
Butanoic acid	240	Cheesy	[37]	39.20 ± 1.55 d	184.10 ± 29.85 ab	94.98 ± 15.13 cd	130.21 ± 19.32 bc	200.72 ± 2.80 a	***
Pentanoic acid	70	Sweet	[38]	2.70 ± 1.26	3.20 ± 0.22	3.56 ± 0.48	3.12 ± 0.12	2.91 ± 1.25	ns
Hexanoic acid	420	Fatty, cheese	Farina et al. 2015 [39]	16.41 ± 5.28	8.88 ± 1.17	13.68 ± 1.38	17.30 ± 10.04	8.34 ± 4.01	ns
Heptanoic acid	N/A	Waxy, cheese, fruity	www.thegoodseecompany.com	5.74 ± 2.62	2.41 ± 0.09	2.98 ± 0.26	2.67 ± 0.59	3.02 ± 0.19	ns
Octanoic acid	500	Fatty, cheese	Farina et al. 2015 [39]	13.52 ± 8.22	3.68 ± 0.34	5.87 ± 0.16	4.45 ± 1.30	3.89 ± 0.47	ns
Nonanoic acid	3000	Green, fatty	[38]	9.29 ± 2.36 a	1.89 ± 0.26 b	4.03 ± 0.10 ab	1.81 ± 0.32 b	2.13 ± 0.71 b	*
Decanoic acid	1000	Rancid, fat	Farina et al. 2015 [39]	19.40 ± 6.56 a	n.d. b	n.d. b	n.d. b	n.d. b	**
Dodecanoic acid	N/A	Fatty, waxy	www.thegoodseecompany.com	24.07 ± 16.49	5.06 ± 0.13	9.12 ± 1.99	7.06 ± 3.27	17.13 ± 4.15	ns
Acids									
1-Octanal	0.70	Honey, green, fruity	[38]	130.32 ± 41.80 b	209.22 ± 32.07 ab	134.22 ± 14.56 b	166.62 ± 14.65 ab	238.13 ± 5.23 a	*
Nonanal	1	Fatty, citrus, green, floral	[40]	13.13 ± 6.92	21.04 ± 0.51	7.17 ± 0.41	10.45 ± 6.54	7.32 ± 0.16	ns
Decanal	6	Fruity, citrusy, orange	[41]	55.54 ± 3.69 a	53.43 ± 18.55 ab	17.65 ± 5.22 b	47.27 ± 3.45 ab	45.40 ± 10.98 ab	*
Aldehydes									
Benzaldehyde	320	Almond, burnt, sugar	[42] [42]	22.60 ± 10.13 a	8.22 ± 0.77 ab	5.64 ± 2.03 ab	7.19 ± 1.51 ab	20.91 ± 7.52 ab	*
Benzyl isothiocy- anate	0.70	Watercress, papaya	[38] [38]	91.27 ± 6.91 a	82.69 ± 18.30 a	30.46 ± 6.84 b	64.90 ± 8.48 ab	73.62 ± 18.65 ab	*
Benzyl alcohol	2546.21	Floral odour	Pino [33] [36]	359.67 ± 17.32 a	63.85 ± 11.62 b	91.50 ± 28.15 b	195.84 ± 10.98 ab	174.09 ± 104.57 ab	**
Benzenoids									
Ethyl dodecanoate	640	Sweet waxy	Sha et al. 2016 [43]	10,010.09 ± 2,636.10 a	1,258.69 ± 130.01 c	8,134.00 ± 348.91 ab	10,961.08 ± 1,175.49 a	7,849.65 ± 945.73 ab	**
Methyl dodecanoate	N/A	Waxy	www.thegoodseecompany.com	22.91 ± 12.80 b	83.98 ± 12.06 a	28.11 ± 2.32 b	31.01 ± 4.04 b	41.03 ± 0.71 b	**
Methyl tetradecanoate	N/A	Waxy	www.thegoodseecompany.com	41.97 ± 31.39 c	262.61 ± 15.37 a	167.58 ± 19.80 b	158.78 ± 28.92 b	206.02 ± 1.07 ab	***
Methyl 11-tetradecenoate	N/A	Sweet waxy	www.thegoodseecompany.com	11.49 ± 0.38 b	26.05 ± 1.16 a	9.70 ± 0.11 b	9.86 ± 4.18 b	14.72 ± 0.02 b	***
Ethyl tetradecanoate	4000.00	Sweet waxy	www.thegoodseecompany.com	n.d. d	21.24 ± 2.13 b	23.13 ± 1.74 b	7.37 ± 0.98 cd	38.47 ± 2.42 a	***

Table 2 (continued)

	Odor thresh- old (ppb)	Odor quality	Reference	Fresh cut papaya	C	AI	AIQu	AIQuHA	Anova, <i>F</i> test sign
Methyl hexade- canoate	N/A	Waxy	www.thegoodscenutrition.com	8.42 ± 1.88 d	78.66 ± 4.15 a	40.96 ± 5.66 bc	28.09 ± 10.52 cd	63.96 ± 4.43 ab	***
Methyl palmitoleate	N/A	Waxy	www.thegoodscenutrition.com	104.67 ± 20.83 c	326.98 ± 13.39 a	246.45 ± 29.81 ab	199.69 ± 49.78 bc	265.52 ± 3.55 ab	**
Methyl 7-octade- canoate	N/A			4.38 ± 0.48 c	18.06 ± 1.58 a	13.01 ± 1.62 ab	4.95 ± 1.92 c	7.54 ± 0.75 bc	***
Esters									
6-methyl-5-hepten- 2-one	50.00	Citrus	[38] [38]	193.83 ± 67.00 c	836.51 ± 3.09 a	540.69 ± 61.30 b	450.68 ± 89.20 bc	663.85 ± 1.36 ab	**
γ-butyrolactone	N/A	Creamy	www.thegoodscenutrition.com	35.02 ± 17.31	22.53 ± 8.95	19.02 ± 4.07	34.35 ± 7.99	21.90 ± 6.47	ns
				16.50 ± 2.97	18.75 ± 9.31	10.49 ± 0.04	11.18 ± 1.76	12.41 ± 1.58	ns

Data are reported as mean ± standard deviation

The concentration unit of measurement is µg equivalents of 1-heptanol kg⁻¹

Anova *F* test significance: * = 0.01 ≤ *p* value < 0.05, ** = 0.001 ≤ *p* value < 0.01, *** = *p* value < 0.001

and moulds, can grow in fruit and cause spoilage [30]. The greater decrease in fructose compared to glucose observed during storage is explained by the preference of microorganisms, in particular LAB, to use glucose as the primary substrate for the fermentation pathway. Moreover, the fructose content in control samples was not drastically reduced like glucose content because not all microorganisms can utilize fructose as substrate. Considering the changes in both glucose and fructose content during the storage period, the alginate-based coatings without active compound and coatings loaded with AIQuHA showed higher effectiveness in preserving the sugar content of fresh-cut papaya.

Volatile compounds

In fresh papaya fruit, 24 volatile compounds (VOCs) were identified: 8 acids, 8 esters, 3 aldehydes, 3 benzenoids and 2 other compounds (Table 3). The compounds most present were benzenoids, followed by esters, acids and finally aldehydes.

Among the benzenoids, benzyl isothiocyanate (BITC) had significantly higher concentrations than all the identified compounds: its concentrations ranged from about 10.0 µg kg⁻¹ in the fresh fruit to about 3.6 µg kg⁻¹ after 14 days, while at some time it was recorded values of 10.9 µg kg⁻¹ in the AIQu sample and 7.50 µg kg⁻¹ in AIQuHA. Benzyl isothiocyanate is the characteristic odorous substance of papaya with an odour like watercress, spicy horseradish, capers and has anticancer properties [31–33]. The precursors and enzymes linked to the formation of BITC were mainly found in the seeds of the fruit and the concentration of this compound according to some authors decreased during the ripening process [34], in contrast to previous studies, that showed that BITC did not decrease during ripening, how confirmed in a subsequent study by [35], which measured the levels of benzylglucosinolates and BITC in seeds, fruit and peel during ripening. The authors also concluded that ethylene does not influence the accumulation of BITC, which is important for understanding the biogenesis of certain volatile compounds. Benzaldehyde (smell like a crushed almonds) in fresh fruit was about 360 µg kg⁻¹, as already reported elsewhere in the cultivar of papaya fruit *Red Maradol*, [36] and decreased at 14 days by more than 80% in the control C sample and less than 50% in AIQuHA. Benzyl alcohol (floral odour) in the fresh fruit had a content of about 62 µg kg⁻¹, previous research [33] reported that benzyl alcohol reached a maximum when 100% papaya peel turned into yellow color. Its content increased in all samples during storage, with the highest value in AIQuHA (108 µg kg⁻¹). Esters increased significantly in all samples during cold storage, from 194 µg kg⁻¹ in C sample to 664 µg kg⁻¹ in AIQuHA. Methyl tetradecanoate and methyl palmitoleate (wax odour) showed the

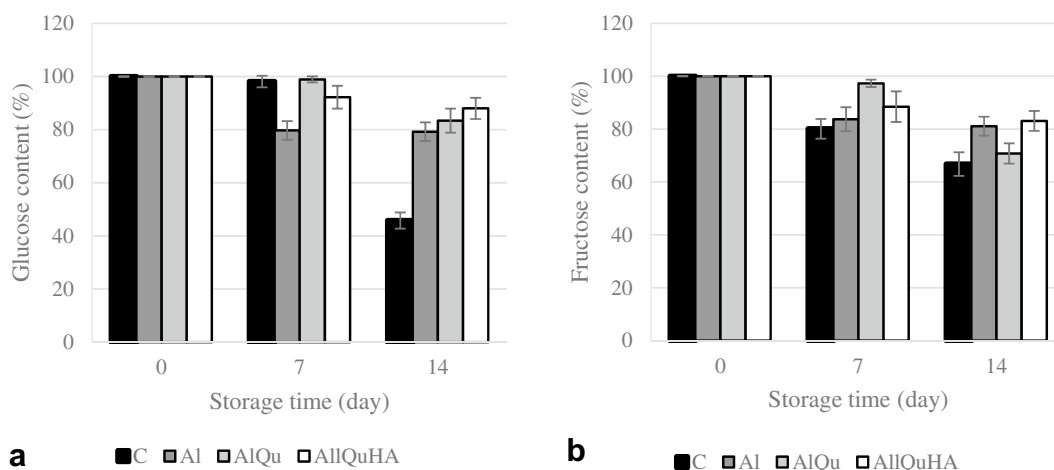


Fig. 3 Changes in sugar content during the storage period: **a** Glucose content; **b** Fructose on fresh cut *Formosa* papaya during cold storage at 6 °C with different coatings. At time 0 the value of 100% was considered, to make the variations more understandable

greatest increases, the former being present in fresh fruit at a concentration of 42 $\mu\text{g kg}^{-1}$, rising to 263 $\mu\text{g kg}^{-1}$ after 14 days. Methyl palmitoleate followed the same trend, with the highest contents in the control and in fruits treated with AlQuHA. Among the acid compounds, there were significant variations for butanoic acid (cheese smell), nonanoic acid (green and fatty smell) and decanoic acid (rancid and fatty smell). Butanoic acid compared to the fresh sample (39 $\mu\text{g kg}^{-1}$) increased significantly after 14 g in all samples, with the highest value in the tests treated with AlQuHA (201 $\mu\text{g kg}^{-1}$). Nonanoic acid decreased significantly in the treated samples compared to the fresh, while decanoic acid was only present in the fresh fruit (19 $\mu\text{g kg}^{-1}$). Aldehydes are olfactory active compounds with low odour threshold values. In papaya fruits, 1-octanal, nonanal and decanal were identified, their content after 14 days decreased or remained constant. Many of these have previously been described as odor-active in papaya, including benzyl isothiocyanate,

benzyl alcohol, nonanal, decanal, butanoic acid, octanoic acid and ethyl dodecanoate [36, 37].

Principal component analysis

The first two principal components explained 44.32% and 33.58% of the total variance, respectively (Fig. 4). PCA showed the potential to discriminate different samples at 14 days of storage in three different quadrants: the second showed AlQuHA and Al samples, the third AlQu, the fourth C sample. The sample of papaya control at time 0 (C) was characterised by the proximity of octanal, nonanal and decanal, aldehydes with a characteristic fruity smell, and γ -butyrolactone, a substance found in sweet wines, with a typical creamy note. It was apparent from the PCA biplot a positive correlation among benzyl isothiocyanate, the papaya's characteristic odorous substance, and Al sample, whilst AlQuHA was close to benzyl alcohol, with positive floral notes, dodecanoic acid with fatty notes and Hue angle. Finally AlQu was correlated with hexanoic acid.

Table 3 Firmness values in cut *Formosa* papaya with different coatings during cold storage

Time (days)	Firmness [N]			
	C	Al	AlQUE	AlQUEHA
0	8.57 ± 0.03 ^{aA}	9.63 ± 0.01 ^{bA}	9.02 ± 0.02 ^{cA}	9.08 ± 0.04 ^{cA}
3	5.02 ± 0.02 ^{aB}	5.34 ± 0.01 ^{bB}	5.41 ± 0.01 ^{cB}	7.96 ± 0.01 ^{dB}
7	3.70 ± 0.02 ^{aC}	3.49 ± 0.02 ^{bC}	3.52 ± 0.02 ^{bC}	6.62 ± 0.02 ^{cC}
10	2.11 ± 0.01 ^{aD}	3.13 ± 0.01 ^{bD}	3.15 ± 0.01 ^{bD}	5.74 ± 0.02 ^{cD}
14	1.45 ± 0.02 ^{aE}	2.33 ± 0.01 ^{bE}	2.48 ± 0.01 ^{cE}	5.06 ± 0.04 ^{dE}

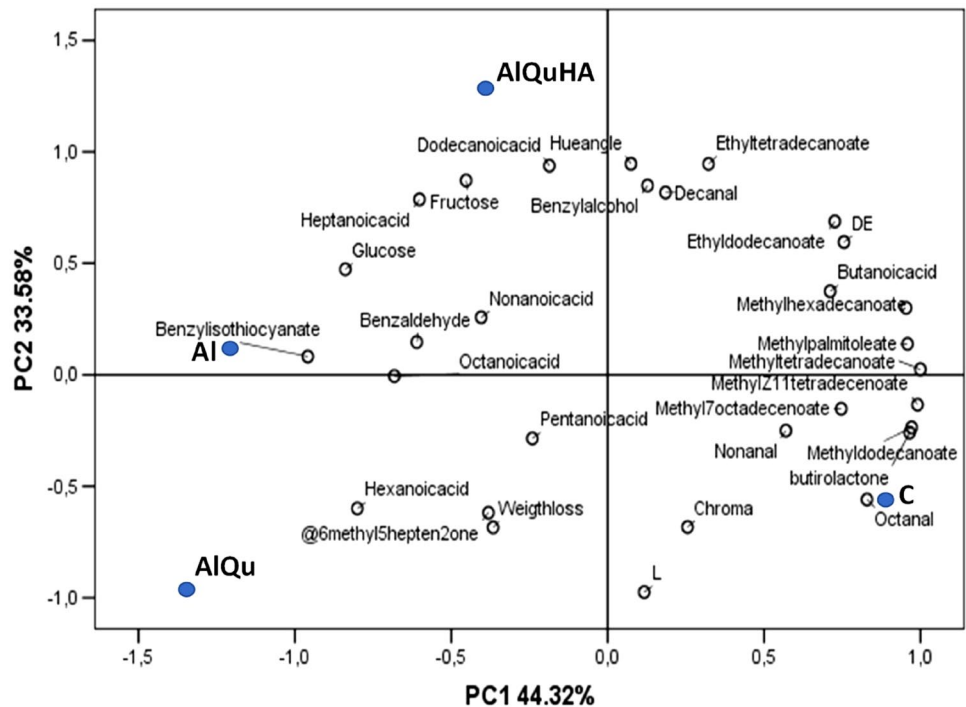
Different letters (a, b, c, d) reveal significant differences ($p < 0.05$) among the samples for each storage time,

different letters (A,B,C,...) reveal significant differences ($p < 0.05$) among treatments during the storage time

Conclusion

The ability of alginate-based coatings, loaded with hydroxyapatite/quercetin complexes, to prolong the shelf-life of fresh-cut papaya stored at 6 °C, was evaluated. Analysis of volatile compounds pointed out benzyl isothiocyanate the most abundant volatile compound characterizing the aroma of papaya fresh fruits. Its concentration was strongly reduced at the end of storage in all papaya samples even if the higher amount was measured in coated papaya with respect to the control. Moreover, alginate coatings charged with free and

Fig. 4 Principal component analysis (PCA) of sugars, color parameters and volatile compounds in fresh cut *Formosa* papaya and after 14 days of cold storage at 6 °C with different coatings



complexed quercetin showed the same efficacy to preserve the glucose content of fresh-cut papaya, while the highest firmness values at the end of storage were registered in samples covered with alginate-based coating charged with complexed quercetin glucosides.

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Declarations

Conflict of interest The authors declare that there is no conflict of interest.

Compliance with ethics requirements The research do not include any human subjects and animal experiments.

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