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Storage Stability of Spray-Dried Blackberry Powder Produced with Maltodextrin or Gum Arabic

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The aim of this work was to evaluate the stability of anthocyanins and antioxidant activity of blackberry powder, obtained by spray drying, using maltodextrin, gum arabic, or a blend of both carrier agents over a period of 5 months. The inlet air temperature was 145°C and the concentration of carrier agent was 7% (w/w). Samples were stored at 25 or 35°C and at relative humidity of 32.8%. Anthocyanin degradation followed the first-order kinetic model. Temperature negatively influenced the stability of anthocyanins, because these pigments are highly thermosensitive. Antioxidant activity increased for the powders stored at 35°C, probably due to the occurrence of the Maillard reaction, leading to the formation of compounds with antioxidant activity. In general, maltodextrin provided greater stability for spray-dried blackberry powder, because particles produced with this carrier agent showed the longest half-life and the lowest anthocyanin degradation rate at 25°C. The use of maltodextrin or the combination of both carrier agents promoted better maintenance of antioxidant potential of blackberry powder. With regard to morphology, all of the samples exhibited a large number of irregular particles with spherical shapes, but powders produced with gum arabic presented the smallest size and shriveled surfaces, which probably affected their stability, resulting in faster anthocyanin degradation during storage.

Keywords Anthocyanin; Antioxidant activity; Carrier agents; Morphology; *Rubus* spp; Spray drying

INTRODUCTION

Anthocyanins are colorful pigments, which are responsible for the red, purple, and blue colors of many plants and fruits. Studies have demonstrated that these bioactive compounds show functional benefits to humans, such as protection against liver injuries, strong anti-inflammatory and antimicrobial activities, as well as prevention of cardiovascular disease and cancer, due to their antioxidant action.[1,2]

Blackberry (*Rubus* spp.) is a small fruit that originated from Asia and grows in temperate regions worldwide. Blackberry fruits are a good source of natural antioxidants, including anthocyanins, and phenolic acids.[3,4] They have a pleasant aroma and a distinct sweet/sour taste that makes them very attractive for the food industry. However, the fragility and high postharvest respiration rate of blackberries contribute significantly to their nutritional and microbiological deterioration, resulting in limited shelf life and reduced quality and health benefits.[5] Another concern that limits the potential application of blackberry in the industry is that anthocyanins are very sensitive to adverse environmental conditions, such as unfavorable temperatures, light, pH, moisture, and oxygen and are susceptible to degradation reactions during processing and storage.[6]

Spray drying of blackberry pulp has economical potential and represents an alternative for improved fruit conservation. The conversion of liquid blackberry juice into a dry form potentially increases product stability, resulting in reduced volume and packaging and easier handling and transportation. Moreover, the short residence time and the use of lower temperatures make spray drying suitable for heat-sensitive food components, such as anthocyanins found in blackberry.[7] On the other hand, fruit juice powders obtained by spray drying may present some difficulties, such as stickiness, hygroscopicity, and low solubility. In addition, the adhesion of droplets to the dryer chamber walls decreases process yield. According to Bhandari et al.,[8] the sticky behavior of sugar- and acid-rich materials is attributed to low-molecular-weight sugars and organic acids, which have low glass transition temperatures. One method to avoid these problems is the addition of carrier agents before atomization, because their high molecular weight increases the glass transition temperature of the product.

The most common carrier agents used in the spray drying of fruit pulps are maltodextrins and gum arabic, mainly due to their high solubility and low viscosity, which are important conditions for the spray-drying process.[9] These carrier agents may also protect the fruit's bioactive compounds from oxidation. The use of maltodextrin or gum

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arabic during spray drying has been studied in several products, such as açai,[10] bayberry,[6,11] cactus pear,[12,13] mussel protein hydrolysate,[14] red raspberry,[15] chicken meat powder,[16] pomegranate,[17] mixed carrot and watermelon juice,[18] and guava.[19] Blends of gum arabic and maltodextrin have also proven to be efficient in spray drying.[20–22] Nevertheless, research on the determination of the stability of anthocyanins in spray-dried blackberry powder during storage has not been reported.

In this context, the aim of this work was to evaluate the influence of different carrier agents (maltodextrin, gum arabic, or a blend of both carrier agents) and temperature (25 or 35°C) on the stability of anthocyanins and the antioxidant capacity of spray-dried blackberry powder during 5 months of storage. The moisture content, water activity, particle size, morphology, and glass transition temperature of blackberry powders were also determined at the beginning of storage time.

MATERIALS AND METHODS

Materials

Frozen blackberry pulp was purchased from De Marchi Ind. e Com. Ltda. (Jundiaí, Brazil). The pulp was stored in a freezing chamber at −18°C and thawed in a refrigerator (4–5°C) for 18 h, according to the amount required for each test. Table 1 shows its physicochemical composition. The carrier agents used were: maltodextrin (Maltogill 20, Cargill, Uberlândia, Brazil) with 20 dextrose equivalent (DE) and a gum arabic (Instantgum, Colloides Naturels, São Paulo, Brazil).

TABLE 1
Physicochemical properties of blackberry pulp subjected to spray drying[a]

Analysis	Mean value	Method
Moisture content (% wb)	91.96 ± 0.14	AOAC[27]b
Ash (%)	0.20 ± 0.01	AOAC[27]
Proteins (%)	<0.1	AOAC[27]
Lipids (%)	0.10 ± 0.01	AOAC[27]
Reducing sugars (%)	5.35 ± 0.26	AOAC[27]
Total sugars (%)	6.43 ± 0.13	AOAC[27]
Titratable acidity (% citric acid)	0.76 ± 0.01	AOAC[27]
Anthocyanins (mg/100 g dry matter)	969.04 ± 26.19	AOAC[27]
Antioxidant Activity (μmol TE/g dry matter)	424.50 ± 14.17	Brand-Williams et al.[29]
pH	3.31 ± 0.02	pH meter

[a]All data are the mean of triplicate measurements ± standard deviation.
[b]AOAC = Association of Official Analytical Chemists.

Sample Preparation and Spray-Drying Process

The carrier agent—maltodextrin, gum arabic, or a blend (1:1 w/w) of both carrier agents—was added to the pulp in a final concentration of 7 g/100 g fresh juice (w/w), which corresponds to 48 g/100 g total solids. Then, the pulp and the carrier agent were homogenized in a colloid mill (model Rex1, Meteor, São Paulo, Brazil) until complete dissolution. About 2 kg of blackberry pulp was used in each experiment.

The process was performed using a laboratory-scale spray dryer (model B290, Büchi, Flawil, Switzerland) at a drying rate of 1.0 kg water/h. The mixture was fed into the drying chamber at room temperature (25°C) through a peristaltic pump with the flow rate was adjusted to 0.49 kg/h. The inlet air temperature was 145°C and the outlet air temperature varied from 75 to 80°C. Spray drying was carried out with a concurrent regime, using a two-fluid nozzle atomizer (0.7 mm diameter), a drying air flow rate of 0.36 m^3/h, and an aspirator flow rate of 35 m^3/h. These conditions were established in a previous work.[23]

Stability Study

The different powders produced were placed in Petri dishes (50 mm diameter × 15 mm height) such that a large surface area was exposed to air during storage. About 3 g of sample was put in each dish. These dishes were stored in airtight plastic containers filled with $MgCl_2$ saturated solution in order to provide relative humidity of 32.8% over 150 days. The containers were stored at two different temperatures: 25°C, representing room temperature, and 35°C, which was recommend by Labuza and Schmidl[24] for accelerated shelf life studies.

Samples were periodically analyzed with respect to anthocyanin content and antioxidant activity (at days 0, 15, 30, 45, 60, 90, 120, and 150). Powder morphology was also evaluated at the beginning of storage and after 150 days. Furthermore, the moisture content, water activity, mean diameter, and glass transition temperature of all the samples were determined after the spray-drying process (at day 0).

Anthocyanin loss during storage was evaluated using a first-order kinetic model. The reaction rate constants (k) and half-lives ($t_{1/2}$) were calculated using the following equations[25]:

$$-\ln\frac{C_t}{C_0} = kt \tag{1}$$

$$t_{1/2} = \frac{\ln 2}{k}, \tag{2}$$

where C_0 is the initial anthocyanin content, C_t is the anthocyanin content at reaction time t, and half-life $t_{1/2}$ corresponds to the time at which the anthocyanin content is reduced by 50% with respect to zero time.

Q_{10} values were determined according to Eq. (3)[26]:

$$Q_{10} = \frac{k_T}{k_{T-10}}, \tag{3}$$

where k_T is the reaction rate constant at temperature T and k_{T-10} is the reaction rate constant at a temperature 10°C lower.

Analytical Methods

Moisture Content

Moisture content was determined gravimetrically. Samples were weighed and dried in a vacuum oven at 70°C for 24 h.[27]

Water Activity

Water activity was measured in an Aqualab 3TE (Decagon Devices Inc., Pullman, WA) hygrometer at 25°C.

Anthocyanin Content

The anthocyanin content of the samples was determined according to the spectrophotometric pH differential method,[27] which is based on the structural transformation of anthocyanin that occurs with a change in pH (colored at pH 1.0 and colorless at pH 4.5). Two dilutions of each sample were prepared with potassium chloride (0.025 M) and sodium acetate (0.4 M), which were used as buffer solutions at pH 1.0 and 4.5, respectively. Anthocyanins were extracted with an acetone solution (70%), according to the methodology described by Falcão et al.,[28] with some modifications. About 2.5 g of powder and 25 mL of acetone solution (70%) were used in each extraction. Absorbance was measured in a spectrophotometer (model 700Plus, Femto, São Paulo, Brazil) at 520 and 700 nm. Total anthocyanin content was calculated using the molar extinction coefficient of 26,900 L/cm · mol for cyanidin-3-glucoside (cyd-3-glu), which is the predominant anthocyanin found in blackberry pulp.[3] Results were expressed as milligrams ofcyd-3-glu per 100 g pulp (db; excluding the mass of carrier agents).

Antioxidant Activity

Antioxidant activity was determined using 2,2-diphenyl-1-picrylhydrazyl (DPPH), according to Brand-Williams et al.[29] This method is based on scavenging of the stable free radical DPPH by antioxidants, causing a decrease in absorbance measured at 515 nm as the result of a color change from purple to yellow.

The extraction was also done using an acetone solution (70%). About 0.25 g of powder and 25 mL of acetone solution (70%) were used in each extraction. Aliquots of 0.1 mL of these extracts were placed in test tubes with 3.9 mL of a 6×10^{-5} mol/L DPPH methanolic solution, followed by vortex agitation. This reaction was allowed to take place in the dark at room temperature for 60 min, after which absorbance was measured in a spectrophotometer at 515 nm. A methanol solution (80%) was used as a blank to calibrate the equipment. The same analysis was performed for Trolox methanolic solutions in six dilutions varying from 0 to 800 μM, which allowed the construction of a standard Trolox curve. Results were expressed as micromoles of Trolox equivalent per gram of pulp (db, excluding the mass of carrier agents).

Glass Transition Temperature

The glass transition temperature (T_g) of the powders was determined using a differential scanning calorimeter (model DSC 2010, TA Instruments, New Castle, DE, USA). Approximately 4–5 mg of blackberry powders was placed into aluminum pans (20 μL) and equilibrated with $MgCl_2$ saturated solution (relative humidity 32.8%) in desiccators at 25°Cuntil equilibrium was reached (about one week). Samples were then hermetically sealed with lids and weighed. The equipment was calibrated with indium ($T_{melting} = 156.6$°C) and dry nitrogen was used as the purge gas (70 mL/mim). Samples were heated at 10°C/min from 10 to 100°C and then cooled to 25°C at 10°C/min. An empty pan was used as a reference. The midpoint values for glass transition temperature of the samples were calculated using the software Thermal Advantage, version 1.1A (TA Instruments).

Particle Size

The particle size was determined using a laser light diffraction instrument (Mastersizer S, model MAM 5005, Malvern Instruments, Malvern, UK). A small amount of powder was dispersed in 99% isopropanol under magnetic agitation, because solubilization of the particles does not occur in this liquid, and the distribution of particle size was monitored during three successive measurements.[25] The particle size was expressed as $D[4,3]$ (De Brouckere mean diameter), the mean diameter over the volume distribution, which is generally used to characterize a particle.

Scanning Electron Microscopy

The microstructure of the particles was evaluated using scanning electron microscopy (SEM). Powders were attached to SEM stubs using a double-sided adhesive tape and coated with gold/palladium under vacuum in a Polaron sputter coater (model SC7620, VG Microtech, Ringmer, UK) at a coating rate of 0.51 Å/s, 3–5 mA, 1 V, and 0.08–0.09 mbar for 180 s. The coated samples were observed with a LEO440i scanning electron microscope (LEICA Electron Microscopy Ltd., Oxford, England).

The SEM was operated at 20 kV and 150 pA with magnification of 2,000×.

Statistical Analysis

The experiments were carried out in duplicate and all analyses were done in triplicate. Results were presented as mean values with standard deviations. Different mean values were statistically evaluated by analysis of variance (ANOVA) using Statistica 8.0 (StatSoft, Inc., Tulsa, OK).Mean separation was determined using Tukey's test at $p \leq 0.05$.

RESULTS AND DISCUSSION

Moisture Content, Water Activity, and Particle Size

The moisture content of blackberry powders varied between 3.25 and 4.42% (Table 2), close to the values obtained for red raspberry[15] and mulberry[22] produced by spray drying. Blackberry powder produced with 7% maltodextrin showed significantly lower moisture content ($p \leq 0.05$) compared to the other samples. Righetto and Netto[30] also observed that maltodextrin (25DE) was more effective than gum arabic in reducting the moisture content of spray-dried acerola powder, probably due to the differences between the chemical structure of both carrier agents, because gum arabic is a complex heteropolysaccharide with a ramified structure, containing shorter chains and hydrophilic groups.

All the samples showed water activity, a_w, values below 0.4, which is very positive for powder stability, because it represents less free water available for microorganism growth and biochemical reactions and thus longer shelf life.[31] Powders produced with maltodextrin presented the lowest water activities, which is in agreement with moisture content values obtained. Similar water activity values were obtained by Quek et al.[9] and Tonon et al.[10] in their studies with watermelon and açai powders.

At the beginning of storage, the total anthocyanin contents of spray-dried blackberry powder produced with maltodextrin, gum arabic, and a blend of both carrier agents were 665.96 ± 2.30, 545.12 ± 0.99, and 637.33 ± 1.72 mg/100 g pulp (db), respectively (Table 2). Considering the mass of carrier agents, these values correspond to 343.84 ± 1.31, 281.44 ± 0.53, and 329.05 ± 0.91 mg/100 g spray-dried powder, respectively.

The mean diameter of particles produced with maltodextrin was statistically higher ($p \leq 0.05$) than that of the other samples, which was related to their better reconstitution properties.[11,32] In addition, the presence of larger particles may decrease the powder exposure to oxygen, protecting the pigments against oxidation. The smaller the particles, the larger the exposed surface area and, consequently, the faster the degradation of compounds susceptible to deterioration.[9] Thus, the lower mean diameter values obtained for spray-dried blackberry powders with gum arabic probably contributed to the lower anthocyanin content observed in this condition.

Stability of Anthocyanins

Figure 1 shows that anthocyanin degradation of blackberry powders produced with different carrier agents followed first-order kinetics throughout storage. A similar trend was verified in research on microencapsulation of anthocyanins[20,33,34] and betalains[13] by spray drying. Tonon et al.[25] observed two first-order kinetics for the anthocyanin degradation of spray-dried açai powder: the first one, with a higher reaction rate constant, up to 45–60 days of storage, and the second with lower degradation rate until the end of storage (120 days). According to the authors, the higher degradation rate can be attributed to the nonencapsulated material, which shows greater contact with oxygen, or even to the material in contact with the oxygen present in the interior of pores. Furthermore, the higher water adsorption at the beginning of storage maybe responsible for the higher degradation rate, because a higher water content implies greater molecular mobility.

The kinetic parameters for anthocyanin degradation in spray-dried blackberry powders are shown in Table 3. The Q_{10} values were higher than 1, meaning that as temperature increased, anthocyanin degradation also increased

TABLE 2
Moisture content, water activity, anthocyanin content, mean diameter (D[4,3]), and glass transition temperature (T_g) of spray-dried blackberry powders produced with maltodextrin (7%MD), gum arabic (7%GA), or a blend of both carrier agents (3.5%MD + 3.5%GA) at the beginning of storage

Sample	Moisture content (%)	Water activity	Anthocyanin content (mg/100 g pulp, db)	Mean diameter D[4,3] μm	T_g (°C)
7%MD	3.25 ± 0.09a	0.259 ± 0.002a	665.96 ± 2.30a	43.67 ± 1.76a	60.23 ± 1.98a
7%GA	4.42 ± 0.13b	0.314 ± 0.003b	545.12 ± 0.99b	10.53 ± 0.03b	51.33 ± 2.17b
3.5%MD + 3.5%GA	3.83 ± 0.12c	0.278 ± 0.003c	637.33 ± 1.72c	28.81 ± 1.17c	57.50 ± 2.06a

Means with different letters in the same column indicate significant differences at $p \leq 0.05$.

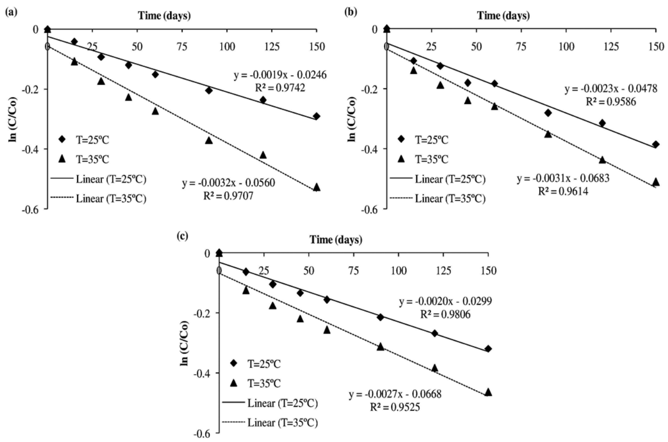

FIG. 1. Anthocyanin degradation kinetics of spray dried blackberry powders produced using different carrier agents: (a) 7% maltodextrin; (b) 7% gum arabic; (c) 3.5% maltodextrin + 3.5% gum arabic.

due to the high sensitivity of these pigments to heat. The negative effect of temperature on the stability of anthocyanins has been reported in many works available in the literature. Fang and Bhandari,[6] working with bayberry powder produced by spray drying, verified anthocyanin losses of about 7–27% after 6 months of storage at 4°C, and the reduction in anthocyanin content at 25°C was around 9–37%. Ersus and Yurdagel[33] evaluated the stability of microencapsulated anthocyanins of black carrots by spray drying and observed a degradation rate three times higher in the samples stored at 25°C compared to the powders stored at 4°C.

The acceleration of anthocyanin degradation at higher temperatures is associated with the Maillard reaction (nonenzymatic browning), which normally occurs in the presence of reducing sugars and proteins during storage for long times and/or food processing and is intensified by the presence of oxygen. The products of the Maillard reaction (furfural and hydroxymethylfurfural) easily condense with the anthocyanins, forming compounds with a brown coloration.[25,35] Ersus and Yurdagel[33] observed that after 8 weeks of storage, the pink color of anthocyanins extracted from black carrots was maintained during storage at 4°C but at 25°C a color change to brown was observed. In a similar study, Osorio et al.[36] verified the color changes (from red to brown) in anthocyanin microcapsules of corozo fruit stored at higher temperatures.

During storage at 25°C, particles produced with maltodextrin had the longest half-life, followed by those produced with the blend of both carrier agents, whereas samples produced with gum arabic showed a higher reaction rate constant and, consequently, a shorter half-life. For samples stored at 35°C, the combination of maltodextrin and gum arabic resulted in longer half-lives, whereas spray-dried blackberry powders with 7% maltodextrin had the fastest degradation rate and the lowest half-life (Table 3). In addition, powders produced with maltodextrin showed the highest Q_{10} value (1.68), indicating that anthocyanin degradation is dependent on temperature.

Righetto and Netto observed that blends of maltodextrin and gum arabic were also more effective in the preservation of vitamin C in acerola powder during storage at 35°C.[21] However, the authors did not observe a significant influence of different formulations on the vitamin C retention in samples stored at 15 or 25°C. In another work, Nayak and Rastogi[20] verified that the combined effect of maltodextrin and gum arabic enhanced the stability of microencapsulated anthocyanins by spray drying, probably due to the emulsifying properties of gum arabic.

Evaluating the stability of spray-dried *Amaranthus* bethacyanins at 25°C for 16 weeks, Cai and Corke[37] observed that the use of maltodextrin (20 or 25DE) resulted in the formation of denser and more oxygen-impermeable wall systems, providing better storage stability for betacyanin pigments. In the present study, because the effect of temperature on the stability of anthocyanins was more pronounced in spray-dried powders produced with maltodextrin, oxygen permeation through the food matrix probably increased at 35°C, accelerating the anthocyanin degradation in these samples.

Working with spray-dried açai powder, Tonon et al.[25] reported longer half-lives for particles produced with maltodextrin 10DE compared to powders produced with maltodextrin 20DE and tapioca starch. According to the authors, the highest anthocyanin retention observed was related to the particle size distribution, because a small number of particles with mean diameter smaller than 1 μm were observed. The smaller the particles, the greater the exposed surface area and, therefore, the faster the degradation of compounds susceptible to deterioration. This association between particle size and the stability of anthocyanins was also verified in the present work, because

TABLE 3
Kinetic parameters for anthocyanin degradation in spray-dried blackberry powders produced with maltodextrin (7%MD), gum arabic (7%GA), or a blend of both carrier agents (3.5%MD + 3.5%GA) stored under different temperatures

Sample	T (°C)	k (days^{-1})	$t_{1/2;}$ (days)	R^2	Q_{10}
7%MD	25	0.0019	373.80	0.974	1.68
	35	0.0032	213.86	0.971	
7%GA	25	0.0023	297.48	0.959	1.35
	35	0.0031	225.36	0.961	
3.5MD +	25	0.0020	347.68	0.981	1.35
3.5%GA	35	0.0027	253.15	0.952	

samples produced with 7% maltodextrin showed the largest particle size and the highest anthocyanin content (Table 2) and greater stability at 25°C (Table 3). However, at 35°C, powders produced with maltodextrin presented a large number of agglomerates with the formation of link bridges between the particles (Fig. 2b), in addition to greater anthocyanin degradation (Table 3) after 150 days of storage. Thus, the morphological characteristics, as well as the influence of storage temperature on anthocyanin degradation, prevailed over the particle size effect in blackberry powders formulated with maltodextrin and stored at 35°C.

Antioxidant Activity

The antioxidant activities throughout the 150 days of storage are presented in Fig. 3. Powders produced with maltodextrin or gum arabic and stored at 35°C showed significantly higher antioxidant activity values ($p \leq 0.05$) during storage compared to the samples stored at 25°C (Figs. 3a and 3b). For particles produced with the blend of both carrier agents, a significant effect of temperature on the antioxidant activity was observed from day 45 onwards (Fig. 3c). Tonon et al.[25] also verified higher antioxidant activity values in spray-dried açai powder as

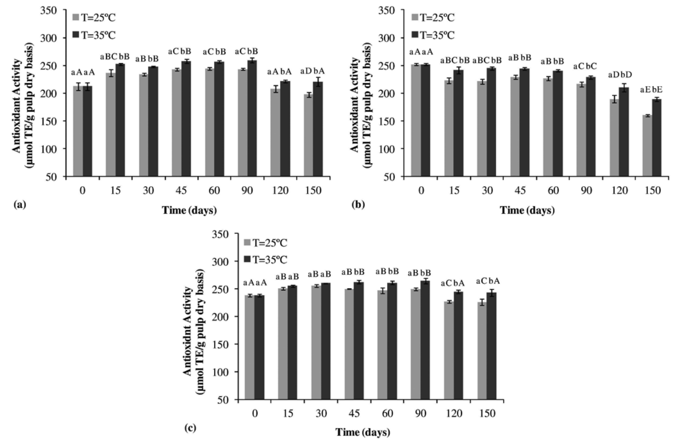

FIG. 3. Antioxidant activity of spray dried blackberry powders produced using different carrier agents along storage. (a) 7% maltodextrin; (b) 7% gum arabic; (c) 3.5% maltodextrin + 3.5% gum arabic. Different letters indicate significant differences at $p \leq 0.05$ (small letters among different temperatures for the same time, capital letters among different times for the same temperature). Bars represent the mean standard error.

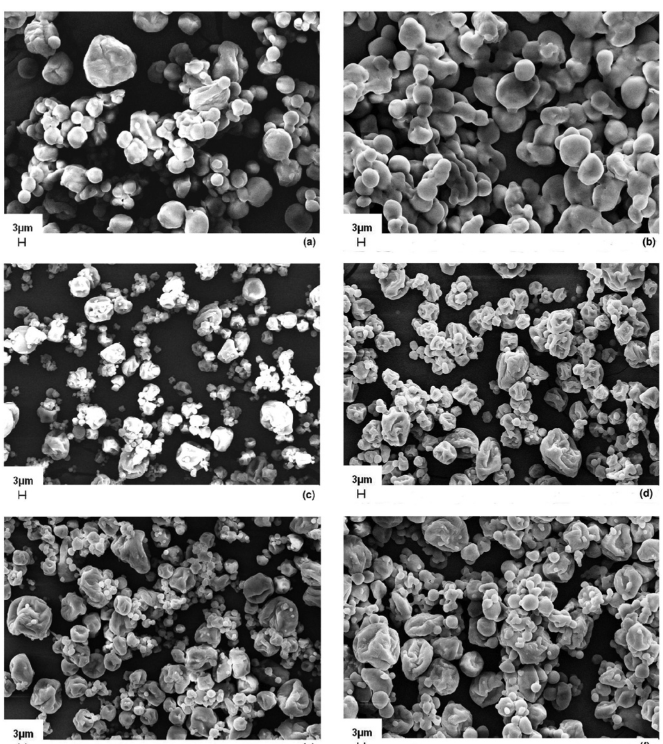

FIG. 2. Scanning electron microscopy micrographs of spray dried blackberry powders produced using different carrier agents at the end of storage. (a) and (b): 7% maltodextrin; (c) and (d): 7% gum arabic; (e) and (f): 3.5% maltodextrin + 3.5% gum arabic. (a), (c), and (e): samples stored at T = 25°C; (b), (d), and (f): samples stored at T = 35°C. Magnification = 2000×.

storage temperature increased. The authors attributed this behavior to two possible factors: The occurrence of the Maillard reaction and the presence of some compounds in açai, other than polyphenols, that contribute to its antioxidant capacity. Storage at 35°C could have increased the bioavailability of these unknown compounds, thus increasing the product's antioxidant potential.

The Maillard reaction was observed in acerola powder obtained by spray drying during 9 months of storage.[21] The reaction followed a zero-order kinetic model; that is, a linear increase with time. Samples produced with the blend 15% maltodextrin + 5% gum arabic presented the lowest reaction rate constants at higher temperatures (35 or 45°C), indicating that the combination of these carrier agents offered the best protection against nonenzymatic browning and vitamin C degradation.

Particles produced with gum arabic showed higher antioxidant activity at day 0 (around 250 μmol TE/g pulp, db) compared to the other samples (Fig. 3b). It is possible that the protein fraction of gum arabic may have contributed to the occurrence of the Maillard reaction during the spray-drying process, resulting in a significant increase in antioxidant activity in this sample at the beginning of storage. A statistically significant decrease in antioxidant activity ($p \leq 0.05$) in powders produced with gum arabic was also observed overtime, reaching values around 160 or 190 μmol mol TE/g pulp (db) at 25 or 35°C, respectively, after 150 days (Fig. 3b). This reduction was related to the faster anthocyanin degradation and higher reaction rate constants observed in spray-dried samples containing gum arabic during storage (Fig. 1b and Table 3), meaning that the protective effect of this carrier agent on the maintenance of antioxidant properties of blackberry powder was less pronounced. On the other hand, Pitalua et al.[35] reported a significant increase in antioxidant activity of beetroot powder produced by spray drying, using gum arabic as carrier agent, during storage at 30°C for 45 days. The authors stated that the protein fraction of gum arabic favored the Maillard reaction, resulting in the formation of intermediary compounds, which may increase the antioxidant activity of the final product. Nevertheless, this behavior was not noticed for powders produced with gum arabic in the present study, suggesting that the reduction in anthocyanin content throughout storage prevailed over the possible formation of degradation compounds.

The use of 7% maltodextrin resulted in a significant increase ($p \leq 0.05$) in antioxidant activity in blackberry powder up to the 90th day, followed by a statistically significant reduction ($p \leq 0.05$) until the end of storage at 25 or 35°C (Fig. 3a). Because the protein content of blackberry pulp was lower than 0.1% (Table 1), the increase in antioxidant activity in these samples was probably due to hydrolysis of phenolic compounds during the drying process or storage.[13,34] The same trend was verified for samples produced with the blend of both carrier agents (Fig. 3c). This behavior could be also related to the hydrolysis of phenolic compounds or even to the formation or release of compounds with antioxidant potential able to quench free radicals, such as the intermediary compounds of the Maillard reaction.[35]

Powder Morphology

The morphological characteristics of spray-dried blackberry powders at the beginning of storage are shown in Fig. 4. All of the particles showed predominantly spherical shapes of several sizes, which is typical of materials produced by spray drying. Particles produced with gum arabic were smaller and had shriveled surfaces (Fig. 4b), whereas larger and more agglomerated particles with smooth surfaces were obtained when maltodextrin or the combination of both carrier agents was used (Figs. 4a and 4c). These results are in accordance with particle size values previously observed (Table 2).

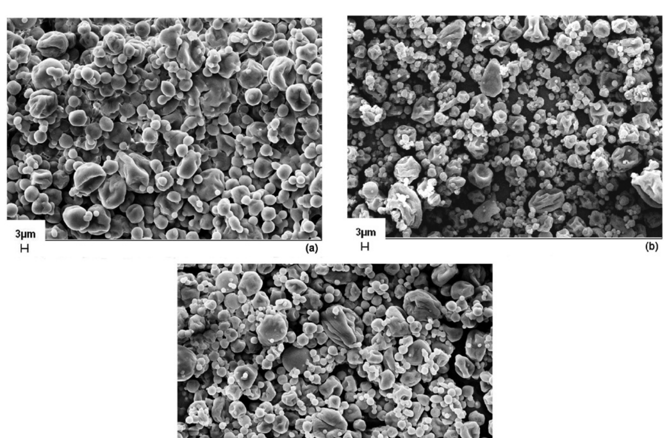

FIG. 4. Scanning electron microscopy micrographs of spray dried blackberry powders produced using different carrier agents at the beginning of storage. (a) 7% maltodextrin; (b) 7% gum arabic; (c) 3.5% maltodextrin + 3.5% gum arabic. Magnification = 2000×.

Figure 2 shows the SEM micrographs of spray-dried blackberry powders after 150 days of storage at 25 or 35°C.

At the end of the storage period, samples produced with maltodextrin and stored at 35°C showed a strong tendency to agglomerate, with formation of link bridges between the particles (Fig. 2b). At 25°C, despite the beginning of agglomeration, spherical-shape particles as well as smooth surfaces were observed (Fig. 2a). On the other hand, micrographs of blackberry powder with 7% gum arabic revealed a large number of irregular and smaller particles as well as a wrinkled structure after 150 days (Figs. 2c–2d), as also verified at the beginning of storage. Powders produced with both carrier agents presented some wrinkled particles of various sizes (Figs. 2e–2f).

According to Saénz et al.,[13] dents are formed due to the shrinkage of particles during drying and cooling, and the presence of these dents has an adverse effect on the flow properties of powder particles. Moreover, smooth spheres are desirable for the stability of encapsulated ingredients and for controlled release, as pointed out by Osorio et al.[36] In the present work, blackberry powders obtained with 7% maltodextrin and stored at 25°C presented a large number of smooth particles and were more stable, showing the lowest anthocyanin degradation and the longest half-lives, as discussed earlier. However, the highest Q_{10} value obtained (Table 3) indicated that these powders were more sensitive to temperature changes. The faster degradation rate of anthocyanin in powders produced with gum arabic and stored at 25°C is associated with the greater number of wrinkled particles. These wrinkled particles are the result of collapsed hollow spherical structures, due to the fast water evaporation, which may lead to the formation of microfissures.[7] The presence of microfissures on the surface of the particles contributes to the increase of nonencapsulated core, reducing the protection of anthocyanins against oxidation reactions. Moreover, determination of the encapsulation efficiency was based on the anthocyanin retention after spray drying. Anthocyanin retention of powders produced with maltodextrin, gum arabic, or a blend of both carrier agents was around 85, 81, and 70%, respectively, meaning that maltodextrin was more effective in the preservation of these pigments.

In spray drying of mulberry juice, Fazaeli et al.[22] observed that particles produced with maltodextrin 20DE were larger, amorphous, piled up, and had a strong attraction to each other, but when gum arabic was used, the particles tended to become more spherical and scattered.

On the other hand, Tonon et al.[10] verified that spray-dried açai powder with gum arabic or maltodextrin (10 or 20DE) showed similar morphological characteristics, exhibiting mostly spherical particles and shriveled surfaces.

Glass Transition Temperature

The glass transition temperature (T_g) of a spray-dried powder can be used as an indicator of stability during long periods of storage.[38] According to Table 2, the T_g values of spray-dried blackberry powders ranged from approximately 51 to 60°C, indicating that all of the samples were in the glassy state at 25 or 35°C ($T_{storage} < T_g$). These T_g values were in the same range as those reported for açai powder obtained by spray drying using maltodextrin (10 or 20DE) or gum arabic.[39] Righetto and Netto[30] found lower T_g values for spray-dried acerola powder produced with maltodextrin 25DE or gum arabic compared to blackberry, which can be attributed to the higher sugar and acid contents present in acerola. The authors also stated that, regardless of the carrier agent used, the T_g values for all of the powders were similar (between 39.5 and 41.6°C) at a relative humidity of 33%.Because all of the encapsulated samples contained the same amount of solids derived from the juice (44%) and from the encapsulating agents (56%), as well as similar water contents, the T_g values of the encapsulated juices were expected to be similar, as was indeed the case.

Particles produced with gum arabic showed the lowest T_g values. This behavior suggests that, although all of the blackberry powders were in the glassy state, samples produced with gum arabic were less stable, which is consistent with the results of this work, because these powders showed faster anthocyanin degradation and a significant reduction in antioxidant activity during storage at 25°C. Furthermore, these samples showed higher moisture contents and water activities at the beginning of storage (Table 2), which probably contributed to the lower glass transition temperatures, as also reported by Righetto and Netto.[30]

Studying the microencapsulation of anthocyaninsin *Garcinia indica* Choisy by spray drying, Nayak and Rastogi[20] observed that microcapsules produced with maltodextrin 33DE had lower stability, as well as a lower glass transition temperature and the lowest anthocyanin contents and antioxidant activities. However, no significant differences were seen between the T_g values of microencapsulated samples using maltodextrin (20DE) or a blend of maltodextrin (20DE), gum arabic, and tricalcium phosphate.

CONCLUSIONS

Anthocyanin degradation in spray-dried blackberry powders exhibited first-order kinetics throughout storage. Temperature negatively affected the stability of anthocyanins due to the high thermosensitivity of these pigments. However, antioxidant activity increased with increasing temperature as a consequence of the Maillard reaction, which promotes the formation of compounds with antioxidant activity. The use of maltodextrin or the combination of both carrier agents resulted in better maintenance of antioxidant potential of spray-dried blackberry powder. Particles produced with 7% maltodextrin presented the longest half-life and lowest anthocyanin degradation rate at 25°C in addition to the highest glass transition temperature. However, these powders showed the highest Q_{10} value, indicating that they were more sensitive to temperature changes. The morphological analysis of powders produced with maltodextrin revealed the presence of larger particles and smooth surfaces, which probably contributed to the greater protection of pigments observed in this condition during storage at 25°C. Therefore, spray drying of blackberry pulp using maltodextrin resulted in more stable powders, rich in anthocyanins and with high antioxidant activity, that can be incorporated into different food products as a functional ingredient.

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