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Effect of encapsulating agent and drying air temperature on the characteristics of microcapsules of anthocyanins and polyphenols from *juçara* (*Euterpe edulis* Martius)

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Abstract

Anthocyanins are natural pigments that provide attractive colours to food products and have potential health benefits. These pigments are present in large quantities in *juçara* palm plant (*Euterpe edulis* Martius). However, anthocyanins are unstable under certain technological processes, thereby motivating the use of microencapsulation to maintain their stability. The present work was therefore aimed to evaluate the microencapsulation of anthocyanins from *juçara* palm plant by spray drying using different encapsulating agents (maltodextrin, gum Arabic, inulin) and outlet air temperatures (50, 55, 60, 65, 70°C). To this end, the anthocyanins retention, total phenolic contents, antioxidant activity, hygroscopicity, wettability, scanning electron microscopy (SEM), and X-ray diffraction were evaluated. These responses were simultaneously optimised using the desirability tool, and it was observed that microcapsules produced with 10 DE maltodextrin at 50°C, gum Arabic at 70°C, and inulin at 70°C showed the most desirable characteristics, while those with maltodextrin had the highest desirability (0.85). SEM analysis indicated the presence of spherical capsules of uniform size and X-ray diffraction allowed the identification of the microcapsules amorphous structure. These results demonstrate the effectiveness of microencapsulation under such optimised conditions.

Introduction

The market demand for natural pigments and the development of food products comprising natural dyes instead of their synthetic analogues have increased, thereby encouraging researchers to investigate the stability of these pigments in food matrices (Nayak and Rastogi, 2010; Mahdavi *et al*., 2014). Anthocyanins are a group of naturally occurring phenolic compounds derived from plant pigments and are of great interest for the food industry. They provide attractive colours to food products as well as having various beneficial health effects (Mahdavi *et al*., 2014; Zaidel *et al*., 2014) due to their antioxidant activity which protects organisms against oxidative damages, thereby preventing various diseases such as cancer, cardiovascular diseases and diabetes (Olatunya and Akintayo, 2017).

A promising source for this pigment is the fruit of *juçara* palm plant (*Euterpe edulis* Martius), a tropical and exotic fruit with great consumption potential. The skin of this fruit naturally has a dark purple colour due to the presence of anthocyanins. Its sensory and physicochemical characteristics are similar to those of the Amazon *açaí* berry (*E. oleracea* Martius; Carvalho *et al*., 2016). *Juçara* fruits can be used as functional foods because of their antioxidant capacity (Lima *et al*. 2012; Bicudo *et al*. 2016). However, the use of such pigments might be limited due to their instability under certain technological processes.

Microencapsulation is a technique often used to mitigate changes that occur in natural dyes over time (Bakowska-Barczak and Kolodziejczyk, 2011; Bernstein and Noreña, 2015), and might be applied to overcome some of the restrictions of antioxidants in order to increase their applicability (Aguiar *et al*., 2017). It is a promising alternative to stabilise pigments during food processing and storage as it might provide greater stability to heat, light and pH, thus increasing the food shelf life (Nayak and

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Rastogi, 2010; Murugesan and Orsat, 2011; Zaidel *et al.*, 2014; Santhalakshmy *et al.*, 2015). Spray drying is one of the most common methods to encapsulate food ingredients due to its economic feasibility, simplicity, flexibility, ease of handling and ability to produce high quality and highly stable particles (Mahdavi *et al.*, 2014; Di Battista *et al.*, 2015; Muzaffar and Kumar, 2015; Aguiar *et al.*, 2017) resulting in longer shelf life, lower water activity and therefore suitability for transportation and storage (Muzaffar and Kumar, 2017). The application of this technique might result in nutritionally rich products by promoting the retention of anthocyanins and preserving their antioxidant activity during food processing and storage (Tonon *et al.*, 2010).

The effectiveness of microencapsulating depends on the correct choice of the encapsulating agent, temperature, drying conditions, juice extraction, additives and other processing parameters, as recently studied by other authors (Murugesan and Orsat, 2011; Bernstein and Noreña, 2015; Khattab *et al.*, 2016; Chong and Wong, 2017; Muzaffar and Kumar, 2016, 2017). The encapsulating agent influences the powder properties and stability (Santhalakshmy *et al.*, 2015), and should have some favourable characteristics including the ability to form films, high solubility in food-grade solvents, low hygroscopicity, high emulsifying power, economic viability, usefulness and biodegradability (Barros and Stringheta, 2006; Robert and Fredes, 2015). Some polysaccharides have been widely used as encapsulating agents including (i) maltodextrin, which is obtained by acid hydrolysis of various starches and extensively used in the food industry (Saenz *et al.*, 2009; Chong and Wong, 2017); (ii) gum Arabic, which is a natural resin extracted from two sub-Saharan acacia tree species and often used as thickener and stabiliser (Murugesan and Orsat, 2011; Bernstein and Noreña, 2015); and (iii) inulin, which is a polysaccharide from the fructan group with prebiotic effects and high solubility in water, being extracted primarily from chicory (*Cichorium intybus*) roots (Toneli *et al.*, 2010; Fernandes *et al.*, 2014).

The objective of the present work was therefore to microencapsulate anthocyanins extracted from the pulp of *juçara* fruits using different encapsulating agents (maltodextrin, gum Arabic, and inulin) and outlet air temperatures during spray drying (50, 55, 60, 65, 70°C) in order to select the best parameters that lead to powders with desirable characteristics.

Materials and methods

Materials

Frozen *juçara* pulp was acquired from an agricultural company located in the southern Espírito Santo state, Brazil. Three encapsulating agents were used in the microencapsulation process, namely: maltodextrin (Maltogill® 10 DE, Cargill), inulin (ORAFTI (Beneo) GR, Clariant), and powdered gum Arabic (Synth).

Anthocyanin extraction

Anthocyanins were extracted as detailed by Francis (1982) with modifications, using 70% (v/v) ethanol and 70% (w/v) citric acid for acidification to pH 2.5. Extraction was performed in the dark for 24 h under refrigeration (8 ± 2°C) condition. The extract was filtered using Whatman no. 1 paper in Buchner funnel attached to a vacuum pump, and then transferred to a rotary evaporator (Fisatom, model 801) for vacuum concentration to 40% of the initial volume at 60°C. These extract concentrations were defined in preliminary experiments (data not shown).

Encapsulating agents and microcapsule preparation

Encapsulating agents at 30% (w/v) were added to the concentrated extracts at a 1:3 ratio (extract:agent, v/v) according to Silva *et al.* (2013). Mixtures were homogenised using a magnetic stirrer and dried on a mini spray dryer (Yamato, model ADL 311S) with a maximum compressed air pressure of 0.1 MPa, a flow rate of 2.0 mL/min, and a drying air flow of 0.21 m^3/min. For each encapsulating agent, five outlet air temperatures of the spray dryer were tested: 50, 55, 60, 65, and 70°C. Powders were then transferred to polyethylene flasks containing a laminated layer and maintained at –18 ± 2°C.

Experimental design and statistical analysis

A completely randomised design (CRD) with a factorial arrangement comprising two factors and three replicates was used, with three levels of encapsulating agents and five levels of outlet air temperatures in the spray dryer. In order to analyse the effects of specific factors on response variables, analysis of variance (ANOVA) and Tukey's test were performed.

Desirability analysis was conducted to simultaneously optimise the response variables using the Statistica® software, version 10 (StatSoft In., Tulsa, USA) in a process involving two steps: (i) finding the levels of the independent variables that simultaneously produced the most desired responses (dependent variables), and (ii) determining the overall desirability considering all dependent variables after obtaining the desired responses for each dependent variable. Each dependent variable, y_i, was converted to an individual desirability function, d_i, in the range of $0 \leq d_i \leq 1$ using Equation 1 for variables that were maximised and Equation 2 for variables that were minimised (Derringer and Suich, 1980).

$$d_i = \begin{cases} 0 & \hat{y}_i < L_i \\ \left(\frac{y_i - L_i}{T_i - L_i}\right)^{r_i} & L_i \leq \hat{y}_i \leq T_i \\ 1 & \hat{y}_i > T_i \end{cases} \qquad \text{(Equation 1)}$$

$$d_i = \begin{cases} 1 & \hat{y}_i < T_i \\ \left(\frac{y_i - T_i}{U_i - T_i}\right)^{r_i} & L_i \leq \hat{y}_i \leq T_i \\ 0 & \hat{y}_i > T_i \end{cases} \qquad \text{(Equation 2)}$$

where T_i = target values, L_i = minimum values for the responses to be maximised, and U_i = maximum values for the responses to be minimised.

Individual desirability values were combined using the geometric mean which provided the overall desirability, D, where k = number of response variables to be optimised (Equation 3).

$$D = (\prod^{k}_{i} = 1)^{1/k} \qquad \text{(Equation 3)}$$

Responses related to anthocyanin retention, antioxidant activity and total phenolic content were maximised, whereas the remaining responses were minimised, because the goal was to produce powders with a high content of bioactive compounds, high antioxidant activity, low hygroscopicity and short wetting time.

Physicochemical characterisation of microcapsules

Anthocyanins retention

One gram of powder was reconstituted in 16 mL acidified water and diluted in an extraction solution of 1.5 N ethanol:HCl (85:15 v/v). The anthocyanin contents in the concentrated extracts and powders were determined by reading the absorbance in a spectrophotometer (BEL Photonics, model SP 2000 UV) at 510 nm using an absorption coefficient of 98.2 L/cm·g (Lees and Francis, 1972). Anthocyanin retention after each drying condition was calculated by measuring the total anthocyanin content in the concentrated extract, in mg/100 g of dry matter, values which were compared with the concentrations obtained in each powder (Tonon *et al*., 2010; Silva *et al*., 2013).

Total phenolic contents

The total phenolic contents (TPC) were determined via Folin-Ciocalteu reagent assay, adapted from the methodology proposed by Singleton and Rossi (1965). The extract obtained by powder reconstitution was diluted in 70% ethanol (v/v) in a 10 mL volumetric flask and centrifuged at 2,260 g for 15 min (Fanem Excelsa II, model 206 BL). A 0.6 mL aliquot of the extract was mixed with 3.0 mL Folin-Ciocalteu reagent diluted in distilled water (1:10 v/v). After 3 min of reaction in the dark, 2.4 mL saturated Na2CO3 solution (7.5% w/v) was added. The absorbance was read at 760 nm in a spectrophotometer after 1 h of reaction in the dark. The TPC was determined using a standard curve of gallic acid (0-150 mg/L) and results were expressed in mg of gallic acid equivalent per 100 gram of sample (mg GAE/100 g).

Antioxidant activity using ABTS

The antioxidant activity (AA) was analysed using 2,2'-azinobis-(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS) reagent according to Re *et al*. (1999). Radical ABTS$^{\bullet+}$ was prepared by mixing 10 mL ABTS aqueous solution at 7 mM and 10 mL of 2.45 mM potassium persulphate solution mixture which was maintained in the dark for 16 h. The absorbance at 734 nm was corrected to 0.700 in a spectrophotometer with the addition of 80% ethanol (v/v). The extract obtained by powder reconstitution was diluted in 80% ethanol (v/v) in a 10 mL volumetric flask and centrifuged at 2,260 g for 15 min (Fanem Excelsa II, model 206 BL). Afterwards, 3.5 mL ABTS$^{\bullet+}$ was added to 0.5 mL of each extract, and the spectrophotometric reading was performed after 6 min of reaction. The antioxidant activity was determined using a standard curve of Trolox (0-150 mM), and results were expressed in Trolox equivalents (mM Trolox/g).

Hygroscopicity

The hygroscopicity was measured by storing approximately 2.5 g dried samples in a desiccator containing saturated solutions of NaCl (75% relative humidity, 0.75 a_w) at 25°C. After 1 w, samples were weighed and the hygroscopicity was expressed in grams of absorbed moisture per 100 g of dry matter (g/100 g) (Cai and Corke, 2000; Silva *et al*., 2013).

Wettability

The wettability was evaluated according to Hla and Hogekamp (1999) with modifications (Vissoto *et al*., 2006), by measuring the wetting time, which is the period needed for a powder sample to be fully submerged after being placed on the surface of a liquid. It consisted of dropping 2.0 g powder sample into 400 mL distilled water at 25°C in a 1 L beaker, and the period required for all particles to become wet was recorded as visually determined.

Scanning electron microscopy (SEM)

The morphology and size of the microcapsules were analysed by SEM. A small amount of sample was fixed onto metallic stubs with double-sided adhesive carbon tape. Samples were then coated with a thin layer of gold under vacuum using a sputter coater (Balzers, model FDU-010). Samples were analysed at magnifications of 220 – 10,000× in a scanning electron microscope with an excitation voltage of 20 kV (Silva *et al*., 2013; Rutz, 2013).

X-ray diffraction

The microparticle structure (crystalline or amorphous) was characterised by an X-ray diffractometer (BRUKER, model D8 Discover) using copper radiation as the X-ray source, a voltage of 40 kV, a current of 40 mA, and steps of 0.05° at 1 sec per step. Measurements were performed at 2θ ranging from 4° to 45° (Rutz *et al*., 2013).

Results and discussion

Effect of encapsulating agent and temperature on response variables

Through ANOVA (data not shown), an isolated effect ($p < 0.05$) of the encapsulating agent factor on anthocyanin retention, total phenolic compounds and hygroscopicity was observed.

Inulin yielded the lowest anthocyanin average retention (59.00 ± 4.86%), whereas gum Arabic yielded the highest average retention (82.37 ± 18.26%). However, these values were not significantly different ($p > 0.05$) from that of maltodextrin (74.56 ± 14.82%) (Table 1). Carvalho *et al*. (2016) found that anthocyanin retentions ranged from 88 to 98% in spray dried *juçara* powder, which were significantly influenced by the type of encapsulating agent (maltodextrin, gum Arabic, or a mixture of both). Bernstein and Noreña (2015) evaluated the retention of red cabbage anthocyanins microencapsulated by gum Arabic and polydextrose and found the highest retention for 15% gum Arabic (97.10%). Cai and Corke (2000) microencapsulated amaranthus betacyanins, and observed that maltodextrins of 25 and 10 dextrose equivalents (DE) presented the highest pigment retention (97.30% and 88.70%, respectively). Therefore, it could be concluded that maltodextrin and gum Arabic effectively boosted anthocyanin retention, thus indicating that these materials could be used to increase the retention of microencapsulated natural pigments.

Similar ANOVA results for anthocyanins were observed regarding total phenolic compounds. This could be because anthocyanins constitute a class of phenolic compounds and might have similar behaviour. Different materials yielded different concentrations of phenolic compounds: inulin showed the least desirable results (187.67 ± 12.93 mg GAE/100 g) ($p < 0.05$), while powder with maltodextrin presented the highest value (234.20 ± 15.58 mg GAE/100 g) (Table 1). According to Murugesan and Orsat (2011), maltodextrin and gum Arabic turned out to be suitable wall materials for spray dried elderberry juice with low phenolic content loss. In the present work, this was also observed for anthocyanins and phenolic compounds from *juçara* pulp.

Table 1: Equations used for each variable response to calculate desirability, and parameters of individual desirability for each response

Variable response	Maltodextrin	Gum Arabic	Inulin	T_i	L_i	U_i
Anthocyanins retention (%)	$\hat{Y} = \bar{Y} = 74.56$	$\hat{Y} = \bar{Y} = 82.37$	$\hat{Y} = \bar{Y} = 59.00$	80.03	56.66	–
TPC (mg GAE/100 g)	$\hat{Y} = \bar{Y} = 234.20$	$\hat{Y} = \bar{Y} = 203.07$	$\hat{Y} = \bar{Y} = 187.67$	229.55	183.02	–
AA (mM Trolox/g)	$\hat{Y} = 304.460 – 7.056T + 0.0420T^2$	$\hat{Y} = \bar{Y} = 34.02$	$\hat{Y} = 48.273 – 0,6742T + 0.008786T^2$	70.54	29.96	–
Hygroscopicity (%)	$\hat{Y} = \bar{Y} = 13.07$	$\hat{Y} = - 26.35 + 1.54T + 0.014T^2$	$\hat{Y} = 15.77 – 0.024T$	13.49	–	17.73
Wettability (min)	$\hat{Y} = 57.8786 – 1.9295T + 0.001680T^2$	$\hat{Y} = 26.2152 – 0.6820T + 0.005357T^2$	$\hat{Y} = 8.5928 – 0.2807T + 0.002395T^2$	0.87	–	5.57

TPC: Total phenolic content; AA: antioxidant activity

$\hat{Y}$: variable responses; $\bar{Y}$: mean; T: temperature.

T_i: target values; L_i: minimum values for the responses to be maximised, U_i: maximum values for the responses to be minimised.

For hygroscopicity, both temperature and encapsulating agent exerted significant effects ($p < 0.05$) when analysed separately. For Tukey's test, each tested agent contributed differently to powder hygroscopicity, indicating that each agent had a distinct degree of hygroscopicity, and this characteristic should be evaluated because agents with low water absorption capacity are desirable (Figure 1). The anthocyanin powder hygroscopicity was found to be significantly lower with maltodextrin (13.07 ± 0.74%), while a higher value was obtained for powder produced with inulin (14.31 ± 0.34%). These results confirm the efficacy of 10 DE maltodextrin as a carrier agent considering its ability to reduce the hygroscopicity of spray dried products, as also observed by Cai and Corke (2000) when analysing betacyanin powders produced by maltodextrin 10, 15, 20, and 25 DE. They observed lower hygroscopicity for powders with 10 DE maltodextrin, contrary to 25 DE. According to Cai and Corke (2000) and Carvalho *et al*. (2016), hygroscopicity could be associated with the number of hydrophilic groups in the structure of each encapsulating agent. Materials with higher occurrence of hydrophilic groups (such as gum Arabic and maltodextrin 20, 25, and 30 DE) present easier moisture adsorption from the environment, whereas maltodextrin 10 DE presents less hydrophilic groups and a lower degree of hydrolysis.

The effect of temperature for each agent was evaluated by regression analysis. It was possible to fit a quadratic mathematical model ($R^2 = 0.7840$) for gum Arabic and a linear model ($R^2 = 0.7217$) for inulin. For maltodextrin, a constant hygroscopicity was observed at different drying temperatures (Figure 1), which could be attributed to fewer hydrophilic groups that could provide increased stability. Santhalakshmy *et al*. (2015) observed that spray dried *jamun* fruit powder produced at higher inlet temperatures was more hygroscopic. Conversely, Tonon *et al*. (2010) noted that the use of different outlet temperatures significantly affected the hygroscopicity of *açaí* juice microcapsules. However, this difference was considered small by the authors, as observed here.

Antioxidant activity can undergo changes caused by microencapsulation process and/or interactions with the encapsulating agent (Aguiar *et al*., 2017). In the present work, the effect of the material at each of the tested temperature was assessed using Tukey's test. The average values at 65 and 70°C were not significantly different, while at the other temperatures maltodextrin yielded the highest antioxidant activity. The effect of temperature for each encapsulating agent is presented in Figure 1. For maltodextrin and inulin, the quadratic model was significant, and the coefficients of determination (R^2) were 0.8995 and 0.6614, respectively. The antioxidant activity was constant for powders obtained using gum Arabic. For powders obtained with maltodextrin, antioxidant activity decreased as the temperature increased. For inulin and gum Arabic, there was a constant trend, i.e., antioxidant activity was maintained at higher temperatures. Similar results were observed by Bernstein and Noreña (2015) when evaluating the antioxidant activities of anthocyanin

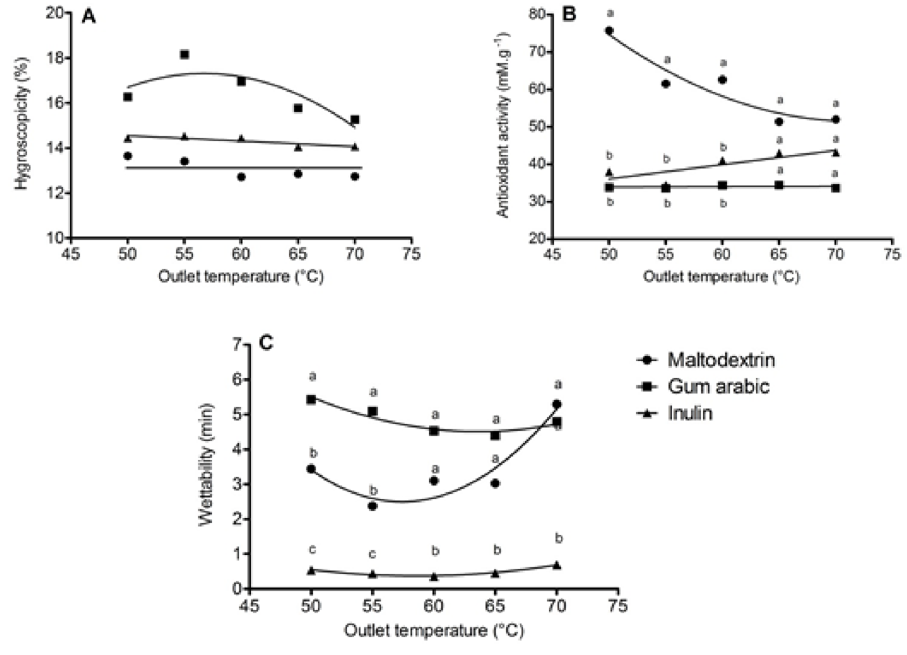

Figure 1: Hygroscopicity (A), antioxidant activity (B) and wettability (C) of powders obtained using maltodextrin, gum Arabic and inulin as encapsulating agents in different temperatures. Means followed by same letter within the same temperature did not differ ($p > 0.05$) by Tukey's test.

microcapsules produced with gum Arabic and polydextrose. Furthermore, an increase in the outlet air temperature did not significantly ($p > 0.01$) affect the antioxidant activities of the powders, indicating that the encapsulating agents protected the bioactive compounds, including anthocyanins. Therefore, as demonstrated in the present work, it is thus possible to produce high antioxidant microcapsules regardless of the encapsulating agent, although preference is to be given to maltodextrin for processing at lower temperatures.

Wettability can be characterised as the ability of a solid surface to be wetted by a liquid (Di Battista *et al*., 2015), and this is a limiting step throughout the reconstitution process. In general, fine powders exhibit low wettability (Tonon *et al*., 2010). By ANOVA (data not shown), temperature and encapsulating agent jointly affected microcapsule wettability (Figure 1). Results of Tukey's test indicated that at initial temperatures (50 and 55°C) all averages differed from each other, whereas at the other evaluated temperatures (60, 65, and 70°C), only the wettability of the powder produced with inulin differed from those produced with the other treatments. Inulin yielded the shortest wetting times as compared to other tested temperatures. Fernandes *et al*. (2014) microencapsulated rosemary essential oil and observed that the shortest wetting times were found for inulin-containing formulations, suggesting that this agent promoted particle solubility. This result could be explained by the properties of inulin, which has a high number of hydrophilic groups, thereby favouring interaction with water. Inulin structure is composed of a primary chain of fructose units with a terminal glucose unit, which favours solubility in water (Saenz *et al*., 2009). In the present work, it was possible to fit quadratic mathematical models, and the coefficients of determination (R^2) were 0.8971 for maltodextrin, 0.9115 for gum Arabic, and 0.9645 for inulin. The high coefficients found herein indicate that the second-degree polynomial models were appropriate for correlating these two variables and allowed the prediction of wettability at the tested temperatures (Figure 1). Improved powder wettability is essential for the quality of the final product, characteristics which can be optimised by the proper choice of parameters and drying technique. Several factors affect this feature, including the chemical composition of the product, physical factors involved in the analysis, reconstitution water temperature (Tonon *et al*., 2010), particle size, and air drying temperature (Santhalakshmy *et al*., 2015). Therefore, inulin should be used as the encapsulating agent when the purpose of microencapsulation is the rapid release of the microcapsule core (e.g., the bioactive compound) into the dispersion medium because this agent promotes wettability and is highly soluble in water. If the purpose of microencapsulation was to slow down compound release (e.g., increased retention of pigments, release of compounds during processing, or increased shelf-life), encapsulating agents with lower solubility in water are recommended, including gum Arabic and maltodextrin, which had the longest wetting time as demonstrated in the present work.

Simultaneous optimisation of responses using the desirability function

It is important to optimise the drying parameters to obtain a high quality powder, considering that the optimal conditions for the response variables were distinct (Toneli *et al*., 2010; Murugesan and Orsat, 2011; Muzaffar and Kumar, 2015; Chong and Wong, 2017).

The simultaneous optimisation of response was performed using the desirability function (Derringer and Suich, 1980). The variables anthocyanin retention, total phenolic content and antioxidant activity were maximised, whereas hygroscopicity and wettability were minimised. The response values, $\hat{y}i$, were estimated using the fitted regression models or the average values when the temperature effect was not significant or when it was not possible to fit any model (Table 1).

In the present work, a linear desirability function was used ($r_i = 1\ \forall i$). The values T_i (desired or target values), U_i, and L_i (minimum and maximum desired values, respectively) considered for each response variable were statistically determined. A delta value was calculated for each response variable (Δ = maximum value – minimum value) and subtracted from or added to the experimentally obtained values in order to define a range that ensures that any treatment achieves a maximum desirability ($d_i = 1$) and that no treatment achieves null desirability ($d_i = 0$) (Table 1). Using the individual desirability values, the overall desirability value, D, was calculated. The optimal conditions were those that achieved maximum values of overall desirability. The maximum values were 0.8540 for maltodextrin at 50°C, 0.3729 for gum Arabic at 70°C and 0.3133 for inulin at 70°C. Figure 2 shows the results of overall desirability as a function of temperature for the three encapsulating agents.

Other authors observed similar results. Bakowska-Barczak and Kolodziejczyk (2011) microencapsulated currant extract with maltodextrin (different DE) and inulin, and also observed better

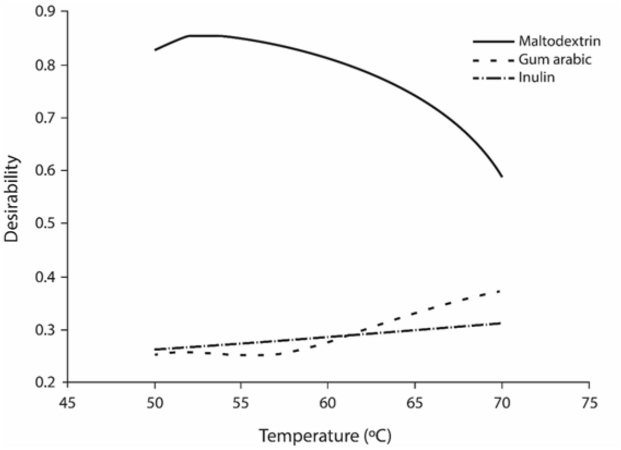

Figure 2: Overall desirability versus temperature for the tree types of encapsulating agents tested

results when maltodextrin was used as the coating material. In a study on blackberry powder spray drying by Ferrari *et al*. (2013), maltodextrin provided greater powder stability because particles showed high half-life and low anthocyanin degradation rate. Chong and Wong (2017) concluded that *Sapodilla* fruit powder spray dried at 200°C inlet added by 20% or 30% (w/v) of maltodextrin was adequately effective to produce highly antioxidant powders featuring acceptable colour. Bicudo *et al*. (2015) observed via response surface analysis that inlet air temperature that achieved the highest concentration of powdered anthocyanins (from *juçara* extract) was between 147 and 165°C for all tested encapsulating agents, including maltodextrin. Considering the variation between the employed apparatus, one could consider that these temperatures were similar to the optimal temperatures found in the present work. In the equipment used in the present work, the inlet air temperature that was equivalent to the outlet air of 50°C was 136 ± 5.29°C. For an outlet air temperature of 70°C, the equivalent inlet air temperature was 179 ± 6.80°C.

Scanning electron microscopy (SEM)

For SEM and X-ray diffraction analyses, samples produced at 50°C for maltodextrin, 70°C for gum Arabic, and 70°C for inulin were selected based on the results obtained in the simultaneous optimisation of response variables (Figure 2).

Figure 3 shows that all microcapsules were spherical, which is typical of spray dried powders, and also fit into the microscale range due to the formation of capsules ranging in size between 0.2 and 5,000 µm (Barros and Stringheta, 2006). The addition of large particles to food matrices could affect texture; therefore, particles smaller than 100 µm in diameter are the most suitable (Annan *et al*., 2008).

Microcapsules obtained with maltodextrin presented a similar morphology, predominantly smooth and spherical, similar to those observed in other studies about anthocyanin microencapsulation by maltodextrin (Nayak and Rastogi, 2010; Tonon *et al*., 2010; Silva *et al*., 2013; Bicudo *et al*., 2015). Smoother microcapsules showed greater anthocyanin retention, and this might be associated with a better accommodation of the pigment in the microparticle (Carvalho *et al*., 2016). The first image shows that the particles were slightly overlapped because of the amount of sample placed on stubs; however, it was possible to identify each capsule, indicating that they were not clustered. The cracks observed at 10,000× might be caused by vacuum sputtering upon particle coating with a thin gold layer, which might have occurred irregularly over the surface. Bicudo *et al*. (2015) observed spherical anthocyanin microcapsules with solid walls and slightly shrunken external surfaces, in addition to the slight clustering of smaller particles onto larger-diameter capsules. Silva *et al*. (2013) observed that, among the tested encapsulating agents, maltodextrin yielded more homogeneous capsules with lower surface roughness. The same characteristics were observed in the present work, indicating the potential of maltodextrin as an encapsulating agent for anthocyanin.

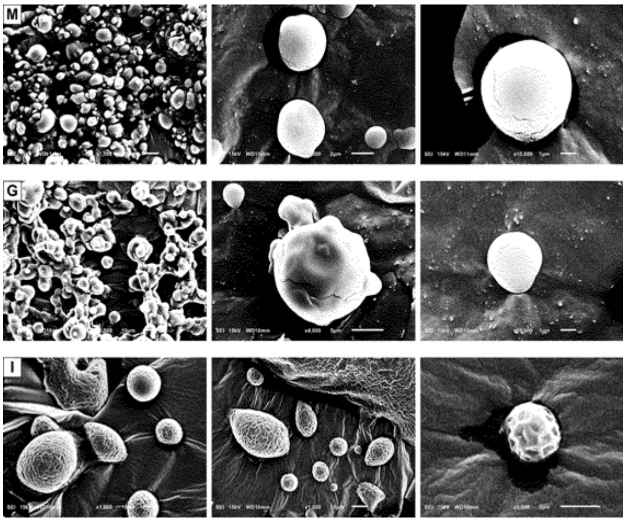

Figure 3: Photomicrographs of the microcapsules from juçara extracts formulated with maltodextrin (M), gum arabic (G) and inulin (I). Magnifications of 1,000-10,000×.

Microcapsules obtained with gum Arabic showed a predominantly spherical shape and smooth morphology with few indentations. A connection between the capsules was also observed, which suggests subtle clustering. Like maltodextrin, small spheres were found to adhere to the surface of larger-diameter spheres, as also observed by Bernstein and Noreña (2015). They also found roughened surfaces and cavities, suggesting the contraction of the spheres due to the rapid water evaporation during drying and subsequent cooling. Ferrari *et al*. (2013) observed that powders produced with the same material presented shrivelled surfaces, which probably affected their stability, resulting in faster anthocyanin degradation during storage. Tonon *et al*. (2010) observed that the surfaces of *açaí* juice microcapsules presented high degree of roughness when lower drying temperatures were used, but smoother surfaces when higher temperatures were applied. This result indicates that increased temperature favours the production of capsules with smoother surfaces. In the present work, an outlet air temperature of 70°C was tested for gum Arabic, which is equivalent to an inlet air of approximately 180°C.

The photomicrographs of the microcapsules produced with inulin revealed characteristics that were distinct from those of microcapsules produced with the other agents. The highly rough surface was due to the high wettability of this powder. When in contact with the glue from the carbon tape placed in the stubs prior to sputtering, the sample instantly solubilised, and since sputtering was performed under vacuum, moisture might have been removed from the samples, contributing to the wrinkling of the capsules, which partially lost their conformation. The roughened surface of the particles adversely affected the release properties of powders (Rosenberg *et al*., 1985). Therefore, processing conditions that eliminate or minimise the development of roughness are preferred.

X-ray diffraction

Figure 4 shows the diffractograms of the powders obtained with maltodextrin, gum Arabic and inulin as well as a differentiated powder with less interference from the encapsulating agent, with a ratio of 1:1 (concentrated extract:maltodextrin v/v) (named "anthocyanin").

The shape of the peaks (intensity or height and width) characterises sample crystallinity. The crystal

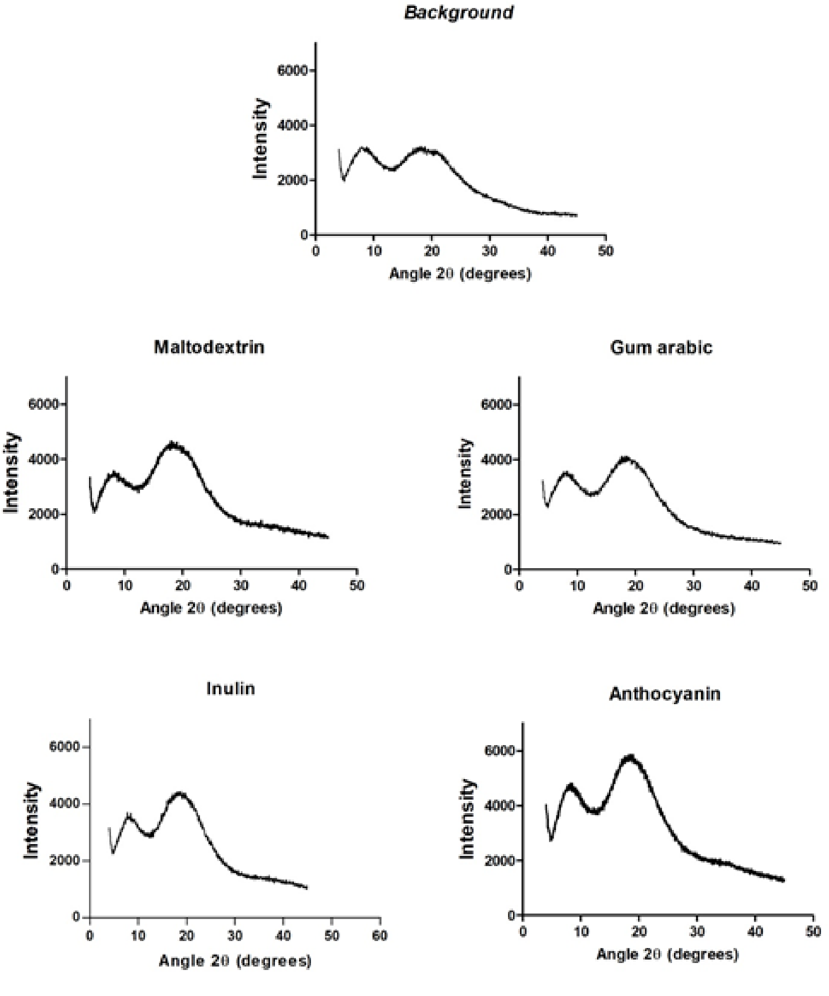

Figure 4: Diffractograms of microcapsules from *juçara* extracts formulated with maltodextrin, gum Arabic and inulin.

structure of all samples was similar to that observed in the background (i.e., without sample). Therefore, none of the tested materials contributed to peak diffraction, indicating the presence of powders with primarily amorphous structures in all samples. In the spray drying process, crystallinity might depend on the atomisation characteristics (including the short drying period and solution viscosity). Since samples are dried almost instantaneously, there is no sufficient time for peak formation. In addition, the tested coating materials had amorphous characteristics; thus, the presence of amorphous structures was already expected, as also observed by other authors (Alves and Santana, 2004; Rutz, 2013).

Moreover, the peak widths in all samples were similar and tended towards a constant value starting at an angle of 30°. Alves and Santana (2004) found that narrower peaks indicate the presence of crystalline structures, whereas wider or smaller peaks indicate a predominance of amorphous structures. The intensity of the obtained peaks in the anthocyanin-rich microcapsules with less interference from the encapsulating agent ("anthocyanin" – powder produced using 1:1 concentrated extract:maltodextrin v/v) was higher than that of the peaks produced by the encapsulating agents, outcome which was also observed by Rutz (2013). The formation of complexes can be assessed by comparing the intensities of the characteristic peaks of the molecule of interest with the peak intensities of the complex. Decreased peak intensities could indicate partial complexation (Rutz, 2013). In the present work, the intensities of the peaks assigned to “anthocyanin" microcapsules were greater than those of the microcapsules produced by the encapsulating agents; however, these peaks were similar to those observed in the other diffractograms, demonstrating the interaction among the encapsulating agent and the guest molecule as well as the formation of complexes.

Conclusion

Microencapsulation by spray drying has proven to be a safe and stable technique to obtain anthocyanins from the *juçara* palm plant. Simultaneous optimisation of response variables allowed the selection of the best processing conditions that yielded powders with desirable characteristics, including spray dryer outlet air temperatures of 50°C for maltodextrin 10 DE and 70°C for gum Arabic and inulin, with maltodextrin displaying the highest desirability (0.85). Therefore, maltodextrin or gum Arabic should be used when the purpose of microencapsulation is the controlled release of the compound, and inulin should be used should the quick release of the compound be the objective due to the high wettability of such agent. SEM confirmed microencapsulation efficiency as evidenced by the spherical capsules of uniform size, whereas X-ray diffraction indicated the presence of microcapsules with amorphous structures.

Future studies should use a combination of encapsulating agents because isolated agents might not exhibit all desired properties, and novel formulations of encapsulating agents should be developed by combining desired technological properties such as the retention of bioactive compounds (e.g., maltodextrin and gum Arabic) and functional properties (e.g., inulin).

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