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Gum arabic/starch/maltodextrin/inulin as wall materials on the microencapsulation of rosemary essential oil

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ABSTRACT

The effects of the partial or total replacement of gum arabic by modified starch, maltodextrin and inulin on the characteristics of rosemary essential oil microencapsulated by spray drying were evaluated in this study. The lowest level of water absorption under conditions of high relative humidity was observed in treatments containing inulin. The wettability property of the powders was improved by the addition of inulin. The total replacement of gum arabic by modified starch or a mixture of modified starch and maltodextrin (1:1, m/m) did not significantly affect the efficiency of encapsulation, although higher T_g values were exhibited by microcapsules prepared using pure gum arabic or gum arabic and inulin. 1,8-cineol, camphor and α-pinene were the main components identified by gas chromatography in the oils extracted from the microcapsules. The particles had smoother surfaces and more folds when gum arabic or inulin was present. Larger particles were observed in the powders prepared with pure gum arabic or modified starch.

1. Introduction

Microencapsulation can potentially offer numerous benefits to the food ingredients being encapsulated. Various properties of active materials may be changed by encapsulation. For instance, handling and flow properties can be improved by converting a liquid to a powdered encapsulated form (Jafari, Assadpoor, He, & Bhandari, 2008). The main compounds of the essential oils, responsible for the flavour and the functional properties, are volatiles and chemically unstable in the presence of oxygen, moisture and heat. Stability of essential oils can be enhanced through microencapsulation by spray drying. Spray drying is the most commonly used encapsulation technique in the food industry (Ré, 1998; Reineccius, 2004). The process of spray drying is economical and flexible, uses equipment that is readily available, and produces powder particles of good quality (Jafari et al., 2008). Some examples of encapsulated flavours are oregano essential oil using gum arabic, maltodextrin and modified starch as wall materials (Botrel et al., 2012), oregano, citronella and marjoram flavours encapsulated into milk protein-based matrices (Baranauskienė, Venskutonis, Dewettinck, & Verhé, 2006) and cardamom oleoresin microencapsulated using gum arabic and modified starch (Krishnan, Krishirsagar, & Singhal, 2005).

Flavours are essential to some foods, play important roles in consumer satisfaction and can promote the consumption of those products. However, the stability of flavours in foods, especially in food processing, has attracted intense attention due to its relationship to the quality and acceptability (Jun-Xia, Hai-Yan, & Jian, 2011). *Rosmarinus officinalis* L. is widely accepted as one of the herb spices with the strongest aroma and highest antioxidant activity. Rosemary has also been extensively studied due to its antimicrobial activity (Genena, Hense, Smânia Junior, & Souza, 2008). Gachkar et al. (2007) reported that antibacterial, antioxidant and free radical-scavenging activities were exhibited by rosemary essential oil extracted using steam distillation.

The selection of a suitable wall material is critical to a microencapsulation spray-drying process that avoids changes due to oxidation, chemical interactions or volatilisation (Botrel et al., 2012) and maximises the retention of the essential oil after the drying process is completed. Research on microencapsulation spray drying has concentrated on improving the encapsulation efficiency and extending the shelf life of the product to produce high quality encapsulated powders. The main factors that affect the encapsulation efficiency are the properties of the wall and core materials (Gharsallaoui, Roudaut, Chambin, Voilley, & Saurel, 2007; Goula & Adamopoulos, 2012; Jafari et al., 2008; Reineccius, 2004).

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In this context, it is of utmost importance to compare the effects of different carriers on the properties of the spray-dried essential oils. Gum arabic, which it is one of the most common wall materials used in microencapsulation by spray drying, is a polymer consisting of D-glucuronic acid, L-rhamnose, D-galactose and L-arabinose, including approximately 2% protein (Dickinson, 2003) and can produces stable emulsions with most oils (Gharsallaoui et al., 2007; Jafari et al., 2008; Reineccius, 2004). Capsul® is a starch that is chemically modified by incorporating a lipophilic component aimed at conferring emulsifying properties (Rocha, Fávaro-Trindade, & Grosso, 2012). When modified with octenyl succinic anhydride, the normally hydrophilic starch gains hydrophobic elements in the form of octenyl groups, resulting in molecules with an amphiphilic character (Sweedman, Tizzotti, Schäfer, & Gilbert, 2013). This modification gives the material an excellent capacity for retaining volatiles during atomisation in a spray-dryer (Rocha et al., 2012). Maltodextrin is a hydrolysed starch produced by partial hydrolysis of starch with acid or enzymes that is commonly used as the wall material in microencapsulation of food ingredients (Gharsallaoui et al., 2007; Goula & Adamopoulos, 2012). It offers advantages such as relatively low cost, neutral aroma and taste, low viscosity at high solids concentrations and good protection of flavours against oxidation. However, the greatest limitation of this wall material is its low emulsifying capacity and marginal retention of volatiles (Buffo & Reineccius, 2000; Krishnan et al., 2005), so it is generally used in mixtures with other wall materials. Inulin is composed of fructose units with β(2-1) links with glucose at the end of the chain (Bakowska-Barczak & Kolodziejczyk, 2011) and, as the maltodextrin, it is an interesting encapsulating agent. It is a dietary fibre which shows prebiotic effects and can improves calcium bioavailability (Robert, García, Reyes, Chávez, & Santos, 2012).

Although gum arabic is considered to be an excellent wall material, several problems are associated with the use of this material for microencapsulation, including its high cost and limited supply (Kanakdande, Bhosale, & Singhal, 2007; Krishnan et al., 2005). Thus, the search for complete or partial substitutes for gum arabic has been encouraged. For instance, modified starch and maltodextrin have become a viable alternative to gum arabic because they are abundant and low-cost materials (Peng, Li, Guan, & Zhao, 2013) and inulin is beneficial for human health. There are no published works reporting the effect of different types of wall materials, particularly inulin, on the encapsulation efficiency, retention of volatiles and the particle properties of microencapsulated rosemary essential oil. This study evaluated the effects of gum arabic, modified starch, maltodextrin and inulin on the microparticles' properties, such as the oil retention, product stability, retention of volatiles and the morphology and size of the powders.

2. Materials and methods

2.1. Materials

Tunisian rosemary (*R. officinalis* leaf oil) essential oil (Ferquima, Vargem Grande Paulista, Brazil) was used as the core material. Gum arabic (Colloides Naturels Brasil, São Paulo, Brazil), high-performance inulin (degree of polymerisation > 23, Orafti®HP, BENEO-Orafti, Tienen, Belgium), maltodextrin (Maltogil DE 10, Gargil, São Paulo, Brazil) and modified starch (Capsul®, National Starch Food Innovation, São Paulo, Brazil) were used as wall materials.

2.2. Experimental design

The experiments were conducted in a completely randomised design with three replications, as shown in Table 1. An analysis of variance was performed using Statistica software (ver.8, Stat Soft. Inc., Tulsa, USA) to evaluate the effects of the six encapsulation formulations on the characteristics of powders of microencapsulated rosemary essential oil. The differences between the mean values obtained were analysed using the Tukey test at 5% probability ($p < 0.05$).

Table 1
Composition of the wall materials for the each treatment used as a feed solution for the spray-drying process.

#	Wall material ($g\ 100\ g^{-1}$ of solution)				Core material ($g\ 100\ g^{-1}$ of solution)
	Gum arabic (GA)	Modified Starch (MS)	Maltodextrin (MD)	Inulin (IN)	Rosemary essential oil
1	20.0	–	–	–	5.0
2	–	20.0	–	–	5.0
3	–	10.0	10.0	–	5.0
4	–	10.0	–	10.0	5.0
5	10.0	–	10.0	–	5.0
6	10.0	–	–	10.0	5.0

2.3. Preparation of emulsions

The wall materials were dissolved in distilled water with stirring. The solutions were prepared one day before being emulsified and were kept overnight at room temperature to ensure full saturation of the polymer molecules. Then, rosemary essential oil was gradually added to the wall material solution with stirring at 3500 rpm over 10 min, using a rotor–stator blender (Ultra-Turrax IKA T18 basic, Wilmington, USA), to form an emulsion. The emulsion was used as the feed liquid for the spray-drying process. For each treatment, approximately 1 L of sample was prepared for the production of microencapsulated powders. The wall material concentration was 20% (Fernandes, Borges, & Botrel, 2013a; Fernandes et al., 2013b) and the amount of rosemary essential oil used was 25% of the mass of the wall materials (Jafari et al., 2008).

2.4. Microencapsulation by spray drying

The emulsions were dried using a spray-dryer (model MSD 1.0; Labmaq do Brasil, Ribeirão Preto, Brazil) equipped with a two-fluid nozzle atomiser. The following operational conditions were used, as described in previous studies: inlet temperature of 170 °C and feed rate of $0.9\ L\ h^{-1}$ (Fernandes et al., 2013a, 2013b). The dried powder was collected and stored in opaque airtight containers at 4 °C until further analysis.

2.5. Characterisation of the microcapsules

2.5.1. Moisture content

The moisture content of the powder was determined gravimetrically by oven-drying at 105 °C to constant weight (Association of Official Analytical Chemists [AOAC], 2007).

2.5.2. Wettability and solubility

The wettability of the powders was determined using the method described by Fuchs et al. (2006). One gram of powder was sprinkled over the surface of 100 mL of distilled water at 20 °C without agitation. The time taken for the powder particles to sediment, sink, be submersed and disappear from the water's surface was recorded and used for a comparison of the extent of wettability of the samples.

The solubility of the powders was evaluated according to the method proposed by Cano-Chauca, Stringheta, Ramos, and Cal-Vidal (2005), with modifications. The powders were weighed (1 g) and stirred into 25 mL of distilled water for 5 min using a blender. The solution was then centrifuged at 760 × *g* for 10 min. An aliquot of 20 mL of the supernatant was transferred to a pre-weighed Petri dish and oven-dried at 105 °C overnight. The solubility (%) was calculated as the percentage of dried supernatant in relation to the amount of powder originally added (1.0 g).

2.5.3. Bulk density (ρd) and bulk tapped density (ρb)

The powders were gently loaded into a 100 mL tared graduated cylinder filled to the 100-mL mark and weighed. The volume read directly from the loaded cylinder was then used to calculate the bulk density (ρd) according to the mass/volume relationship (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 powder bulk density was calculated as m/V (g/cm^3) (Goula & Adamopoulos, 2008).

2.5.4. Oil retention

The total oil content of the spray-dried microencapsulated products was determined by distilling 10 g of the microencapsulated powder for 3 h in a Clevenger-type apparatus (Jafari, He, & Bhandari, 2007). Ethyl ether was used to successively extract the essential oil from the water phase three times. After evaporating the solvent at room temperature (25 °C for 24 h), the resulting oil was weighed and the percentage of total oil in the particles was calculated. The oil retention was defined as the ratio of the total oil in the final powder to that of the initial oil load (dry basis) and was calculated as follows (Eq. (1)):

$$\text{Oil retention}\,(\%) = \frac{\text{Total oil}\,(\%)}{\text{Initial oil load}\,(\%)} \times 100$$

2.6. Moisture sorption isotherms

The sorption isotherms for the optimised conditions were determined using the gravimetric static method with a saturated saline solution at 25 °C. The seven saturated saline solutions ($NaCl$, K_2CO_3, $MgCl_2$, $LiCl$, $Mg(NO_3)_2$, KCl and $NaNO_3$), which were used at different temperatures, had water activities ranging from 0.113 to 0.843. The moisture sorption isotherm data were correlated to the water activity (relative humidity) using the following mathematical models: GAB, Halsey, Henderson and Oswin and Smith. The models used for adjustment were selected as described in the review article of Al-Muhtaseb, Mcminn, and Magee (2002).

The parameters of these equations were estimated by correlating the mathematical models to the experimental data via a quasi-Newton nonlinear regression using Statistica software version 8.0, with a 5% significance level. The model that was considered most suitable was based on the high coefficient of determination (R^2) and the low mean relative percentage deviation modulus (E), defined as follows in Eq. (2):

$$E = \frac{100}{N}\sum_{i=1}^{N}\frac{|m_i - m_{pi}|}{m_i} \tag{2}$$

where m_i is the experimental value, m_{pi} is the predicted value and N is the population of experimental data.

2.7. Differential scanning calorimetry

Differential scanning calorimetry (DSC60, Shimadzu Corporation, Kyoto, Japan) was used to determine the glass transition temperatures (T_g) of the spray-dried powders. Approximately 1.5 mg of sample was prepared in aluminium pans under nitrogen gas at 50 mL min^{-1}. An empty pan was used as the reference. A baseline was constructed using an empty pan over the same temperature range and scanning rate. The curves were obtained according to the following heating programme: a 10 °C min^{-1} scanning rate and a temperature range of 20–140 °C. The glass transition value was taken as the midpoint of the glass transition range. DSC curves were examined to determine the onset temperature and end-point temperature of the glass transition region. The glass transition midpoint value was calculated as the average of the onset and end-point values and reported as the glass transition temperature (T_g) (Ahmed, Akter, Lee, & Eun, 2010).

2.8. Gas chromatography–mass spectrometry

After dilution in diethyl ether (1 μL in 1000 μL), the pure rosemary essential oil and samples of the oils obtained when determining the total oil retention values (as described above) were analysed using a Shimadzu CG-MS-QP2010 Plus gas chromatography mass spectrometer equipped with an Equity-5 capillary column, 95%-polydimethylsiloxane and 5%-phenyl (30-m length, 0.25-mm i.d.; 0.25-μm film thickness; Supelco, St. Louis, USA). The operating conditions were the following: the injector temperature was 220 °C; the oven temperature was programmed to hold at 40 °C for 1 min, increase from 40 °C to 180 °C at 4 °C min^{-1}, then further increase to 250 °C at 30 °C min^{-1}, where it was held for 2 min; the helium carrier gas flowed at a linear velocity of 40 cm s^{-1}; the split ratio was 1:20; the type of ionisation used was EI 70 eV; and the spectra were acquired by scanning at 45–500 m/z. The compounds were identified by comparison with spectra available in the literature (Wiley 8 and FFNSC 1.2) and the analyses were repeated at least two times. The components profile was expressed as percentage according to the relative peak area.

2.9. Particle morphology and size distribution

The particle morphology of the six samples was evaluated using scanning electron microscopy (SEM). The powders were attached to a double-sided adhesive tape mounted on SEM stubs with a diameter of 1 cm and a height of 1 cm, coated with gold in a vacuum evaporator and examined using an MEV 1430 VP – LEO scanning electron microscope (Electron Microscopy Ltd., Cambridge, UK). The SEM was operated at 20 kV with magnification of 900–1200×.

The particle size distribution was determined for all of the samples using a Mastersizer 2000 laser light diffraction instrument (model Hydro 2000 MU, Malvern Instruments, Malvern, UK). A small sample of powder was suspended in isopropyl alcohol with agitation and the particle size distribution was monitored during each measurement until successive readings were consistent. The volume-weighted mean diameter (D[4,3]) was measured and the distribution of the sizes of the particles in the powder (span) was calculated using Eq. (3), as follows:

$$\text{Span} = \frac{d_{90} - d_{10}}{d_{50}} \tag{3}$$

where d_{90}, d_{50} and d_{10}, are the volume diameters at 90%, 50% and 10% of the cumulative volume, respectively (Jinapong et al., 2008).

3. Results and discussion

3.1. Particle characterisation

The particle characterisation results are shown in Table 2. The moisture content of the microcapsules ranged from 1.40% to 3.56%. The moisture content values found were very similar to those reported in other studies, such as oregano essential oil microencapsulated by spray drying using gum arabic, maltodextrin and modified starch as wall materials (1.30–3.65%) (Botrel et al., 2012) and D-limonene microencapsulated in matrices of modified starch, whey protein concentrate and maltodextrin (1.20–2.70%) (Jafari et al., 2007). The samples prepared with inulin (MS:IN and GA:IN) were significantly different ($p < 0.05$) from the samples prepared with pure gum arabic and starch (GA and MS). The addition of inulin increased the moisture content of the powders. This fact was most likely due to the higher drying rate of these particles, which led to the rapid formation of a crust that hindered water diffusion and evaporation.

The wettability, or ability to absorb water, of microcapsules is one of the most important physical properties related to reconstituting the powders (Bae & Lee, 2008), and it is directly affected by the molecular interactions between the two phases (Cuq, Rondet, & Abecassis, 2011). In the present study, the time needed for the powders to become completely wet ranged from 84 s to 307 s. The type of wall material significantly affected this property. The shortest wettability time was observed when inulin was used in the formulation, suggesting that the inulin improved the instantising characteristics of the particles. This fact can be explained by the higher moisture content of the powders prepared using inulin and the properties of inulin itself, which most likely contributed to a higher number of hydrophilic groups on the particles, thus reducing the instantising time through greater interaction with water. Agglomeration, which usually occurs in powders with higher moisture content, may contribute to their wetting ability because the liquid penetrates into the pores more easily (Buffo, Probst, Zehentbauer, Luo, & Reineccius, 2002). In addition, inulin is very soluble in water at 20–25 °C (Glibowski & Pikus, 2011), which favours the wettability of the particles prepared using this component to the formulation.

To be practical, the powders used as ingredients for the food industry must exhibit good solubility. Solubility is the last particle dissolution step and is a decisive factor for the quality of these products (Jayasundera, Adhikari, Howes, & Aldred, 2011). All of the particles were relatively soluble despite the hydrophobic nature of the core material, yielding results ranging from 41.85% to 47.72%. Pure rosemary essential oil is not soluble in pure water at room temperature, whereas encapsulating the essential oil resulted in better solubility. The type of encapsulant used did not affect this property.

The bulk density values of the samples ranged from 0.23 g mL^{-1} to 0.35 g mL^{-1}. Values close to these were obtained for encapsulated soy milk (0.21–0.22 g mL^{-1}), (Jinapong et al., 2008) and for the microcapsules of rosemary essential oil prepared using gum arabic as the wall material (0.25–0.36 g mL^{-1}) (Fernandes et al., 2013a). The samples with modified starch present in the matrix displayed in general the lowest average bulk density. When inulin was applied together with starch and gum arabic, the bulk density showed higher values when comparing to starch and gum arabic only.

The tapped density is an important factor related to the transport, packaging and marketing of powers; thus, this variable is useful for determining of the weight and amount of material that will fit inside a container (Finney, Buffo, & Reineccius, 2002). A high-density dry product can be stored in a smaller container, compared with a low-density product (Quispe-Condori, Saldaña, & Temelli, 2011). The results obtained ranged from 0.35 g mL^{-1} to 0.49 g mL^{-1}. The highest density was observed for the treatment prepared with gum arabic and inulin, which significantly differed ($p < 0.05$) from all the other samples, except for the treatment prepared with gum arabic and maltodextrin.

One of the most important quality parameters for the encapsulation of an essential oil is the microencapsulation efficiency, which is the percentage of the initial amount of essential oil that is encapsulated. The encapsulation efficiency values ranged between 26.31% and 61.81%. There were no significant difference ($p > 0.05$) among the oil retention capacity of samples GA, MS and MS:MD and between those of samples MS:IN and GA:MD; however, treatment 6 was less effective in retaining the oil. The nature of the wall material is one of the main factors in the retention of volatile constituents. Among all of the encapsulants studied, gum arabic is the most popular and commonly used ingredient for encapsulating essential oils by spray drying, due to its emulsifying properties and excellent retention of volatiles during drying (Jafari et al., 2008). However, this wall material has a high cost and limited availability. Mixing gum arabic with other materials or completely replacing it is an alternative strategy for encapsulating essential oils or other substances. For efficient encapsulation, the wall material must have suitable properties, with its emulsification capacity being an important factor. Most likely, emulsification was not effective when inulin was added to gum arabic based on low oil retention of this treatment. Emulsification of the dryer feed is an essential requisite for efficient retention of volatiles in the sense that the stability acquired in the formed emulsion leads to higher encapsulation efficiency and, thus, a lower loss of volatiles.

The mixture of modified starch and maltodextrin proved to be an effective matrix for retaining rosemary essential oil. Its oil retention capacity did not differ from those of the pure gum arabic or pure starch. The substitution of part of the modified starch by maltodextrin resulted in encapsulation similar to that obtained using pure starch and superior to that obtained using gum arabic, and therefore this mixture may be an alternative wall material for the food industry. Although maltodextrin should be used in combination with another encapsulating agent because it does not have an emulsifying capacity, it has the advantage of being relatively inexpensive and provides excellent protection of the encapsulated

Table 2
Mean values and standard deviations for the moisture content, wettability, solubility, bulk and tapped density and oil retention of the particles produced.

Wall material	Variables					
	Moisture (%)	Wettability (s)	Solubility (%)	Bulk density (g mL^{-1})	Bulk tapped density (g mL^{-1})	Oil retention (%)
GA (1)	1.64 ± 0.17^{a}	301 ± 6 ^{d}	46.57 ± 1.15^{a}	0.28 ± 0.01^{a,b}	0.41 ± 0.01^{a,b}	56.83 ± 3.21^{c}
MS (2)	1.55 ± 0.15^{a}	254 ± 35^{b,c}	46.00 ± 0.54^{a}	0.25 ± 0.01^{a}	0.38 ± 0.01^{a}	56.79 ± 0.00^{c}
MS:MD (3)	2.25 ± 0.85^{a,b}	232 ± 17^{b}	44.82 ± 1.68^{a}	0.25 ± 0.02^{a}	0.38 ± 0.03^{a}	60.22 ± 1.59^{c}
MS:IN (4)	3.48 ± 0.08^{b}	131 ± 8^{a}	42.38 ± 0.53^{a}	0.29 ± 0.01^{a,b}	0.41 ± 0.01^{a,b}	45.45 ± 0.01^{b}
GA:MD (5)	2.05 ± 0.45^{a,b}	274 ± 15^{c,d}	45.82 ± 0.26^{a}	0.31 ± 0.02^{a,b}	0.46 ± 0.02^{a,b,c}	45.45 ± 0.00^{b}
GA:IN (6)	3.27 ± 0.08^{b}	93 ± 9^{a}	44.32 ± 2.38^{a}	0.34 ± 0.01^{b}	0.48 ± 0.01^{c}	29.53 ± 3.22^{a}

[a,b,c,d] Values with different letters in the same column differ significantly ($p < 0.05$). GA, gum arabic; MS, modified starch; MD, maltodextrin; IN, inulin.

materials. Modified starch leads to good retention of volatiles and low amounts of oil on the particle surface, in addition to having an emulsifying property (Jafari et al., 2008). Although treatments MS:IN and GA:MD presented lower encapsulation efficiency than did treatments GA, MS and MS:MD, the presence of inulin together with modified starch (treatment MS:IN) would be an alternative based on the prebiotic properties of inulin and on the consumer seeking for food with additional health benefits.

3.2. Moisture sorption isotherms

The estimated values of the coefficients and the statistical parameters used to evaluate the adequacy of the models for the moisture adsorption behaviour are shown in Table 3. The equilibrium moisture content in the treatments formulated with gum arabic was greatly increased when exposed to relative humidity higher than 0.60. On the other hand, the equilibrium moisture content of the treatments containing starch remained relatively constant, with the relative humidity variation, except for the treatment applying starch and maltodextrin. At low water activities values, water can be adsorbed on the surface of carbohydrates at the polar sites, whereas at high water activity values, the dissolution of carbohydrates occurs (Ayranci, Ayranci, & Dogantan, 1990).

The model that best fit to the variations in isotherm data for all the treatments was the GAB model, when considering both the lowest value of the average relative deviation (E) and the highest coefficient of determination (R^2). Regarding the GAB parameters, as shown in Table 3, the X_m or moisture content of the monolayer of gum arabic and gum arabic plus maltodextrin were very high when comparing to those of the other treatments, indicating the greater availability of active sites bond with water (Quirijns, van Boxtel, van Loon, & van Straten, 2005). The use of inulin together with gum arabic caused decrease of the hygroscopicity of the storage powders at different relative humidities (Fig. 1). For the powders elaborated with starch, lower hygroscopicity was observed when maltodextrin was also applied (relative humidities below 70%). In general, starch- and inulin-containing products presented low X_m values.

The GAB model provides important information about food products because estimating the moisture content of the monolayer (X_m) is important to establish appropriate storage conditions for dehydrated foods.

The physical characteristics of the powders subjected to different humidity levels demonstrated that there was no apparent phase change in the particles produced with inulin (Fig. 2) at all of the tested conditions. The starch plus inulin and gum arabic plus inulin were the only treatments in which the powders visibly remained in the glassy state. The other treatments underwent changes from a glassy state to a rubbery state. These results suggest that inulin is an interesting additive for the encapsulation of spray dried active compounds. For better particle conservation and stability, lower water absorption values are desirable, which will also improve the reconstitution properties, while reducing the caking occurrence.

3.3. Differential scanning calorimetry

The temperature at which the polymeric material changes from a glassy amorphous state to a rubbery state is known as glass transition temperature (T_g), which is specific to each amorphous material. The glass transition temperature is affected by several parameters, such as the molecular weight, the chemical structure and the moisture content of the material. Materials with higher T_g produce particles that are more stable during processing and, more importantly, during storage (Beristain, Azuara, & Vernon-Carter, 2002; Bhandari & Hartel, 2005). The T_g was obtained from the midpoint of the glass transition range and the analysed powders presented the moisture content described in Table 2. The DSC curves demonstrated T_g of 99.6 °C, 85.1 °C, 80.6 °C, 89.3 °C, 86.4 °C and 100.4 °C for treatments GA, MS, MS:MD, MS:IN, GA:MD and GA:IN, respectively (Fig. 3). The highest T_g values were found for treatments GA and GA:IN. Most likely, gum arabic increased the T_g because, among all of the encapsulants studied, it has the highest molar mass (47,000–3,000,000 g mol^{-1}) (Anderson, 1977) and the T_g is positively related to the molar mass (Truong, Bhandari, & Howes, 2005). Maltodextrin (DE 10) exerted an influence in the opposite direction. Because it is the encapsulant with the lowest molar mass among all of those studied (1.800 g mol^{-1}) (Bhandari & Howes, 1999), the addition of this type of wall material decreased the T_g of the powders. A T_g value of 160 °C was reported for anhydrous maltodextrin (DE 10) (Bhandari & Howes, 1999) and a T_g value of 170 °C was reported for anhydrous gum arabic (Collares, Finzer, & Kieckbusch, 2004). In their study of different encapsulants for spray drying pomegranate juice, Yousefi, Emam-Djomeh, and Mousavi (2011) also found lower T_g values when maltodextrin (DE 20) was used and higher T_g values when gum arabic was employed (40.0 °C and 52.8 °C, respectively). The particles prepared with modified starch and inulin (T_g = 89.3 °C) presented relative higher T_g demonstrating that this formulation also has some potential for application as a wall material in the food industry.

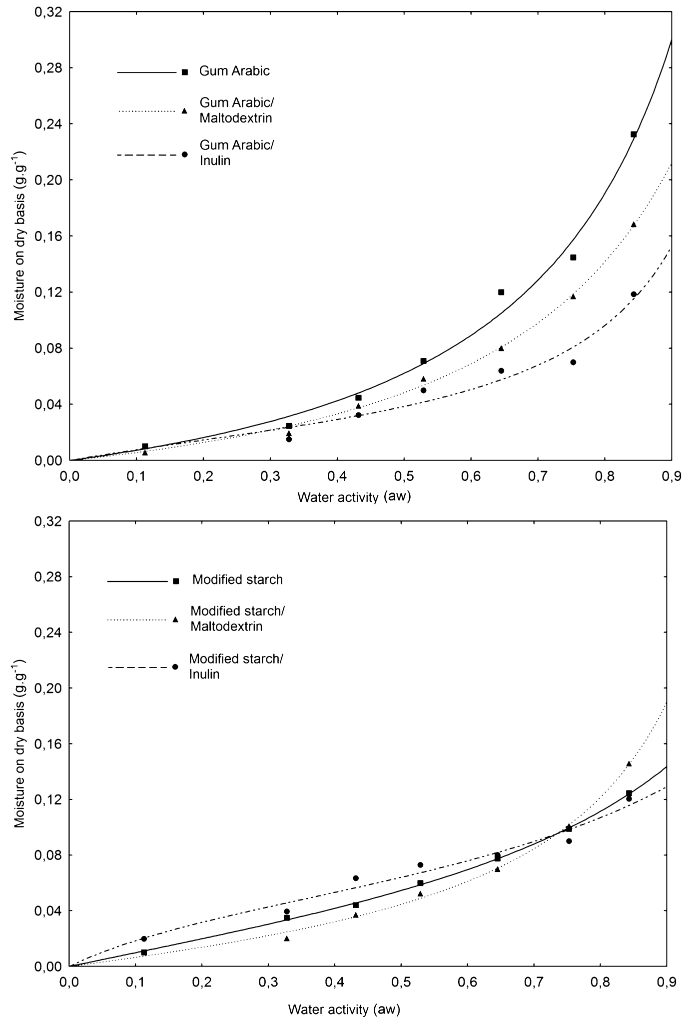

Fig. 1. Sorption isotherms of the particles produced using different wall materials, adjusted using the GAB model for all of the treatments.

Table 3
Estimated values of the coefficients and statistical parameters that were used to evaluate the adequacy of the models of adsorptive behaviour of the rosemary essential oil microcapsules.

(Model) Equation		MS	MS:MD	MS:IN	GA	GA:MD	GA:IN
(GAB) $X_{eq}=\frac{X_m CKa_w}{(1-Ka_w)(1-Ka_w+CKa_w)}$	X_m	0.064	0.044	0.056	0.092	0.090	0.029
	C	2.190	1.605	6.150	0.831	0.703	3.143
	K	0.718	0.887	0.676	0.859	0.806	0.915
	E (%)	3.264	8.661	7.430	11.078	7.789	16.668
	R^2	0.999	0.997	0.968	0.988	0.997	0.963
(Halsey) $X_{eq}=\left(\frac{a}{\ln a_w}\right)^{1/b}$	*a*	−0.002	−0.002	−0.002	−0.003	−0.002	−0.002
	b	0.071	0.071	0.071	0.068	0.070	0.071
	E (%)	28.552	17.233	39.100	30.384	39.682	20.065
	R^2	0.803	0.970	0.411	0.972	0.972	0.923
(Henderson) $X_{eq}=\left[\frac{\ln(1-a_w)}{-a}\right]^{1/b}$	*a*	4.342	4.255	4.312	2.683	2.794	5.983
	b	3.243	3.193	3.227	3.309	4.253	2.815
	E (%)	10.834	15.353	29.226	33.508	32.692	21.471
	R^2	0.982	0.983	0.782	0.954	0.974	0.958
(Oswin) $X_{eq}=a\left[\frac{a_w}{(1-a_w)}\right]^b$	*a*	0.053	0.045	0.062	0.063	0.049	0.039
	b	0.526	0.704	0.397	0.777	0.743	0.654
	E (%)	17.863	8.840	14.551	18.766	25.885	17.331
	R^2	0.986	0.995	0.958	0.984	0.991	0.964
(Smith) $X_{eq}=a+b\log(1-a_w)$	*a*	0.007	−0.007	0.023	−0.021	−0.014	−0.002
	b	−0.065	−0.079	−0.053	−0.130	−0.095	−0.061
	E (%)	11.527	18.899	16.639	37.612	29.534	22.625
	R^2	0.993	0.990	0.943	0.978	0.993	0.959

X_{eq}: equilibrium moisture content (g g^{-1} dry powder); X_m: monolayer moisture content (g g^{-1} dry powder); C,K: model constants related to the monolayer and monolayer properties; aw: water activity; *a*,*b*: model parameters; *E*: mean relative deviation modulus; R^2: coefficient of determination.

3.4. Gas chromatography with mass spectrometry

Fig. 4 demonstrates the variation in the contents of the 6 major components (from a total of 24 components) that were identified in the samples of rosemary essential oil. 1,8-cineol, camphor, limonene, α-pinene, β-pinene and camphene were the main components identified. Zaouali, Bouzaine, and Boussaid (2010) found that 1,8-cineol, camphor and α-pinene were also the main components of rosemary essential oil, which represented approximately 40%, 18% and 10% of the composition of rosemary oil originating from Tunisia. Pintore et al. (2002) studied the composition of rosemary oil and found that α-pinene, camphor and 1,8-cineol were among the main components. In studying the encapsulation of flavoured compounds, it is important to evaluate changes caused by the process, particularly during the drying phase. The compositions of the pure rosemary oil and the rosemary oil that were encapsulated using all the different matrices were very similar; however, some differences in the components profile were observed. The levels of 1,8-cineol and β-pinene in the pure oil were higher than those found in the oil recovered from the microcapsules. In contrast, the

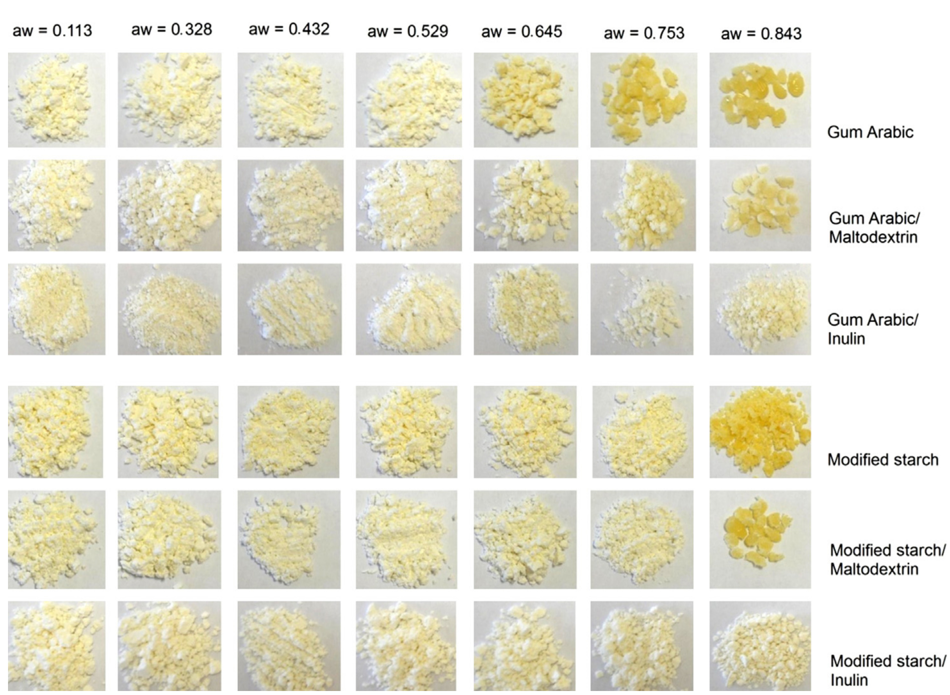

Fig. 2. Physical characteristics of the powders produced with the various formulations of encapsulants at different relative humidities during the determination of the moisture adsorption isotherms.

level of the other components in the oil recovered from the microcapsules were greater than those in the pure oil, which is most likely due to a lower loss by evaporation during the heating process. Baranauskiené et al. (2006) suggested that the volatile hydrophobic compounds of encapsulated essential oils, which are present mainly on the surface of the particles, are less protected and hence more susceptible to evaporation, which could explain the reduction in the relative amounts of components such as 1,8-cineol and β-pinene in the in the oil recovered from the microcapsules.

3.5. Morphology

The scanning electron microscopic images (SEM) (Fig. 5) showed no evidence of cracking in the particles produced using all the encapsulant formulations, which is important to ensure low gas permeability and better protect the rosemary essential oil. Barely perceptible differences in the surface characteristics of each type of particle were observed; in general, the particles had a spherical shape. Spray-dried materials are typically hollow spheres. Vacuole formation results from the shrinking process that occurs after the hardening of the outer surface followed by the expansion of the air bubbles trapped inside the droplet (Ré, 1998). The mechanisms underlying the formation of voids are related to the expansion of the particles during the latter stages of the drying process. Thermal expansion of air or steam inside the drying particles can reduce shrinkage (Teixeira, Andrade, Farina, & Rocha-Leão, 2004), depending on the drying rate and the viscoelastic properties of the matrix material. The microcapsules prepared with starch alone or with starch and maltodextrin possessed a higher proportion of spherical particles, most likely because these matrices provided elasticity during the drying process.

3.6. Particle size distribution

The particles produced using starch and gum arabic presented the higher particle sizes, 13.4 μm and 13.5 μm, respectively, expressed as D[4,3] (De Brouckere mean diameter). When inulin and maltodextrin were applied to both formulations, the particle size was decreased and an average value of 12.1 μm was obtained, with no significant difference between these treatments. The scattering of the particles, calculated using the span equation was low (1.75–2.47) which indicate a homogeneous distribution. According to the literature, the diameter of spray-dried particles depends on the atomisation method used, the properties of the material, the concentration and viscosity of the encapsulated material and the drying conditions (Cai & Corke, 2000; Jafari et al., 2008). The particle size was significantly affected ($p < 0.05$) by the type of wall material, with the largest sizes resulting from using only starch or gum arabic as the wall materials. There are reports that larger particles have an increased encapsulation efficiency (Jafari et al., 2008). The presence of inulin or maltodextrin caused a reduction in the average particle size. The production of particles with the highest average size using only starch or gum arabic can be explained by the higher viscosity of these polymers. According to Masters (1991), the higher the feed viscosity, the larger the droplets formed during atomisation. Maltodextrin has the characteristic of having low viscosity at high concentrations (Jafari et al., 2008). The size of spray-dried particles is an important factor because of its strong influence on their appearance, flowability and dispensability (Reineccius, 2004).

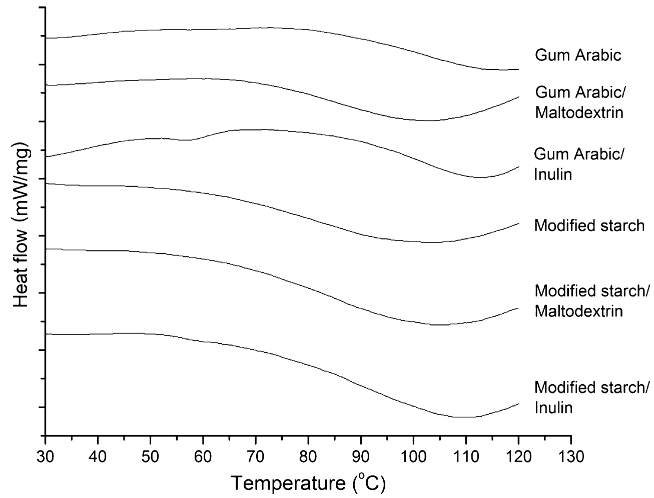

Fig. 3. DSC curves obtained at a heating rate of 10 °C min^{-1} for the particles produced using the specified wall materials.

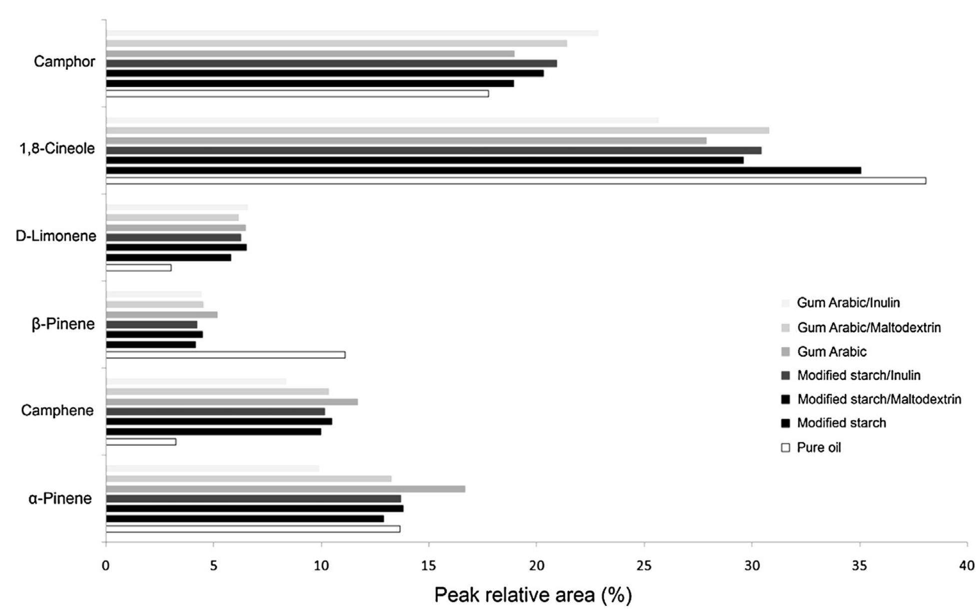

Fig. 4. Variations in the profile of the major components of the rosemary essential oil.

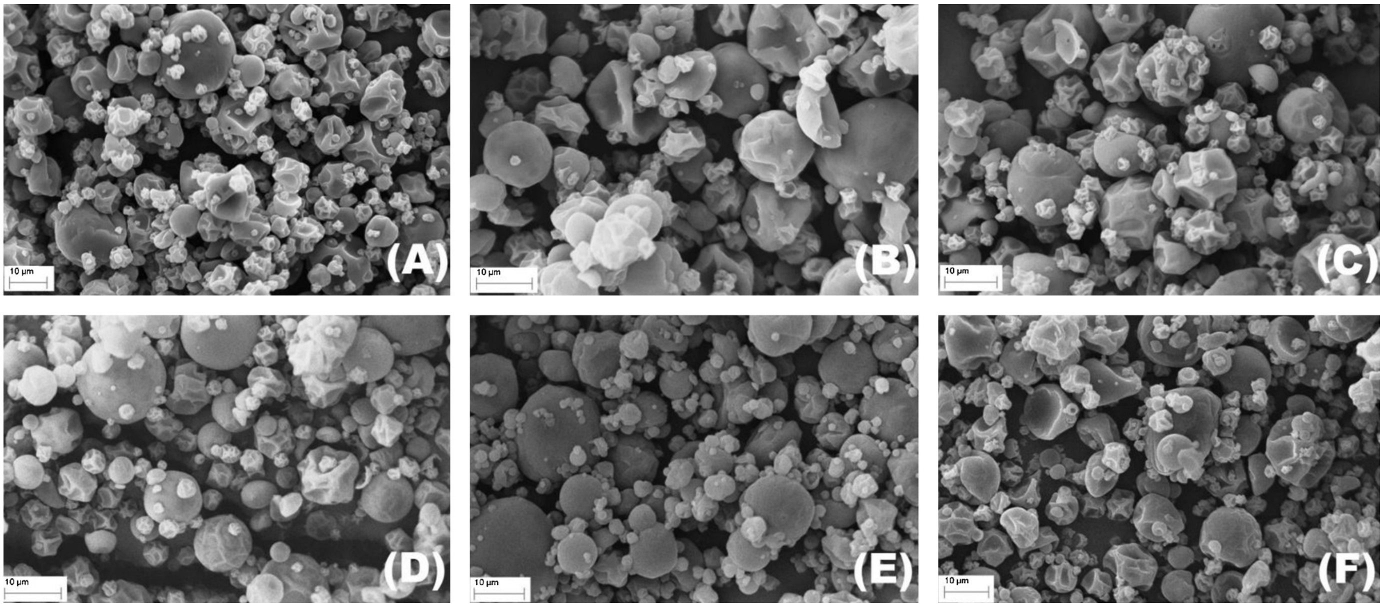

Fig. 5. Scanning electron micrographs of the particles containing rosemary essential oil using the following wall materials (A) gum arabic, (B) gum arabic/maltodextrin (C) gum arabic/inulin (D) starch; (E) modified starch/maltodextrin; and (F) modified starch/inulin.

4. Conclusions

The importance of the use of carbohydrates with a high capacity for emulsification (i.e., gum arabic and modified starch) as wall materials was reaffirmed in this study, which showed that such materials are more efficient in retaining volatiles. The presence of inulin improved the wettability of the particles, decreased the hygroscopicity under high relative humidity but decreased the encapsulation efficiency. An interesting alternative for the encapsulation of rosemary essential oil would be a mixture of modified starch and maltodextrin, which are relatively inexpensive wall materials with good properties, including high retention of volatiles. Although adding inulin decreased the oil retention of the particles, the combination of modified starch and inulin was shown to be a viable substitute for gum arabic in foods. This combination was observed to retain oil better than the combination of gum arabic and inulin and was similar to the combination of gum arabic and maltodextrin. This mixture also presented a high glass transition temperature, which is important for processing and storage. These results indicate that inulin, a fibre with proven functional activity, is an alternative encapsulating material for the production of foods with functional claims, increasing the possibilities of developing new formulations of encapsulants.

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