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ORIGINAL PAPER

Utility of Blended Polymeric Formulations Containing Cellulose Nanofibrils for Encapsulation and Controlled Release of Sweet Orange Essential Oil

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Abstract
The characteristics and encapsulating potential of blended polymeric formulations containing gum arabic (GA), maltodextrin (MD), and cellulose nanofibrils (CNF) for microencapsulation of sweet orange essential oil were evaluated in this study. CNF acted as a thickener, increasing emulsion viscosity. The droplet size was affected by the partial replacement of GA in the formulations without CNF; however, the presence of CNF contributed to decreasing the droplet size. CNF-containing formulations had the best encapsulation efficiency. Images obtained by microscopy showed no cracks on the surface of the microparticles. CNF-containing formulations released more essential oil at 25 °C and presented different behaviors when compared to formulations without CNF at 45 °C. The presence of CNF in the wall material formulations was associated with higher encapsulation efficiency of the particles containing essential oil produced by the spray drying.

Keywords Gum arabic · Maltodextrin · Cellulose · Spray drying · Oil retention

Introduction

Essential oils have been widely used around the world, and their use is increasing because of the high demand for pure and natural ingredients in various market segments (Raut and Karuppayil 2014). Chemically, essential oils comprise terpenes, alcohols, acids, esters, epoxides, aldehydes, ketones, and amines (Bakkali et al. 2008; Calo et al. 2015); however, they are susceptible to several undesirable changes. The application of essential oils in food products is limited due to the high volatility and instability in presence of light, temperature, and oxygen and also due to the physical state of the oil which make it difficult to be used in powdered food formulations.

The encapsulation processes have the ability to improve the appearance and properties of several components of interest. Their use is intended to meet the specific needs of the food industry, e.g., to reduce environmental interactions of the encapsulated material and facilitate manipulation thereof, to ensure controlled release of certain substances, to mask unpleasant taste and odor, and to promote homogenous dilution of the encapsulated material in the food formulation (Rebello 2009). A large number of different methods for microencapsulation of active and functional compounds have been developed (Dordevic et al. 2015; Jafari et al. 2008). One of the most widely used techniques is spray drying, where a liquid product is converted into a powder by spraying the material in a hot air stream (Gharsallaoui et al. 2007). A spray dryer may be used with sensitive or heat-resistant products, without major changes in their overall quality (Perdana et al. 2014; Wu et al. 2014).

The wall material of microencapsulation systems for containment of essential oils consists of polymers with hydrophilic and hydrophobic chemical groups, such as modified starches, milk and soy proteins, and gums, which form a

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polymeric network holding the encapsulated material of interest within the created matrix. Use of combinations of polymers is generally preferred, because it ensures better barrier properties than when a single polymer is used. In addition to possessing emulsifying properties and ability to form films, solutions of wall materials should have low viscosity at high concentrations of solids. Furthermore, they must not have a strong taste or odor and should be able to release the core component at the necessary rate (Do et al. 2015).

The increase in the concentration of the wall material has a positive effect on the yield of the encapsulated product, although the determination of optimal concentrations for each process and each type of essential oil is usually required. High concentrations of solids in the feed reduce the time for the formation of the semipermeable membrane allowing microencapsulation of a larger amount of oil. However, excessively high concentrations of solids may reduce the yield of the encapsulated material because the emulsion viscosity will be directly affected (Fernandes et al. 2014; Soottitantawat et al. 2005). Despite their low emulsifying capacity and poor retention of volatile compounds, some carbohydrate polymers, such as maltodextrin (MD), are used for microencapsulation of essential oils due to their good oxygen barrier properties. They are recommended for use with other wall materials, such as gum arabic (GA) (Uekane et al. 2016), which produces stable emulsions and increases retention of volatile encapsulated agents, such as essential oils.

With the development of new technologies in the manufacturing processes of materials, alternative types of nano-scale components, such as cellulose nanofibrils (CNF) (Assis et al. 2012), become available. These polymeric materials can provide unique characteristics to the formulations according to the degree of dispersion and orientation in the matrix. They also confer smaller volume and larger surface area to the droplets. CNF offer rheological and physical-chemical properties and also act as a physical barrier allowing stabilization of the interface oil/water (Löbmann and Svagan 2017). The presence of solid fine particles, such as CNF, dispersed in emulsions may also control coagulation, keeping the oil droplets apart by means of either steric repulsion mechanism or by thickening the continuous phase (Chevalier and Bolzinger 2013). Besides, CNF is a low-density material and has the ability to form a stable aqueous suspension, making possible several applications, mainly as thickener and emulsifier for food formulations (Habibi et al. 2009), and in the production of aerogels and nanocomposites (Moon et al. 2011). However, the application of CNF in encapsulation processes and its effects are still limited although such materials may have considerable potential. Thus, the objective of this study was to evaluate the characteristics of encapsulant polymer blends containing GA, MD, and CNF and their potential for microencapsulation of sweet orange essential oil.

Material and Methods

Materials

Sweet orange essential oil extracted by the hydrodistillation method from *Citrus aurantium* var. dulcis was provided by Ferquima Industry and Trade Ltda (Vargem Grande Paulista, Brazil) and used as the encapsulated material. Gum arabic (GA) (Instantgum BA, Nexira, São Paulo, Brazil), maltodextrin (MD) (DE 9–12) (Agro Industry Commercial Cassava SA, Santa Catarina, Brazil), and cellulose nanofibrils (CNF) extracted from the eucalyptus waste (bleached kraft pulp) were used as wall materials.

Preparation of the Suspension Containing CNF

Bleached kraft pulp (eucalyptus residue) was dispersed for 5 min using a domestic pulper to obtain a homogenized suspension. To obtain CNF, the suspension of homogenized fibers was dispersed in water at a concentration of 1% *w*/*w* (dry basis) and then mechanically processed by 10 passes through a grinder (Masscolloider Masuko Sangyo Super Mill, MKCA6–3; Masuko Sangyo Co., Ltd. Kawaguchi, Japan) at 1500 rpm. The grinder consisted of a rotating disk and a static disk with an adjustable gap between them. The distance between the disks was adjusted to about 10 μm. As a result of this manipulation, the cellulose suspension acquired gel-like properties.

Preparation of Emulsions

The solutions containing GA and MD were prepared before emulsification and maintained overnight at room temperature to ensure complete hydration of the polymer molecules. Sweet orange essential oil was gradually added to the solution while stirring at 3000 rpm for 5 min using a homogenizer (Ultra-Turrax T18 IKA, Wilmington, USA). Then, the solution was ultrasonicated (Branson Digital Sonifier®, model 102C, Branson Ultrasonics Corporation, Danbury, USA) for 2 min at 240 W. For the formulations in presence of CNF, a suspension of the latter material (20% *v*/*v*) was added to the solution containing the solubilized polymers and oil, substituting the same volume of water. This final solution was again homogenized and ultrasonicated as described above. The ratio obetween sweet orange oil and wall material was 1:4 (*w*/*w*), which is the commonly used value for the encapsulation of essential oils by spray drying (Rascón et al. 2011).

Experimental Design

Encapsulation process was assessed for the formulations produced using the different wall materials in the presence or absence of CNF. The drying process was performed in triplicate for each treatment. Experimental design details and the amount of wall materials are described in Table 1.

Table 1 Design of the experiment evaluating formulations of different wall material biopolymers

Treatments	Wall materials (g/100 g solution)		
	Gum arabic	Maltodextrin	CNF* (%)
GA	30.0	0.0	0.0
GA/MD (3:1)	22.5	7.5	0.0
GA/MD (1:1)	15.0	15.0	0.0
GA/CNF	30.0	0.0	20.0
GA/MD (3:1) CNF	22.5	7.5	20.0
GA/MD (1:1) CNF	15.0	15.0	20.0

GA, gum Arabic; *MD*, maltodextrin; *CNF*, cellulose nanofibrils

*CNF suspension contained 1.5% of dry matter

Physical Characteristics of CNF

The samples were analyzed using Electron Microscope JEC 1200EXII (600 thousand X) for visualization of the cellulose nanofibrils structures. The suspension was diluted about 10,000 times in distilled water and dripped onto the sieve surface. The samples were left to dry at room temperature before observation using the transmission electron microscope. The fiber diameters, determined after the chemical and mechanical treatment of the fibers, were obtained using an image processing program Digital Micrograph (Gatan).

Rheological Analysis

The rheological study of the produced emulsions was carried out at 25 °C by using a rheometer (HAAKE ReoStress 6000, Thermo Scientific, Karlsruhe, Germany) equipped with a thermostatic bath (HAAKE A10, Thermo Scientific) and a universal temperature controller (HAAKE UTM, Thermo Scientific, Karlsruhe, Germany) coupled to a set of concentric cylindrical geometry sensors with a 5.3-mm gap for all samples. Samples were analyzed using a 16.1-mL volume for each trial. Each sample was subjected to a shear rate continuous ramp in the range of 0 to 300 s^{-1} over 2 min for the ascending and descending curves. After this procedure, a flow curve was generated for the rheological characterization of the samples by varying the shear rate from 0 to 300 s^{-1} over a period of 2 min. The experimental flow curve data were adjusted to the Newton law, power law, and Herschel-Buckley models using Statistical Analysis System 9.1.2 (SAS Institute Inc., Cary, USA, 2008).

Emulsion Droplet Size

The microstructure of the emulsions was evaluated immediately after homogenization and ultrasonication. Aliquots of the samples were placed on glass slides, covered with coverslips, and observed with a Carl Zeiss AG optical microscope (MF-AKS 24 × 36 Expomet, Zeiss, Germany) equipped with a digital Axiocam ICC camera with × 40–100 magnification. Five images of each sample were obtained in order to sweep across the slide and to obtain a representative result. The microscopy images were analyzed according to the methodology described by (Frascareli et al. 2012) with some modifications. A hundred droplets were measured for each image sample by using Zeiss software. The average droplet surface diameter (Sauter d_{32}) was calculated using the following Eq. (1):

$$d_{32} = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} \quad (1)$$

where d_i is the average droplet diameter; n_i is the number of drops.

Microencapsulation by Spray Drying

Emulsions were dried by using a spray dryer (Model MSD 1.0; Labmaq Brazil, Ribeirao Preto, Brazil) equipped with a pneumatic dual fluid nozzle. The inlet air temperature was 160 °C, and the feed flow rate was 0.9 L h^{-1} based on the review made by Jafari et al. (2008), and the drying air flow was maintained at 40 L min^{-1}. After drying, the powders were stored in dark, oxygen-free containers at 4 °C until analysis.

Characterization of the Microparticles

Moisture Content

The moisture content of the powders was determined by the AOAC method (Association of Official Analytical Chemists (ASSOCIATION OF OFFICIAL ANALYTICAL CHEMISTS—AOAC 2007). The percentage weight loss of the powders after drying at 105 °C until constant weight was obtained, and the moisture content (%) was calculated.

Reconstitution Properties

Powder wettability was determined using the method proposed by (Fuchs et al. 2006) with some modifications. Powder samples (0.1 g) were spread on the surface of a beaker containing 100 mL of distilled water at 20 °C without stirring. The time until the last powder particle has sunk or become wet was used to compare the degree of wettability between samples. Solubility of the powders in cold water was evaluated based on the method proposed by (Cano-Chauca et al. 2005) with some modifications as follows. Ten milliliters of distilled water was measured and transferred to a 50-mL beaker. A 2.0-g powder sample was weighed and added to the water in the beaker while stirring at a low speed for 2 min. The material was transferred to a 50-mL centrifuge tube and centrifuged at 1950×*g* for 5 min. A 5-mL aliquot was removed from the

supernatant, transferred to a Petri dish, and dried in an oven at 105 °C for 5 h. The cold water solubility was calculated according to the following Eq. (2):

$$\text{Sol}\ (\%) = \frac{\text{supernatant dry weight (g)} \times 2}{\text{initial sample dry weight (g)}} \times 100 \quad (2)$$

Oil Retention

The amount of encapsulated oil was determined using hexane as an extractant according to the methodology described by Lu et al. (2014) with some modifications. The spray dried powder (1.0 g) was dissolved in 20 mL of distilled water at 50 °C and vortexed for 1 min. Then, the sample was ultrasonicated for 1 min at 240-W power. Afterwards, 20 mL of hexane was added and the resulting solution was vortexed again for 1 min. The sample was centrifuged at 3300 rpm for 5 min and the supernatant was transferred to a 50-mL flask. Ten milliliters of hexane was added to the remaining volume, vortexed, and centrifuged again for 5 min. This procedure was repeated four times. Following these extraction steps, 50 mL of the solution was obtained. The amount of sweet orange essential oil was determined by measuring the absorbance at 252 nm with a UV-VIS spectrophotometer (SP 2000, Bel Photonics, Piracicaba, Brazil) using a calibration curve based on measurements of 0.063–2.000 ppm solutions of sweet orange essential oil in hexane. The linear equation Abs = 0.2859.[c] + 0.00005 with a coefficient of determination (R^2) of 0.9998 was obtained, where Abs was the absorbance value at 252 nm and [c] was the concentration of essential oil. The oil retention is defined as the ratio between the total amount of oil (g) extracted and the initial amount of oil (g) on a dry basis, and was calculated by the following Eq. (3):

$$\text{Oil retention}\ (\%) = \frac{\text{total oil extracted (g)}}{\text{initial oil (g)}} \times 100 \quad (3)$$

Morphology and Particle Size Distribution

The surface morphology of the microparticles was analyzed by scanning electron microscopy (SEM). The microparticles were fixed in the aluminum stubs and metalized with gold by using a SCD-050 vacuum coater. Visualization of samples at various magnifications (× 110–12,000) was done with a scanning electron microscope LEO Evo 40 at 15-kV acceleration voltage.

The particle size distribution was determined after spray drying using the images obtained from SEM. Three images of each sample were obtained in order to sweep across the sample and obtain a representative result. The images were analyzed according to the methodology described by (Frascareli et al. 2012) with some modifications. A hundred microparticles were measured in each image sample by using Zeiss software. These measurements were then used for the calculations of the average Sauter (d_{32}) surface diameter and volume mean diameter (d_{43}) according to Eq. (4) and Eq. (5), respectively:

$$d_{32} = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} \quad (4)$$

$$d_{43} = \frac{\sum n_i d_i^4}{\sum n_i d_i^3} \quad (5)$$

where d_i is the average particle diameter and n_i is the number of particles.

Controlled Release of the Essential Oil

The dried powders were used to study the release characteristics according to the methodology described by (Silva et al. 2016) with some modifications. One gram of powder was suspended in 50 mL of hexane at low speed and at constant stirring. At 10-min intervals, 1.5-mL solution aliquots were taken, centrifuged at 1950×g and used for analysis of absorbance through a UV-VIS spectrophotometer (SP 2000, Bel Photonics, Piracicaba, Brazil) at the pre-determined wavelength for sweet orange essential oil (252 nm). After the readings, the samples used were returned to the initial suspension. The readings were carried out over 140 min. The controlled release was analyzed at 25 and 45 °C to investigate the influence of different storage/processing temperatures.

Statistical Analysis

Analysis of variance of the data was carried out to evaluate the effect of wall material formulations on the characteristics of the produced emulsions and the microencapsulated powders. The Scott-Knott test was done to examine the significance of differences between the mean values obtained. Differences were considered to be significant if $P < 0.05$.

Results and Discussion

Physical Characteristics of CNF

Images obtained by transmission electron microscopy (Fig. 1) showed the thin, twisted, and elongated structure of the CNF. The diameters found in the CNF used in this study were between 17 and 40 nm. Diameters between 70 and 90 nm were found by Lavoratti et al. (2016) in the production of CNF, obtained from softwood residues of (Pinus sp.) and

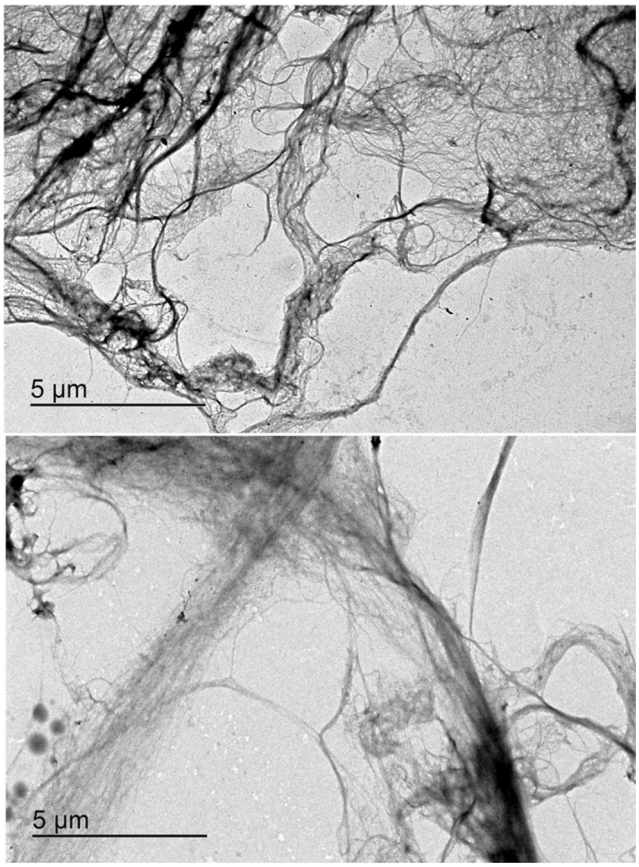

Fig. 1 Physical aspects of the cellulose nanofibrils obtained after 10 passes through a grinder

eucalyptus. Similar values (30–40 nm) were found for agricultural residues nanofibers from wheat straw and soybean hulls (Alemdar and Sain 2008). As these nanofibers form a non-individual fiber network, it is not possible to measure the exact length of the CNFs. In water absorption tests performed by Lavoratti et al. (2016), it was observed that the CNF absorbed more water than the pure residues, because of the nanocellulose hydrophilic nature (Dufresne 2013).

The mechanical treatment performed on eucalyptus fibers resulted in the defibrillation of nanofibers from the cell walls and the images showed the separation of the nanofibres from the microdimensioned fibers.

Rheological Analysis

The rheological data obtained for the emulsions without CNF were adequately described by Newton's law model, in which viscosity is independent of the shear rate values (Carmona et al. 2013). In contrast, the results obtained for the CNF suspension and CNF-containing emulsions were better fitted by the power law model. As shown in Table 2, the rheological parameters determined according to each model used were viscosity (μ) by Newton's law and consistency index (K) and flow behavior index (n) by the power law. Based on the adjustments of the experimental data, the models studied were adequate because they had high values of the coefficient of determination R^2 and acceptable root-mean-square error.

There was a significant effect of treatments ($P < 0.05$) on the viscosity of emulsions without CNF. The emulsion produced with GA had the highest viscosity, whereas the emulsions produced using 3:1 and 1:1 GA/MD blends had sequentially lower viscosity values. In emulsions containing CNF, statistically significant differences ($P < 0.05$) between treatments were observed in both consistency (K) and flow behavior (n) indices. Figure 2 shows the relation between apparent viscosity and shear rate for different treatments at 25 °C: (a) Newton law e, (b) Power law.

As indicated by the rheograms (Fig. 2a), a linear relationship between the apparent viscosity and shear rate, i.e., a typical Newtonian behavior, was observed for emulsions of sweet orange essential oil produced with GA and MD formulations without CNFs. However, the rheological behavior of the CNF suspension and of the emulsions in presence of CNF was more similar to that of non-Newtonian fluids, since the viscosity changes with the increase in the shear rate, characteristic of pseudoplastic fluid. Confirmation of pseudoplasticity of these samples can be illustrated by the flow behavior index (n), which was lower than unity and ranged from 0.779 to 0.872 (Table 2).

The emulsions that contained only GA exhibited Newtonian behavior and had higher viscosity than those made of GA/MD formulations. As described by Madene et al. (2006), maltodextrin is a traditional wall material for encapsulation of aromatic compounds, because it presents low cost and confers good film-forming properties and low viscosity. GA exhibits good emulsion-stabilizing properties and has a branched structure with long chains, which accounts for its higher viscosity (Gharsallaoui et al. 2007; Carneiro et al. 2013).

It was evidenced that the viscosity of the CNF-containing emulsions was higher than that of the CNF-free emulsions. This could be due to the high dispersibility of CNF in the emulsions. The increase in the viscosity could have positive effects on emulsion stability, by hindering the droplet coalescence, and consequently improving the encapsulation efficiency after the drying process. In Fig. 2, it is observed that the presence of CNF resulted in a change on the rheological behavior of the emulsions, also showing increase in viscosity. Some previous studies have shown that aqueous dispersions of CNF exhibit non-Newtonian rheological behavior at concentrations above the gelling threshold (Jowkarderis and Van De Ven 2015; de Kort et al. 2016; Marto et al. 2016). Recent studies have investigated the effects of the cellulose source (Tanaka et al. 2016) on the rheology of CNF dispersions.

Emulsion Droplet Size

The emulsion droplet size from the 1:1 GA/MD blend was significantly smaller ($P < 0.05$) than that in other formulations.

Table 2 Rheological parameters of different emulsion preparations

Wall material	Newton law			
	μ	R^2	RMSE	
GA	0.242 ± 0.002^{a}	0.9997	0.3504	
GA/MD (3:1)	0.172 ± 0.002^{b}	0.9999	0.1649	
GA/MD (1:1)	0.100 ± 0.001^{c}	1.0000	0.0411	
Wall material	Power law			
	K	n	R^2	RMSE
GA/CNF	0.985 ± 0.017^{a}	$0.872^{a} \pm 0.001$	0.9999	0.4561
GA/MD (3:1) CNF	0.837 ± 0.004^{b}	$0.831^{b} \pm 0.002$	0.9998	0.3814
GA/MD (1:1) CNF	0.857 ± 0.027^{b}	$0.779^{c} \pm 0.005$	0.9996	0.4328
C CNF suspension	0.276 ± 0.232^{a}	$0.439^{a} \pm 0.008$	0.9965	0.0438

Means followed by the same lowercase letters in the column are not statistically different ($P > 0.05$)

μ, viscosity (Pa s^{-1}); K, consistency index (Pa s^{n}); n, dimensionless flow behavior index; R^2, coefficient of determination; *RMSE*, root-mean-square error; *GA*, gum Arabic; *MD*, maltodextrin; *CNF*, cellulose nanofibrils

In general, droplet diameters were similar for the different formulations that contained GA, MD, and CNF ($P > 0.05$). However, CNF-containing formulations had lower droplet diameter than CNF-free formulations (Fig. 3).

The observed droplet size values (Table 3) were close to those reported in a study that studied the spray-drying process of refined soybean using GA, MD, and alginate as encapsulating agents (3.8–4.8 μm) (Maisuthisakul and Gordon 2012). MD is considered a good encapsulating agent, because it has high solubility in solutions and low viscosity at high solid content. Nevertheless, it presents no interfacial properties and needs to be used in combinations with other encapsulation agents, such as GA (Yoshii et al. 2001).

CNF suspensions have high degree of dispersion, interfacial adhesion, and orientation in the matrix, as well as a small volume and large surface area (Wu and Wu 2006). Thus, CNF acted as a thickener in the emulsion, improving the interfacial adhesion of the carbohydrates with the orange oil and increasing emulsion stability.

Characterization of the Microparticles

The results of the characterization of microparticles containing sweet orange essential oil produced using the different compositions of wall materials are shown in Table 3.

The study of particle reconstitution properties of powdered food products is necessary for understanding their behavior during processing, marketing, and consumption of the final product. Powdered product wettability, i.e., the ability of water to spread over the microparticles' surface, is a very important feature that influences various stages of the food production process, including agglomeration, granulation, coating, as well as final product characteristics such as dispersibility and solubility (Forny et al. 2011). These properties are directly affected by the molecular interaction between the two phases. In this study, the time required for the powders to become fully wet ranged from 164 to 373 s. The type of the wall material had a significant effect on wettability, where microparticles prepared using MD in formulation exhibited, in general, low

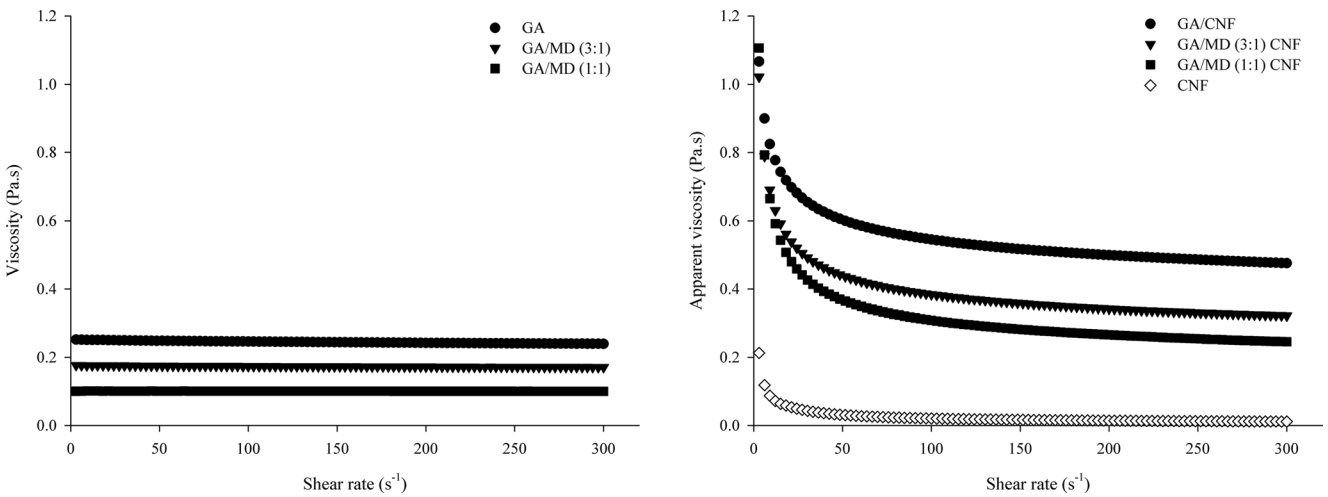

Fig. 2 The relationship between viscosity and apparent viscosity and shear rate for the different emulsions at 25 °C

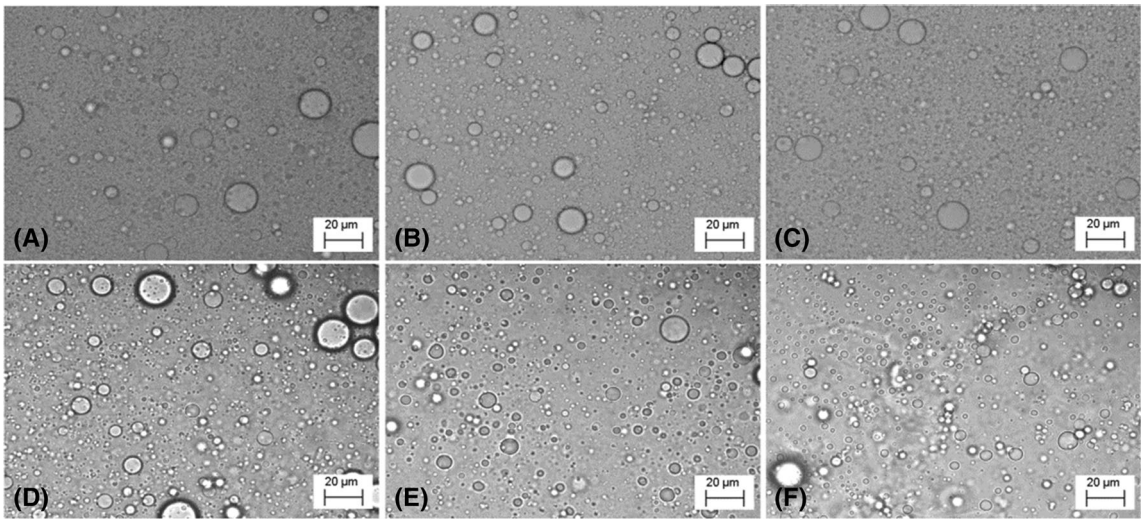

Fig. 3 Optical microscopy of the emulsion droplets containing sweet orange essential oil using different wall materials. Gum Arabic—(a), gum Arabic/maltodextrin (3:1)—(b), gum Arabic/maltodextrin (1:1)—(c), gum Arabic/CNF—(d), gum Arabic/maltodextrin (3:1)/CNF—(e), and gum Arabic/maltodextrin (1,1)/CNF—(f)

wettability times. This was probably due to stronger interactions of MD molecules with water, which likely contributed to a more frequent occurrence of hydrophilic groups on the particles. The latter circumstance reduced the instantiation time by increasing the interaction with water. On the other hand, according to Buffo et al. (2002), powders with higher humidity can contribute to the wetting ability and water absorption, because the liquid penetrates into porous substrates more easily. In the study conducted by Fernandes et al. (2014), similar wettability values were also found for rosemary essential oil GA- and GA/MD-based formulations (301 and 274 s, respectively). The wetting times for the CNF-containing formulations were higher than those for the CNF-free ones, except for GA formulation.

Solubility is an important property and a decisive factor for the quality of powdered products when applied in certain situations. Despite the hydrophobic nature of the encapsulated bioactive material, microparticles in all formulations had similar solubility, which was probably determined by the type of the wall material (Yousefi et al. 2011). GA was present in all formulations, making their surface properties and relative protein fraction (2%) similar (Frascareli et al. 2012), which ensured similar results for the solubility. The carbohydrate polymers used as wall materials in the present study are highly soluble in water, even at high concentrations. CNF have functional hydroxyl groups that contributed to their hydrophilicity (Gardner et al. 2008). Bulk sweet orange essential oil cannot be solubilized in water, whereas following microencapsulation, it can be used in aqueous media. Therefore, the encapsulation of sweet orange essential oil in microparticles helped to disperse the oil in cold water.

The moisture content is an essential property that determines stability of the dehydrated product during storage (Phisut 2012). Low moisture values for particulates prevent the formation of agglomerates, whereas high moisture levels significantly reduce glass transition temperature and decrease product stability. Particles produced using GA as wall material had a statistically lower moisture content value (2.06%)

Table 3 Mean values and standard deviations of the parameters characterizing emulsions and microparticles of sweet orange essential oil encapsulated within different formulations

Wall material	Droplet size (μm)	Wettability (s)	Solubility (%)	Moisture content (%)	Oil retention (%)	D_{32} (μm)	D_{43} (μm)
GA	6.2 ± 1.9^{a}	343 ± 8^{a}	85.8 ± 0.6^{a}	2.06 ± 0.21^{b}	71.33 ± 3.05^{d}	17.5 ± 0.6^{d}	20.1 ± 0.9^{d}
GA/MD (3:1)	5.7 ± 0.5^{a}	205 ± 24^{c}	84.2 ± 1.2^{a}	2.73 ± 0.29^{a}	61.67 ± 1.15^{f}	14.5 ± 0.5^{e}	16.9 ± 0.2^{e}
GA/MD (1:1)	4.4 ± 1.0^{b}	164 ± 10^{c}	83.7 ± 0.6^{a}	2.83 ± 0.83^{a}	65.33 ± 2.08^{e}	10.8 ± 0.6^{f}	12.4 ± 0.6^{f}
GA/CNF	4.4 ± 1.0^{b}	275 ± 60^{b}	80.7 ± 1.4^{a}	3.03 ± 0.64^{a}	84.30 ± 0.57^{a}	31.1 ± 0.9^{a}	36.6 ± 1.7^{a}
GA/MD (3:1) CNF	4.9 ± 2.1^{b}	373 ± 37^{a}	82.8 ± 2.4^{a}	3.03 ± 0.35^{a}	80.31 ± 0.57^{b}	29.0 ± 1.0^{b}	33.0 ± 1.1^{b}
GA/MD (1:1) CNF	3.8 ± 0.9^{c}	236 ± 57^{b}	82.9 ± 1.4^{a}	2.97 ± 0.29^{a}	74.33 ± 0.57^{c}	21.0 ± 0.9^{c}	23.8 ± 1.6^{c}

Values with different letters in the same column are significantly different ($P < 0.05$)

GA, gum Arabic; *MD*, maltodextrin; *CNF*, cellulose nanofibrils

than other formulations ($P < 0.05$), showing that although CNF confers hydrophilic characteristics and swelling capacity, the use of CNF does not influence the powder moisture content. The moisture content values obtained in this study were comparatively low and should not affect powder storage stability.

Encapsulation efficiency of the formulations without CNF ranged from 61.7 to 71.3%. There was a significant effect of the type of wall material formulation on the retention of oil ($P < 0.05$), where GA/MD (3:1) mixture exhibiting the lowest oil retention. The results show that replacement of GA with MD reduced the retention of sweet orange essential oil due to decreased viscosity of the emulsion and increased surface tension. These properties likely facilitated coalescence of droplets (Burgess et al. 1998). According to the study of (Rajabi et al. 2015), the same trend was observed during encapsulation of the bioactive components of turmeric by spray drying using GA, MD, and gelatin as wall materials. Similar efficiency level (73.57%) was found during microencapsulation of basil essential oil using GA-based formulation (Garcia et al. 2012). The increase in the emulsion viscosity until a certain optimal level may enhance oil retention due to the reduction of internal circulations of the semipermeable droplets, occurring rapid formation of the membrane (Jafari et al. 2008). Encapsulation efficiency of the formulations containing CNF ranged from 74.33 to 84.30%. The presence of CNF in the GA and MD formulations contributed to improving the encapsulation efficiency. This results could be possibly attributed to the thickening effect conferred by CNF, because of its nanosized structure which was able to increase the viscosity of the system and thereby improved oil retention during the spray-drying process. Cellulose also has unique properties, such as extremely high surface area, low thermal expansion coefficient, and high barrier function (Lavoine et al. 2012), along with its hydrophilic nature. Oil retention of the CNF-containing GA-based formulation was 18.2% higher than that of the CNF-free GA formulation. In general, the spray-drying process used to encapsulate essential oils has the ability to maintain the volatile components during the drying process. This characteristic is related to the formation of a semipermeable membrane during the process. Some studies have reported effective encapsulation of essential oils using spray drying technique for rosemary (Fernandes et al. 2014) and oregano (Baranauskiené et al. 2006) for example.

SEM images (Fig. 4) did not reveal cracks or flaws in the surface of microparticles produced by different formulations. The formation of a failure-free structure is an important factor for minimizing the loss of volatile compounds and for limiting their contact with external agents such as oxygen, light, and heat. There were no visible differences in the surface area and morphology of the microparticles of different compositions. All particles had a similar spherical shape with some dents, which is characteristic of microparticles stabilized by the spray-drying process. Therefore, differences in the wall material did not affect the morphological characteristics of the microparticles.

Formulations with higher amount of GA (GA and GA/CNF) had larger particle diameters: 20.14 and 36.61 μm, respectively (Table 3). According to Cai and Corke (2000), microparticle diameter depends on the atomization method as well as on the physicochemical properties, concentration, viscosity, and the type of the encapsulating material. Thus, larger particle diameter in formulations with higher concentration of GA is explained by their higher viscosity. GA presence exerts a physical protective effect promoting greater retention of the bioactive compound. Furthermore, a relation between greater particle diameters and high encapsulation efficiency was observed in this study. Microparticles produced in presence of CNF showed greater diameters and also higher encapsulation efficiency. The higher oil retention in presence of CNF could also be due to the emulsion stabilizer effect promoted by the CNF, contributing to a better oil droplet distribution which ensures lower loss of components by volatilization during the spray-drying process. Besides, it is possible that the presence of CNF has increased the emulsifying effect of GA. Jafari et al. (2008) also found correlation between the particle size and encapsulation efficiency, where increasing the viscosity of the emulsion leads to an increase in the diameter of the microparticles, providing higher oil retention, although there is great difficulty in the formation of microparticles in systems with high viscosities.

Formulations containing CNF were more prone to produce smaller microparticles superposed on the surface of larger ones. Furthermore, smaller particles were most frequent in presence of MD in the formulations. In this study, the total levels of MD in the formulations ranged from 25 to 50%.

3.5. Controlled Release of Essential Oil

The controlled release of encapsulated bioactive compounds is a good tool to predict the availability of the core material through the process or storage. Hexane was used as release media in order to simulate conditions regarding lipophilic foods, such as oils and fats, which are potential food matrices to apply encapsulated essential oils. Figure 5 shows the release profile of sweet orange essential oil from microparticles of different formulations at temperatures of 25 and 45 °C. At 25 °C, the release rate from CNF-free formulations was similar, with higher released content (42%) for the 1:1 GA/MD blend. The presence of MD, specially at (1:1) ratio allows higher release. In presence of CNF, at 25 °C, there was an increase in the oil released, reaching 54%. At 45 °C, different behaviors were observed for the formulations studied and no trend was observed, likely due to the higher temperature used. The presence of CNF increased the amount of oil released from GA

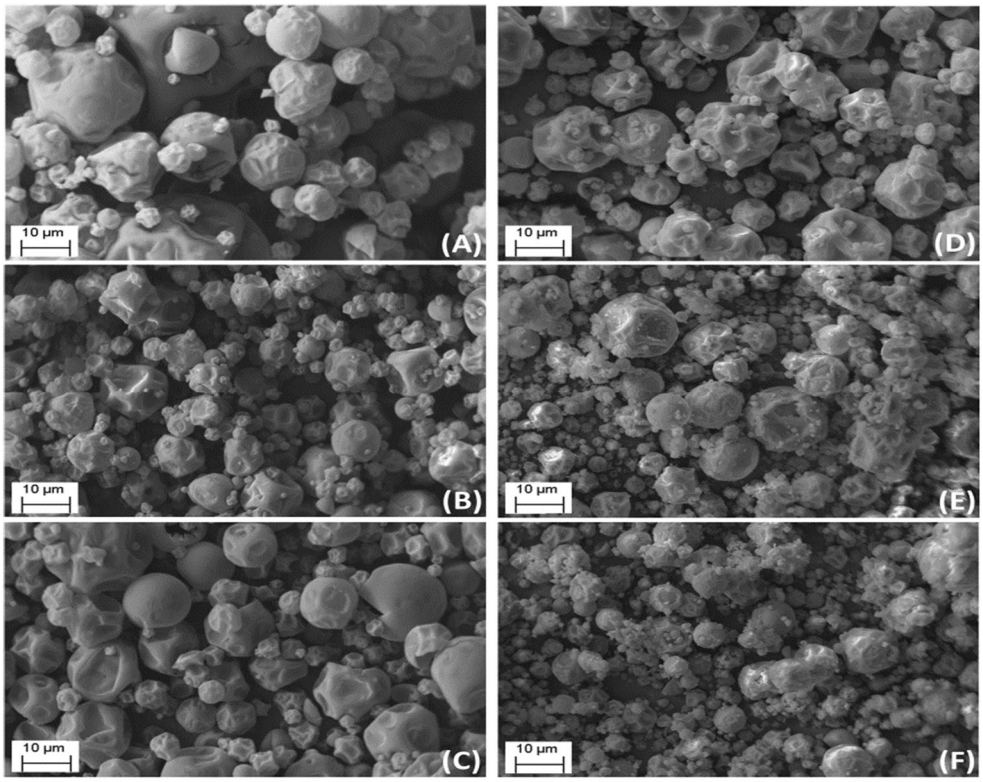

Fig. 4 Images of the microparticles containing sweet orange essential oil obtained by scanning electron microscopy after spray drying. Gum Arabic—(a), gum Arabic/maltodextrin (3:1)—(b), gum Arabic/maltodextrin (1:1)—(c), gum Arabic/CNF—(d), gum Arabic/maltodextrin (3:1)/CNF—(e), and gum Arabic/maltodextrin (1:1)/CNF—(f)

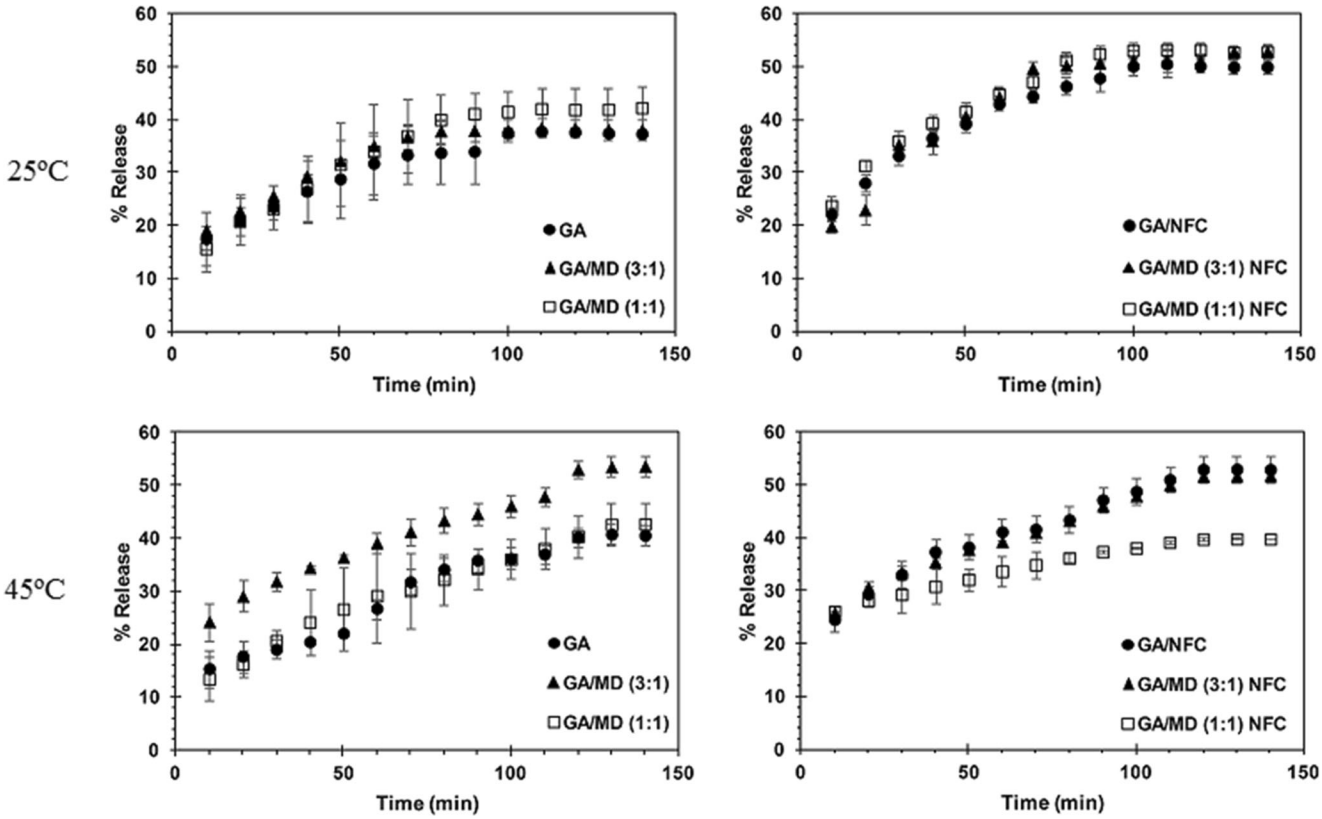

Fig. 5 Profiles of controlled release of sweet orange essential oil from CNF-containing and CNF-free microparticles at 25 and 45 °C. GA gum arabic, GA/MD blend of gum arabic and maltodextrin, CNF cellulose nanofibrils

microparticles. According to Löbmann and Svagan (2017), CNF matrix particles have great potential to provide longer-lasting sustained released; however, due to the high viscosity of a CNF suspension, spray-drying process should be possible only at low concentrations. Therefore, determination of an optimal concentration of CNF regarding the release of essential oils is worthy of being studied.

In this study, by comparing the formulations with and without CNF, at 25 °C, higher amount of essential oil was released by CNF-containing formulations. Features such as the lack of retention of cellulose in the liquid medium and favorable permeation properties to liquid and gas, even at low concentrations, allowed greater amount of oil to be released into the surrounding medium. The presence of some heterogeneity or the lack of a continuous interface between the wall material components could contribute to the higher amount released by CNF-containing formulations. However, such phenomena should be further investigated.

Conclusions

The substitution of gum arabic by maltodextrin and the use of cellulose nanofibrils significantly affected the properties of the produced emulsions and microparticles containing sweet orange essential oil. The presence of CNF increased viscosity, as indicated by the rheological analysis. The droplet size, which is important for emulsion stability, was affected by replacing GA with MD in CNF-free formulations. However, the addition of CNF lowered droplet size, increased the final particle size, and increased encapsulation efficiency in all formulations. Microparticles produced had similar solubility levels with varied wettability. Reduction of the amount of GA in all formulations was associated with the decrease in encapsulation efficiency. The latter parameter was maximal in CNF-containing formulations, especially in the formulation containing only GA and CNF. The produced particles from all formulations had no cracks or flaws on their surface. This finding shows that the combination of GA/MD/CNF formed a matrix with great potential to protect the core material from external influences. By comparing the formulations with and without CNF, in general, it was observed that higher amount of essential oil was released by CNF-containing formulations at 25 °C. This study demonstrated that different wall material formulations had variable capacities to retain and release sweet orange essential oil. The use of CNF combined with other carbohydrate polymers increased the emulsion viscosity presenting positive effects on the microencapsulation efficiency. Further investigations of the application of cellulose nanofibrils in microencapsulation by spray drying are therefore warranted.

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