LWT - Food Science and Technology 118 (2020) 108842

Contents lists available at ScienceDirect

LWT - Food Science and Technology

journal homepage: www.elsevier.com/locate/lwt

Storage stability of freeze-dried arazá (*Eugenia stipitata* Mc Vaugh) powders. Implications of carrier type and glass transition

Camilo Andrés Reyes-Álvarez[a,b], María Cecilia Lanari[a,b,*]

[a] Centro de Investigación y Desarrollo en Criotecnología de Alimentos (CIDCA), CONICET - La Plata, Facultad de Ciencias Exactas Universidad Nacional de La Plata (UNLP), Calle 47 y 116 S/N°, La Plata, B1900AJJ, Buenos Aires, Argentina
[b] Members of Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina

ARTICLE INFO

Keywords:
Arazá
Eugenia stipitata
Water-activity
Glass transition
Antioxidant activity

ABSTRACT

Arazá, a flavorsome fruit rich in antioxidants (phenolics/carotenoids/flavonoids/ascorbic acid) may be appropriate for preparing powdered-functional foods and beverages. Variations in water-activity (a_w) and matrix physical state (glassy/rubbery) can induce undesirable changes in dehydrated products color antioxidant composition/activity reducing shelf-life. Solving this problem requires a thorough analysis of the a_w/physical state effects on the arazá powder physicochemical properties. Objectives were to: (a) analyse a_w, glass-transition temperature (T_g) and carrier-type (maltodextrin-DE10/Arabic-gum) effects on freeze-dried arazá color, antioxidant composition/activity; (b) Determine storage-time influence on antioxidant content/activity/polyphenol composition considering the best performing a_w values previously determined. Critical a_w values calculated from T_g/a_w interrelationship overestimated the a_w limit corresponding to samples color/antioxidant composition/activity maximum stability, therefore, T_g was not a reliable indicator of the properties stabilities. Antioxidant content/activity storage behavior (20 °C/$a_w = 0.11$ (best performing a_w optimized across all properties)) were satisfactorily predicted by the Weibull equation. Shelf-lives, calculated considering 90% properties retention as the acceptability limit, were 34 (arazá/maltodextrin) and 50 (arazá/Arabic-gum) days. Polyphenolic profile included 6 phenolic acids, one coumaric acid derivative, 4 flavonoids and one ellagitannin. Using a mix of maltodextrin-DE10/Arabic-gum might improve antioxidant content/activity stability obtained with the single carriers and extend their shelf-life.

1. Introduction

Arazá (*Eugenia stipitata* Mc Vaugh) is an amazonian fruit rich in heat-sensitive antioxidants (phenolics/carotenoids/flavonoids/ascorbic-acid) with proven antigenotoxic and antimutagenic properties; however, its high perishability hinders its commercialization in regions far from its production zones (Borghi-Virgolin, Fortunato-Seixas & Soares-Janzantti, 2017). Freeze-drying can be a viable solution to this problem since the low processing temperatures used and the absence of liquid water protects heat-sensitive compounds resulting in a high quality final product (Marques, Ferreira, & Freire, 2007). However, drying or freeze-drying fruit juices or other products with high sugar content presents technical difficulties, the low glass-transition temperature (T_g) of some components (low molecular weight sugars and organic acids) and their high hygroscopicity causes stickiness, collapse and flow problems during processing and storage (Orjuela-Palacio & Lanari, 2016). Since in comparison with other tropical fruits, arazá's level of low molecular weight sugars (0.48 g glucose 100 mL^{-1}; Borghi-Virgolin, Fortunato-Seixa, & Soares-Janzantti, 2017) is 9–10 times less, the incidence of these issues in the powder might be lower.

Several researchers reported that incorporating carrier agents like maltodextrin (MD) and/or Arabic-gum (AG) before drying increased T_g, prevented caking, reduced hygroscopicity and improved physical stability of vacuum-dried mango (Jaya & Das, 2004) and spray-dried acai (Tonon et al., 2009).

Water-activity (a_w) and physical state (glassy/rubbery) of the matrix play a fundamental role in dehydrated food stability. The glassy/rubbery transition occurs at a specific temperature (glass-transition temperature, T_g) which depends on the a_w/water content of the powder. At $T < T_g$, the dehydrated food system is in the highly viscous glassy state associated to low levels of molecular mobility and diffusion-controlled reaction rates. At $T > T_g$, the product is in the rubbery state which

---

[*] Corresponding author. Centro de Investigación y Desarrollo en Criotecnología de Alimentos (CIDCA), CONICET - La Plata, Facultad de Ciencias Exactas Universidad Nacional de La Plata (UNLP), Calle 47 y 116 S/N°, La Plata, B1900AJJ, Buenos Aires, Argentina.

E-mail address: cecilialanari@gmail.com (M.C. Lanari).

https://doi.org/10.1016/j.lwt.2019.108842
Received 21 June 2019; Received in revised form 9 November 2019; Accepted 11 November 2019

implies a sharp viscosity decrease and an enhancement in certain processes rates. Water content/a_w increments can also reduce T_g through water plasticization and consequently induce glass-transition (Syamaladevi, Sablani, Tang, Powers, & Swanson, 2011).

Although food stored under glassy state conditions can be shelf stable, discoloration caused by non-enzymatic browning, antioxidant content/activity losses may still occur (Syamaladevi et al., 2011) therefore optimum product stability requires a thorough analysis on the T_g/a_w effect on the product physicochemical stability within the glassy and rubbery states ranges.

The aim of this study was to determine the relative humidity/a_w necessary for preserving color, antioxidant content and activity of arazá samples freeze-dried with maltodextrin or Arabic-gum stored at 20 °C. Specific objectives were:

(a) To analyse the relationship between a_w, glass-transition and carrier type (maltodextrin DE 10 and Arabic-gum) at 20 °C on the stability of freeze-dried arazá color, antioxidant concentration and activity.
(b) To determine the effect of storage time on the antioxidant content and activity and polyphenol composition considering the best performing a_w values previously determined.

2. Materials and methods

2.1. Fruit selection and processing

Fresh arazá (moisture (H) 96 ± 2.4%, totals soluble solids (TSS) 3.9 ± 0.4°Brix) purchased at a local market in Ibagué (Colombia), was selected according to its color (yellow-green) and size (10–14 cm diameter). After washing, peeling and cutting, the fruit was manually pressed to form a paste and mixed with different concentrations (0, 2.5, and 5%) of (a) maltodextrin Dextrose Equivalent 10 (AMD; Productos de Maız S.A., Buenos Aires, Argentina) or (b) Arabic-gum (AAG; Quimica Oeste S.A., Buenos Aires, Argentina) and freeze-dried with a FIC L1-1-E300-CRT freeze-dryer (Buenos Aires, Argentina; $T = -35$ °C, vacuum < 13.32 Pa).

2.2. Glass-transition temperature/water content/water-activity relationship

The adsorption isotherms of AMD and AAG powders were determined at 20 °C with the static gravimetric method (Orjuela-Palacio & Lanari, 2016). Triplicate samples were placed in hermetic containers filled with saturated solutions of different salts (LiCl (11.3%); CH_3COOK (23.4%); $MgCl_2$ (33%); K_2CO_3 (43.2%); $Mg(N0_3)_2$ (54.4%) and NaCl (76%)). The samples were weighed every 3 days until reaching equilibrium (difference between 2 consecutive weights < ± 0.003 g), the equilibration period lasted 2–3 weeks. At this point, the a_w of the equilibrated samples can be considered equal to the corresponding relative humidity (RH)*100^{-1}.

The relationship between the equilibrium moisture content (*Wc*) and the a_w of the powder drinks was predicted with the GAB equation (1)

$$W_c = \frac{W_m K\ C\ a_w}{(1 - K\ a_w)(1 - K\ a_w + C\ K\ a_w)} \tag{1}$$

W_c and W_m represent the equilibrium and monolayer water contents (kg H_2O*(kg d.m. (dry matter))$^{-1}$) respectively while C and K are constants related to the monolayer (C) and multilayer (K) sorption heats.

To determine the T_g values, the samples (5–10 mg), placed in DSC aluminum pans (TA Instruments; USA) andequilibrated at each RH as described previously, were hermetically sealed, weighed and scanned with a differential scanning calorimeter (DSC, Q-100 TA 5000; TA Instruments; USA) using an empty pan as reference. The heating rate was 10 °C/min and the temperature ranged from -20 °C to 120 °C. Two runs were performed for each sample; the second scan reduced the relaxation enthalpy of the amorphous powder, shown in the first scan, enhancing the accuracy of T_g measurement on the DSC thermogram.

The onset (T_{gonset}), mid (T_{gI}) and end (T_{gend}) temperatures were determined in duplicate with the TA Universal Analysis 2000 software (TA Instruments Waters LLC, DE USA).

The powder T_g/water content relationship was predicted with the Gordon–Taylor equation (Eq. (2); Gordon & Taylor, 1953) considering $T_g = T_{g\ onset}$.

$$T_g = \frac{X_s T_{gs} + k X_w T_{gw}}{X_s + k X_w} \tag{2}$$

X_s and X_w represent the solids and water weight fractions (kg*(kg d.m)$^{-1}$), T_{gw} and T_{gs} (°C) the glass-transition temperatures of the water (−135 °C; Tonon et al., 2009) and the anhydrous matrix respectively and $\mathbf{k_{GT}}$ a constant related to the matrix/water interaction. Eqs. (1) and (2) parameters were estimated using nonlinear regression analysis with the OriginPro v 8.0 (OriginLab Corp., Northhampton, MA USA) and Systat 12 (Systat Software Inc; San Jose, CA USA) softwares. Models performance were evaluated with the mean relative deviation modulus (%E) and the adjusted determination coefficient (R_{adj}^2).

The critical moisture content (CW_c) and water-activity (Ca_w) values corresponding to the glass/rubbery transition at 20 °C were determined as described by Tonon et al. (2009).

2.3. Physico-chemical analysis

Flowability (Repose angle (°)), hygroscopicity (Hyg %), degree of caking (DC %), pH, total soluble solids (TSS), total and reducing sugars were only measured in non-equilibrated samples while water content, T_g, color, antioxidants contents and activities determinations were done for the whole a_w range.

2.3.1. Water-activity, moisture content

All determinations were done at least in triplicate. Water-activity was measured at 25 °C in an AquaLab series 3 (Decagon Device, Pullman, Washington, USA), calibrated with the saline solutions used for the sorption experiments.

Samples water content (H; %) was analyzed according to AOAC (1998) method part. 934.06.

2.3.2. Microstructure

The powders microstructure was analyzed by scanning electron microscopy (SEM; FEI Quanta 200 microscope, Netherlands) under high-vacuum conditions and 20 kV acceleration voltage (Deladino, Anbinder, Navarro, & Martino, 2007) The samples, attached to stubs with two-sided adhesive tape, were coated with a gold layer (40–50 nm).

2.3.3. Flowability, hygroscopicity and degree of caking

The powder bulk densities (g (cm^3)$^{-1}$) were evaluated measuring the volume occupied by a given weight of powder (40 g) in a graduated cylinder with (compact density (CD)); (100 taps, rate = 60 taps min^{-1}) and without compacting loose density (LD); (Deladino, Navarro, & Martino, 2007).

The powders flowability was determined with the dynamic repose angle chamber (Solids handling study bench, CEN, Armfield, UK; Geldart, Abdullah, Hassanpour, Nwoke, & Wouters, 2006) and the Hausner index (Ha), defined as the compact to loose bulk density ratio (CD (LD)$^{-1}$).

Samples hygroscopicity (Hyg; Eq. (3)) and degree of caking (DC; Eq. (4)) were determined as described by Jaya and Das (2004).

$$Hyg\,(\%) = \frac{{}^{b}\!/_{a} + W_i}{1 + {}^{b}\!/_{a}} 100 \tag{3}$$

a (g) and b (g) and W_i (%, wet matter (w.m)) are the mass of powder,

Table 1
Physicochemical properties of the non-equilibrated freeze-dried arazá powders encapsulated with maltodextrina DE10 (AMD) or arabic gum (AAG) 5% (w/w).

	AMD/AAG[1]		AMD	AAG
Repose angle (°)	53.19 ± 3.83	a_w	$0.08 \pm 2{*}10^{-3a}$	$0.09 \pm 2{*}10^{-3b}$
Hausner Index (Ha)	1.39 ± 0.22	H	$0.02 \pm 2{*}10^{-3a}$	$0.03 \pm 2{*}10^{-3b}$
L*	85.35 ± 2.03	Hyg (%)	22 ± 0.06^a	25 ± 0.23^b
SI	34.12 ± 1.19	DC (%)	51.5 ± 2.14^a	56.5 ± 0.91^b
HA (°)	89.54 ± 5.05	T_g (°C)	116.89 ± 3.33^a	99.12 ± 0.41^b
Solubility (Sol %)	81.01 ± 1.34	TP	99.16 ± 0.79^a	92.59 ± 0.34^b
TSS (°Brix)	7.75 ± 0.07	TF	17.81 ± 0.28^a	14.59 ± 0.47^b
AA	$92 \pm 1{*}10^{-3}$	TC	44.29 ± 0.78^a	38.83 ± 0.43^b
ARA (%)	71.19 ± 2.49	pH	2.79 ± 0.030^a	2.93 ± 0.030^b
FRAP	1306.96 ± 6.22			
Total sugars (°Brix)	5.55 ± 0.02			
Reducing sugars	3.32 ± 0.01			

[1] Statistical difference between samples was not significant ($P > 0.05$); Means within a row with different superscripts are significantly different ($P < 0.05$); d.m: dried matter; TSS: Total soluble solids; Total sugars/Reducing sugar (mg GluE (glucose eq)) (g d.m)$^{-1}$; AA: Ascorbic acid:(mg AA (100 g d.m ^{1})); ARA: Antiradical activity; DC: degree of caking; FRAP: Ferric Reducing Antioxidant Power (μM Fe^{+2}(g d.m)$^{-1}$); H: Water content (kg H_2O (kg d.m)$^{-1}$); HA: Hue Angle; Hyg: Hygroscopicity; L*:Lightness; SI: Saturation Index; T_g: glass transition temperature; TP: Total polyphenols (mg GAE (gallic acid eq) (g d.m)$^{-1}$); TF: Total Flavonoids (mg CAT (catechin eq) (g d.m)$^{-1}$); TC: Total carotenoids (mg β-carotene eq(g d.m)$^{-1}$) content.

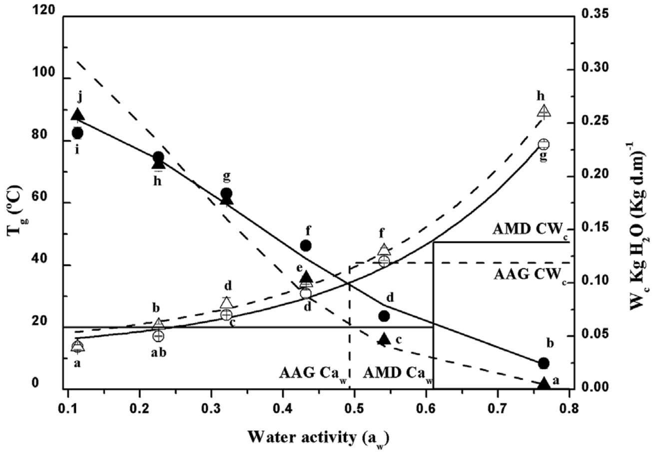

Fig. 1. Water activity effect on the equilibrium moisture content (W_c) (AAG --Δ; AMD -○-) and glass transition temperature (T_g) (AAG - -▲; AMD -●-) of samples freeze-dried with MD10/AG (5%w/w). Solid and broken lines represent W_c and T_g values predicted by the GAB (Eq. (1)) and Gordon-Taylor (Eq. (2)) models. Ca_w; critical water activity; CW_c: critical water content.

the weight increment and the initial water content respectively.

$$DC(\%) = \frac{c}{d} * 100 \tag{4}$$

d (g) and c (g) are the total and filter-retained powder weights.

2.3.4. Color, pH, total soluble solids (TSS) and solubility in cold water

Color was expressed with the CIE L*a*b* coordinates and measured with a Minolta CR-400 Chroma Meter (Minolta, Osaka, Japan), each value was the average of 9 measurements on triplicate samples. The total color differences relative to the non-equilibrated freeze-dried samples (ΔE) were calculated from Eq. 5

$$\Delta E = \sqrt{L*^2 + \Delta a*^2 + \Delta b*^2} \tag{5}$$

to measure the pH and the TSS (°Brix), the powders were reconstituted with a H_2O volume similar to that lost during drying. Determinations were done by duplicate at 25 °C with a pHmeter (Hach Sension + pH3 Lab; Hach Company, Lovely, CO, USA) or a refractometer Atago N2 (Tokyo, Japan).

Samples solubility (Sol; Eq. (6)) in water at 4 °C was determined in duplicate according to Chen and Jane (1994).

Table 2
GAB (W_m, C, K) and Gordon–Taylor (k_{GT}, T_{gs}, T_{gw}, W_s) estimated parameters, critical values of water content (CW_c) and water activity (Ca_w) of freeze-dried arazá encapsulated with maltodextrin DE10 (AMD) or arabic gum (AAG) 5% (w/w).

Parameters	AAG[a]	Error	AMD[b]	Error
GAB model				
W_m (kg H_2O (kg d.m)$^{-1}$)	0.05	3.4×10^{-5}	0.046	2.3×10^{-6}
C	0.95	0.07	0.89	0.07
K	1.04	5.9×10^{-3}	1.04	6.9×10^{-3}
R^2_{adj}	0.97		0.97	
Gordon-Taylor model				
T_{gs} (°C)	105.86	11.79	97.96	6.98
k_{GT}	2.84	0.59	2.48	0.37
X_s	0.43	2.1×10^{-3}	0.4	1.2×10^{-3}
T_{gw} (°C)	−135		−135	
R^2_{adj}	0.98		0.95	
Critical parameters				
Ca_w	0.49		0.61	
CW_c (kg H_2O (kg d.m)$^{-1}$)	0.12		0.14	

d.m.: dried matter; W_m: monolayer water content; $\mathbf{k_{GT}}$: Gordon-Taylor constant; T_{gw}/T_{gs}: water and anhydrous solids glass transition temperatures; X_s: solid fraction.

$$Sol(\%) = \frac{(p_{ss} * FD * 100)}{pt} \tag{6}$$

p_{ss} and pt represent the dried weights (g) of the supernatant and the sample respectively and FD the dilution factor.

2.3.5. Total/reducing sugars content and antioxidant composition

Total and reducing sugars concentration (g Glu (glucose equivalents)*(g d.m.)$^{-1}$) were analyzed with the anthrone/sulfuric acid colorimetric test (Leyva et al., 2008) using a UVmini-1240 UV–Vis Spectrophotometer (Shimadzu Scientific Instruments, Japan).

Antioxidants were extracted with a methanol/H_2O (50:50 v/v, pH = 2.0) mixture (Saura-Calixto, Serrano, & Goñi, 2007). The total phenolic content of the extracts (TP; mg GAE (gallic acid equivalents)*(g d.m)$^{-1}$) was assessed with the Folin-Ciocalteu method (Schlesier, Hawat, Böhm & Bitsch, 2002).

Total flavonoids (TF; mg CAT (catechin equivalents)*(g d.m)$^{-1}$) and carotenoids levels (TC; mg β-carotene equivalents*(g d.m)$^{-1}$) were determined according to Chang, Yang, and Wen (2002) and Ordoñez-Santos, Hurtado-Aguilar, Ríos-Solarte, and Arias-Jaramillo (2014).

Ascorbic acid (AA; mg AA*(100 g d.m)$^{-1}$) concentration was analyzed by high performance liquid chromatography (Waters, model R-414, Milford, MA, USA; Orjuela-Palacio & Lanari, 2016).

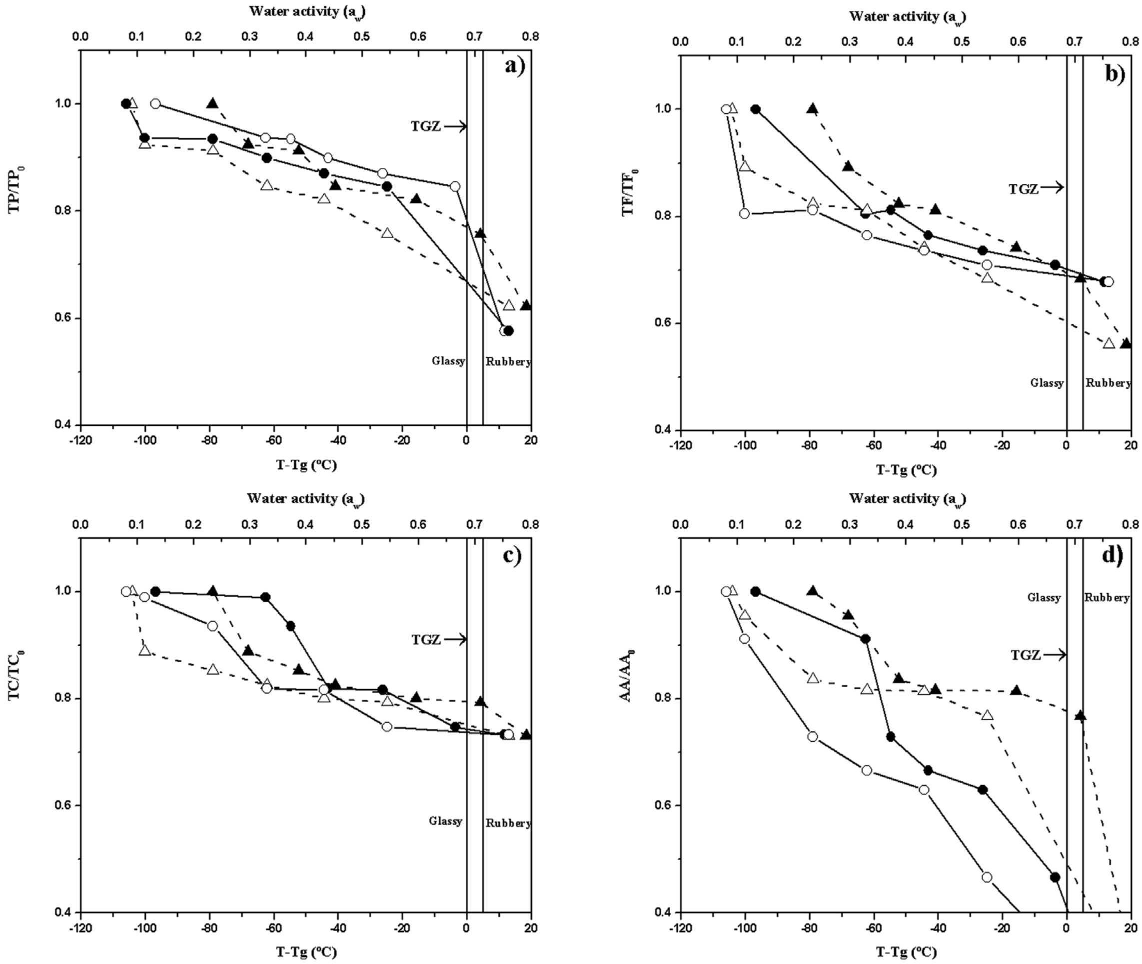

Fig. 2. a, b, c, d Water activity (AAG - -Δ; AMD -○-) and T_{stor}-T_g (AAG - -▲; AMD -●-) influence on the total polyphenol (TP, a), total flavonoids (TF; b), total carotenoids (TC; c) and ascorbic acid (AA; d) contents of the samples freeze-dried with MD10/AG (5% w/w) TGZ: glass transition zone. T_{stor} = 20 °C.

Polyphenol composition was determined following Soares et al. (2019) protocol with a Waters Model 6000 A LC system (Milford, MA, USA) equipped with a diode array detector (DAD) and a C-18 Altex-Ultrasphere™-ODS column (250 mm × 4.6 mm i.d, 5 µm part size). Compound identification was done comparing their DAD spectra and retention times with those from commercial standards (Caffeic (CAF), Cinnamic (CIN), Chlorogenic (CLO), Coumaric (COU) trans-Ferulic (tFER), Gallic (GA)) acids and Rutin tri-hydrate (R3H_2O; Sigma-Aldrich, Argentina) and from Soares et al. (2019) publication.

2.3.6. Antiradical activity and ferric reducing antioxidant power

The AMD and AAG antiradical activities (ARA; Eq. (7)) were determined with the DPPH scavenging assay (Brand-Williams, Cuvelier, & Berset, 1995).

$$ARA = [(Absb_0 - Abss_t)\ Absb_0^{-1}]*100 \tag{7}$$

$Absb_0$ and $Abss_t$ are the absorbancies of the blank (b) and the sample (s) at time = 0 and at t = 120 min.

Ferric Reducing Antioxidant Power (FRAP; µM Fe^{+2}*(g d.m.)$^{-1}$) was evaluated according to Pulido, Bravo, and Saura-Calixto (2000) after 30 min of reaction time.

2.4. Storage stability

To analyse the influence of storage time and its interaction with carrier type on the powders antioxidant composition, ARA and FRAP, the samples were stored as described in Sect. 2.2 for 90 days at 20 °C using the RH/a_w that provided maximum stability to all properties obtained from the a_w/glass-transition relationship with color, antioxidant concentration and activity analysis.

Antioxidant content and activity retention (RY) during storage was analyzed using the Weibull equations (Eqs. (8) and (9); Oms-Oliu, Odriozola-Serrano, Soliva-Fortuny, & Martín-Belloso, 2009).

$$RY_t = RY_0\ \exp(-(kt)^{\gamma}) \tag{8}$$

$$RY_t = RY_0 - (RY_0 - RY_f)\ \exp(-(kt)^{\gamma}) \tag{9}$$

$$RY_t = Y/Y_0 \tag{10}$$

RY_t represents the fraction of the property Y (TP, TC, TF, AA, ARA, FRAP) retained at t days, RY_0 and RY_f correspond to the RY value at days 0 and 90 while k (days^{-1}) and γ are the kinetic and shape constants respectively.

Eq. (8), and (9) parameters were determined by regression analysis with the OriginPro v8.0. The model "goodness of fit" was evaluated considering the highest adjusted regression coefficients (R^2_{adj}) and minimal error of the parameters.

2.5. Statistical analysis

Results were expressed as the mean ± standard error of at least three replicates. The effect of temperature, carrier type and water-activity on the color, antioxidant content, antiradical activity and FRAP were analyzed with the Infostat (v. 2013) software. Significant differences among means were determined by analysis of variance followed

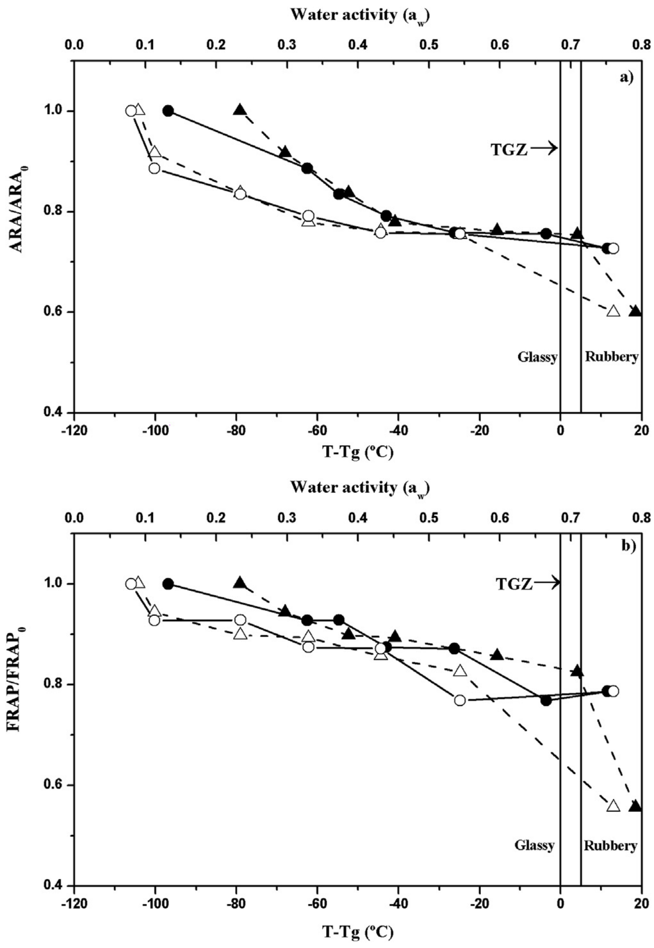

Fig. 3. a, b Water activity (AAG - -Δ; AMD -○-) and T_{stor}-T_g (AAG - -▲; AMD -●-) influence on the antiradical activity (ARA; a) and the Ferric Reducing Antioxidant Power (FRAP; b) of the samples freeze-dried with MD10/AG (5% w/w). TGZ: glass transition zone. $T_{stor} = 20$ °C.

by pairwise comparisons with the Tuckey test considering $P < 0.05$ as statistically significant.

3. Results and discussion

The AMD and AAG samples prepared with 5% carrier showed lower a_w levels (0.08–0.09; Table 1) than those obtained with 0 or 2.5% (0.36–0.13) therefore, this concentration was used in the rest of the experiments.

3.1. Samples characterization

AAG and AMD physicochemical properties before equilibration are listed in Table 1; flow capacity Hausner index (Ha), repose angle and color parameters (L*, SI, HA) as well as solubility (Sol), total soluble solids (TSS), ascorbic acid concentration (AA) and antioxidant activities (ARA, FRAP) were independent of the carrier type ($P > 0.05$), therefore individual AAG and AMD results were replaced by their average.

UPS United States Pharmacopeia Convention (2012) and Geldart et al. (2006) reported that powders with repose angles > 50° or Hausner index > 1.5 have flow problems during processing.

Although the samples repose angle was 6.4% higher than the limit (50°), the difference was not significant ($P > 0.05$); in addition, AMD/AAG Hausner ratio (Table 1) also fulfilled Geldart et al. (2006) conditions (Ha > 1.5), indicating that the samples flowability was acceptable for manufacturing purposes.

AAG and AMD microstructures before equilibration (Appendix Fig. 1a and b non-eq) were consistent with the samples low humidity since the particles shapes and sizes were highly irregular with sharp edges and shriveled surfaces suggesting absence of agglomeration even though AAG particles were bigger and thicker.

Juliano and Barbosa-Cánovas (2010) concluded that powders fluidity depended on particle size, shape and surface characteristics. Compared with smooth round particles, those with smaller size, irregular shapes and rough surfaces have more inter-particles contact points resulting in a higher cohesiveness and a lower flowing capacity (Juliano & Barbosa-Cánovas, 2010). AMD and AAG irregular flaky shape and rough surfaces (Appendix Fig. 1a and b) fulfilled this condition, therefore their flow behavior could be partially explained by their morphology.

3.2. Glass-transition temperature/equilibrium water content/water-activity relationships

Table 1 shows the a_w, moisture content, hygroscopicity and degree of caking levels of the non-equilibrated samples. Water-activity values were within the range ($a_w < 0.25$) recommended by Labuza and Altunakar (2007) for preserving biochemical stability and microbiological safety. Moisture level (H), hygroscopicity (Hyg; Eq. (3)) and degree of caking (DC; Eq. (4)) were higher in AAG than in AMD, possibly due to AG higher content of hydrophilic groups. According to GEA Niro Research Laboratory. (2003), Hyg and DC values indicated that, the samples were very hygroscopic and prone to caking.

Both products had high $T_{g,}$ possibly due to their low level of reducing sugars (Table 1), Tonon et al. (2009) reported similar results for spray dried açai with 6% MD10.

Fig. 1 shows the water-activity effect on AAG and AMD equilibrium water content and T_g at 20 °C. For a_w ranging 0.08–0.23, AMD moisture content remained stable but further enhancements up to 0.76 increased it by 464%; in contrast, AAG moisture gain was continuous reaching 529%.

Both isotherms were satisfactorily predicted by the GAB equation (Eq. (1)), Table 2 presents the regression parameters, the determination coefficient (R^2_{adj}) and the mean relative deviation modulus (%E).

W_m^{AAG} was higher than W_m^{AMD} ($P < 0.05$), this could be caused by AG higher concentration of hydrophilic groups in comparison with MD10 which favor a greater interaction solute/sorbent (Silva, Kurozawa, Park, & Hubinger, 2012).

W_m represents the moisture level corresponding to optimum food stability (Orjuela-Palacio & Lanari, 2016). Labuza and Ball (2002) concluded that $W_m > 0.1$ kg H_2O (kg d.m.)$^{-1}$ may compromise food stability. Results showed that the predicted W_m values satisfied this condition (Table 2) therefore the processing conditions used in the current study were appropriate for producing powders with good stability.

Water-activity and carrier type strongly ($P < 0.05$) affected T_g (Fig. 1); at $a_w = 0.11$, T_g drop in AMD was 3 times higher than in AAG. Further a_w increments to 0.33 reduced the sample T_g by 26.5%, however, at a_w 0.43–0.76, T_g^{AAG} stability was 14% lower.

The Gordon-Taylor equation (Eq. (2)) satisfactorily predicted the T_g/a_w relationship (Fig. 1; Table 2). k_{GT} represents the effectiveness of water plasticizing capacity in a given matrix (Ramoneda, Ponce-Cevallos, Buera, & Elizalde, 2011) therefore an enhancement of this property implies a faster T_g drop at low water contents. Statistical analysis showed that AMD and AAG k_{GT} values were similar ($P > 0.05$) hence the water plasticization effect was independent from the carrier type.

The critical moisture content (CW_c) and water-activity (Ca_w) values corresponding to the samples glass/rubbery transition at 20 °C (Table 2; Fig. 1) indicated that to preserve the AMD or AAG glassy state during the whole storage period, samples should be kept at relative

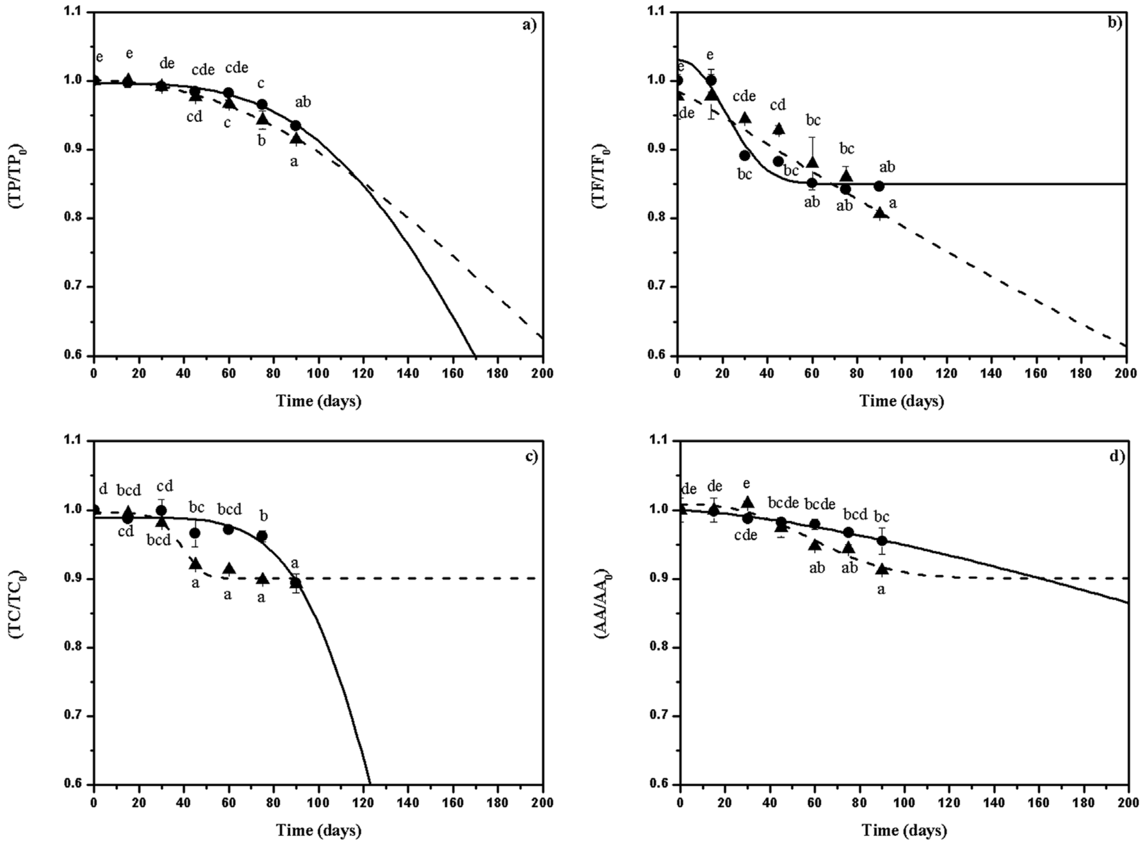

Fig. 4. a, b, c, d Storage time effect on the total polyphenol (TP, a), total flavonoids (TF; b), total carotenoids (TC; c) and ascorbic acid (AA; d) contents of AMD (●) and AAG (▲) samples freeze-dried with MD10/AG (5% w/w). Solid and dash lines represent the values predicted by the Weibull model (Eqs. (8) and (9)).

humidities < 61 or 49% respectively.

To determine the influence of physical state (glassy/rubbery) on ΔE (Appendix Fig. 2), antioxidant concentration (Fig. 2a–d) and activity (Fig. 3a–b), the T_g effect was analyzed considering $\Delta T = T_{stor}\text{-}T_g$ ($T_{stor} = 20\,^\circ C$).

Results showed that within the glassy-state zone, discoloration and antioxidant content/activity losses were considerable. At $a_w = 0.43$, ΔE_{AAG} and ΔE_{AMD} values increased 14.75 and 1.75 times respectively in comparison with their levels in non-equilibrated samples. Karmas, Buera, and Karel (1992) observed significant discoloration caused by non-enzymatic browning in freeze-dried potatoes under glassy-state conditions.

Antioxidant retention decreased by 26% for TP and 20% for TC and TF (Fig. 2a–c). Carrier-type influence on AA content was highly significant ($P < 0.05$), at $a_w = 0.43$, AAG and AMD retention dropped 19 and 37% respectively (Fig. 2d). Ismail and Mauer (2019) detected significant ascorbic-acid degradation in glassy state model systems whereas Prado, Buera, and Elizalde (2006) showed that β-carotene degradation was faster in the glassy than in the rubbery state.

In accordance with antioxidant content results, ARA and FRAP also diminished in the glassy area ($P < 0.05$; Fig. 3 a, b), at $a_w = 0.43$, antioxidant activities retention decreased by 14% and was not affected by carrier type ($P > 0.05$).

Syamaladevi et al. (2011) reported that although molecular mobility were greatly reduced in the glassy state, undesirable chemical reactions may still occur caused by changes in water-activity. Bell and Hageman (1994) reported that aspartame degradation was more affected by a_w than by T_g.

Deladino, Navarro, & Martino, (2005) concluded that although maltodextrin and Arabic-gum can encapsulate the bioactives protecting them from adverse environmental conditions, their efficiency is reduced because spray or freeze-drying encapsulation leaves a significant proportion of the antioxidants unprotected in the microcapsule surface resulting in increments of the degradation rates.

Results showed that to retain 90% of the color, antioxidant content/activity values from the samples before equilibration, the powders must be kept at $a_w \leq 0.11$.

The SEM micrographs (Appendix Fig. 1a and b) shows the water-activity effect on the microstructure of the powders, a_w increments up to 0.33 (GLASSY STATE) did not produced visible signs of agglomeration; particles had wrinkled surfaces, pores and visible dents. In contrast, in the phase transition ($0\,^\circ C < \Delta T \leq 20^\circ C\text{-}T_{gend}$) and rubbery state ($T\text{-}T_g > 20^\circ C\text{-}T_{gend}$) regions, the formation of inter-particle bridges was noticeable at $a_w = 0.54$ and enhanced at 0.76.

3.3. Storage stability

To determine the antioxidant content and activity variations during storage, AAG and AMD samples were kept for 90 days at 20 °C and $a_w = 0.11$. Results showed that antioxidant concentration/activity losses were: 10% (TP/TC/TF), 6–9% (AA), 9–12% (ARA) and 10–14% (FRAP; Fig. 4a–d, Fig. 5a–b).

Degradation rates followed two different patterns;

a) Continuous decline ($TP_{AMD/AAG}$, TF_{AAG}, TC_{AMD}, AA_{AMD} and $FRAP_{AMD}$) or
b) An initial stable period followed by a sharp drop until reaching an asymptotic level (TF_{AMD}, TC_{AAG}, AA_{AAG}, $FRAP_{AAG}$ and $ARA_{AMD/AAG}$).

Results were satisfactorily predicted by Eq. (8) in the first case and Eq. (9) in the latter. Table 3 shows the regression parameters and their corresponding errors along with the models adjusted determination coefficients (R^2_{adj}).

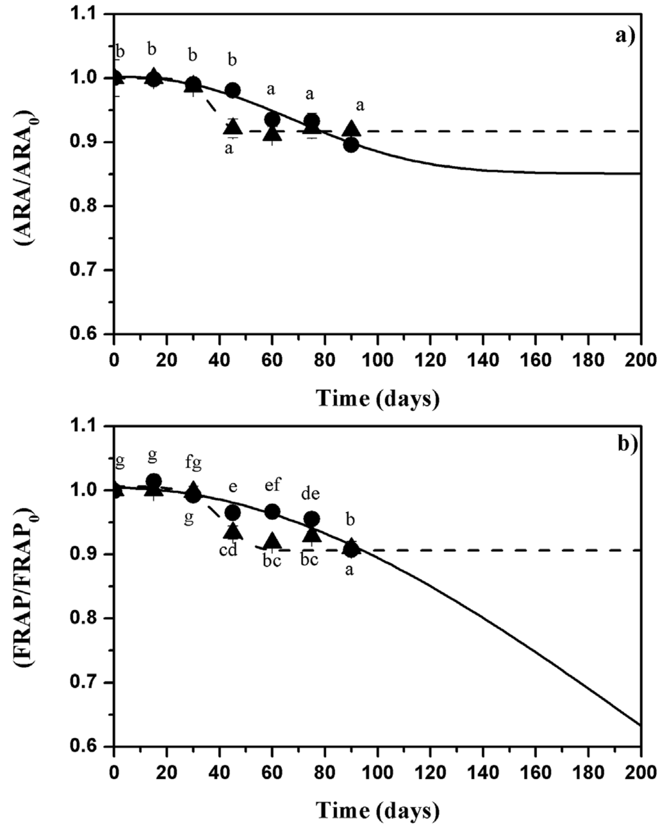

Fig. 5. a, b Storage time effect on the antiradical activity (ARA; a) and the Ferric Reducing Antioxidant Power (FRAP; b) of the freeze-dried AMD (●) and AAG (▲) samples freeze-dried with MD10/AG (5% w/w). Solid and dash lines represent the values predicted by the Weibull model (Eqs. (8) and (9)).

Table 3
Weibull parameters corresponding to the antioxidants (TP, TF, TC, AA) content and activity (ARA, FRAP) retention (Eqs. (8) and (9)) during 90 days storage (20 °C) of freeze-dried arazá encapsulated with maltodextrin DE10 (AMD) or arabic gum (AAG) 5% (w/w).

		Weibull parameters					
Sample	Y	RY_0	γ	k (days^{-1})	RY_f	R^2_{adj}	Shelf-life (days)
AMD	TP	1.00	3.30	4.80E-03		0.96	109
	TF	1.03	2.18	3.00E-02	0.84	0.92	34
	TC	0.99	5.17	7.10E-03		0.83	93
	AA	1.00	1.48	1.35E-03		0.84	178
	ARA (%)	1.00	2.40	1.18E-02	0.85	0.92	99
	FRAP	1.00	2.01	3.40E-03		0.87	103
AAG	TP	1.00	2.10	3.49E-03		0.97	105
	TF	0.97	2.51	5.31E-03		0.71	50
	TC	1.00	5.51	2.42E-02	0.90	0.96	> 200
	AA	1.01	2.59	1.43E-02	0.90	0.86	> 200
	ARA (%)	1.00	7.08	2.59E-02	0.92	0.95	> 200
	FRAP	1.01	5.00	2.29E-02	0.91	0.81	> 200

Y: property measured; RY_0/RY_f: Y retention at 0/90 day; k/γ: kinetic/shape constants. d.m: dried matter; TP: Total polyphenols (mg GAE (Gallic acid eq). (g d.m)$^{-1}$); TF: Total Flavonoids (mg CAT (catechin eq) (g d.m)$^{-1}$); TC: Total carotenoids (mg β-carotene eq (g d.m)$^{-1}$); AA: Ascorbic acid (mg AA eq (100 g d.m)$^{-1}$); ARA: Antiradical activity; FRAP: Ferric Reducing Antioxidant Power (μM Fe^{+2}(g d.m)$^{-1}$).

The TP retention values predicted by the model between days 0 and 109 were slightly higher in AMD than in AAG, however, the difference was marginal ($P > 0.05$). In contrast, after an initial period ranging from 15 to 75 days where no carrier effect was detected ($P > 0.05$), TF, TC and AA showed a strong time × carrier interaction ($P < 0.05$). From days 30–90 (TC) or days 36–157 (AA), TC and AA stabilities were more pronounced in AMD than in AAG ($P < 0.05$) whereas, between days 22–67, TF retention was higher in AAG than in AMD ($P < 0.05$). Following these periods, AAG had higher TP, TC and AA and lower TF concentrations than AMD ($P < 0.05$).

FRAP and ARA stabilities during storage followed similar behaviors: an initial 30 days period with no changes ($P > 0.05$) followed by a drop where the stability order was:

$ARA_{AMD} > ARA_{AAG}$ (31–77 days)
$FRAP_{AMD} > FRAP_{AAG}$ (31–92 days)

After these periods, AAG presented higher levels of both ARA and FRAP than AMD ($P < 0.05$).

AAG and AMD shelf lives (SL) were calculated assuming 90% retention of the different properties as the acceptability limit. The results (Table 3) indicated that using AG as the carrier increased SL from 34 to 50 days; however, if only antioxidant activity contribution is taken into consideration then the shelf-life values were 99 and at least 200 days for AMD and AAG respectively.

Storage time and carrier type produced significant changes ($P < 0.05$) in the arazá polyphenolic profile (Table 4). In accordance with Soares et al. (2019), we detected 6 phenolic acids: gallic (GA), chlorogenic (CLO), coumaric (COU), cinnamic (CIN), caffeic (CAF) and transferulic (tFER) as well as one coumaric acid derivative identified as coumaric acid hexoside (COUHex). In addition, both samples contained 4 flavonoids (rutin mono-hydrate (RH_2O) and trihydrate ($R3H_2O$); Quercetin-3-O-rutinoside (QRut), eriodictyol-7-O-glucoside (EGlu)) and one ellagitannin; di-HHDP (hexahydroxydiphenoyl)-galloyl-glucose (casuarictin/potentillin) derivative (CPDer).

Carrier type affected the freeze-drying influence on polyphenols content (Table 4; $P < 0.05$), Comparison between both samples showed that AAG contained 130–204% more Ga, QRut, $R3H_2O$ and RH_2O whereas CAF, CLO. CIN, COU, COUHex and CPDer were 172–283% higher in AMD.

At day 90, phenolic acids losses were 16–68% (AAG) and 16–70% (AMD) while in the case of the flavonoids and the di-HHDP-galloyl-glucose derivative the reductions were: 4–51% (AAG) and 10–71% (AMD; Table 4), in contrast, rutin monohydrate content remained constant through the whole storage period.

Polyphenols stability ranking was:

AAG
- tFER > COUHex ≈ GAL > COU > CLO ≈ CIN ≈ CAF
- RH_2O > QRut > $R3H_2O$ > CPDer > EGlu

AMD
- GAL > tFER > COUHex > CLO > CAF ≈ CIN ≈ COU
- RH_2O > QRut > EGlu > $R3H_2O$ > CPDer

Results obtained from contrasting the carrier effects on polyphenol stability showed that using AG reduced QRut, COU, CPDer and RH_2O/$R3H_2O$ storage losses 28–59% whereas MD10 improved COUHex, GA and EGlu stabilities 20–58%.

4. Conclusions

The critical water-activity values determined from the T_g/a_w interrelationship (0.61 (AMD), 0.49 (AAG)) overestimated the a_w limits corresponding to the samples color and antioxidant content/activity stability levels therefore, in these cases, T_g was not a reliable criterion for stability prediction.

Assuming 90% retention of all the different properties as the acceptability limit, AAG and AMD shelf-lives (20 °C, $a_w = 0.11$) were 50 and 34 days.

Total flavonoids and total carotenoids levels were key factors in determining the samples shelf-lives. Although AAG had the longest

Table 4
Storage time effect on polyphenol composition of freeze-dried arazá encapsulated with Arabic gum (AAG) or maltodextrin DE10 (AMD) 5% (w/w).

Bioactives	Rt (min)^{b}	AAG		AMD		Stor. Loss (%)^{a}	
		0 days	90 days	0 days	90 days	AAG	AMD
Caffeic acid (CAF)^{c}	11.3	66.49 ± 5.52^{b}	21.14 ± 3.09^{a}	187.87 ± 7.07^{c}	70.64 ± 4.62^{b}	68.21	62.42
Chlorogenic acid (GA)^{c}	9.6	96.94 ± 1.83^{c}	38.12 ± 4.15^{a}	166.98 ± 4.76^{d}	71.70 ± 7.48^{b}	60.68	57.42
Cinnamic acid (CIN)^{c}	27.5	126.58 ± 2.54^{c}	41.82 ± 0.84^{a}	288.95 ± 5.07^{d}	87.72 ± 1.29^{a}	66.96	69.58
Coumaric acid (COU)^{c}	15.1	128.55 ± 3.48^{b}	67.86 ± 2.04^{a}	354.23 ± 6.19^{c}	121.24 ± 2.75^{b}	47.21	65.77
Coumaric acid-O-hexoside (COUHex)^{1}	13.9	57.15 ± 1.79^{b}	36.60 ± 1.54^{a}	119.87 ± 9.25^{d}	85.51 ± 0.94^{c}	35.96	28.66
Galic acid (GA)^{c}	4.4	166.02 ± 3.39^{d}	106.01 ± 0.88^{c}	81.08 ± 2.45^{b}	68.19 ± 1.83^{a}	36.15	15.90
Trans-ferulic acid (tFER)^{c}	17.4	468.44 ± 10.10^{b}	395.21 ± 10.86^{a}	524.68 ± 6.99^{c}	419.15 ± 6.12^{a}	15.63	20.11
Di-HHDP-galloyl-glucose (casuarictin/potentillin)derivate (CPD)^{2}	14.7	235.21 ± 6.94^{b}	164.242 ± 2.57^{a}	586.78 ± 3.69^{c}	170.06 ± 10.79^{a}	30.17	71.02
Eriodictyol-7-O-glucoside (EGlu)^{3}	25.0	575.15 ± 13.37^{c}	281.15 ± 8.14^{a}	581.21 ± 4.79^{c}	455.75 ± 8.57^{b}	51.12	21.59
Quercetin 3-O-rutinoside (QRut)^{4}	3.1	699.75 ± 11.82^{d}	643.63 ± 5.14^{c}	417.51 ± 4.02^{b}	347.27 ± 4.28^{a}	8.02	18.02
Rutin (trihydrate; R3H_2O)^{5}	18.9	171.81 ± 8.14^{c}	143.21 ± 3.68^{b}	132.53 ± 8.57^{b}	100.81 ± 3.06^{a}	16.65	23.93
Rutin (hydrate form; RH_2O)^{5}	3.5	413.33 ± 12.34^{b}	395.75 ± 5.99^{b}	214.78 ± 4.97^{a}	192.72 ± 5.14^{a}	4.25	10.26

1: COUHex: mg COU eq (100 g d.m)$^{-1}$; 2: CPD: mg Gallic acid eq (GAE) (100 g d.m)$^{-1}$, 3: EGlu: mg GAE (100 g d.m)$^{-1}$, 4: QRut: mg R3$\mathbf{H_2O}$ eq (100 g d.m)$^{-1}$, 5: R$\mathbf{H_2O}$/R3$\mathbf{H_2O}$: mg R3$\mathbf{H_2O}$ eq (100 g d.m)$^{-1}$.

[a] Storage loss.

[b] Rt: retention time.

[c] mg (100 g dry matter (d.m))$^{-1}$.

shelf-life, AMD had a higher TP, TF and TC content therefore using a mix of maltodextrin-DE10/Arabic-gum might improve the antioxidant content/activity stabilities and extend the samples shelf-life.

Declaration of competing interest

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Acknowledgements

We thank Eng. Chris Young for assisting with the english translation, Claudio Reyes for the ascorbic-acid analysis, Dr Juliana Orjuela-Palacio, Dr Jonh Mendez and Universidad del Tolima for their contribution. C.A. Reyes-Álvarez was supported by the Argentinean Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET).

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.lwt.2019.108842.

References

AOAC (Association of Official Analytical Chemists) (1998). *Official methods of analysis Part. 934.06* (16th ed.). (Gaithersburg, USA).

Bell, L. N., & Hageman, J. (1994). Differentiating between the effects of water activity and glass transition dependent mobility on a solid state chemical reaction: Aspartame degradation. *Journal of Agricultural and Food Chemistry, 42*, 2398–2401.

Borghi-Virgolin, L., Fortunato-Seixa, F., & Soares-Janzantti, N. (2017). Composition, content of bioactive compounds, and antioxidant activity of fruit pulps from the Brazilian Amazon biome. *Pesquisa Agropecuária Brasileira, 52*(10), 933–941.

Brand-Williams, W., Cuvelier, M. E., & Berset, C. (1995). Use of a free radical method to evaluate antioxidant activity. *Lebensmittel-Wissenschaft und -Technologie- Food Science and Technology, 28*(1), 25–30.

Chang, C., Yang, M., & Wen, H. (2002). Estimation of total flavonoid content in propolis by two complementary colorimetric methods. *Journal of Food and Drug Analysis, 10*(3).

Chen, J., & Jane, J. (1994). Properties of granular cold-water-soluble starches prepared by alcoholic-alkaline treatments. *Cereal Chemistry, 71*(6), 623–626.

Deladino, L., Anbinder, P. S., Navarro, A. S., & Martino, M. N. (2007a). Co-crystallization of yerba mate extract (*Ilex paraguariensis*) and mineral salts within a sucrose matrix. *Journal of Food Engineering, 80*(2), 573–580.

Deladino, L., Navarro, A., & Martino, M. N. (2007). Encapsulation of active compounds: Ionic gelation and cocrystallization as case studies. In C. E. Lupano (Ed.). *Functional properties of food components* (pp. 125–157). Trivandrum: Kerala Research Signpost.

GEA Niro Research Laboratory (2003). *Analytical methods dry milk products (Niro Analytical Methods, No. 15 a).* (Soeborg).

Geldart, D., Abdullah, E. C., Hassanpour, A., Nwoke, L. C., & Wouters, I. (2006). Characterization of powder flowability using measurement of angle of repose. *China Particuology, 4*(3), 104–107.

Gordon, M., & Taylor, J. S. (1953). Ideal copolymers and the second-order transitions of synthetic rubbers. I. Noncrystalline copolymers. *Rubber Chemistry and Technology, 26*(2), 323–335.

Ismail, Y., & Mauer, L. J. (2019). Phase transitions of ascorbic acid and sodium ascorbate in a polymer matrix and effects on vitamin degradation. *Journal of Food Process Engineering,* e13073.

Jaya, S., & Das, H. (2004). Effect of maltodextrin, glycerol monostearate and tricalcium phosphate on vacuum dried mango powder properties. *Journal of Food Engineering, 63*(2), 125–134.

Juliano, P., & Barbosa-Cánovas, G. V. (2010). Food powders flowability characterization: Theory, methods, and applications. *Annual Review of Food Science and Technology, 1*(1), 211–239.

Karmas, H., Buera, M., & Karel, M. (1992). Effect of glass transition on rates of non-enzymatic browning in food systems. *Journal of Agricultural and Food Chemistry, 40*(5), 873–879.

Labuza, T. P., & Altunakar, L. (2007). Water activity prediction and moisture sorption isotherms. *Water activity in foods: Fundamentals and applications, 1*, 109–154.

Labuza, T. P., & Ball, L. N. (2002). Moisture sorption: Practical aspects of isotherm measurement and use. *Minessota: American association of cereal chemists*(2nd ed.). .

Leyva, A., Quintana, A., Sánchez, M., Rodríguez, E. N., Cremata, J., & Sánchez, J. C. (2008). Rapid and sensitive anthrone–sulfuric acid assay in microplate format to quantify carbohydrate in biopharmaceutical products: Method development and validation. *Biologicals, 36*(2), 134–141.

Marques, L. G., Ferreira, M. C., & Freire, J. T. (2007). Freeze-drying of acerola (*Malpighia glabra* L.). *Chemical Engineering and Processing: Process Intensification, 46*(5), 451–457.

Oms-Oliu, G., Odriozola-Serrano, I., Soliva-Fortuny, R., & Martín-Belloso, O. (2009). Use of Weibull distribution for describing kinetics of antioxidant potential changes in fresh-cut watermelon. *Journal of Food Engineering, 95*(1), 99–105.

Ordoñez-Santos, L. E., Hurtado-Aguilar, P., Ríos-Solarte, O. D., & Arias-Jaramillo, M. E. (2014). Concentración de carotenoides totales en residuos de frutas tropicales. *Producción + Limpia, 9*(1), 91–98.

Orjuela-Palacio, J. M., & Lanari, M. C. (2016). The impact of moisture sorption properties on the color and bioactives concentrations of black currant-yerba mate instant drinks. *Journal of Berry Research, 6*(3), 303–319.

Prado, S. M., Buera, M. P., & Elizalde, B. E. (2006). Structural collapse prevents β*-carotene loss in a supercoolled polymeric matrix. *Journal of Agricultural and Food Chemistry, 54*, 79–85.

Pulido, R., Bravo, L., & Saura-Calixto, F. (2000). Antioxidant activity of dietary polyphenols as determined by a modified ferric reducing/antioxidant power assay. *Journal of Agricultural and Food Chemistry, 48*(8), 3396–3402.

Ramoneda, X. A., Ponce-Cevallos, P. A., Buera, M. del P., & Elizalde, B. E. (2011). Degradation of β-carotene in amorphous polymer matrices. Effect of water sorption properties and physical state. *Journal of the Science of Food and Agriculture, 91*(14), 2587–2593.

Saura-Calixto, F., Serrano, J., & Goñi, I. (2007). Intake and bioaccessibility of total polyphenols in a whole diet. *Food Chemistry, 101*(2), 492–501.

Schlesier, K., Harwat, M., Böhm, V., & Bitsch, R. (2002). Assessment of antioxidant activity by using different in vitro methods. *Free Radical Research, 36*(2), 177–187.

Silva, V. M., Kurozawa, L. E., Park, K. J., & Hubinger, M. D. (2012). Water sorption and glass-transition temperature of spray-dried mussel meat protein hydrolysate. *Drying Technology, 30*(2), 175–184.

Soares, J. C., Rosalen, P. L., Lazarini, J. G., Massarioli, A. P., da Silva, C. F., Nani, B. D., et al. (2019). Comprehensive characterization of bioactive phenols from new

Brazilian superfruits by LC-ESI-QTOF-MS, and their ROS and RNS scavenging effects and anti-inflammatory activity. *Food Chemistry, 281*, 178–188.

Syamaladevi, R. M., Sablani, S. S., Tang, J., Powers, J., & Swanson, B. G. (2011). Stability of anthocyanins in frozen and freeze-dried raspberries during long-term storage: In relation to glass-transition. *Journal of Food Science, 76*(6), 414–421.

Tonon, R. V., Baroni, A. F., Brabet, C., Gibert, O., Pallet, D., & Hubinger, M. D. (2009). Water sorption and glass-transition temperature of spray dried açai (*Euterpe oleracea* Mart.) juice. *Journal of Food Engineering, 94*(3–4), 215–221.

United States Pharmacopeia Convention (2012). *The United States Pharmacopeia 35 and the national formulary 30.* Rockville, MD: The United States Pharmacopeia Convention, Inc.