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Brea gum as wall material in the microencapsulation of corn oil by spray drying: Effect of inulin addition

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ABSTRACT

This study aimed to evaluate the potential of Brea gum (BG) in the microencapsulation of corn oil in comparison with gum arabic (GA) and evaluate the effect of adding inulin at the matrix formulation. Different concentration of BG and inulin were used to emulsify pure corn oil using a homogenizer followed by an ultrasonic treatment. Then, emulsions were spray dried in laboratory scale equipment to obtain the microcapsules. Overall, powders presented spherical shape with surface concavities, no apparent cracks and high polydispersity. However, some powders containing inulin showed particles that seem to have fused together reflecting a coating effect of inulin. Moisture content of BG powders were low but increased with inulin addition, while water activities ($\leq$0.4) were not affected by inulin. The color analysis showed that BG powders presented lower luminosity and higher red and yellow parameters than GA powder, and adding inulin decreased the lightness, redness and yellowness resulting in powders with more pale color. Encapsulation efficiency increased with BG concentration, reaching 76.12% with 20% of BG. Further efficiency improvement was achieved in presence of inulin, reaching the highest value (91.72) with 20% BG/20% inulin formulation, which was higher than the efficiency achieved with GA (88.66%). It was concluded that the combination of BG and inulin could be used as an alternative wall material for microencapsulation of hydrophobic compounds in replacement of GA.

1. Introduction

Microencapsulation is a technology in which sensitive ingredients or 'core' materials are physically entrapped in a protective matrix or 'wall' material (Hogan, McNamee, O'Riordan, & O'Sullivan, 2001a). The encapsulation is widely used in food and pharmaceutical industries for (1) improving the chemical stability of sensitive compounds, protecting them from deteriorative reactions or adverse environmental conditions, (2) providing controlled release of active compounds and (3) transforming liquids such as essential oils and flavours into stable free-flowing powders that are easy to handle, minimize volume/weight, facilitate storage, transportation and incorporation into a dry mix enhancing their range of applications (de Barros Fernandes et al., 2016; Jafari, Assadpoor, Bhandari, & He, 2008; Kim & Morr, 1996).

In food applications, encapsulation is typically employed to solve formulation problems resulting from the limited chemical or physical stability of the active ingredient, an incompatibility between the active ingredient and the food matrix, or to control the release of an active compound or the bioavailability of a nutrient (Ubbink & Krüger, 2006). Currently, the most commonly applied process for encapsulation is spray-drying, mainly due to the low cost and available equipment but also because it results in good quality powders with low water activity and it is appropriate for heat sensitive components. Spray-drying technique generally involves the emulsification of the core material, usually a lipid, with a dense solution of wall material such as proteins, gums, carbohydrates, followed by the atomization of the emulsion into a drying medium with high temperature, resulting in a very fast water evaporation, which results in a quick formation of a crust that entrap the core material (Rodea-González et al., 2012). It is well described that emulsion properties (stability, viscosity and droplet size) play a key role in the encapsulation efficiency and the microencapsulated product stability (Carneiro, Tonon, Grosso, & Hubinger, 2013; Jafari et al., 2008; Klinkerson, Sophanodora, Chinachoti, Decker, & McClements, 2006; Rodea-González et al., 2012; Savary, Hucher, Bernadi, Grisel, & Malhiac, 2010). Therefore, it is important to select an appropriate emulsifying system, as well as a wall materials that forms a continuous matrix between the oil droplets in the powder particles. Gum arabic (GA) is a wall material widely used in microencapsulation by spray drying because of its high solubility, low viscosity and good emulsifying properties. However, the fluctuation in supply, as well as the increasing prices, are leading researches to look for complete or partial substitutes for GA (de Barros Fernandez, Vilela

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Borges, & Alvarenga Botrel, 2014).

The Brea gum (BG), which is a hydrocolloid exudated from *Cercidium praecox* tree, is a potential replacement for GA in many purposes, mainly due to its physicochemical characteristics and functional properties similar to gum arabic (Bertuzzi, Slavutsky, & Armada, 2012; Castel, Rubiolo, & Carrara, 2017). Chemically, both gums are composed of polysaccharide and protein that are responsible for a high interfacial activity and good emulsifying properties (Castel et al., 2016). In a previous work, it has been shown that BG emulsifying properties were similar to GA properties (Castel et al., 2017). Results showed that corn oil emulsions stabilized with BG presented no difference in the particle size distribution with emulsions stabilized with GA at same concentration, however, BG emulsion resulted more stable than the GA, possibly due to a high viscosity of BG emulsion. These findings suggested that BG could replace GA in some applications such as microencapsulation.

On the other hand, the use of blends of biopolymers having different functional properties may allow the increase of encapsulation efficiency and shelf life of microcapsules (Rodea-González et al., 2012).

In this sense, adding inulin at the encapsulation matrix is an interesting concept not only because of its functional properties and low price but also for its benefits to human health. Inulin is a natural carbohydrate commercially obtained from chicory where it is present in high quantity. In the last years, inulin has attracted much attention from various industries, especially because of its prebiotic nature (i.e. it is not digested in the small intestine, only being degraded by certain colon bacteria like bifidobacteria) (Beirão-da-Costa et al., 2012). Then, the consumption of inulin produces a selective stimulation of these gut bacteria which is beneficial for human health (Roberfroid, 2000). Other biological effect attributed to consumption of inulin are the dietary fiber actions, calcium bioavailability improvements (Saénz, Tapia, Chávez, & Robert, 2009), anticancer (Korbelik & Cooper, 2007) and immunomodulatory properties (Beirão-da-Costa et al., 2013; Bustos-Garza, Yáñez-Fernández, & Barragán-Huerta, 2013; Silva, Cooper, & Petrovsky, 2004). Besides the health related benefits of inulin, its low hydrolysis capacity allows the preparation of microcapsules resistant to pH variations (Dima, Pătraşcu, Cantaragiu, Alexe, & Dima, 2016). This property suggest that inulin is suitable for protection of bioactive compounds that are susceptible to degradation along the human digestive tract, since their release take place only in the intestine, where they are be absorbed (Beirão-da-Costa et al., 2013). In the pharmaceutical field, inulin is used as excipient, stabilizer and slow release drug delivery medium (Barclay, Ginic-Markovic, Cooper, & Petrovsky, 2010). Overall, the evaluation of new matrix system, a mix of BG and inulin, can extend the application possibilities of hydrophobic compounds in encapsulation.

The objective of this work was to evaluate the potential of pure BG and in combination with inulin as alternative materials for encapsulation of corn oil (a model of hydrophobic compound) by spray-drying. The microcapsules were characterized for morphology, moisture content, water activity and encapsulation efficiency.

2. Materials and methods

2.1. Materials

BG exudate nodules were collected and supplied by a native community of Tartagal city (Salta, Argentina).

The crude gum was purified by dissolution, centrifugation, filtration and freeze-drying steps. A 15% w/w aqueous solution of the exudate was allowed to stand for 24 h to reach a complete hydration of the sample. The gum solution was then centrifuged and filtered through Whatman No. 1 filter paper to separate any undissolved materials. The solution was then vacuum filtered through a 0.5 μm fiberglass membrane to remove impurities further. Finally, the purified solution was freeze-dried, and then ground to obtain a powder. BG sample used for color analysis was purified by the same later steps of dissolution, centrifugation and filtration but instead of being freeze-dried, it was spray dried in laboratory scale equipment (Spray Dryer. ADL311 Yamato), using an inlet and outlet air temperatures of 150 ± 5 °C and 60 ± 5 °C respectively, with an atomization pressure of 0.1 MPa. BG powder contained 1.14% w/w of fat and 4.23% w/w of ash as determined by standard methods (AOAC, 1995), and 7.52% w/w of protein determined by Kjeldahl method using 6.6 as N protein conversion factor (Renard, Lavenant-Gourgeon, Ralet, & Sanchez, 2006), 1.25% w/w of phenolic compounds determined according to Castel, Andrich, Netto, Santiago, and Carrara (2014), 4.38% of moisture and 82.06% of polysaccharides determined from the difference between the rest of the components (Castel et al., 2016).

GA was purchased from Colloïdes Naturels International (Rouen, France) and the inulin (Orafti GR, Beneo, Germany) was kindly supplied by Saporiti S.A.

2.2. Emulsion preparation

The wall materials were added to distilled water and stirred until complete dissolution at 25 °C. The solutions were kept overnight to warrant full saturation of the polymer molecules. The composition of wall material solutions are shown in Table 1. First, three concentration of pure BG were evaluated (5, 10 and 20% w/w) and compared with GA at 20% w/w. Then, since BG presented high viscosity solutions at concentrations above 20% w/w, inulin was added to BG20 formulation in order to reach 30% and 40% of total solids as they are the concentration generally used for encapsulation by spray drying (Barbosa, Borsarelli, & Mercadante, 2005; Boiero et al., 2014; Hogan et al., 2001a; Jafari et al., 2008).

Then, 10% w/w pure corn oil was added to the wall material solutions (90% w/w) and was homogenized with an Omni mixer (Ivan Sorvall, Inc., Norwalk, Conn.) for 5 min at 5000 rpm. Pre-emulsions were further emulsified by an ultrasonic treatment at 75% AMP for 2 min with temperature controller setup to stop the treatment when sample reaches 30 °C. A 20 kHz sonicator was used (Ultrasound generator, Sonics and Materials VCX-750, Newton, CT).

2.3. Emulsion droplet size measurement

Emulsion droplet sizes were determined by dynamic light scattering using a Zetasizer Nano-ZS90 device (Malvern Instruments, Ltd., Worcestershire, UK) at 25 °C. After appropriate dilution of the emulsion samples with Milli-Q ultrapure water, ten reads per sample were carried out and Z-average was automatically calculated by the instrument.

Table 1
Composition of wall material solutions for emulsion preparation.

	Wall material[a]			Total solid[a]	Core material[b]
	Brea gum (BG)	Gum arabic (GA)	Inulin (I)		Corn oil
BG5	5	–	–	5	10
BG10	10	–	–	10	10
BG20	20	–	–	20	10
BG20 + I10	20	–	10	30	10
BG20 + I20	20	–	20	40	10
GA20	–	20	–	20	10
GA20 + I10	–	20	10	30	10
GA20 + I20	–	20	20	40	10

[a] g/100 g of solution.
[b] g/100 g of emulsion.

2.4. Microencapsulation by spray drying

Emulsions were spray dried in laboratory scale equipment (Spray Dryer. ADL311 Yamato), using an inlet and outlet air temperatures of 150 ± 5 °C and 60 ± 5 °C respectively, with an atomization pressure of 0.1 MPa. Powders were named as BG5, BG10, BG20, GA20, BG20 + I10, BG20 + I20. GA20 + I10 and GA20 + I20 according to the wall material composition (Table 1).

2.5. Scanning electronic microscopy (SEM)

The morphology and microstructure of the powders were observed by scanning electronic microscopy (JSM-35C, JEOL, Japan). The powders were placed on the SEM stubs using a two-sided adhesive tape and subsequently coated with gold using a magnetron sputter coater. Examinations were made at 3000 × and 10,000 × magnifications. An approximate range of particle size was obtained by measuring particle diameters with an image processing program, Image J 1.48v. Different micrographs of the same sample were observed to make a representative measurement.

2.6. Moisture content and water activity determinations

The moisture content was determined gravimetrically by drying in a vacuum oven at 40 °C until constant weight. Powders' water activity (a_w) was measured with a team Aqua-Lab Water Activity Meter. Temperature was maintained at 25 ± 0.1 °C during the tests.

2.7. Color analysis

Color analysis was performed in a colorimeter Minolta 508d. The color of the samples was reported in term of the tristimulus coordinates L^*, a^*, and b^*. The total difference of color (ΔE^*) between the measured values of a white standard plate and the samples was calculated according to Verruck, Schwinden Prudêncio, Olivera Müller, Beddin Fritzen-Freire, and Dias de Mello Castanho Amboni (2015), as described in Eq. (1),

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

where ΔL^* is the difference of luminosity between the white standard plate and each of the samples, Δa^* represents the intensity of the red color and Δb^* the intensity of the yellow color.

2.8. Free oil determination

The microcapsule free oil was determined according to Klinkerson, Sophanodora, Chinachoti, Decker and McClements (2006) method with modifications. Fifteen milliliters of petroleum ether were added to 2.5 g of powder in a glass jar with a lid, which was shaken by hand for 2 min and then allowed to stand for 5 min at room temperature. The mixture was filtered through a Munktell 00R filter paper and collected in a round-bottomed flask. The petroleum ether was evaporated in rotary evaporator at 70 °C and the solvent-free extract was dried at 105 °C until constant weight (about 1 h). The amount of free oil was calculated based on the difference between the weight of the initial clean flask and that containing extracted oil residue.

2.9. Total oil determination

The total oil content was determined according to the method of Klinkerson et al. (2006) with modifications. Four millilitres of ultrapure water were added to 0.5 g of powder and the mixture was stirred until completely dissolved. Then, 25 mL hexane/isopropanol (3:1 v/v) was added to the solution and the tube was shaken for 10 min using a vortex mixer and centrifuged for 15 min at 12,000*g*. The clear organic phase was filtered through a Munktell 00R filter paper and collected in a round-bottomed flask. The solvent was evaporated in a rotary evaporator at 70 °C and the residue dried to constant weight. The amount of oil extracted was determined gravimetrically as described in free oil method.

2.10. Encapsulation efficiency

Encapsulation efficiency (EE) was calculated from the ratio between the amount of encapsulated oil and total oil present in the powders (Eq. (2)) determined by gravimetric methods:

$$EE\ (\%) = \frac{\left[\text{Total oil}\left(\frac{g}{100g\ powder}\right) - \text{Free oil}\left(\frac{g}{100g\ powder}\right)\right] \times 100}{\text{Total oil}\left(\frac{g}{100g\ powder}\right)} \quad (2)$$

2.11. Statistical analysis

All experiments were performed at least in triplicate and data were reported as means ± standard deviation. Statistical analyses were performed using Statgraphics Centurion XVsoftware. One-way analysis of variance (ANOVA) with a LSD test at $p \leq 0.05$ was used to detect statistical differences in microcapsule characteristics. If data could not meet ANOVA assumptions, non-parametric analysis of variance (Kruskall-Wallis) was performed, and box and whisker plot was used to determine which median are significantly different from other.

3. Results and discussion

3.1. Surface morphology of BG and GA microcapsules

Corn oil emulsions stabilized with BG and GA were spray dried to obtain the microcapsules. Fig. 1 shows the scanning electron micrographs of the powders obtained.

In general, BG and GA microcapsules showed similar external morphology: quasi-spherical shape with some dents or concavities on the surface. These surface irregularities are attributed to the fast water evaporation and consequent contraction of the particles during the drying process (Bustos-Garza et al., 2013). No cracks or fissures were observed in most microcapsules indicating that they have low permeability to gases which increases the protection and retention of the core material. Occasionally, some pores were found in few particles of BG5 (Fig. 1B). Some authors suggest that pores probably arise from an uneven shrinkage of the material during the last phase of the drying process (Klinkerson et al., 2006). The porosity may affect the free oil measured using solvent extraction since considerable part of the encapsulated oil could be extracted from the interior of the microcapsules due to possible solvent penetration through the pore. Similar spherical morphologies were found by several authors using spray-drying as microencapsulation process (Carneiro et al., 2013; Klinkerson et al., 2006; Rodea-González et al., 2012).

Particle size of the powders, measured from the micrographs with an image processing program, exhibited a wide range, with diameters varying from 0.6 to 26 μm. The size polydispersity is a typical characteristic of particles produced by spray-drying (Carneiro et al., 2013). BG5 showed particle sizes from 1.8 to 10 μm and particles with a trend to form clumps that seem to have fused together. This appearance could be related to the presence of high surface oil on the powders (McNamee, O'Riordan, & O'Sullivan, 1998). BG10 and BG20 powders presented wider size distributions than BG5, with particles of diameters varying from 0.8 to 10 μm for BG10 and from 0.9 to 26 μm for BG20. Although the polydispersity of the particle size distribution increased with the gum concentration, in BG10 and BG20, the smaller particles were the majority population. This may be due to the higher concentration of wall material available to form more interfacial area

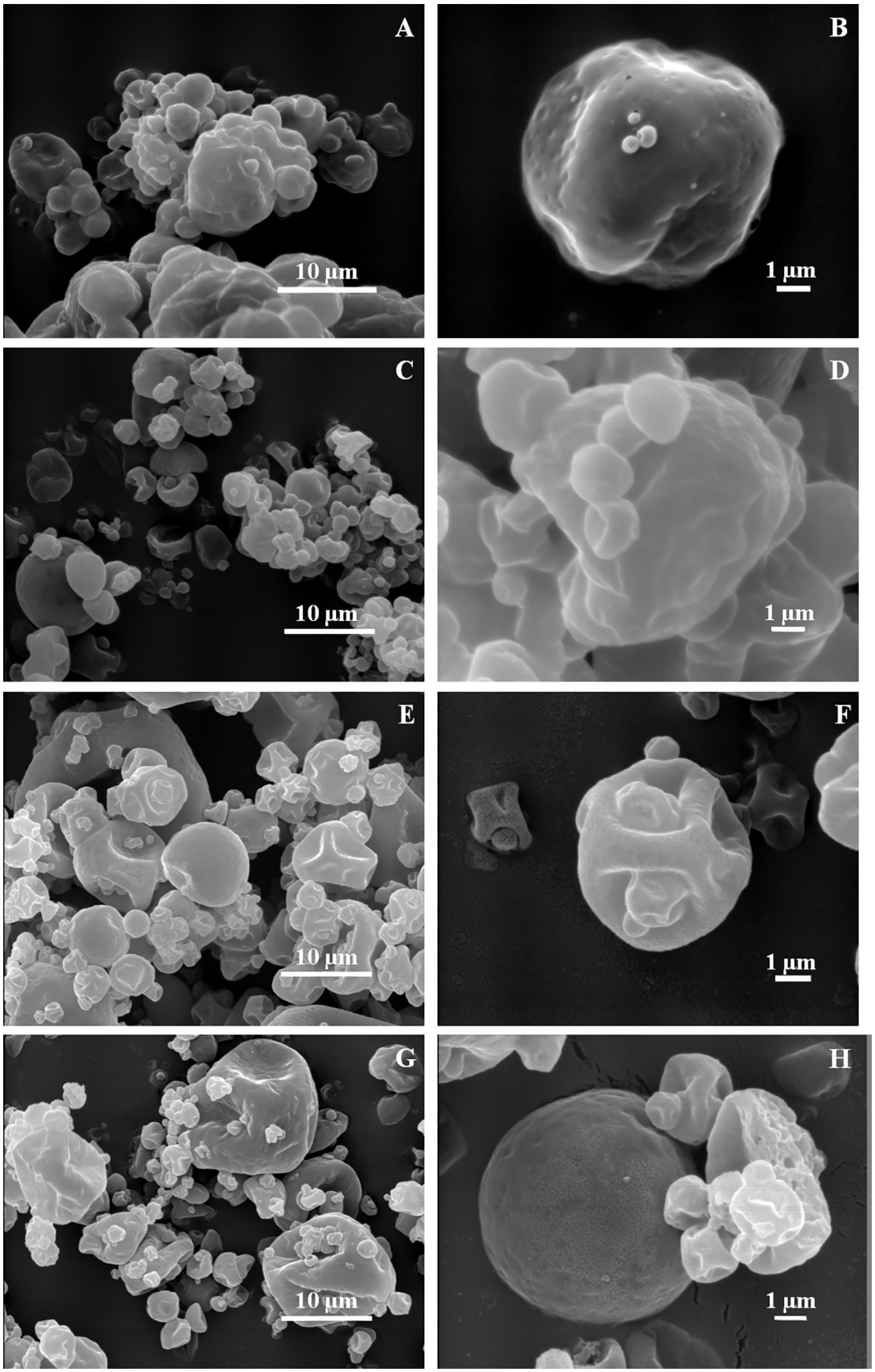
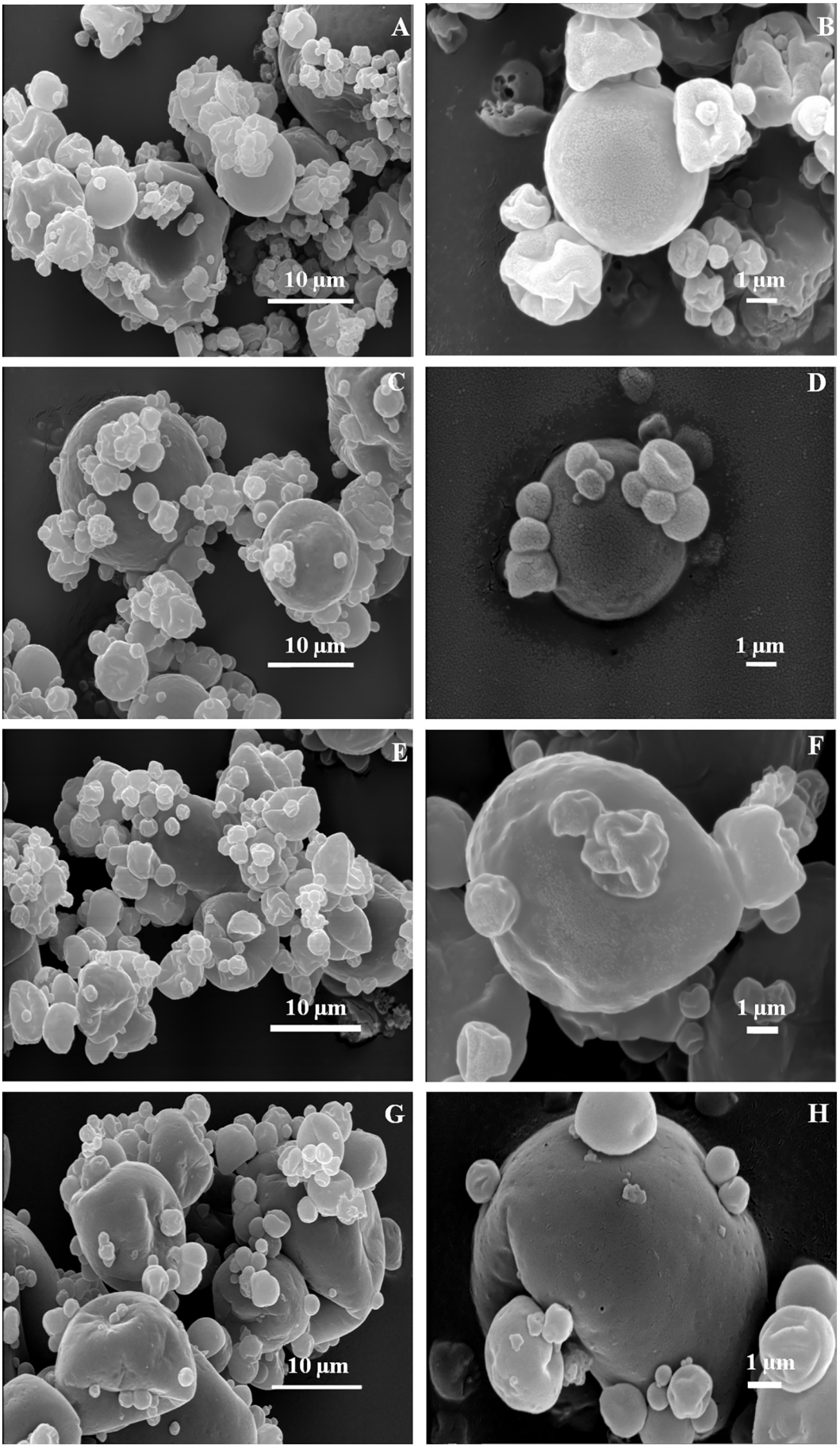


Fig. 1. SEM images of microcapsulated corn oil produced with BG and GA: BG5 (A at 3000 × and B at 10,000 ×), BG10 (C at 3000 × and D 10,000 ×), BG20, (F at 3000 × and E 10,000 ×) and GA20 (G 3000 × and H at 10,000 ×).



(caption on next page)

Fig. 2. SEM images of microcapsulated corn oil produced with BG and GA combined with inulin: BG20 + I10 (A at 3000 × and B at 10,000 ×), BG20 + I20 (C at 3000 × and D at 10,000 ×), GA20 + I10 (E at 3000 × and F at 10,000 ×) and GA20 + I20 (G at 3000 × and H at 1000 ×).

allowing the formation of more particles with smaller diameters. Microcapsules prepared with GA presented similar aspect to those of BG20, although some particles with higher diameter were observed.

On the other hand, the effect of adding inulin to the wall material formulation was evaluated and the SEM micrographs of the powders are shown in Figure 2. BG20 + I10 presented several broken particles and some particles with pores which were not observed in BG20 + I20. This fact indicates that the latter formulation produces particles with better coverage. Although these morphological differences, particle size distribution of BG20 + I10 and BG20 + I20 were similar to those prepared without inulin, with diameters in a range of 0.8 to 18 μm showing high polydispersity as well.

GA20 + I10 and GA20 + I20 presented similar morphologies and particles sizes to those of GA20, but particularly GA20 + I20 showed a majority population of large particles of around 15 μm and some particles with pores.

3.2. Moisture content and water activity

Particle moisture contents and water activities (a_w) are shown in Table 2. The moisture content of the BG microcapsules ranged from 1.16% to 3.68% which was lower than GA20 microcapsule moisture (4.37%). No trend was observed in moisture content with varying BG concentration. BG5 had the lowest moisture content. Also, these moisture values were lower than the values reported in other studies, such as orange oil encapsulated by spray drying using GA as wall material with 5.7% of moisture content (Kim & Morr, 1996). Rodea-González et al. (2012) reported moisture contents ranged from 4.35 to 5.26% for chia essential oil microcapsules prepared with whey protein concentrate, GA and mesquite gum. However, using maltodextrin, WPC and modified starch as wall materials for encapsulation of different oils similar moisture values than those of BG microcapsules were obtained (1–3%) (Carneiro et al., 2013; Hogan, McNamee, O'Riordan, & O'Sullivan, 2001b; Jafari et al., 2008). According to Hogan et al. (2001b) and Carneiro et al. (2013) moisture content values were not affected by the type of wall material. Instead, moisture content was related to the temperatures used in the spray drying process (Klinkerson et al., 2006).

All BG microcapsules showed low a_w values, ranging from 0.280 to 0.375 which were lower than GA20 water activity (0.414). Moreover, all these a_w values are considered to be adequate for this type of product since low a_w inhibit microbial growth and decrease relative rate of oxidative reactions (Quirino Lacerda et al., 2016).

The addition of inulin significantly increased ($p < 0.05$) the moisture contents and a_w of BG powders. According to de Barros Fernandez et al. (2014), particles containing inulin dried faster than the others which led to rapid formation of a crust that hindered water diffusion and evaporation.

Table 2
Moisture contents and water activities (a_w) of corn oil microcapsules.

Sample	Moisture content (%)	a_w
BG5	1.16 ± 0.01^{a}	0.355 ± 0.001^{e}
BG10	3.68 ± 0.07^{e}	0.375 ± 0.001^{f}
BG20	2.74 ± 0.05^{d}	0.319 ± 0.001^{c}
BG20 + I10	4.20 ± 0.01^{h}	0.358 ± 0.001^{e}
BG20 + I20	4.11 ± 0.01^{f}	0.349 ± 0.006^{e}
GA20	4.37 ± 0.01^{i}	0.414 ± 0.002^{g}
GA20 + I10	4.16 ± 0.01^{g}	0.307 ± 0.001^{b}
GA20 + I20	2.14 ± 0.07^{c}	0.336 ± 0.02^{d}

Data expressed as average ± standard deviation ($n = 3$). Different superscript letters in the same column indicate statistical difference.

On the other hand, it was observed that the addition of inulin to the GA20 formulation produced the decrease of both the moisture content and the a_w, opposed to the effect observed in BG microcapsules.

3.3. Color analysis

Results of color coordinates (L^*, a^* and b^*) and the total difference of color (ΔE^*) of BG, GA and the microcapsules are presented in Table 3. First, it can be noticed that although BG presented slightly lower L^*, a^* and b^* values than GA, the ΔE^* of both samples showed no significant difference ($p < 0.05$), indicating that both wall materials were similar in color. However, this value of ΔE^* for pure samples decreased significantly when obtaining both GA and GB microencapsulated powders, which could be attributed to the color interference of the oil when incorporated in the microcapsules composition. It also bears noting that this effect was more pronounced in GA powders, as ΔE^* dropped from 15.25 to 5.66 when preparing GA20 microcapsules. On the other hand, clear differences between BG and GA microencapsulated powders were observed in the color coordinates and the ΔE^* as well as visually. BG powders presented lower L^* values and higher b^* and a^* values than GA powders, corresponding to a brownish color of BG powders and a pale yellow color of GA powders. Moreover, ΔE^* values of BG powders were more than two-fold higher regarding to those of GA20, and close to that observed for the pure BG sample. A possible reason for this would be that BG presents higher phenolic compound content than GA (Castel et al., 2016), and among these phenolic compounds, it is possible that some pigments are present which influenced the final color of the powders.

All powders prepared with pure BG presented similar pale brownish color showing slight visual differences and no clear trend when varying BG concentration. In agreement with this, BG microcapsules presented high L^* (lightness) values, a^* values close to zero and low b^* values corresponding to a brownish to yellowish color.

When adding inulin, BG microcapsules showed lower b^* values (less yellowness) and lower L^* in the case of BG20 + I20 resulting in lower ΔE^* values than the powders without inulin which corresponds with the more pale colors observed. This is probably due to the color interference of inulin in the microcapsules color. In contrast, when adding inulin to GA microcapsules, powders presented lower L^* values and higher a^* and b^* values than GA20, which resulted in colors less similar to the white standard (higher ΔE^* values).

Finally, it is important to note that all BG powders (with or without inulin) presented lower ΔE^* values than the initial wall material (BG), being more similar to the white standard which is a convenient characteristic for this kind of products that are going to be added in different formulation.

3.4. Encapsulation efficiency

In order to evaluate BG ability for lipophilic compounds encapsulation in comparison with GA, total and free oil of the powders were determined and an encapsulation efficiency (EE) was calculated. According to literature, free oil is considered as the oil that can be extracted with organic solvents and strongly depends on the extraction conditions used (Klinkerson et al., 2006). Therefore, EE values reflect not only the presence of oil at the particles surfaces but also the degree to which the encapsulation matrix can prevent extraction of encapsulated oil by a leaching process (Hogan et al., 2001a). Overall, as concentration of BG increased in the emulsion from 5% to 20%, free oil values decreased from 40.29% to 9.50%, respectively (Table 4). The high free oil value determined for BG5 could be explained by different effects: (i) high amount of oil on the surface of BG5 particles, as was

Table 3
Color coordinates values of BG, GA and corn oil microcapsules.

Sample	L^*	a^*	b^*	ΔE^*
BG	85.34 ± 0.04^{a}	0.66 ± 0.02^{c}	11.00 ± 0.03^{h}	15.36 ± 0.08^{h}
GA	87.15 ± 0.25^{b}	1.26 ± 0.04^{d}	12.31 ± 0.07^{i}	15.25 ± 0.20^{h}
BG5	85.59 ± 0.38^{a}	0.60 ± 0.06^{c}	10.21 ± 0.47^{f}	14.62 ± 0.30^{g}
BG10	88.03 ± 0.43^{c}	0.58 ± 0.05^{c}	9.76 ± 0.05^{e}	12.65 ± 0.24^{e}
BG20	86.35 ± 0.19^{a}	0.70 ± 0.03^{c}	10.41 ± 0.12^{g}	14.25 ± 0.13^{g}
BG20 + I10	85.98 ± 0.45^{a}	0.74 ± 0.09^{c}	9.48 ± 0.17^{d}	13.84 ± 0.40^{f}
BG20 + I20	87.39 ± 0.61^{b}	0.62 ± 0.06^{c}	8.62 ± 0.16^{c}	12.23 ± 0.49^{d}
GA20	92.43 ± 0.48^{f}	0.10 ± 0.03^{b}	4.33 ± 0.10^{a}	5.66 ± 0.27^{a}
GA20 + I10	91.45 ± 0.29^{e}	−0.03 ± 0.04^{a}	4.26 ± 0.07^{a}	6.27 ± 0.24^{b}
GA20 + I20	88.78 ± 0.17^{d}	0.52 ± 0.05^{c}	7.76 ± 0.19^{b}	10.64 ± 0.24^{c}

Data expressed as average ± standard deviation (n = 3). Different superscript letters in the same column indicate statistical difference.

Table 4
Free oil, total oil and encapsulation efficiency (EE) of corn oil microcapsules.

Sample	Free oil (g/100 g powder)	Total oil (g/100 g powder)	EE (%)
BG5	40.29 ± 2.28^{g}	61.20 ± 0.70^{c}	34.16 ± 3.16^{a}
BG10	29.75 ± 1.08^{f}	47.59 ± 1.69^{b}	37.48 ± 0.72^{a}
BG20	9.50 ± 2.82^{e}	33.12 ± 3.40^{a}	76.12 ± 0.29^{b}
BG20 + I10	4.54 ± 2.19^{e}	23.56 ± 0.97^{a}	74.15 ± 1.06^{b}
BG20 + I20	1.63 ± 0.23^{a}	19.61 ± 0.35^{a}	91.72 ± 1.02^{d}
GA20	3.83 ± 0.01^{d}	33.80 ± 0.44^{a}	88.66 ± 0.12^{c}
GA20 + I10	2.86 ± 0.06^{c}	24.66 ± 0.82^{a}	88.39 ± 0.14^{c}
GA20 + I20	2.54 ± 0.08^{b}	20.29 ± 1.01^{a}	87.48 ± 0.48^{c}

Data expressed as average ± standard deviation (n = 3). Different superscript letters in the same column indicate statistical difference.

reflected in SEM images where the formation of aggregates and fused particles were observed (Fig. 1A), (ii) oil extracted from the interior of the particle through the pores observed in some BG5 particles (Fig. 1B), and (iii) rupture of some particles during the process of extraction because of a thin and fragile matrix. In BG5, the lack of sufficient wall material for core entrapment could have caused fragile microcapsules (Karaca, Nickerson, & Low, 2013; McNamee et al., 1998; Polavarapu, Oliver, Ajlouni, & Augustin, 2011). On the other hand, many authors agreed that a smaller size of droplets in the emulsion usually represents a greater stability and this is strongly related to a low concentration of surface oil in the powders (Barbosa et al., 2005; Carneiro et al., 2013; Jafari et al., 2008; Kim & Morr, 1996; Liu et al., 2001; Soottitantawat et al., 2005). Previously, we have shown that BG5 emulsions presented larger droplet sizes (783.8 nm) and lower stability than BG10 and BG20 emulsions (674.4 and 529.6 nm, respectively), which would be in agreement with the high free oil determined for BG5 microcapsules (Castel et al., 2017). As a consequence of this the EE of BG5 was low (34.16%).

Although the amount of free oil was lower when BG concentration increased to 10% (BG10), EE did not increase significantly (Table 4). A significant increase in EE was achieved in BG20 (76.12%), approaching the EE obtained with GA20 (88.66%). In BG20, the free oil was drastically reduced which is important to provide storage stability of the encapsulated material (Anandaraman & Reineccius, 1987). EE of BG20 was in the range of those obtained by Kim and Morr (1996) in the encapsulation of orange oil with GA (75.9%) and WPI (72.7%) as wall materials. Rodea-González et al. (2012) obtained EE in the range of 70.7 to 80.7% by encapsulating chia essential oil with WPC combined with mesquite gum or GA but using a higher total solid content (30 and 40%). Carneiro et al. (2013) reported an EE of 62.3% using GA/maltodextrin as wall materials to encapsulate flaxseed oil. The same authors reached EE of 95.7% using a matrix of modified starch combined with maltodextrin.

When 10% of inulin was added to BG20 formulation, no effect was observed neither in free oil values nor in EE. In contrast, a significant impact on free oil and EE was observed when 20% of inulin was added to BG20. Free oil of BG20 + I20 was the lowest value achieved among the samples and EE was the highest (91.72%), even higher than all GA formulations. Besides, it was observed that the addition of inulin on GA formulations produced no effect regarding EE improvement. Therefore, BG20 + I20 was the optimum formulation at which the efficiency was the greatest. According to da Silva Carvalho et al. (2016), low-molecular-weight sugar can act as a plasticizer, avoiding irregular shrinkage of the microparticle surface during the drying process. This effect could be contributing to a better coverage of the microcapsules improving the efficiency of the powders containing inulin. On the other hand, although free oil decreased and EE increased in presence of inulin, emulsions containing inulin presented bigger particle sizes than emulsion without inulin in each formulations (821.4, 1491.0, 617.3 and 624.3 nm for BG10 + I20, BG10 + I30, BG20 + I10 and BG20 + I20, respectively). This may be due to coating effect of inulin that produces a thicker matrix layer around the particle. However, these emulsions presented high stability without phase separation after 7 days of analysis (data not shown), which is related to the low free oil and the high EE presented by these samples.

Finally, results suggest that the use of inulin together with BG is more advantageous in relation to pure BG in loading oil, since these polysaccharides may offer different functional properties: BG mainly acts as an emulsifying agent and matrix forming material while inulin serves as coating agent.

4. Conclusions

BG proved to be a good wall material for the encapsulation of hydrophobic compounds particles by spray drying process. BG powders presented good quality in terms of moisture, a_w and morphology, showing no cracks or fissures reflecting a good protection of the encapsulated material. EE increased with increasing BG concentration which was related to smaller droplet size and higher emulsion stability.

The presence of inulin as a secondary wall material showed a significant impact on EE, being BG20 + I20 the optimum formulation showing the highest efficiency. According to the results, the blend of BG and inulin, which are relatively inexpensive natural materials, can be selected as good alternative carrier agents for hydrophobic compounds.

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References

Anandaraman, S., & Reineccius, G. A. (1987). Analysis of encapsulated orange peel oil. *Perfumer and Flavorist, 12*, 33–39.

Barbosa, M. I. M. J., Borsarelli, C. D., & Mercadante, A. Z. (2005). Light stability of spray-dried bixin encapsulated with different edible polysaccharide preparations. *Food Research International, 38*, 989–994.

Barclay, T., Ginic-Markovic, M., Cooper, P. D., & Petrovsky, N. (2010). Inuline a versatile polysaccharide with multiple pharmaceutical and food chemical uses. *Journal of Excipients and Food Chemistry, 1*(3), 27–50.

de Barros Fernandes, R. V., Alvarenga Botrela, D., Silva, E. K., Vilela Borges, S., Rodrigues de Oliveira, C., Yoshidad, M. I., ... Monteiro de Paula, R. C. (2016). Cashew gum and inulin: New alternative for ginger essential oil microencapsulation. *Carbohydrate Polymers, 153*, 133–142.

de Barros Fernandez, R. V., Vilela Borges, S., & Alvarenga Botrel, D. (2014). Gum arabic/starch/maltodextrin/inulin as wall materials on the microencapsulation of rosemary essential oil. *Carbohydrate Polymers, 101*, 524–532.

Beirão-da-Costa, S., Duarte, C., Bourbon, A. I., Pinheiro, A. C., Nunes Januário, M. I., Vicente, A. A., ... Delgadillo, I. (2013). Inulin potential for encapsulation and controlled delivery of oregano essential oil. *Food Hydrocolloids, 33*, 199–206.

Beirão-da-Costa, S., Duarte, C., Bourbon, A. I., Pinheiro, A. C., Serra, A. T., Moldão Martins, M., ... Beirão da Costa, M. L. (2012). Effect of the matrix system in the delivery and in vitro bioactivity of microencapsulated oregano essential oil. *Journal of Food Engineering, 110*, 190–199.

Bertuzzi, M. A., Slavutsky, A. M., & Armada, M. (2012). Physicochemical characterisation of the hydrocolloid from Brea tree (*Cercidium praecox*). *International Journal of Food Science and Technology, 47*, 776–782.

Boiero, M. L., Mandrioli, M., Vanden Braber, N., Rodriguez-Estrada, M. T., García, N. A., Borsarelli, C. D., & Montenegro, M. A. (2014). Gum arabic microcapsules as protectors of the photoinduced degradation of riboflavin in whole milk. *Journal of Dairy Science, 97*, 5328–5336.

Bustos-Garza, C., Yáñez-Fernández, J., & Barragán-Huerta, B. E. (2013). Thermal and pH stability of spray-dried encapsulated astaxanthin oleoresin from *Haematococcus pluvialis* using several encapsulation wall materials. *Food Research International, 54*, 641–649.

Carneiro, H. C. F., Tonon, R. V., Grosso, C. R. F., & Hubinger, M. D. (2013). Encapsulation efficiency and oxidative stability of flaxseed oil microencapsulated by spray drying using different combination of wall materials. *Journal of Food Engineering, 115*, 443–451.

Castel, V., Andrich, O., Netto, F. M., Santiago, L. G., & Carrara, C. R. (2014). Total phenolic content and antioxidant activity of different streams resulting from pilot-plant processes to obtain *Amaranthus mantegazzianus* protein concentrates. *Journal of Food Engineering, 122*, 62–67.

Castel, V., Rubiolo, A. C., & Carrara, C. R. (2017). Droplet size distribution, rheological behavior and stability of corn oil emulsions stabilized by a novel hydrocolloid (Brea gum) compared with gum arabic. *Food Hydrocolloids, 63*, 170–177.

Castel, V., Zivanovic, S., Jurat-Fuentes, J. L., Santiago, L. G., Rubiolo, A. C., Carrara, C. R., & Harte, F. M. (2016). Chromatographic fractionation and molecular mass characterization of *Cercidium praecox* (Brea) gum. *Journal of the Science of Food and Agriculture, 96*(13), 4345–4350.

Dima, C., Pătraşcu, L., Cantaragiu, A., Alexe, P., & Dima, S. (2016). The kinetics of the swelling process and the release mechanisms of *Coriandrum sativum* L. essential oil from chitosan/alginate/inulin microcapsules. *Food Chemistry, 195*, 39–48.

Hogan, S. A., McNamee, B. F., O'Riordan, E. D., & O'Sullivan, M. (2001a). Emulsification and microencapsulation properties of sodium caseinate/carbohydrate blends. *International Dairy Journal, 11*, 137–144.

Hogan, S. A., McNamee, B. F., O'Riordan, E. D., & O'Sullivan, M. (2001b). Microencapsulating properties of whey protein concentrate. *Journal of Food Science, 66*, 675–680.

Jafari, S. M., Assadpoor, E., Bhandari, B., & He, Y. (2008). Nano particle encapsulation of fish oil by spray drying. *Food Research International, 41*(2), 172–183.

Karaca, A. C., Nickerson, M., & Low, N. H. (2013). Microcapsule production employing chickpea or lentil protein isolates and maltodextrin: Physicochemical properties and oxidative protection of encapsulated flaxseed oil. *Food Chemistry, 139*, 448–457.

Kim, Y. D., & Morr, C. V. (1996). Microencapsulation properties of gum arabic and several food proteins: Spray-dried orange oil emulsion particles. *Journal of Agricultural and Food Chemistry, 44*, 1314–1320.

Klinkerson, U., Sophanodora, P., Chinachoti, P., Decker, E. A., & McClements, D. J. (2006). Characterization of spray-dried tuna oil emulsified in two-layered interfacial membranes prepared using electrostatic layer-by-layer deposition. *Food Research International, 39*(4), 449–457.

Korbelik, M., & Cooper, P. D. (2007). Potentiation of photodynamic therapy of cancer by complement: the effect of gamma-inulin. *British Journal of Cancer, 96*, 67–72.

Liu, X. D., Atarashi, T., Furuta, T., Yoshii, H., Aishima, S., Ohkawara, M., & Linko, P. (2001). Microencapsulation of emulsified hydrophobic flavors by spray drying. *Drying Technology, 19*, 1361–1374.

McNamee, B. F., O'Riordan, E., & O'Sullivan, M. (1998). Emulsification and microencapsulation properties of gum arabic. *Journal of Agricultural and Food Chemistry, 46*, 4551–4555.

Polavarapu, S., Oliver, C. M., Ajlouni, S., & Augustin, M. A. (2011). Physicochemical characterisation and oxidative stability of fish oil and fish oil–extra virgin olive oil microencapsulated by sugar beet pectin. *Food Chemistry, 127*(4), 1694–1705.

Quirino Lacerda, E. C., de Araújo Caladob, V. M., Monteiroc, M., Finotellid, P. V., Guedes Torresa, A., & Perrone, D. (2016). Starch, inulin and maltodextrin as encapsulating agents affect the quality and stability of jussara pulp microparticles. *Carbohydrate Polymers, 151*, 500–510.

Renard, D., Lavenant-Gourgeon, L., Ralet, M.-C., & Sanchez, C. (2006). Acacia senegal gum: continuum of molecular species differing by their protein to sugar ratio, molecular weight, and charges. *Biomacromolecules, 7*, 2637–2649.

Roberfroid, M. B. (2000). Chicory fructooligossacharides and the gastrointestinal tract. *Nutrition, 16*, 677–679.

Rodea-González, D.A., Cruz-Olivares, J., Román-Guerrero, A., Rodríguez-Huezo, M.E., Vernon-Carter, E.J. & Pérez-Alonso, C. (2012). Spray-dried encapsulation of chia essential oil (*Salvia hispanica* L.) in whey protein concentrate-polysaccharide matrices. Journal of Food Engineering, 111 (1), 102-109.

Saénz, C., Tapia, S., Chávez, J., & Robert, P. (2009). Microencapsulation by spray drying of bioactive compounds from cactus pear (*Opuntia ficus-indica*). *Food Chemistry, 114*, 616–622.

Savary, G., Hucher, N., Bernadi, E., Grisel, M., & Malhiac, C. (2010). Relationship between the emulsifying properties of *Acacia* gums and the retention and diffusion of aroma compounds. *Food Hydrocolloids, 24*, 178–183.

da Silva Carvalho, A. G., Teixeira da Costa Machado, M., Martins da Silva, V., Sartoratto, A., Ferreira Rodrigues, R. A., & Dupas Hubinger, M. (2016). Physical properties and morphology of spray dried microparticles containing anthocyanins of jussara (*Euterpe edulis* Martius) extract. *Powder Technology, 294*, 421–428.

Silva, D. G., Cooper, P. D., & Petrovsky, N. (2004). Inulin-derived adjuvants efficiently promote both Th1 and Th2 immune responses. *Immunology and Cell Biology, 82*, 611–616.

Soottitantawat, A., Bigeard, F., Yoshi, H., Furuta, T., Ohkawara, M., & Linko, P. (2005). Influence of emulsion and powder size on the stability of encapsulated D-limonene by spray drying. *Innovative Food Science and Emerging Technologies, 6*(1), 107–114.

Ubbink, J., & Krüger, J. (2006). Physical approaches for the delivery of active ingredients in foods. *Trends in Food Science & Technology, 17*, 244–254.

Verruck, S., Schwinden Prudêncio, E., Olivera Müller, C. M., Beddin Fritzen-Freire, C., & Dias de Mello Castanho Amboni, R. (2015). Influence of *Bifidobacterium* Bb-12 on the physicochemical and rheological properties of buffalo Minas Frescal cheese during cold storage. *Journal of Food Engineering, 151*, 34–42.