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PHYSICOCHEMICAL PROPERTIES OF COFFEE OIL MICROCAPSULES PRODUCED BY SPRAY DRYING

E.C. Frascareli[1], V.M. Silva[1], R.V. Tonon[1,2], M.D. Hubinger[1]

[1]Department of Food Engineering, School of Food Engineering.
Monteiro Lobato Street, 80, Campinas, 13083-862, Brazil
Tel.:+55 19 35214036, E-mail: mhub@fea.unicamp.br

[2]Embrapa Food Technology
Americas Avenue, 29501, Rio de Janeiro, 23020-470, Brazil
Tel.:+55 21 36229600, E-mail: renata.tonon@ctaa.embrapa.br

Abstract: The aim of this study was to evaluate some physicochemical properties of coffee oil microcapsules produced with mixtures of maltodextrin: gum Arabic and maltodextrin: whey protein isolate, in the proportions 25:75, 50:50 and 75:25, as well as the pure encapsulating agents. For this purpose, the emulsions properties, encapsulation efficiency, oil retention, powders moisture content, bulk density, hygroscopicity and particles morphology were determined. As main results, powders produced with gum Arabic and with mixtures of maltodextrin: gum Arabic were more hygroscopic, while those produced with whey protein and the mixtures of maltodextrin: whey protein showed the best values of encapsulation efficiency and oil retention.

Keywords: coffee oil, microencapsulation, physicochemical properties, encapsulating agents.

INTRODUCTION

Brazil is the largest coffee producer in the world and coffee oil represents an important industry byproduct, which has several applications as flavoring agent in food and cosmetic products. It is composed by a major lipid fraction (around 75%) (Lucas and Cocero, 2006), which makes it susceptible to lipid oxidation, besides a typical fraction of coffee aroma volatiles and pigments that provide it a dark brown aspect (Oliveira et al., 2005). Since the oil exposure to the atmospheric air can lead to lipid oxidation and, consequently, to the formation of unpleasant tastes and odors, microencapsulation has been proposed as an alternative to avoid such degradation processes. The most used technique to encapsulate flavors is spray drying.

One of the key steps in oils and flavors encapsulation by spray drying is the emulsion preparation, which plays an important role in the surface oil content present in the final encapsulated powder. The significant parameters to be considered in the emulsion formation are: total solid concentration, oil content, viscosity, stability, droplet size and emulsification method. If the emulsion is sufficiently stable and presents optimal conditions of viscosity and droplet size, then the encapsulation efficiency can be maximized by the right choice of the spray drying parameters (Jafari et al., 2008).

Gum Arabic is generally used as wall material in the spray drying of oils and flavors. It produces stable emulsions with most oils over a wide pH range, and it also forms a visible film at the oil interface. However, its high cost, limited supply and quality variations have restricted its use, leading researchers to search for alternative materials for that purpose (Gharsallaoui et al., 2007). Maltodextrins are considered good encapsulating agents because they exhibit low viscosity at high solids contents and good solubility. However, they have no emulsifying properties, which are required for an appropriate encapsulation process. This can be improved by the combination of maltodextrin with other encapsulating materials, such as proteins or gums. Whey protein isolate represents an alternative of wall material for volatile and non-volatile cores and some studies reveals that it offers effective protection against core oxidation (Lee and Rosenberg, 1999; Partanen et al., 2008).

Physical characteristics of powders produced by spray drying, such as bulk density, moisture content, particle size and shape (morphology) are important since they influence powders stability, flowability and have a bearing on transport and packaging costs (O'Hagan et al., 2005).

The aim of this work was to evaluate the emulsions characteristics (droplet size and viscosity) and some physicochemical properties (moisture content, hygroscopicity, bulk density) of coffee oil microcapsules produced by spray drying, using as encapsulating agents gum Arabic, whey protein isolate and mixtures of maltodextrin: gum Arabic and maltodextrin: whey protein isolate.

MATERIALS AND METHODS

Materials

Roasted coffee oil was supplied by Companhia Cacique de Café Solúvel (Barueri, SP, Brazil). Gum Arabic Instantgum BA® (Colloids Naturels, Sao Paulo, SP, Brazil), maltodextrin 10 DE (Corn Products, Mogi Guacu, SP, Brazil) and whey protein isolate, with 89% of protein (Alibra, Sao Paulo, SP, Brazil) were used as wall materials.

Emulsion formation

At first, each wall material (30% w/w) was dispersed in distilled water, under magnetic stirring, until complete dissolution. Gum Arabic, whey protein isolate and the mixtures (maltodextrin: gum Arabic, maltodextrin: whey protein) in the proportions of 25:75, 50:50 and 75:25 were studied. Then emulsions were prepared by blending the coffee oil (15% w/w oil to total solids) and the wall solution, using a rotor-stator homogenizer (Ultra-turrax IKA T18 Basic, Wilmington, NC, USA) operating at 14,000 rpm for 5 minutes. The emulsions were characterized in terms of droplet size and viscosity.

Emulsion droplet size

Emulsions were analyzed immediately after preparation and each sample was measured in triplicate. Samples were poured into microscope slides, covered with glass cover slips and observed using a conventional optical microscope (Carl Zeiss Model mf-AKS 24 × 36 Expomet, Zeiss, Germany), using 40× and 100× objective lenses. Ten images of each emulsion sample were analyzed with the public domain software Image J v1.36b (http://rsb.info.nih.gov/ij/). The volume-surface mean diameter (d_{32}) was calculated from 500 droplets according to Equation (1), considering spherical oil droplets.

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

Where n_i is the number of droplets with diameter d_i.

Emulsion viscosity

Emulsion viscosity was analyzed by the determination of steady-shear flow curves, using a controlled stress rheometer (Physica MCR 301 Rheometer, Anton Paar, Ostfildern, Germany) at 25 °C. Parallel stainless steel plates of 75 mm diameter were used for the measurements with a 0.2 mm gap. Analyses were performed at least in triplicate. Flow curve measurements were carried out with a shear rate ranging from 0 to 300 s^{-1} in three sweeps (up, down and up-cycles), in order to eliminate the influence of thixotropy. The data obtained in the third sweep were fitted to the power law model (Equation 2) and Newtonian model (Equation 3), where σ is the shear stress (Pa), $\dot{\gamma}$ is the shear rate (s^{-1}), k is the consistency index (Pa s^n), n is the flow behavior index (dimensionless) and μ is the viscosity (Pa.s). Flow curves were adjusted by a non-linear regression analysis using the Statistica 5.0 software (StatSoft, Tulsa, Oklahoma, USA). Viscosity was calculated as the relationship between shear stress and shear rate.

$$\sigma = k \cdot \dot{\gamma}^n \qquad (2)$$

$$\sigma = \mu \cdot \dot{\gamma} \qquad (3)$$

Microencapsulation by spray drying

Emulsions were spray dried in a laboratory scale spray dryer (Labmaq MSD 1.0, Ribeirao Preto, SP, Brazil) equipped with a dual fluid nozzle of 1.2 mm diameter. The emulsion was fed into the main chamber of 500 mm × 150 mm, by a peristaltic pump, at 0.8 l/h of feed flow rate. The others conditions were fixed: air flow rate at 36 m^3/h, compressed air flow rate at 2.4 m^3/h and air drying temperature at 170 °C.

Encapsulation efficiency

Encapsulation efficiency (EE) was determined by the fraction of encapsulated oil over the total amount of oil (Equation 4).

$$EE = \frac{\left(Oil_{Total} - Oil_{Surface}\right)}{Oil_{Total}} \times 100 \qquad (4)$$

Where Oil_{Total} is the total amount of oil and $Oil_{Surface}$ is the amount of non-encapsulated oil presented in the surface of microcapsules.

The non-encapsulated oil present in the particles surface was determined according to the method described by Bae and Lee (2008). Fifteen milliliters of hexane were added to two grams of powders in a sealed glass bottle, which was shaken for two minutes at room temperature in order to extract the free oil. Then the solvent mixture was passed through a number 1 Whatman paper filter. The powder collected in the filter was washed three times with 20 ml of hexane. The solvent was evaporated at 60 ºC until constant weight and the non-encapsulated oil was calculated based on the difference between the initial clean flask and that containing the extracted oil residue (Jafari et al., 2008).

Total oil was determined gravimetrically by ether extraction, according to the Rose-Gottlieb method (Bradley et al., 1993).

Oil retention

Oil retention (OR) was determined by dividing the total oil quantified in the particles after spray drying by the total oil initially added to the emulsion preparation (Equation 5).

$$OR = \frac{Oil_{Total}}{Oil_{Initial}} \quad (5)$$

Moisture content

Particles moisture content (U_{bs}) was determined gravimetrically by drying in a vacuum oven at 70 ºC until constant weight (AOAC, 1997).

Bulk density

Powders bulk density (ρ) was measured by weighing 2 g of sample and placing it in a 50 ml graduated cylinder. The cylinder was tapped by hand five times and the bulk density was calculated by dividing the mass of the powder by the volume occupied in the cylinder (Goula and Adamopoulos, 2004).

Hygroscopicity

Hygroscopicity (H) was determined according to the method proposed by Cai and Corke (2000), with some modifications. Samples of about one gram were placed in desiccators with a saturated solution of NaCl (relative humidity of 75.3%). After one week, samples were weighed and hygroscopicity was expressed as the amount of adsorbed moisture per 100 g of sample (g/100 g).

Powders morphology

Powders produced with gum Arabic, whey protein isolate and the mixture of whey protein isolate: maltodextrin, in the proportions 75:25 and 25:75, were observed by scanning electron microscopy (SEM). Particles were attached to SEM stubs using double adhesive tape, coated with 3–5 mA gold/palladium under vacuum, and examined with a scanning electron microscope (Leica, LEO440i model, Cambridge, England). SEM was carried out at 5 kV with magnification of 5000 times.

RESULTS AND DISCUSSION

Table 1 shows the values of encapsulation efficiency and oil retention while the results of droplets diameter and emulsions viscosity are shown in Table 2. Physicochemical properties of coffee oil microcapsules produced with different encapsulating agents are shown in Table 3.

Table 1 shows that oil retention ranged from 85.25 to 96.38% and encapsulation efficiency ranged from 74.60 to 93.60%. The higher values of encapsulation efficiency were obtained for powders produced with whey protein isolate and the mixtures of maltodextrin: whey protein. The increase of whey protein and gum Arabic concentration led to an increase in the encapsulation efficiency, which can be related to the emulsion properties. Higher concentrations of gum Arabic and whey protein isolate resulted in smaller oil droplets (which implies in higher emulsion stability) and higher emulsion viscosity (which makes difficult the droplets movements inside the emulsion, avoiding droplets coalescence). Fernandes et al. (2008) also observed an increase of this response with the increase on gum Arabic concentration in the mixture maltodextrin: gum Arabic of *Lippia sidoides* essential oil microcapsules.

Table 1. Encapsulation efficiency and oil retention

Materials	OR (%)	EE (%)
GA	96.18 ± 0.62	85.15 ± 0.37
75:25 MD:PS	88.40 ± 0.29	87.59 ± 0.74
50:50 MD:PS	89.11 ± 2.63	88.87 ± 1.26
25:75 MD:PS	94.20 ± 2.19	90.74 ± 0.17
25:75 GA:MD	85.25 ± 3.99	74.60 ± 1.57
50:50 GA:MD	95.44 ± 1.40	79.27 ± 2.16
75:25 GA:MD	96.38 ± 0.49	81.51 ± 0.19
PS	93.05 ± 1.62	93.60 ± 1.05

Where: GA = gum Arabic, MD = maltodextrin 10 DE and PS = whey protein isolate.

According to Table 1, mixtures produced with whey protein showed higher encapsulation efficiency (EE) values than those produced with gum Arabic, due to the higher amount of emulsifier in the emulsion, which may have increased its stability during spray drying process. Other possible reasons could be powder collapse of mixtures of maltodextrin: gum Arabic, which consequently delivered the encapsulated oil (Drusch et al., 2006), reducing encapsulation efficiency; and/or the formation of large vacuoles inside the particles, immediately after the crust development, that increased surface oil content and also reducing encapsulation efficiency (Keogh, 2001). Lower values (45 to 66%) were obtained for avocado oil microcapsules produced with mixtures of maltodextrin: whey protein isolate (Bae and Lee, 2008) and higher encapsulation efficiency (99.3%) was obtained for orange oil microcapsules produced with whey protein isolate (Kim and Morr, 1996). Higher values of oil retention (OR) were observed for microcapsules produced with gum Arabic and whey protein. In the mixtures of encapsulating agents, a reduction on oil retention (OR) with the increase on maltodextrin concentration can be seen, probably due to the reduction of emulsifying properties and consequently lower emulsion stability and oil retention. Lower values of oil retention ranging from 54.5 to 84.8% were observed by Huynh et al. (2008) in microencapsulation of lemon myrtle oil with mixtures of maltodextrin with modified starch or maltodextrin with whey protein, observing that oil retention was influenced by the kind of wall material and total solids content.

Table 2. Emulsions properties of coffee oil mixtures with encapsulating agents

Materials	$d_{3,2}$	μ (Pa.s)
GA	2.16 ± 0.12	0.0924
75:25 MD:PS	5.08 ± 0.39	0.0159
50:50 MD:PS	4.62 ± 0.34	0.0161
25:75 MD:PS	3.67 ± 0.13	0.0222
25:75 GA:MD	4.49 ± 0.13	0.0244
50:50 GA:MD	3.05 ± 0.21	0.0436
75:25 GA:MD	2.51 ± 0.27	0.0752
PS	2.86 ± 0.11	0.0279

Where: GA = gum Arabic, MD = maltodextrin 10 DE and PS = whey protein isolate.

Table 2 shows the results of droplets diameter and emulsions viscosity. Smaller diameters were obtained for powders produced with pure encapsulating agents. All the mixtures showed a reduction in the droplets diameter with the reduction of maltodextrin concentration, which can be attributed to the excellent emulsifying properties of whey protein and gum Arabic. The experimental data of shear rate/shear stress, for all emulsions, presented excellent fit to both Newtonian and power law models, with determination coefficients above 0.998 and mean relative error less than 3.66%. However, as n was close to 1, the emulsions were characterized as Newtonian fluids. The emulsions produced with gum Arabic were more viscous than those produced with whey protein. Similar results were obtained by Fernandes et al (2008). Bae e Lee (2008) studied the influence of the proportion of maltodextrin and whey protein isolate on the emulsions viscosity and observed that higher concentrations of maltodextrin 5 DE led to higher emulsion viscosity. In the present work, an opposite tendency was observed due to the chemical structure of maltodextrin 10 DE, that is more hydrolysed than 5 DE, which presents viscosity characteristics of large molecules as starch.

Table 3 shows that powders moisture content for all samples were similar and ranged from 1.25 to 2.13%. Higher values were obtained for microcapsules produced with gum Arabic and with the mixture maltodextrin: gum Arabic, due to the more hydrophilic characteristics of this encapsulating agent. Similar results were obtained for microcapsules of avocado oil produced with whey protein and maltodextrin and for microcapsules of *d*-Limonene produced with maltodextrin and gum Arabic (Bae and Lee, 2008; Soottitantawat et al., 2003).

Table 3. Physicochemical properties of coffee oil microcapsules produced with different encapsulating agents

Materials	X_{wb} (%)	ρ (g/cm^3)	H (g/100 g)
GA	1.79 ± 0.04	0.376 ± 0.003	17.41 ± 0.35
75:25 MD:PS	1.30 ± 0.07	0.269 ± 0.006	10.72 ± 0.13
50:50 MD:PS	1.54 ± 0.06	0.262 ± 0.002	11.28 ± 0.07
25:75 MD:PS	1.38 ± 0.01	0.258 ± 0.001	11.54 ± 0.28
25:75 GA:MD	1.47 ± 0.03	0.367 ± 0.004	13.01 ± 0.11
50:50 GA:MD	2.13 ± 0.08	0.346 ± 0.007	14.33 ± 0.14
75:25 GA:MD	1.87 ± 0.13	0.340 ± 0.007	15.71 ± 0.10
PS	1.25 ± 0.03	0.238 ± 0.009	12.99 ± 0.08

Where: GA = gum Arabic, MD = maltodextrin 10 DE and PS = whey protein isolate

The results obtained for bulk density showed that powders produced with gum Arabic presented higher values of this property than those produced with whey protein isolate. The increase in the maltodextrin concentration led to higher bulk densities, for the particles produced with gum Arabic and maltodextrin, while the samples produced with whey protein did not show significant difference between themselves. Bae and Lee (2008) found similar values (0.25 to 0.28 g/cm^3) of bulk density for avocado oil microcapsules using mixtures of maltodextrin: whey protein and Kim and Morr (1996) obtained values of 0.13 g/cm^3 and 0.27 g/cm^3, for samples produced with whey protein isolate and gum Arabic, respectively.

In relation to powders hygroscopicity, the results showed that higher values were observed for samples produced with gum Arabic, followed by those produced with the mixture maltodextrin: gum Arabic and maltodextrin: whey protein. The differences can be explained by the chemical structure of wall materials. Gum Arabic presents a high number of ramifications with hydrophilic groups that easily bind to water molecules, while whey protein has less of these groups available to interact with water, showing lower hygroscopicity. Maltodextrin 10 DE, which is a hydrolyzed starch, also exhibits some ramifications with hydrophilic groups with contributes to water adsorption.

Fig 1 to 4 show powders micrographs. All samples have spherical shape, shriveled particles, with roughness. Specifically those produced with whey protein presented a continuous wall and no apparent fissures or cracks, which is important for core protection from oxidation reaction. Moreover, powders produced with gum Arabic presented some agglomeration points that can be related to free oil surface content.

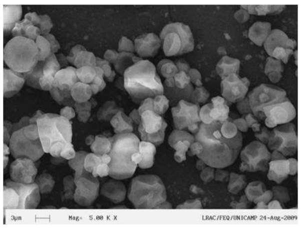

Fig. 1. Micrograph of powders produced with gum Arabic (5000 x)

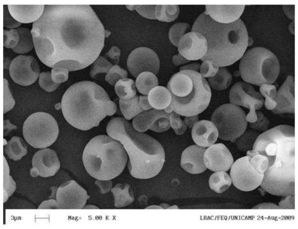

Fig. 2. Micrograph of powders produced with whey protein isolate (5000 x)

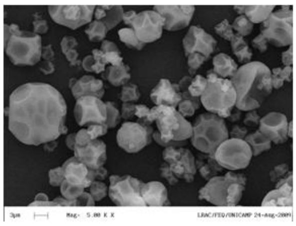

Fig. 3. Micrograph of powders produced with 75:25 maltodextrin: whey protein isolate (5000 x)

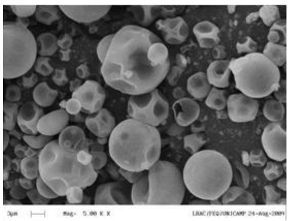

Fig. 4. Micrograph of powders produced with 25:75 maltodextrin: whey protein isolate (5000 x)

CONCLUSIONS

Powders produced with the mixture maltodextrin:whey protein isolate showed good physicochemical properties and the best results of encapsulation efficiency and oil retention. Then they can replace gum Arabic as encapsulating agent in spray drying process.

NOMENCLATURE

$d_{3,2}$	volume-surface mean diameter	μm
d_i	mean diameter	μm
EE	encapsulation efficiency	%
H	hygroscopicity	g/100g
n_i	number of droplets	-
OR	oil retention	%
X_{wb}	moisture content (wet basis)	%

Greek letters

ρ	bulk density	g/cm^3
μ	viscosity	Pa.s

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