Acta Scientiarum

http://periodicos.uem.br/ojs
ISSN on-line: 1807-8664
Doi: 10.4025/actascitechnol.v44i1.56598

Maltodextrin- modified starch microparticles containing benzoic acid: Physical properties and thermal stability

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ABSTRACT. The microencapsulation of benzoic acid by spray drying can provide amorphous characteristics, which is necessary for its application in foods. In addition, it facilitates the use of this component in a food matrix and prolongs the shelf life of the product. Thus, wall materials with high encapsulation efficiency should be used, such as modified starch and maltodextrin and their combinations. The aim of this study was to evaluate the effect of modified starch (MS) and/or maltodextrin (M) used as encapsulating agents on the chemical and physical properties, morphological parameters, and thermal stability of spray-dried benzoic acid. Three treatments were evaluated: modified starch (MS), maltodextrin (M), and a blend containing modified starch and maltodextrin (MS/M). In general, the variables studied have a significant effect on the responses. The highest efficiency was observed for the treatment MS/M (82.65%); although it presented a lower drying process yield (50%). It was observed that the use of maltodextrin contributed to improving the wettability and solubility of the microparticles since this component is highly water-soluble. The largest microparticle diameter was 19.15 µm (MS/M), and the *Span* ranged from 1.94 to 2.15 for all treatments, indicating good homogeneity in relation to the particle size distribution. Concerning the particle morphology, the treatment MS/M exhibited partially rough microparticles, while the treatments MS and M led to a higher amount of brittle microparticles. The GAB model was chosen as the best model to explain the isotherm behavior. In addition, the adsorption isotherms of the samples using blend showed a Type-III behavior (non-sigmoidal), common for many foods rich in soluble components. The treatment MS/M has proven to be the most suitable for the encapsulation of benzoic acid being a good and viable option for the food industry.

Keywords: Modified starch; maltodextrin; blend; spray drying; microencapsulation.

Received on November 10, 2020.
Accepted on March 23, 2021.

Introduction

Benzoic acid has many applications in pharmaceuticals, cosmetics, and hygiene products, and also in packaging. In addition, the use of this additive is very common in processed foods, mainly, as a preservative and an antioxidant (Silva & Lidon, 2016) which is commonly used as antibacterial and antifungal preservatives and as flavoring agents. Benzoic acid is an aromatic carboxylic acid naturally present in plants, fruits, and dairy products, which can also be produced by microorganisms (Del Olmo, Calzada & Nuñez, 2017) and has no toxic effects at the recommended concentrations.

There is a growing demand to initiate new technologies suitable for the protection of additives, mainly due to food processing, since these compounds are recognized as highly sensitive to heat, light, oxygen, and moisture. One technique that ensures improved controlled release over storage time, bioavailability, stability, and delivery of these materials is microencapsulation, since it prevents interaction with the food matrix and convert the ingredients into the easily handled, free-flowing, and dispersible powders; as well as masks or preserves flavors and aromas (Nahum & Domb, 2021).

The microencapsulation by spray drying plays an important role, is the most used process in the food industry, which consists in dispersing the product in the form of droplets in contact with hot air to obtain a powder (Corti, Bittencourt, & Drunkler, 2017). The prime atomization function is to provide high evaporation rate at high temperatures and to produce microparticles with controlled shape, size, and density (Leimann,

Gonçalves, Machado, & Bolzan, 2009). A previous study was conducted to determine the optimum of benzoic acid concentration and the drying air temperature of spray dryer. With this research, it was realized the need to explore the influence of wall materials that should be used with the previously optimized independent variables, since the additive present in the microparticle is released under the influence of different factors depending on wall material (Marques, Fernandes, Borges, & Botrel, 2016).

Among the variables that affect the microencapsulation efficiency, carriers or encapsulating agents with different emulsifying and film-forming properties stand out, which is necessary for an effective encapsulation. The encapsulating material must be able to create a network for entrapping the core material (Medina-Torres et al., 2016). Therefore, they should have the ability to form a film cohesive with the active material and to provide chemical and physical compatibility, which should confer the desired properties to the microparticles, such as flexibility, strength, impermeability, and stability. In addition, it is necessary to have low viscosity at high solid concentrations, low hygroscopicity, and great availability (Soukoulis & Bohn, 2018; Telis & Martínez-Navarrete, 2010).

The encapsulating materials can be selected from a wide variety of natural and synthetic polymers, depending on the core material and the desired characteristics in the final product (Botrel et al., 2012; Paris et al., 2016). The use of modified starch is a potential option, with the objective of overcoming the limitations of the native starches and, thus, to increase the industrial applications of this polymer. When starch is modified with octenyl succinic anhydride, the partially hydrolyzed waxy starch gains a hydrophobic element as octenyl groups, resulting in whole molecules with an amphiphilic character. This modification can lead to a product with an excellent emulsifying capacity to aid in spray drying, which can be used in the system at high concentrations, and produce solutions with good stability (Naseri, Shekarchizadeh, & Kadivar, 2019; Sweedman, Tizzotti, Schäfer, & Gilbert, 2013).

Modified starches reproduce the functional properties of gum Arabic, extensively used as encapsulant, and have shown good encapsulation efficiency when blended with maltodextrin (Cano-Higuita, Malacrida, & Telis, 2015). Maltodextrin is a polysaccharide obtained from the partial hydrolysis of starch, formed by D-glucose bound in the α- (1 → 4) position. It also has a low cost, high solubility in water (> 75%) and low viscosity in aqueous solutions, and should have an equivalent dextrose value (DE) < 20 (Medina-Torres et al., 2016). In this context, the use of a blend made with modified starch and maltodextrin may be a cost-effective and promising alternative for the encapsulation process. The aim of this study was to evaluate the encapsulating agents modified starch and/or maltodextrin on the microencapsulation efficiency and the physical and thermal properties of the spray-dried benzoic acid.

Material and methods

Materials

Benzoic acid (Brenntag Química Brasil Ltda, São Paulo, Brazil) was used for the microencapsulation process; maltodextrin (Maltogil DE 10, Cargill, São Paulo, Brazil) and modified starch with octenyl succinic anhydride (Capsul®, National Starch Food Innovation, São Paulo, Brazil) were used as encapsulating materials; and polysorbate 80 (Emfal Ltda, Betim, Brazil) was used as an emulsifying agent.

Preparation of the solutions

Three treatments 100% MS - modified starch, 100% M - maltodextrin, and a 50%/50% MS/M - blend containing modified starch and maltodextrin were done for each formulation. The polysaccharides were hydrated with distilled water for 12 hours at room temperature to ensure the complete saturation of the molecules. The concentration of the encapsulating material was set at 40% (w w^{-1}). Benzoic acid was previously dissolved in 5 mL ethanol, at the concentration of 6% in relation to the total solids (Marques et al., 2016). Polysorbate 80 (0.5% w v^{-1}) was used as an emulsifying agent. The final solution was heated to 60°C and homogenized at 2500 rpm for 10 min. (Ultraturrax, TECNAL Piracicaba, Brazil).

Microencapsulation by spray drying

The solutions were dried using a spray dryer (model MSD 1.0, Labmaq do Brasil, Ribeirão Preto, Brazil) equipped with a two-fluid nozzle atomizer, 3 mm diameter, in a drying chamber measuring 670 mm x 200 mm. A peristaltic pump was used to feed the system at an air flow of 40 L·min^{-1} and air pressure of 400 kPa.

The dryer temperature was established using the inlet air temperature of 169°C, outlet temperature from 78-96°C, and the feed flow rate of 0.70 $L \cdot h^{-1}$ (Marques et al., 2016).

Microcapsule powder analysis

Microencapsulation efficiency

The microencapsulation efficiency was determined in a modular Shimadzu® high performance liquid chromatography system (Kyoto, Japan), composed of LC 20 AT pump, CTO 20A furnace, SIL 10A automatic sampler, SPD-20A variable wavelength detector, and LC Solution software. For sample preparation, 5 g of spray-dried benzoic acid was placed into a 100 mL amber volumetric flask and 50 mL of 70% hydroethanolic solution was added. The solubilization of the samples was performed by sonication for 30 min. at 50°C, and then the volume was completed to 100 mL with 70% hydroethanolic solution. The samples were filtered on a 0.45 µm membrane (Tfouni & Toledo, 2002).

For the chromatographic analyses, an Acclaim Organic Acid OA column (250 × 40 mm, 5 µm) was used, and 25 µL of the supernatants were injected. The analyses were carried out in isocratic mode, using ammonium acetate 0.005 M/acetonitrile/water at a ratio of 2:17:81, pH 4.2, and flow rate of 1 $mL \cdot min^{-1}$, at 25°C. The UV detection was recorded at 228 nm. A benzoic acid calibration curve was constructed in the range of 1.0 to 5.0 $mg \cdot mL^{-1}$. The benzoic acid concentration in the microparticle was calculated using the equation $y = 1.39 \times 10^5 - 2.1 \times 10^3 x$, $R^2 = 0.9989$, where y is the absorbance and x is the benzoic acid concentration. The microencapsulation efficiency was calculated according to the Equation (1) (Tonon, Grosso, & Hubinger, 2011).

$$Microencapsulation\ efficiency\ (\%) = \left(\frac{Q_{Eba}}{Q_{ba}} \right) x\ 100 \quad (1)$$

where, Q_{Eba} is the amount of spray-dried benzoic acid, and Q_{ba} is the amount of benzoic acid in the feeding.

Process yield

The yield of the spray drying process was expressed as a percentage (%), calculated as the relationship between total solids content (g) in the resulting powder and total solids content (g) in the feed mixture (Tonon, Brabet, & Hubinger, 2008).

Moisture content

The moisture content was determined by the gravimetric method, 5 g of the powder samples were put in a vacuum oven at 70ºC (Association of Official Analytical Chemists [AOAC], 2005). Moisture content was calculated in terms of weight loss.

Wettability and solubility

In order to determine the wettability of the powder, the sample (1 g) was sprinkled over the surface of 100 mL of distilled water at 20ºC without agitation. The time it took until the last powder particles submerged was recorded (Fuchs et al., 2006). For the solubility analysis, 1 g of the powder was stirred in 100 mL of distilled water. The solution was transferred to a tube and centrifuged at 2600 rpm for 5 min. An aliquot (25 mL) of the supernatant was placed in the Petri dish and oven dried at 105°C. The amount of powder present in the supernatant was quantified and considered as the soluble fraction of the powder (Cano-Chauca, Stringheta, Ramos, & Cal-Vidal, 2005).

Bulk and tapped density

Bulk density (ρ) of powders was measured by weighing 2 g of sample in a 50 mL graduated cylinder, being calculated by dividing the mass of powder by the volume occupied in the cylinder (Jinapong, Suphantharika, & Jamnong, 2008). Approximately 5 g of powder was poured into a 25 mL graduated cylinder and then the cylinder was repeatedly tapped by lifting and dropping it under its own weight until a negligible difference in volume between successive measurements was observed. Given the mass (m) and the apparent (tapped) volume (V) of the powder, the density of the powder bulk was calculated as $m\ V^{-1}$ ($g \cdot cm^{-3}$) (Goula & Adamopoulos, 2008).

Mean droplet diameter and size distribution

The microparticle size distribution was measured by laser diffraction particle sizing technique (Mastersizer 2000, Hydro 2000 UM model, Malvern Instruments, Worcestshire, UK). The dispersion of the microparticles was performed in the dispersion unit of the equipment, using pure isopropanol. The stirring time of the solution was 15 min., and five replicates were made within 10 seconds. The particle size distribution was determined using the mean volumetric diameter of the microparticles (D[4.3]), and the microparticle homogeneity (*Span*) was calculated according to Equation (2) (Jinapong et al., 2008).

$$Span = \frac{d_{90} - d_{10}}{d_{50}} \quad (2)$$

Span is the polydispersity index (PDI) and the variables, d_{10}, d_{50}, and d_{90} are the droplet diameter (μm) at 10%, 50%, and 90% cumulative volume, respectively.

Morphology

The morphology of the microparticles was evaluated by scanning electron microscopy (SEM). The particles were spread on double-coated carbon adhesive tapes fixed on metal stubs (1 x 1 cm) and gold sputter-coated. The samples were placed in the vacuum chamber and examined with the scanning electron microscope (MEV 1430 VP-LE Electron Microscopy Ltd., Cambridge, UK). The SEM was operated at 20 kV at a magnification of 900 – 1200x.

Thermal stability

The thermal stability of the spray-dried benzoic acid was evaluated by thermogravimetric analysis using Shimadzu 50 H DTA-TG equipment (Shimadzu Corporation, Kyoto, Japan). The analyses were performed under a nitrogen atmosphere at a flow rate of 50 mL·min^{-1}, from 25ºC to 600ºC and a heating rate of 10ºC·min^{-1}.

Moisture adsorption isotherm

The adsorption isotherms were determined by the static gravimetric method, where 1 g of sample was weighed in a Petri dish, and placed in seven desiccators containing saturated saline solutions (LiCl, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, $NaNO_3$, NaCl, and KCl), with water activity ranging from 0.11 to 0.84, and stored in a climatic chamber at 25°C. The samples were weighed at predetermined time intervals until constant weight (Spiess & Wolf, 1987). The moisture sorption isotherm data correlated with the mathematical models (Al-Muhtaseb, McMinn, & Magee, 2002): GAB (Guggenheim, Anderson, and de Boer), Halsey, Oswin, and Peleg. The equation parameters were estimated by the correlation of the mathematical models with the experimental data, using a non-linear regression model and the Quasi-Newton method, with a convergence criterion of 10^{-4}, with the aid of Statistica software (v. 8. Stat Soft Inc., Tulsa, USA), at a level of 5% of significance. The model was considered the most adequate, based on the highest coefficient of determination (R^2) and the smallest relative deviation (E%), as shown in the Equation (3).

$$E = \frac{100}{N}\sum_{i=1}^{N}\frac{\left|m_i - m_{pi}\right|}{m_i} \quad (3)$$

where E is the standard error (%), *n* number of data observed, m_i experimental value, and m_{pi} value estimated by the model.

Statistical analysis

To evaluate the effects of the three treatments on the characteristics of the spray-dried benzoic acid, analysis of variance was performed using the Statistica software (see 8. Stat Soft Inc., Tulsa, USA) and the means were compared by the Tukey's test ($p < 0.05$).

Results and discussion

Microencapsulation efficiency, moisture, bulk density, mean droplet diameter, and size distribution

The use of different encapsulating materials in the microencapsulation of benzoic acid significantly affected ($p < 0.05$) its physical and chemical parameters (Table 1).

Table 1. Physicochemical parameters (mean ± SD) of spray-dried benzoic acid using different encapsulating materials.

Variables	Treatment		
	MS	M	MS/M
Microencapsulation efficiency (g·100 g^{-1})	68.47±1.11[b]	67.10±1.05[b]	82.65±3.52[a]
Process yield (%)	55.00±0.30[b]	55.00±0.71[b]	50.00±1.05[a]
Moisture (%)	1.55±0.24[a]	1.56±0.14[a]	2.16±0.01[b]
Wettability (s·g^{-1})	68.41±2.02[a]	52.64±3.17[b]	58.72±3.84[ab]
Solubility (g·100 g^{-1})	75.92±0.87[b]	77.90±0.43[a]	76.78±0.84[c]
Bulk density (g·cm^{-3})	0.68±0.03[a]	0.58±0.01[b]	0.59±0.01[b]
Tapped density (g·cm^{-3})	0.58±0.01[a]	0.50±0.01[b]	0.41±0.01[c]
$D_{[4,3]}$ (µm)	15.93±0.07[b]	14.88±0.09[c]	19.15±0.01[a]
Span	2.12±0.00[a]	2.15±0.03[a]	1.94±0.00[b]

[a,b,c]Values with different letters in the same line differ significantly ($p < 0.05$) by the Tukey's test at the 5% probability level. MS: modified starch; M: maltodextrin; MS/M: modified starch and maltodextrin blend.

One of the most important quality parameters in the microencapsulation process is the encapsulation efficiency, which is considered indispensable for the characterization of the final product. This variable is strongly related to the encapsulating material used, the solids concentration of the feeding solution, and the process temperature. The encapsulation efficiency can be improved by using encapsulating materials with different functional properties (Botrel et al., 2012). The highest efficiency was observed for the treatment MS/M, which differed statistically ($p < 0.05$) from the treatments MS and M; although it presented a lower drying process yield (50%). It is observed that the use of the encapsulating material (modified starch or maltodextrin) may have facilitated the formation of a crust during drying, thus reducing the diffusion of the spray-dried acid onto the particle surface and reducing the loss of core material. High encapsulation efficiency (84%) of curcumin spray-dried using gum Arabic, maltodextrin, and modified starch blend was also found by Cano-Higuita et al. (2015), compared to treatments using encapsulation agents alone. These results suggest that the carbohydrate-based matrices are more protective.

Moisture content is the main factor affecting the stability and the physical properties of the microparticles, once a small increase in moisture content is able to decrease the glass transition temperature (*Tg*) of the microparticles, leading to an increase in mobility of the spray-dried material during storage, negatively impacting the physical and technological properties of these materials. The blend containing modified starch and maltodextrin led to an increase in moisture of the powder, due to the increased viscosity of the blend, once the particles had a relatively large diameter. Thus, the higher the viscosity of the encapsulating material, the larger the droplets formed in the spray-drying (Goula & Adamopoulos, 2008). In addition, according to Tonon et al. (2008), the increase on feed viscosity can cause more solids to paste in the main chamber wall of spray dryer, reducing the process yield, which justifies the result found for this treatment (MS/M).

Wettability can be characterized by the susceptibility of the microparticles to be penetrated by water, which is influenced by physical factors, especially the particle size and shape (Santana, Oliveira, Pinedo, Kurozawa, & Park, 2013). It was observed that the use of maltodextrin contributed to improving the wettability of the microparticles since this component is highly water-soluble, which can reduce the time required for the microparticles to be fully absorbed by water. GEA Group (2009) reported that samples with wetting times in excess of 60 seconds are considered non-instant; therefore, a good parameter can be a maximum of 60 seconds for 90% of the product to be absorbed by water. In this study, both the treatments M and MS/M reached these values.

High solubility is an essential property for using powders as ingredients in the food industry. Solubility is the last stage of dissolution of a microparticle in the food matrix and is considered essential for the quality of these products. In this study, the values for the powders to become completely solubilized in water ranged from 75.92 to 77.90 g 100 g^{-1}. Du et al. (2014) studied different maltodextrin concentrations for the microencapsulation of persimmon pulp and observed an average value of 76.22% solubility.

The particle density is an essential parameter to evaluate the packaging and transport conditions in the industry. Significant differences ($p < 0.05$) were observed for the treatments M and MS/M when compared to the treatment MS, probably due to the size of these components, once the maltodextrin molecules are smaller than those of the modified starch. Ribeiro, Costa, and Afonso (2019) found that the high agglomeration of powder particles and structure collapse were related to the maltodextrin content, which can lead to a decrease in particle volume. On the other hand, the tapped density is influenced by the particle shape and size, thus the spherical microparticles exhibit better organization and higher densities (Lourenço, Martins, & Alves, 2020).

Measuring the particle size distribution is fundamental because it affects the appearance, fluidity, and dispersibility of the product (Francisquini et al., 2020). In the present study, a significant effect was observed in the

particle size of the microparticles ($p < 0.05$) as a function of the encapsulating material. The particle size values found in this study ranged from 5 to 100 µm, which is in accordance with studies using the spray drying technique (Cislaghi, Silva, Freire, Lorenz, & Sant'Anna, 2012). The addition of maltodextrin to the modified starch formulation led to an increase in the particle size of the microparticles, probably due to the particle morphology, as discussed below in the morphology analysis. The microparticles showed lower shrinkage in the presence of modified starch and maltodextrin, thus contributing to an increase in particle size. The dispersibility value (span) is related to the degree of uniformity of the size distribution (Tonon et al., 2011). Thus, the lower the span, the smaller the dispersion of the particle size distribution, which indicates a homogeneous system that allows establishing a better product standardization, besides improving the properties of the microparticles. The microparticles of the present study presented span values from 1.94 to 2.15, indicating a homogeneity of the spray drying process.

Morphology

The microparticles showed variety in size, which is a typical characteristic of the microparticles produced by spray drying. Although some differences in morphology were observed in the particles of this study, most of them presented a spherical shape with some concavities (Figure 1), presumably due to the drying process. Surface imperfections (cracks, roughness, and collapses) can be formed during a slow film-forming process during drying of the atomized droplets together with surface depressions, due to the collapse of droplets in the initial drying stages (Alves et al., 2017; Carneiro, Tonon, Grosso, & Hubinger, 2013). Costa et al. (2015) studied the encapsulation of Swiss cheese bioaroma by spray drying, using maltodextrin and modified starch as encapsulating materials, and observed hollow spherical shapes with the formation of vacuoles probably from the shrinkage process occurring shortly after surface hardening. The mechanisms associated with the formation of voids are related to the expansion of the microparticles in the final drying stages. Teixeira, Andrade, Farina, and Rocha-Leão (2004) have shown that the thermal expansion of the air inside the microparticles can reduce shrinkage. In this study, small holes were observed in some microparticles, which may have occurred in the final drying stages (Garcia, Tonon, & Hubinger, 2012).

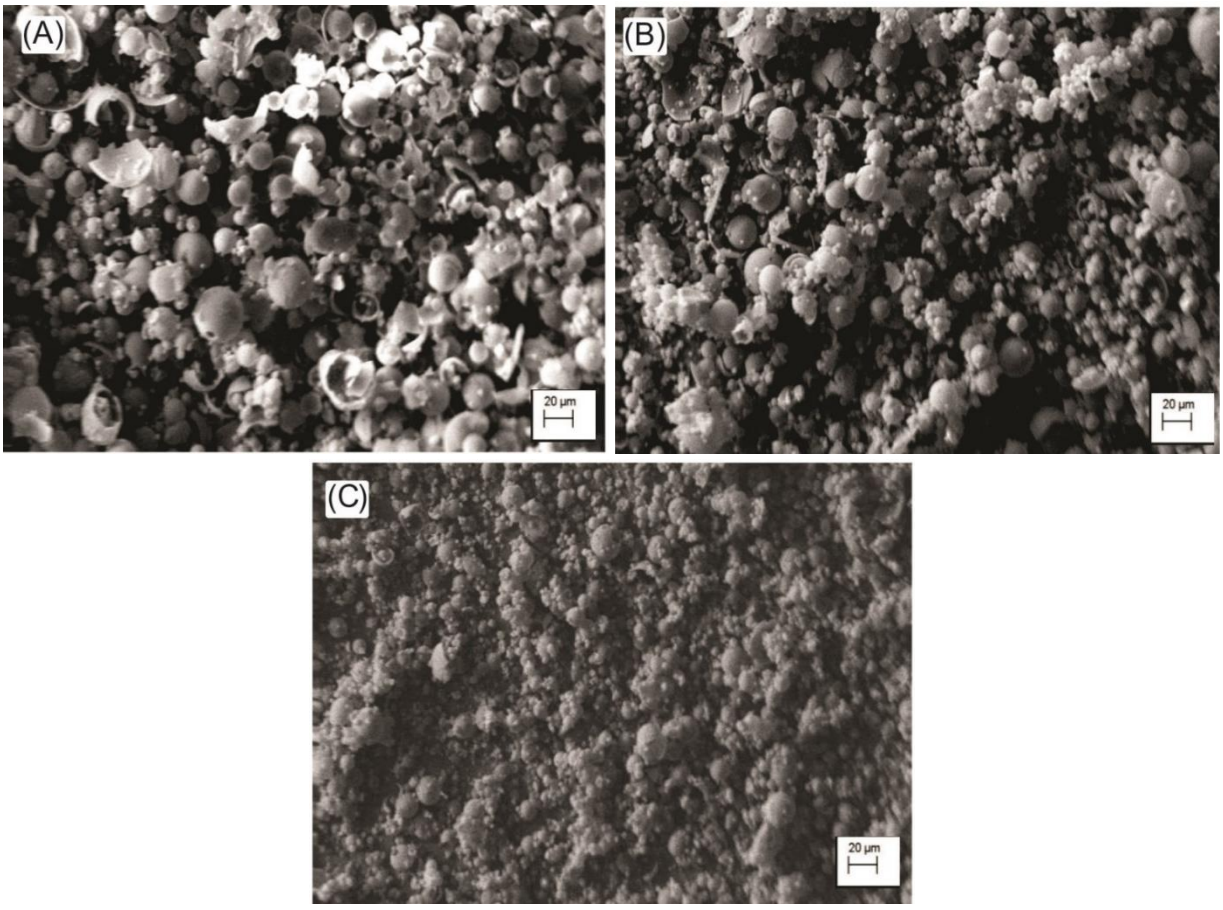

Figure 1. Scanning electron micrographs of the benzoic acid microparticles produced with the encapsulating agents: A: MS - modified starch, B: M - maltodextrin, C: MS/M - modified starch/maltodextrin.

Moisture adsorption isotherms

The GAB model was chosen as the best model to explain the isotherm behavior due to the high coefficient of determination (R^2) and the lowest mean relative deviation (E%) (Table 2). The monolayer moisture content (X_m) shows the amount of water that is strongly adsorbed at specific sites on the food surface, which is an important factor to ensure the product stability (Oliveira, Corrêa, Santos, Treto, & Diniz, 2011). The X_m values of the spray-dried benzoic acid ranged from 0.055 to 0.095 g·g^{-1} among the treatments. The microparticles produced with M as an encapsulating material presented lower X_m values than those produced with MS and MS/M. The X_m values indicated low hygroscopicity of the microparticles, which is similar to the results found for sugar-rich products, with values ranging from 0.040 g·g^{-1} to 0.106 g·g^{-1} for powdered pigment obtained from vinification byproducts, as reported by Souza, Thomazini, Balieiro, and Trindade (2015). Gabas, Telis, Sobral, and Telis-Romero (2007), explain that the moisture in the monolayer decreases with the presence of the maltodextrin that probably modify the balance between hydrophilic/hydrophobic sites, promoting greater sorption of water and, consequently, reduced X_m values.

Table 2. Estimated coefficients and statistical parameters for the GAB, *Halsey*, *Oswin*, and *Peleg* models.

Equation model	Coefficients	MS	M	MS/M
GAB $X_{eq} = \frac{X_m C K a_w}{(1-Ka_w)(1-Ka_w+CKa_w)}$	X_m	0.055	0.095	0.067
	C	0.055	2.915	0.099
	K	0.183	0.619	0.114
	E(%)	0.509	0.509	1.116
	R^2	0.999	0.995	0.994
Halsey $X_{eq} = \left(\frac{a}{\ln(a_w)}\right)^{\frac{1}{b}}$	A	0.002	0.002	0.002
	B	0.070	0.070	0.071
	E(%)	4.204	4.57	4.475
	R^2	0.783	0.760	0.724
Oswin $X_{eq} = a\left(\frac{a_w}{(1-a_w)}\right)^b$	A	0.085	0.079	0.066
	B	0.411	0.400	0.602
	E(%)	1.616	1.464	0.849
	R^2	0.988	0.988	0.996
Peleg $X_{eq} = a.a_w^{K_1} + b.a_w^{K_2}$	A	0.093	0.084	0.016
	K_1	1.019	0.979	1.787
	b	0.093	0.084	0.116
	K_2	1.019	0.979	1.787
	E(%)	0.997	0.916	2.273
	R^2	0.986	0.985	0.992

*X*eq: equilibrium moisture (g g^{-1} powder); X_m: monolayer moisture (g·g^{-1} powder); *C*, *K*: model constants related to monolayer and monolayer properties; aw: water activity; a, b: model parameters; *E*: relative deviation module; R^2: coefficient of determination. MS: modified starch; M: maltodextrin; and MS/M: modified starch and maltodextrin blend.

The GAB model was used to describe the isotherm behavior (Figure 2). The moisture sorption isotherm of both the treatments MS and M showed a Type-II behavior (sigmoidal), while the treatment MS/M showed a Type III behavior (non-sigmoidal) (Roos & Drusch, 1995). According to Fikry and Al-Awaadh (2016) and Ribeiro et al. (2019) the Type III isotherm is common for many foods having rich soluble components.

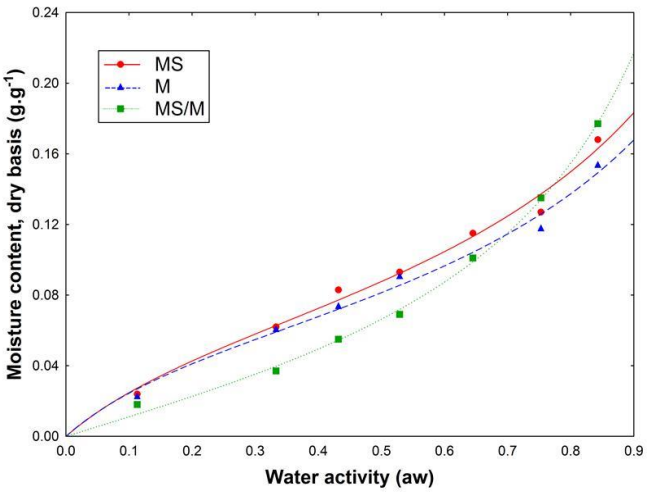

Figure 2. Moisture sorption isotherm of the spray-dried benzoic acid adjusted to the GAB model.

The effect of moisture on the behavior of each material should be evaluated since the phase change due to moisture adsorption is characteristic of each biopolymer. The powders changed state when stored under different Aw values for all treatments evaluated (Figure 3). The collapse observed in the treatments is an undesirable phenomenon, in which the powder begins to agglomerate, leading to the formation of clods. This phenomenon was observed in the treatment M with Aw from 0.113 to 0.529 and in the treatments MS and MS/M with Aw from 0.113 to 0.645. Both, Siemons, Boom, and Schutyser (2019) reported that the collapse morphology usually begins with the formation of points, with contact surface deformation and adhesion. This collapse was observed in the treatment M with Aw of 0.645. At the final stage, the sample was liquefied, which was observed for all treatments at Aw of 0.843.

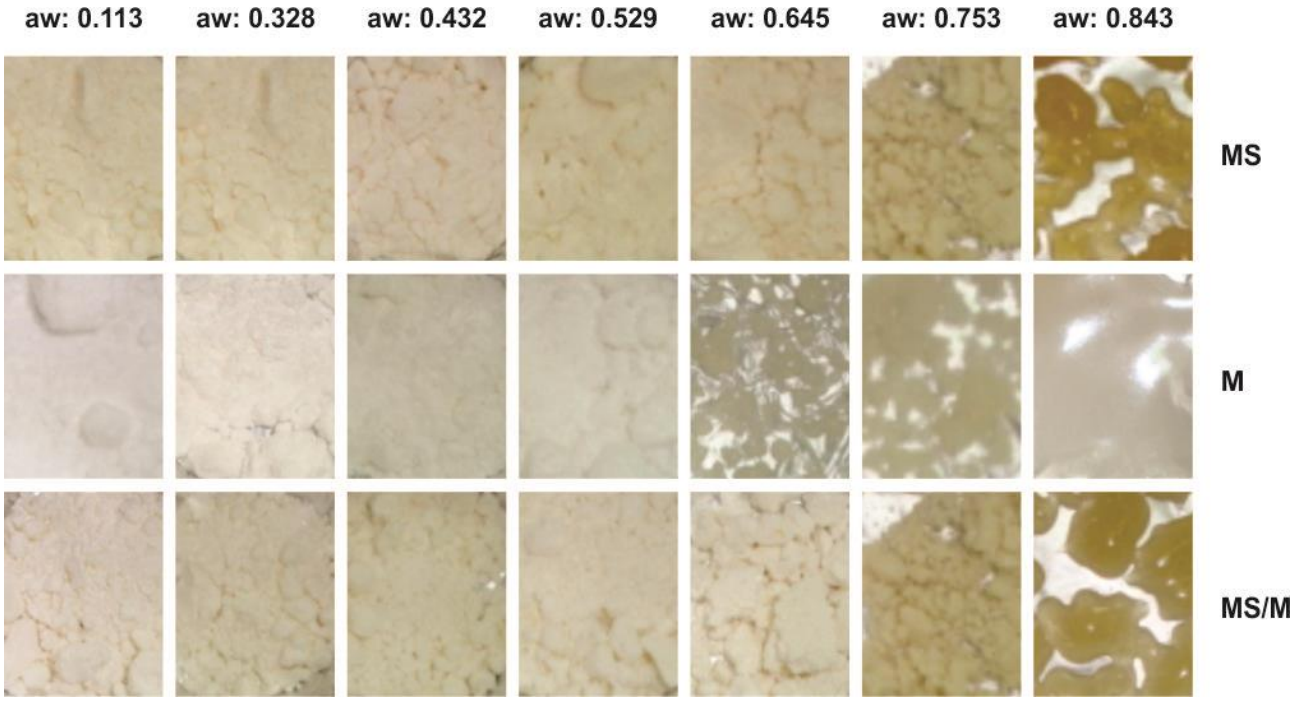

Figure 3. Physical structure of the powders of the spray-dried benzoic acid at the water activity values studied, during the determination of moisture adsorption isotherms.

Differential thermal analysis and mass loss

Thermogravimetric analysis is a method of thermal analysis in which the mass of a sample is measured over time as the temperature changes (Table 3).

Table 3. Differential thermal analysis and mass loss of the encapsulating materials and spray-dried benzoic acid.

Assays	1st stage			2nd stage		
	T_{inlet} °C	T_{outlet} °C	ML %	T_{inlet} °C	T_{outlet} °C	ML %
Benzoic acid pure material	88.20	110.64	1.18	151.12	178.43	99.162
Modified starch pure material	41.90	76.92	5.29	290.79	339.98	79.74
Maltodextrin pure material	48.89	100.13	7.05	286.85	330.77	73.34
MS	41.34	69.97	5.53	294.77	336.99	81.46
M	39.45	68.41	5.02	280.38	332.17	82.06
MS/M	40.03	72.81	5.06	280.92	337.95	80.79

T_{inlet}: inlet temperature; T_{outlet}: outlet temperature; ML: mass loss; MS: modified starch; M: maltodextrin; and MS/M: modified starch and maltodextrin blend.

The benzoic acid showed only one stage of mass loss (Figure 4A,) while the microparticles produced with the encapsulating materials alone exhibited two stages of mass loss (Figure 4B).

The first stage was due to the moisture loss of the samples up to 110°C, for all materials except the benzoic acid, which presented a lower thermal stability when compared to the spray-dried benzoic acid. At temperatures above 110°C, the mass loss corresponded to the decomposition of the materials. In this step, several reactions are observed, including the carbohydrate ring dehydration, depolymerization and decomposition of the polymer units (Hosseini, Zandi, Rezaei, & Farahmandghavi, 2013). When polymeric

materials are subjected to a thermal treatment, they can present structural changes characterized by the rupture of chemical bonds in the main and lateral chains (Costa et al., 2015). Regarding the thermographic curves or the maximum degradation temperature (600°C), it is observed that it was lower for the pure benzoic acid (approximately 180°C) when compared to both the encapsulating agents (Figure 4A) and the spray-dried product (300-330ºC) (Figure 4B), once it is a volatile compound, whose encapsulation is effective to delay the thermal degradation, which is the purpose of the encapsulation process.

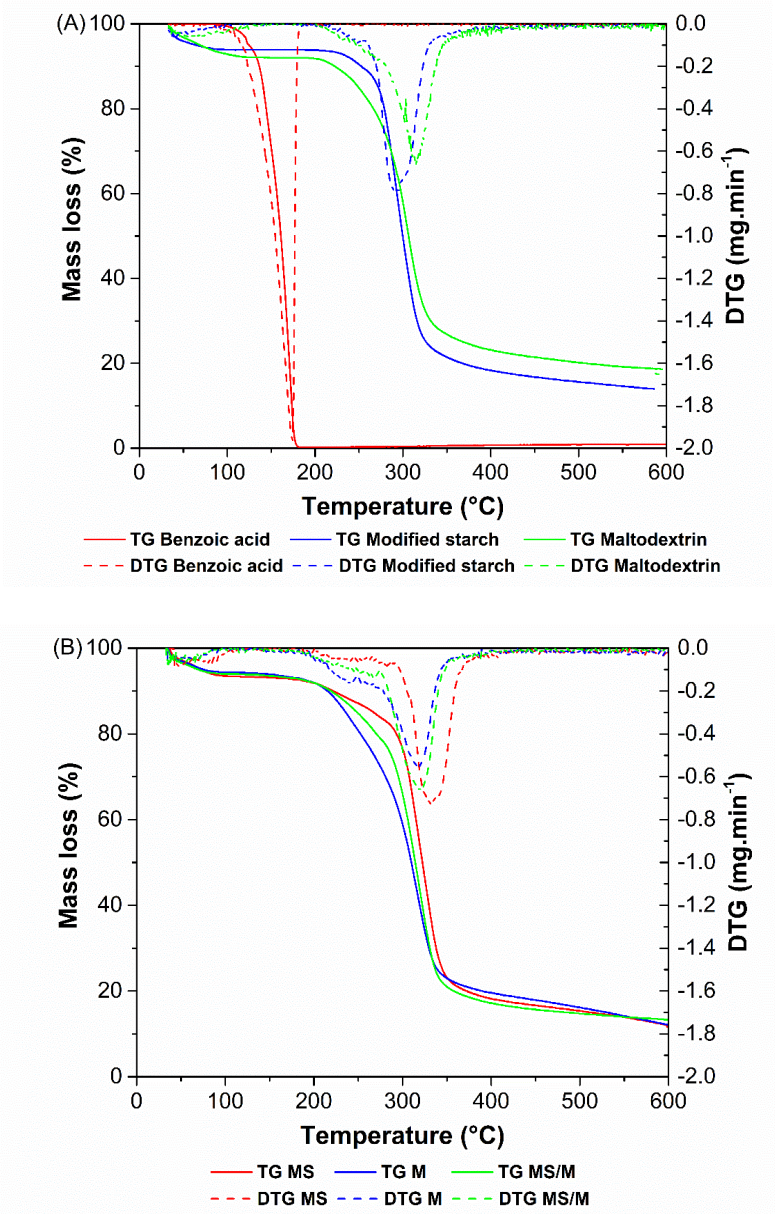

Figure 4. Thermogravimetric curves TG and DTG: pure encapsulating materials (A) and spray-dried benzoic acid in the different matrices (B), under a nitrogen atmosphere. MS: modified starch; M: maltodextrin; and MS/M: modified starch and maltodextrin blend. (Editar nas figuras 4a e 4b a unidade de medida mg/min para mg min.$^{-1}$) – AU: As figuras foram substituídas

Conclusion

The modified starch and maltodextrin blend has proven to be a suitable encapsulating material to produce benzoic acid microparticles, which exhibited the highest encapsulation efficiency, as well as the adsorption isotherms showed a Type-III behavior. The particle morphology presented spherical shape with some concavities and showed an increased thermal stability. Thus, the benzoic acid microparticles has great potential for application in food products, mainly acidic foods such as salad dressings, carbonated drinks (soft drinks), jams, fruit juices, as well as in condiments, prolonging their shelf life, due to their actions as preservatives (bacteriostatic and fungistatic) and flavoring agents.

Acknowledgements

The authors would like to thank the Coordination for the Improvement of Higher Education Personnel – Brazil (CAPES) – Finance Code (001). The authors thank FAPEMIG (Minas Gerais State Foundation for Research Development, Brazil) (CAG-PPM-00318-11) and CNPq (National Council for Scientific and Technological Development, Brazil) (Grant 303269/2016-2) for financial support.

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