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Compositional and functional dynamics of dried papaya as affected by storage time and packaging material

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ABSTRACT

Papaya has been identified as a valuable source of nutrients and antioxidants, which are beneficial for human health. To preserve the nutritional properties after drying, appropriate storage specifications should be considered. This study aimed to investigate the quality and stability of air-dried papaya in terms of quality dynamics and behavior of bio-active compounds during storage for up to 9 months in two packaging materials: aluminum laminated polyethylene and polyamide/polyethylene. Samples with moisture content (MC) of 0.1328 g g^{-1} and water activity (a_w) of 0.5 were stored at 30 °C and relative humidity (RH) of 40–50%. The MC, a_w, degree of browning (DB) and 5-hydroxymethylfurfural (HMF) content were found to notably increase as storage progressed. On the contrary, there was a significant decrease in antioxidant capacity (DPPH, FRAP and ABTS), total phenolic (TP) and ascorbic acid (AA) contents. Packaging in aluminum laminated polyethylene under ambient conditions was found to better preserve bio-active compounds and retard increases in MC, a_w and DB, when compared to polyamide/polyethylene.

1. Introduction

Food security is a critical issue in many countries around the world, while globalization has placed a strain on leading agricultural countries to provide the world's food supply. Thus, innovative solutions that are economically and socio-culturally appropriate must be devised and implemented to ensure food security, not only with respect to food quantity, but also increased attention must be given to food quality attributes, particularly nutritional content and safety. Post-harvest losses not only include physical losses in quantity, but also highly significant degradation of essential bio-active compounds and overall quality attributes. Therefore, minimizing post-harvest losses of agricultural perishables through the entire value chain, from farm to fork, is one of the key pathways of alleviating poverty, increasing food security and improving nutrition.

Papaya is an important fruit crop, which serves as a good source of vitamins A and C as well as calcium, potassium and magnesium. Vitamin C (ascorbic acid) in papaya ranges between 35.4 and 187 mg per 100 g fresh weight, which is higher than that observed in other tropical fruits such as passion fruit, banana and pineapple (Bautisa-Baños, Sivakumar, Bello-Pérez, Villanueva-Arce, Hernández-López, 2013). Also, phenolic compounds such as ferulic acid, caffeic acid and rutin have been detected in papaya fruits (Rivera-Pastrana, Yahia, & González-Aguilar, 2010). Lately, many clinical studies have exemplified that these beneficial bio-active compounds exhibit a protective effect against cancer as well as neurological and cardiovascular diseases. These effects are due to certain biochemical properties, such as free radical scavengers, hydrogen donors, singlet oxygen quenchers and metal ion chelators (Ikram et al., 2009).

Considerable post-harvest losses occur in fresh papaya due to its rapid senescence, which causes high perishability. Consequently, postharvest processing is required to extend shelf life and preserve quality. Convective air drying of papaya is the most common preservation method of fruits that allows for greater flexibility in the availability and marketability of products, regardless of high production volume. By convention, dried papaya can be consumed directly or used as an ingredient in snacks, chocolates, breakfast cereals and other foodstuffs. Nowadays, there is even an increasing demand for natural products, including high quality dried fruits in which nutritional properties have minimal

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alteration. A study by Udomkun, Nagle, et al. (2015) already presented optimal drying parameters for conservation of bioactive compounds during drying of papaya.

In food industries, packaging materials and storage conditions are considered as the last step in product development to extend the conservation of dried fruits. During storage and distribution, dried fruits can experience a wide range of environmental conditions, such as high temperature and humidity as well as exposure to light and oxygen, which can trigger various physicochemical changes. These factors have been reported to facilitate browning reactions, causing undesirable color changes. Additionally, chemical reactions can degrade antioxidants such as polyphenols, carotenoids and vitamin C, which is a particular concern for consumers as it decreases the nutritional value (Hymavathi & Khader, 2005). Lavelli and Vantaggi (2009) found that dried apples were relatively stable during storage and had optimal conservation of antioxidants as long as the proper packaging materials were used. Pua et al. (2008) suggested that aluminum laminated polyethylene (ALP) pouches with storage conditions of 28 °C and relative humidity less than 75% were better suited for preserving qualities of jackfruit powder. Also, Dak, Sagar, and Jha (2014) agreed that ALP is more effective to retain anthocyanins and phenolic compounds in dried pomegranate arils than packaging without aluminum coating. Overall, it should be noted that properties of the packaging materials play an important role for shelf life stability of dried fruits.

Ultimately, the challenge in modern food sciences is not only to minimize the chemical degradation reactions, but also to maximize the conservation of beneficial nutrients during storage. The previous study by Udomkun, Nagle, et al. (2015) mainly focused on the effect of drying parameters on the qualities of dried papaya products. However, a comprehensive investigation about the effects of storage conditions on the quality of dried papaya was not presented. Therefore, the objectives of this study were to examine the effects of two packaging materials, namely aluminum laminated polyethylene and polyamide/polyethylene, on browning occurrence and bio-active compounds properties, particularly antioxidants and ascorbic acid contents, in papaya samples during long-term storage.

2. Materials and methods

2.1. Raw materials

Papayas (*Carica papaya* L. cv. Pluk Mai Lie) harvested from a commercial orchard in Nakhon Nayok province, Thailand, were purchased from a local import company. Fruits of uniform shape, weight (1.0 ± 0.2 kg fruit^{-1}) and ripening stage (three quarters ripeness indicated by 70 ± 10% of skin yellowness) were selected. The initial moisture content (83.5 ± 2 g 100 g^{-1}), soluble solids content (9.8 ± 0.4 °Brix), titratable acidity (0.15 ± 0.02 g citric acid 100 g^{-1}) and pH (5.3 ± 0.2) were measured. Before preparation for drying, fruits were stored under refrigeration at a temperature of 10 ± 1 °C and relative humidity (RH) of 20–35%.

2.2. Sample preparation

2.2.1. Osmotic pretreatment

Papaya samples were treated osmotically according to the procedure described in a previous study (Udomkun, Mahayothee, Nagle, & Müller, 2014). Papayas were hand-peeled and cut into dimensions of 20 × 30 × 20 mm using a specially-designed stainless steel cutter. The samples were rinsed with fresh water and then soaked in 2.5% (w v^{-1}) calcium lactate ($Ca{\cdot}C_6H_{10}O_6$) solution. The samples were allowed to soak for 1 h at controlled temperature (20 ± 2 °C), then blanched at 60 ± 2 °C for 1 min. Subsequently, they were immersed in a hypertonic solution of 30 °Brix at a starting temperature of 60 ± 2 °C and then allowed to stand at room temperature for 6 h. The solution was prepared by dissolving 99.9% refined sucrose in water to obtain the required osmotic concentration and then pH was adjusted to 4.0 using citric acid. The weight ratio of osmotic solution to fruit samples was 1:1. After removal from the solution, the samples were rinsed with water, drained and blotted with absorbent paper to remove the surface water before drying.

2.2.2. Convective drying

After pretreatment, papaya samples were placed on a round 24 cm diameter perforated dryer tray. Convective drying was conducted using the through-flow chamber of a high-precision hot air laboratory dryer (Institute of Agricultural Engineering, Tropics and Subtropics Group, Universität Hohenheim, Germany). A description of the experimental dryer has been given by Argyropoulos, Heindl, and Müller (2011). The drying experiments were carried out according to optimal conditions described in previous studies (Udomkun, Nagle, et al., 2015; Udomkun, Argyropoulos, et al., 2015). Samples were dried at a temperature of 70 °C, constant specific humidity of 10 g kg^{-1} dry air and air velocity of 0.2 m s^{-1} until moisture content of 13.5 ± 0.05 g per 100 g.

2.3. Packaging and storage

Two commercially-available packaging materials were used in this study, namely 15 × 18 cm pouches made from aluminum polyethylene (ALP) and polyamide/polyethylene (PA/PE) barrier films. The ALP laminate consisted of 15 μm polyethylene terephthalate (PET), 95 μm low density polyethylene (LDPE) and 7 μm aluminum layers. The PA/PE film was a laminate of 30 μm polyamide PA6 and 60 μm high density polyethylene (HDPE). Film thickness was measured using a hand-held digital micrometer (Mitutoyo, Mitutoyo Corporation, Kanagawa, Japan) with an accuracy of 0.001 mm. Measurements were performed randomly at fifteen different locations of the film and the mean thickness was computed. Light transmissivity of the packaging materials was determined by measuring the percentage of transmittance (% *T*) using a UV–VIS spectrophotometer UV-3101PC (Shimadzu, Kyoto, Japan) at 600 nm according to ASTM standard D1746. Three replicates of each film were measured and the average value was reported. Oxygen transmission rate (OTR) of packaging materials was analyzed at 38 °C and 90% RH using an oxygen permeability analyzer Model 8003 (Illinois Instruments, Johnsburg, IL, USA) according to ASTM F2622. In addition, water vapor permeability (WVP) was measured at 25 °C and 50% RH using a WVP analyzer Model 7002 (Illinois Instruments, Johnsburg, IL, USA) following ASTM F1249. The properties of packaging materials used in this study can be found in Table 1.

Table 1
Comparison of aluminum laminated polyethylene (ALP) and polyamide/polyethylene (PA/PE) films used in storage packaging.

Materials	Thickness (μm)	Light transmissivity* (%)	Water vapor permeability** (kg m^{-2} day^{-1} Pa^{-1})	Oxygen transmission rate*** (L m^{-2} day^{-1})
ALP	117	0	6.44×10^{-8}	0.0213
PA/PE	90	95	2.25×10^{-7}	0.1200

* At 600 nm.
** At 38 °C, 90% RH.
*** At 25 °C, 50% RH.

For both types of packaging, 200 g of dried papaya samples were filled in pouches and then sealed under normal atmospheric conditions with a packing machine (model A 300/16, Sepp Haggenmüller GmbH and Co.KG, Wolfertschwenden, Germany). The package seal was carefully inspected to avoid any possibility of leakage. Subsequently, the sealed sample pouches were stored in a climate chamber at a temperature of 30 ± 2 °C and RH of 40–45% using saturated potassium carbonate solution for a period of up to 9 months. The product was sampled monthly for chemical analyses.

2.4. Chemical analyses

2.4.1. Chemicals and solvents

The compounds of 2,2-diphenyl-1-picrylhydrazyl (DPPH), 2,4,6-tripiridyl-*s*-triazine (TPTZ), 2,2-azinobis-3-ethyl-benzothiazoline-6-sulfonic acid (ABTS), Folin–Ciocalteu's reagent as well as all standards of 5-hydroxymethylfurfural (HMF), gallic acid and 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox) were purchased from Sigma–Aldrich Chemie GmbH (Taufkirchen, Germany). Ascorbic acid and other reagent-grade solvents were acquired from VWR Chemicals (Darmstadt, Germany). Deionized water was used throughout.

2.4.2. Moisture content and water activity

Moisture content (MC) was determined by volumetric Karl Fischer titration (model 758 KFD Titrino, Metrohm GmbH and Co., Herisau, Switzerland) carried out at 50 °C with the addition of 10 ml of formamide as a solubilizing agent. Samples were subjected to double determination and values were calculated in g per 100 g. Water activity (a_w) was measured using a ventilated hygrometer system (model AW-DIO, Rotronic, Bassersdorf, Switzerland) after 20 min in a thermostatic cell at 25 °C. Results are given as water activity (% ERH/100). Total soluble solids (TSS) were measured using a refractometer (model PR-201, Atago, Tokyo, Japan). Titratable acidity (TA) was determined by alkaline titration method with 0.1 mol L^{-1} NaOH to obtain pH 8.1 (AOAC, 2006) and was expressed in g citric acid per 100 g sample. Pulp pH was obtained with a pH meter (model 340, Wissenschaftlich-Technische Werkstätten GmbH, Weilheim, Germany). All measurements were carried out in triplicate.

2.4.3. Degree of browning

The method described by Baloch, Buckle, and Edwards (1973) was used to determine the degree of browning (DB). Five grams of sample was soaked in 50 ml of 2% (v v^{-1}) acetic acid for 2 h. Subsequently, the sample was homogenized for 1 min and then centrifuged at 14,000×*g* for 20 min (model Z326K, Hermle Labortechnik, Wehingen, Germany). The supernatant was extracted and the absorbance was measured at 420 nm with a UV–VIS spectrophotometer (model UVmini 1240, Shimadzu, Kyoto, Japan). Results were expressed as absorbance unit (AU) per g dry weight (d.w.) of sample.

2.4.4. Non-enzymatic browning

To determine 5-hydroxymethylfurfural (HMF), the method developed by Rattanthanalerk, Chiewchan, and Srichumpoung (2005) was adapted. One gram of sample was mixed with 20 ml of 90% ethanol. The mixture was homogenized for 1 min and subsequently centrifuged at 18,000×*g* for 1 min. Two milliliters of the supernatant was transferred to a test tube and mixed with 2 ml of 12% (w v^{-1}) trichloroacetic acid (TCA) and 2 ml of 0.025 M thiobarbituric acid (TBA). The mixture was incubated at 40 °C for 50 min and then cooled. The sample was subjected to absorbance measurement at 443 nm using the UV–VIS spectrophotometer. A calibration curve was established to quantify the HMF concentration and the result was expressed in mM per g d.w. of sample.

2.4.5. Total phenolics

Extraction of total phenolics (TP) and antioxidants from fresh and dried papayas was carried out identically. Approximately 2 g of dried sample was mixed with methanol at a ratio 1:5 in a conical flask that was wrapped with an aluminum foil. The mixture was experimentally extracted at 35 kHz and 50 °C for 2 h using an ultrasonic bath (model T 780/H, Elma, Singen, Germany) with thermostatic temperature control. The sample was filtered through Whatman No. 4 paper in order to clarify the solution. The extracted sample was stored at −20 °C prior to analysis. Total phenolic contents were evaluated using the Folin–Ciocalteu assay based on the method of Ikram et al. (2009), with slight modification. A total of 200 µl of extracted sample was mixed with 1.50 ml of 10-fold diluted Folin–Ciocalteu reagent in a test tube. The mixture was continuously shaken and allowed to react for 5 min. Subsequently, the sample was mixed with 1.50 ml of 7.5% (w v^{-1}) Na_2CO_3 solution and incubated at ambient temperature in the dark for 90 min. The TP content was measured at 760 nm using the UV–VIS spectrophotometer. A standard calibration curve was plotted using gallic acid. The TP content was expressed as mg gallic acid equivalent (GAE) per g dry weight (d.w.) of sample.

2.4.6. Antioxidant capacity

For the antioxidant assays, a fruit extract obtained as described in Section 2.4.5 was used for all analyses. The method developed by Thaipong, Boonprakob, Crosby, Cisneros-Zevallos, and Byrne (2006) was utilized to determine DPPH radical scavenging capacity. A stock DPPH solution was prepared by dissolving 24 mg DPPH with 100 ml methanol and then stored at −20 °C prior to analysis. The working solution was prepared by mixing 10 ml of stock solution with 45 ml of methanol to obtain an absorbency of 1.1 ± 0.02 units at 515 nm using the UV–VIS spectrophotometer. A total of 150 µl fruit extract was allowed to react with 2850 µl of the DPPH solution for 12 h under dark conditions. The absorbance was measured at 515 nm and the result was expressed in µM trolox equivalent (TE) per g d.w. of sample.

Ferric reducing antioxidant potential (FRAP) assay was also performed using the method of Thaipong et al. (2006). The stock solution included 300 mM acetate buffer solution in 40 mM HCl and 20 mM $FeCl_3{\cdot}6H_2O$ solution. The fresh FRAP reagent was prepared by mixing 25 ml of acetate buffer, 2.5 ml of TPTZ solution and 2.5 ml of $FeCl_3{\cdot}6H_2O$ solution, which was warmed to 37 °C before dispensation. A total of 150 µl fruit extract was allowed to react with 2850 µl of the FRAP solution for 30 min in the dark condition. The absorbance of the colored product was read at 593 nm using the UV–VIS spectrophotometer. Trolox was measured as a standard curve. The result is expressed in µM TE per g d.w. of sample.

ABTS radical cation scavenging capacity was determined using the method proposed by Arnao, Cano, and Acosta (2001), with some modification. The stock solution included 7.4 mM $ABTS^+$ solution and 2.6 mM $K_2S_2O_7$ solution. The working solution was prepared by mixing the two stock solutions in equal quantities and then allowed to react for 12 h at room temperature under dark conditions. The solution was subsequently diluted by mixing 1 ml of $ABTS^+$ solution with 60 ml of methanol to obtain an absorbance of 1.1 ± 0.02 units at 734 nm using the UV–VIS spectrophotometer. A total of 150 µl fruit extract (obtained as described in Section 2.3.5) was allowed to react with 2850 µl of $ABTS^+$ solution for 2 h under dark conditions. The absorbance reading was taken

at 734 nm and the result was expressed in μM TE per g d.w. of sample.

2.4.7. Ascorbic acid

The method of Valente, Albuquerque, Sanches-Silva, and Costa (2011) was modified to analyze ascorbic acid (AA) content. Three grams of dried samples were weighed and then homogenized with 7.5 ml of 10:1 (v v^{-1}) perchloric acid:metaphosphoric acid, by using Ultraturrax for 1 min and then 7.5 ml of extracted solution were added. Suspensions were centrifuged at 10 °C and 11,000×*g* for 30 min. Subsequently, 3 ml of the supernatant was transferred into a volumetric flask and adjusted to 10 ml with mobile phase. The mobile phase consisted of 20 mM ammonium dihydrogen phosphate, pH 3.5, containing 0.015% (w v^{-1}) of metaphosphoric acid. Prior to injection into the high performance liquid chromatograph (HPLC), supernatants were filtered through 0.45 μm membrane filters.

The HPLC system was equipped with the following components (Shimadzu, Kyoto, Japan): binary pump (model SIL-20 AT HT), auto-sampler (model SIL-20 AT HT), a UV-detector (model SIL-20 AT HT) and controller (model SIL-20 AT HT). A Reprosil Pur C18AQ column (4.6 mm I.D. × 250 mm length, Dr. Maisch-GmbH, Ammerbuch-Entringen, Germany) which was protected by a guard column (4.6 mm I.D. × 10 mm length) was used. The total run time was 15 min at a flow-rate of 0.6 ml min^{-1}. Column temperature was kept at 30 °C and the auto-sampler at 5 °C. The chromatographic analyses were performed in duplicate.

2.5. Kinetic modeling and data analysis

Kinetic modeling describes reaction rates as functions of storage time and can be used to predict changes in product quality during storage (Van Boekel, 2008). For a zero-order reaction (with respect to time) kinetics are described by:

$$c = c_0 - kt \quad (1)$$

and for a first-order reaction the relationship is defined as:

$$c = c_0 \exp(-kt) \quad (2)$$

where c is the value for the quality parameter at any time t, c_0 is the initial value and k is the reaction rate constant. Kinetics of browning reactions and degradation of bioactive compounds during storage were modeled using the experimental data. Coefficient of determination (R^2) and mean absolute percentage error (MAPE) were used to evaluate the goodness of fit.

Statistical analysis was performed using SAS software (Ver. 9.4, SAS Institute Inc., Cary, NC, USA). Least significant difference (LSD) was used to estimate the significant differences among the means for each treatment at 5% probability level.

3. Results and discussion

3.1. Moisture content and water activity

The variation in MC and a_w of dried papaya during storage is shown in Table 2. As expected, MC and a_w of samples significantly increased in both ALP and PA/PE pouches as storage time progressed up to 9 months, mainly due to the diffusion of water vapor from the external environment through the packaging materials (Esse & Saari, 2004). A marked change of MC and a_w was found particularly from 5 to 9 months. After storage for 9 months, MC of dried samples packaged in ALP and PA/PE pouches increased by 19.7% and 21.7%, whereas the increase of a_w was 28.3% and 30.5%, respectively. This result can be explained by lower permeability of ALP to water as compared to PA/PE (Table 1). The threshold a_w of 0.6 was reached at 6 months in PA/PE and 8 months in ALP. In agreement with these results, Kumar and Mishra (2004) reported that the moisture gain in mango/soy yogurt powder packaged in transparent pouches was higher than in ALP pouches. Similar observations regarding the increase of MC during storage were reported for sun-dried apricots by Alagöz, Türkyılmaz, Tagĭ, and Özkan (2015). Borges and Cal-Vidal (1994) mentioned that the kinetics of water sorption is governed by several factors such as the amount of water absorbed by the drying material, environmental conditions (mainly temperature and humidity) and microstructure of the products.

3.2. Browning

Browning is a critical quality factor for fruit products during processing and storage, as it directly affects the sensory and nutritional attributes. The change in DB and HMF as influenced by packaging material and storage period is shown in Fig. 1. The initial DB and HMF of dried papayas had average values of 0.325 AU g^{-1} d.w. and 0.245 mM g^{-1} d.w., respectively. The DB and HMF of samples in both ALP and PA/PE packages increased significantly over storage time. After 9 months, the DB and HMF values of dried samples packaged in ALP intensified 1.6 and 1.5-fold, respectively when compared to the initial dried sample, while in the samples packaged in PA/PE the accumulation was 2.1 and 1.7-fold, respectively. The results also signify that not only non-enzymatic browning (NEB) as indicated by HMF formation influenced the DB measurement, but also enzymatic browning. Enzymatic browning reactions are associated with the presence of oxygen and the enzyme

Table 2
Changes in moisture content (MC) and water activity (a_w) of dried papaya during storage in aluminum laminated polyethylene (ALP) and polyamide/polyethylene (PA/PE) packaging.

Storage (month)	MC (g g^{-1})		a_w (−)	
	ALP	PA/PE	ALP	PA/PE
0	0.1328 ± 0.0011^{aG}	0.1328 ± 0.0011^{aJ}	0.512 ± 0.002^{aH}	0.512 ± 0.002^{aI}
1	0.1352 ± 0.0008^{bF}	0.1365 ± 0.0007^{aI}	0.518 ± 0.002^{bG}	0.523 ± 0.002^{aH}
2	0.1374 ± 0.0013^{bF}	0.1407 ± 0.0014^{aH}	0.522 ± 0.001^{bG}	0.538 ± 0.003^{aG}
3	0.1416 ± 0.0005^{bE}	0.1458 ± 0.0012^{aG}	0.533 ± 0.004^{bF}	0.547 ± 0.004^{aFG}
4	0.1452 ± 0.0012^{bD}	0.1502 ± 0.0008^{aF}	0.540 ± 0.002^{bF}	0.552 ± 0.002^{aF}
5	0.1486 ± 0.0016^{bD}	0.1551 ± 0.0011^{aE}	0.554 ± 0.002^{bE}	0.565 ± 0.002^{aE}
6	0.1511 ± 0.0007^{bC}	0.1586 ± 0.0009^{aD}	0.578 ± 0.003^{bD}	0.598 ± 0.003^{aD}
7	0.1544 ± 0.0011^{bB}	0.1612 ± 0.0008^{aC}	0.592 ± 0.003^{bC}	0.624 ± 0.003^{aC}
8	0.1567 ± 0.0009^{bB}	0.1676 ± 0.0010^{aB}	0.615 ± 0.004^{bB}	0.645 ± 0.004^{aB}
9	0.1590 ± 0.0006^{bA}	0.1704 ± 0.0009^{aA}	0.623 ± 0.002^{bA}	0.668 ± 0.002^{aA}

Value is the mean ± standard deviation.
[a–b] Represents the significant differences ($p < 0.05$) of dried papaya stored in different packaging material.
[A–J] Represent the significant differences ($p < 0.05$) of dried papaya stored at different period.

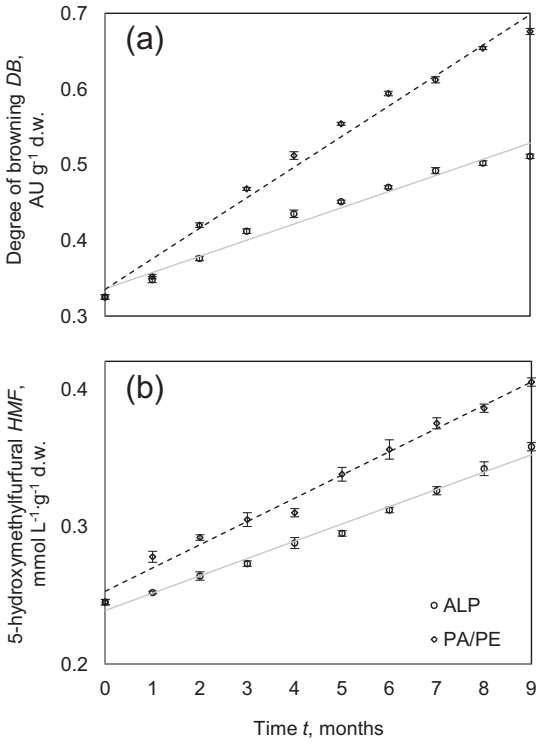

Fig. 1. Effect of storage time and packaging material on (a) degree of browning DB and (b) 5-hydroxymethylfurfural HMF of dried papaya.

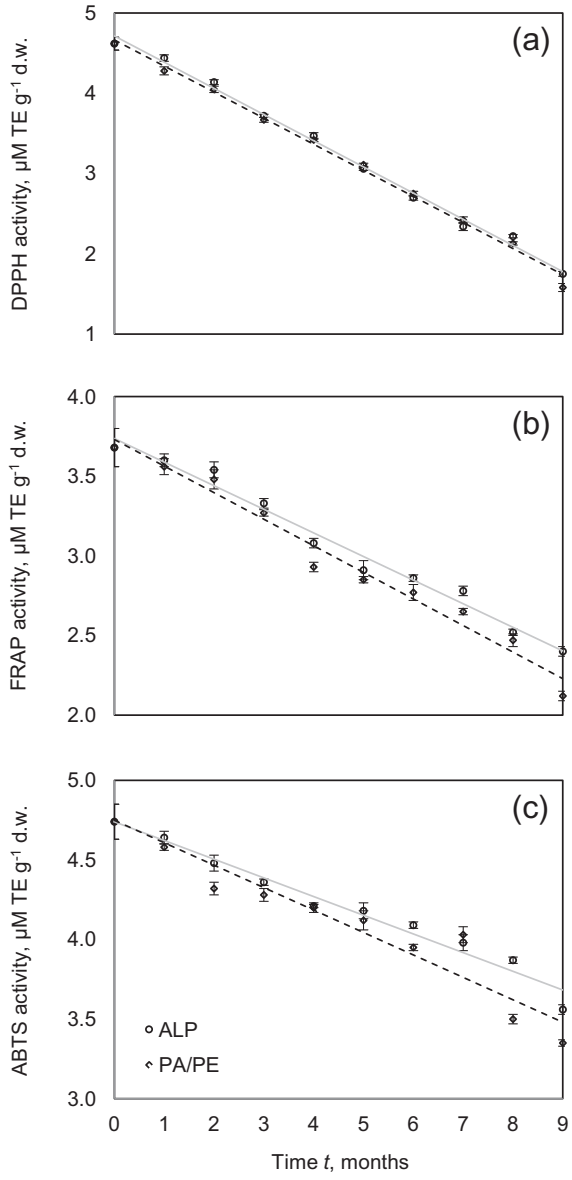

Fig. 2. Effect of storage time and packaging material on antioxidant capacity of dried papaya as defined by (a) DPPH, (b) FRAP and (c) ABTS.

polyphenol oxidase (PPO). The primary oxidation products, named *o*-quinones, are highly reactive and prompt further reactions with phenolic and non-phenolic compounds, resulting in the formation of yellow and brown pigments (Moreno et al., 2013). It can be seen in Fig. 2 that the rate of increase in HMF during the storage period in PE/PA over ALP was a factor of 1.3, but DB had almost double the rate in PA/PE packing as compared to ALP. This difference mainly represents enzymatic browning reactions and can be explained by the lower oxygen transmission rate of ALP respective to PE/PA (Table 1). Pua et al. (2008) reported a similar finding that substantial change in total color (ΔE) was observed in packaging material with high oxygen and water vapor transmission rates.

Likewise, dried papaya approximately contained 11.78 g D-glucose, 10.84 g D-fructose and 1.62 g sucrose per 100 g of weight in dry basis (Udomkun, Argyropoulos, et al., 2015). With high amount of reducing sugars as well as presence of amino acids, NEB (the Maillard reaction) can take place, especially when dried samples are exposed to heat, humidity and oxygen during storage. An increase in MC facilitates the mobility of sugar molecules within the papaya tissue, resulting in greater availability as a reactant for the Maillard reaction. In this study, the rise in MC and a_w distinctively correlated with the occurrence of DB and HMF, showing a strong coefficient of determination ($R^2 > 0.90$). Mahayothee et al. (2009) mentioned that both, enzymatic and non-enzymatic browning reactions were gradually increased in the dried litchi during storage at 25 °C and 45–60% RH for 5 months. As reported by Chong, Law, Figiel, Wojdyło, and Oziembłowski (2013), the oxidation of AA also contributes to the color change of dehydrated papaya. The oxidation of AA to dehydroascorbic acid is followed by hydrolysis of the latter to 2,3-diketogulonic acid. This substance may further undergo polymerization with amino acid such as lysine, glutamic acid and other amino acids, leading to the active formation of brown pigments (Dewanto, Wu, Adom, & Liu, 2002). Normally, these browning products are furan-type compounds, lactones, acids, 3-hydroxy-2-pyrone, furaldehyde and 5-hydroxymethylfuraldehyde (Chong et al., 2013). Furthermore, the degradation of β-carotene, resulting in the generation of NEB products could have also occurred (Hymavathi & Khader, 2005).

3.3. Antioxidant capacity and total phenolics

The effect of packaging type and storage time on antioxidant capacity and TP content is demonstrated in Figs. 2 and 3. The initial DPPH, FRAP and ABTS activities of dried papayas had average values of 4.62, 3.68 and 4.74 µM TE g^{-1} d.w., respectively, while the TP compounds, which exhibit hydrophilic antioxidant capacity, had a content of 25.45 mg GAE 100 g^{-1} d.w. For both ALP and PA/PE packaging materials, antioxidant capacity and TP content decreased significantly during the storage period, particularly after 3 months. Antioxidant capacity as indicated by DPPH, FRAP and ABTS decreased by 62%, 35% and 25%, respectively, when samples were packaged in ALP pouches for 9 months, whereas capacity

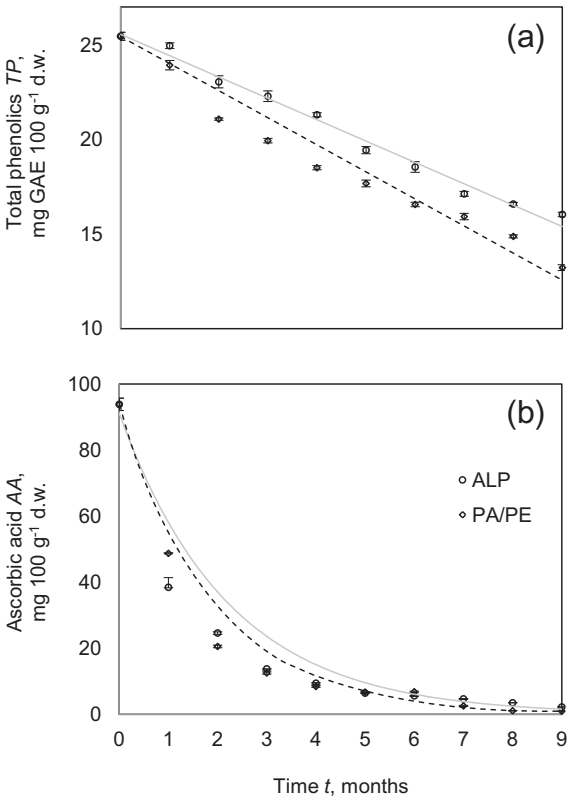

Fig. 3. Effect of storage time and packaging material on (a) total phenolics TP and (b) ascorbic acid AA in dried papaya.

decreased by 66%, 42% and 27%, respectively for samples packaged in PA/PE pouches. Also, the loss of TP contents in ALP reached 37%, whereas in the PA/PE it reached 40%. Phenol compounds are believed to be the major phytochemical constituents responsible for antioxidant capacity in plant materials (Korus, 2011). In this study, the antioxidant capacity as defined by DPPH, FRAP and ABTS were linearly correlated with TP compounds ($R^2 > 0.90$). This result implied that the antioxidant activities in dried papaya samples during storage were directly affected by phenolic compounds, while other constituents such as reducing carbohydrates, tocopherols, carotenoids, terpenes and pigments (and the synergistic effect among them), contributed less to the total antioxidant capacity (Chong et al., 2013). A decrease in antioxidant activities and TP retention might be due to the activation of oxidative enzymes such as polyphenoloxidase or chemical oxidation of phenolic compounds (Manzocco, Calligaris, Mastrocola, Nicoli, & Lerici, 2001). In addition, the loss of phenolics may also be more closely associated with storage temperature, pH as well as exposure to oxygen and light. Sablani (2006) mentioned that elevated moisture content can accelerate the degradation of phenolic compounds. In regard to antioxidant and TP degradation, it was evident that with elevated MC, decreased antioxidant capacities and TP content were observed. The MC and a_w changes in both packing materials were almost linearly related to the TP content and antioxidant activities with $R^2 > 0.95$.

DPPH scavenging capacity and TP content of dried papaya packaged in ALP were found to be more stable than of those packaged in PA/PE pouches. Furthermore, it was noticed that the ALP pouches were better packaging material in preserving FRAP and ABTS activities after 7 months of storage. ALP pouches with lower water vapor permeability and oxygen transmission rate would be expected to better retard the degradation of antioxidant activities and TP in dried fruits during the subsequent storage, yet the results indicated that ALP performed only moderately better than PA/PE pouches. This phenomenon might be related with the formation and accumulation of melanoidins as well as Maillard reaction products (MRP), which also function as antioxidant substances (Miranda, Berna, Salazar, & Mulet, 2009).

3.4. Ascorbic acid

AA content variation of dried papayas during storage in different packaging materials is shown in Fig. 3. The initial AA content of dried sample was 93.82 mg 100 g^{-1} d.w. The degradation of AA accelerated exponentially during the first 3 months of storage and, after 9 months, the AA content of samples packaged in ALP and PA/PE pouches was markedly reduced by 42-fold (2.25 mg 100 g^{-1} d.w.) and 96-fold (0.98 mg 100 g^{-1} d.w.), respectively. Paul, Ghosh, Singh, and Bhowmick (2014) reported that 6 months of storage caused significant losses of AA in osmotically pretreated and vacuum dried pineapple cubes. Due to the instability of AA, progressive degradation of AA during storage might be associated with an increase of a_w as well as MC, since free water can act as a solvent for reactants and as a catalyst. Gregory (2008) inferred that the presence of fructose and sucrose at low pH might increase the rate of anaerobic degradation of AA. Other storage conditions such as pH, temperature and the presence of metal ion catalysis may also lead to the degradation of AA (Lešková et al., 2006). Although ALP pouches cannot preserve AA considerably better than PA/PE for the entire storage period, greater conservation of AA content was observed in the samples packaged in ALP pouches after 7 months of storage. Hymavathi and Khader (2005) demonstrated likewise that the loss of AA in mango powder was higher in polyester poly (PP) pouches as compared to metalized polyester (MPP).

3.5. Quality kinetics

Kinetic coefficients obtained from fitting Eqs. (1) and (2) for the respective quality parameters are reported in Table 3. Based on the R^2 values ($R^2 > 0.95$), it was concluded that quality parameters

Table 3
Kinetics coefficients and statistical parameters from regression analysis of quality parameters during storage of dried papaya in aluminum laminated polyethylene (ALP) and polyamide/polyethylene (PA/PE) packaging.

	c_0		k		R^2		MAPE	
	ALP	PA/PE	ALP	PA/PE	ALP	PA/PE	ALP	PA/PE
Zero-order model								
Degree of browning (DB)	0.336	0.335	−0.0214	−0.0403	0.974	0.984	2.156	2.705
Non-enzymatic browning (5-HMF)	0.239	0.253	−0.0126	−0.0169	0.989	0.988	1.024	1.402
DPPH radical scavenging activity	4.714	4.666	0.3263	0.3250	0.995	0.995	2.074	2.326
Ferric reducing antioxidant power (FRAP)	3.737	3.730	0.1482	0.1684	0.982	0.979	1.553	2.211
ABTS radical cation scavenging capacity	4.739	4.749	0.1173	0.1381	0.972	0.922	1.182	2.304
Total phenolics (TP)	25.550	24.440	1.1280	1.2730	0.987	0.967	1.652	3.121
First-order model								
Ascorbic acid (AA)	91.110	93.450	0.6837	0.6655	0.980	0.992	47.210	37.222

followed zero order reactions, except AA which was described better using a first-order model. The error was low (MAPE < 5) for all models, with the exception of AA, which showed very high percentage error at low values. Examination of the *k*-values shows that rate changes were more drastic for the samples stored in PA/PE packaging in comparison to those from the ALP pouches, meaning that more degradation occurred in dried papaya when packed in PA/PE. This could also been seen when kinetic models were fitted to the experimental data, as shown in Figs. 1–3 where the dotted lines represent models for PA/PE and the gray lines indicate ALP.

4. Conclusions

The main objectives of this study were to examine the effects of ALP and PA/PE materials on the dynamics of browning and bioactive compounds in dried papayas during storage. The results revealed that MC and a_w, DB, HMF, antioxidant activities, TP and AA contents were significantly affected by both, storage time and packaging materials. Color change of dried sample was due to Maillard reaction, enzymatic browning, and ascorbic acid oxidation. As MC and a_w increased over storage, DB and HMF levels also increased, while antioxidant activities, TP and AA contents decreased. The permeability of packaging materials to water vapor and oxygen as well as light transmittance are critical factors determining the quality and bio-chemical stability of dried papaya during storage. ALP pouches, with a greater protective barrier, better preserved the antioxidant activities, TP and AA contents as well as inhibited browning when compared to PA/PE pouches.

In conclusion, the best quality of dried product in terms of color attributes and bio-active compounds could be achieved by the ALP packages. According to the safe storage conditions for the commercialization of dried fruits, the maximum threshold for a_w of 0.6 is used as reference. Therefore, it is suggested that dried papayas in this study can be conserved for 8 months in ALP and 6 months in PA/PE under normal conditions. Nevertheless, further research is still needed in order to understand degradation kinetics of other functional compounds such as carotenoids during storage. Also, other options like vacuum and modified atmosphere (MA) packaging should be explored to serve as a basis to benefit the nutritional value and economic potential for producers and consumers alike.

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References

Alagöz, S., Türkyılmaz, M., Tagĭ, S., & Özkan, M. (2015). Effects of different sorbic acid and moisture levels on chemical and microbial qualities of sun-dried apricots during storage. *Food Chemistry, 174*, 356–364.

Argyropoulos, D., Heindl, A., & Müller, J. (2011). Assessment of convection, hot-air combined with microwave-vacuum and freeze-drying methods for mushroom with regard to product quality. *International Journal of Food Science & Technology, 46*(2), 333–342.

Arnao, M. B., Cano, A., & Acosta, M. (2001). The hydrophilic and lipophilic contribution of total antioxidant activity. *Food Chemistry, 73*, 239–244.

AOAC (2006). *Official methods of analysis* (18th ed.). Gaithersburg, MD: Association of Official Analytical Chemists.

Baloch, A. K., Buckle, K. A., & Edwards, R. A. (1973). Measurement of non-enzymatic browning of dehydrated carrot. *Journal of the Science of Food and Agriculture, 24*, 389–398.

Bautisa-Baños, S., Sivakumar, D., Bello-Pérez, A., Villanueva-Arce, R., & Hernández-López, M. (2013). A review of the management alternatives for controlling fungi on papaya fruit during the postharvest supply chain. *Crop Protection, 49*, 8–20.

Borges, S. V., & Cal-Vidal, J. (1994). Kinetics of water vapour sorption by drum-dried banana. *International Journal of Food Science & Technology, 29*, 83–90.

Chong, C. H., Law, C. L., Figiel, A., Wojdyło, A., & Oziembłowski, M. (2013). Colour, phenolic content and antioxidant capacity of some fruits dehydrated by a combination of different methods. *Food Chemistry, 141*(4), 3889–3896.

Dak, M., Sagar, V. R., & Jha, S. K. (2014). Shelf-life and kinetics of quality change of dried pomegranate arils in flexible packaging. *Food Packaging and Shelf Life, 2*, 1–6.

Dewanto, V., Wu, X., Adom, K. K., & Liu, R. H. (2002). Thermal processing enhances the nutritional values of tomatoes by increasing total antioxidant activity. *Journal of Agricultural and Food Chemistry, 50*, 3010–3014.

Esse, R., & Saari, A. (2004). Shelf-life and moisture management. In R. Steele (Ed.), *Understanding and measuring the shelf-life of food* (pp. 24–41). England: Woodhead Publishing Limited.

Gregory, J. F. III, (2008). Vitamins. In S. Damodaran, K. L. Parkin, & O. R. Fennema (Eds.), *Food chemistry* (pp. 474). Boca Raton: CRC Press.

Hymavathi, T. V., & Khader, V. (2005). Carotene, ascorbic acid and sugar content of vacuum dehydrated ripe mango powders stored in flexible packaging material. *Journal of Food Composition and Analysis, 18*, 181–192.

Ikram, E. H. K., Khoo, H. E., Jalil, A. M. M., Ismail, A., Idris, S., Azlan, A., ... Mokhtar, R. A. M. (2009). Antioxidant capacity and total phenolic content of Malaysian underutilized fruits. *Journal of Food Composition and Analysis, 22*(5), 388–393.

Korus, A. (2011). Effect of preliminary processing, method of drying and storage temperature on the level of antioxidants in kale (*Brassica oleracea* L. var. *acephala*) leaves. *LWT-Food Science and Technology, 44*, 1711–1716.

Kumar, P., & Mishra, H. N. (2004). Storage stability of mango soy fortified yoghurt powder in two different packaging materials HDPP and ALP. *Journal of Food Engineering, 65*, 569–576.

Lavelli, V., & Vantaggi, C. (2009). Rate of antioxidant degradation and color variations in dehydrated apples as related to water activity. *Journal of Agriculture and Food Chemistry, 57*, 4733–4738.

Lešková, E., Kubíková, J., Kováčiková, E., Košická, M., Porubská, J., & Holčíková, K. (2006). Vitamin losses: Retention during heat treatment and continual changes expressed by mathematical models. *Journal of Food Composition and Analysis, 19*, 252–276.

Mahayothee, B., Udomkun, P., Nagle, M., Haewsungcharoen, M., Janjai, S., & Müller, J. (2009). Effect of pretreatments on colour alterations of litchi during drying and storage. *European Food Research and Technology, 229*, 329–337.

Miranda, G., Berna, A., Salazar, D., & Mulet, A. (2009). Sulphur dioxide evolution during dried apricot storage. *LWT-Food Science and Technology, 42*, 531–533.

Manzocco, L., Calligaris, S., Mastrocola, D., Nicoli, M., & Lerici, C. (2001). Review of non-enzymatic browning and antioxidant capacity in processed foods. *Trends in Food Science & Technology, 11*, 340–346.

Moreno, J., Simpson, R., Pizarro, N., Pavez, C., Dorvil, F., Petzold, G., & Bugueño, G. (2013). Influence of ohmic heating/osmotic dehydration treatments on polyphenoloxidase inactivation, physical properties and microbial stability of apples (cv. Granny Smith). *Innovative Food Science and Emerging Technologies, 20*, 198–207.

Pua, C. K., Hamid, N. S. . Abd., Tan, C. P., Mirhosseini, H., Rahman, R. . Abd., & Rusul, G. (2008). Storage stability of jackfruit (*Artocarpus heterophyllus*) powder packaged in aluminium laminated polyethylene and metallized co-extruded biaxially oriented polypropylene during storage. *Journal of Food Engineering, 89*, 419–428.

Paul, P. K., Ghosh, S. K., Singh, D. K., & Bhowmick, N. (2014). Quality of osmotically pre-treated and vacuum dried pineapple cubes on storage as influenced by type of solutes and packaging materials. *Journal of Food Science and Technology, 51*(8), 1561–1567.

Rattanthanalerk, M., Chiewchan, N., & Srichumpoung, W. (2005). Effect of thermal processing on the quality loss of pineapple juice. *Journal of Food Engineering, 66*, 259–265.

Rivera-Pastrana, D. M., Yahia, M. E., & González-Aguilar, G. A. (2010). Phenolic and carotenoid profiles of papaya fruit (*Carica papaya* L.) and their contents under low temperature storage. *Journal of the Science of Food and Agriculture, 90*, 2358–2365.

Sablani, S. (2006). Drying of fruits and vegetables: Retention of nutritional/functional quality. *Drying Technology, 24*, 123–135.

Thaipong, K., Boonprakob, U., Crosby, K., Cisneros-Zevallos, L., & Byrne, D. H. (2006). Comparison of ABTS, DPPH, FRAP, and ORAC assays for estimating antioxidant activity from guava fruit extracts. *Journal of Food Composition and Analysis, 19*, 669–675.

Udomkun, P., Mahayothee, M., Nagle, M., & Müller, J. (2014). Effects of calcium chloride and calcium lactate applications with osmotic pretreatment on physicochemical aspects and consumer acceptances of dried papaya. *International Journal of Food Science & Technology, 49*, 1122–1131.

Udomkun, P., Nagle, M., Mahayothee, B., Nohr, D., Koza, A., & Müller, J. (2015). Influence of air drying properties on non-enzymatic browning, major bio-active

compounds and antioxidant capacity of osmotically pretreated papaya. *LWT-Food Science and Technology, 60*(2), 914–922.
Udomkun, P., Argyropoulos, D., Nagle, M., Mahayothee, B., & Müller, J. (2015). Sorption behaviour of papayas as affected by compositional and structural alterations from osmotic pretreatment and drying. *Journal of Food Engineering, 157*, 14–23.
Valente, A., Albuquerque, T. G., Sanches-Silva, A., & Costa, H. S. (2011). Ascorbic acid content in exotic fruits: A contribution of produce quality data for food composition database. *Food Research International, 44*(7), 2237–2242.
Van Boekel, M. A. J. S. (2008). Kinetic modeling of food quality: A critical review. *Comprehensive Reviews in Food Science and Food Safety, 7*(1), 144–158.