Journal of Food Engineering 115 (2013) 443–451

Contents lists available at SciVerse ScienceDirect

Journal of Food Engineering

journal homepage: www.elsevier.com/locate/jfoodeng

Encapsulation efficiency and oxidative stability of flaxseed oil microencapsulated by spray drying using different combinations of wall materials

Helena C.F. Carneiro [a], Renata V. Tonon [b], Carlos R.F. Grosso [c], Míriam D. Hubinger [a,*]

[a] Department of Food Engineering, Faculty of Food Engineering, University of Campinas, Campinas, SP, Brazil
[b] Embrapa Food Technology, Rio de Janeiro, RJ, Brazil
[c] Department of Food and Nutrition, Faculty of Food Engineering, University of Campinas, Campinas, SP, Brazil

ARTICLE INFO

Article history:
Available online 3 April 2012

Keywords:
Microencapsulation
Spray drying
Flaxseed oil
Wall material
Encapsulation efficiency
Oxidative stability

ABSTRACT

This study aimed at evaluating the potential of maltodextrin combination with different wall materials in the microencapsulation of flaxseed oil by spray drying, in order to maximize encapsulation efficiency and minimize lipid oxidation. Maltodextrin (MD) was mixed with gum Arabic (GA), whey protein concentrate (WPC) or two types of modified starch (Hi-Cap 100™ and Capsul TA®) at a 25:75 ratio. The feed emulsions used for particle production were characterized for stability, viscosity and droplet size. The best encapsulation efficiency was obtained for MD:Hi-Cap followed by the MD:Capsul combination, while the lowest encapsulation efficiency was obtained for MD:WPC, which also showed poorer emulsion stability. Particles were hollow, with the active material embedded in the wall material matrix, and had no apparent cracks or fissures. During the oxidative stability study, MD:WPC combination was the wall material that best protected the active material against lipid oxidation.

the market and this fact has led the food industry to focus their research in products of this nature. Flaxseed oil is a polyunsaturated oil extracted from the flax plant (*Linum usitatissimim*) rich in α-linolenic acid (ALA), the essential fatty acid omega (ω)-3, which represents about 57% of its total fatty acids. The high content of n-3 fatty acid present in this oil allows the attribution of functional food, which means that besides the nutritional functions, its consumption may have beneficial effects on health (Vaisey-Genser and Morris, 2003).

On the other hand, one of the major problems associated with oils rich in polyunsaturated fatty acids (PUFAs) is their high susceptibility to oxidative deterioration and consequent production of undesirable flavor. Thus, there is a need to protect these oils in order to make them more stable during handling, processing and storage (Augustin et al., 2006).

Spray drying is a process widely used for microencapsulation of oils and flavours (Fuchs et al., 2006; Ahn et al., 2008; Bae and Lee, 2008; Partanen et al., 2008). It results in powders with good quality,

* Corresponding author at: Faculty of Food Engineering – UNICAMP, 80 Monteiro Lobato Street, Postal code 13083-862, Cidade Universitaria Zeferino Vaz, Campinas/SP, Brazil. Tel.: +55 19 3521 4036; fax: +55 19 3521 4027.

E-mail addresses: htina01@fea.unicamp.br (H.C.F. Carneiro), renata.tonon@ctaa.embrapa.br (R.V. Tonon), grosso@fea.unicamp.br (C.R.F. Grosso), mhub@fea.unicamp.br (M.D. Hubinger).

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http://dx.doi.org/10.1016/j.jfoodeng.2012.03.033

also protects the th wall material sity and droplet size) can affect the process efficiency and the microencapsulated product stability. A successful microencapsulation must result in a powder with minimum surface oil and maximum retention of the active material.

Gum Arabic is one of the most common wall materials used in microencapsulation by spray drying. Although it presents many desirable characteristics to be a good encapsulating agent (high solubility, low viscosity and good emulsifying properties), the oscillation in supply, as well as the increasing prices, is leading researches to look for alternative wall materials that could replace it or be used in combination with it (Charve and Reineccius, 2009).

Maltodextrin is a hydrolyzed starch commonly used as wall material in microencapsulation of food ingredients (Gharsallaoui et al., 2007). It offers advantages such as relatively low cost, neutral aroma and taste, low viscosity at high solids concentrations and good protection against oxidation. However, the biggest problem of this wall material is its low emulsifying capacity. Therefore, it is desirable to use maltodextrin in combination with other surface active biopolymers, such as gum Arabic (Fernandes et al., 2008; Bule et al., 2010), modified starches (Soottitantawat et al., 2003; Bule et al., 2010) and proteins (Hogan et al., 2003; Bae and Lee, 2008) in order to obtain an effective microencapsulation by spray drying.

The selection of wall material combinations affects both the emulsion properties and the particles' characteristics after drying

and during storage. It is well described that emulsion characteristics such as stability, viscosity, droplets size, as well as powder properties such as surface oil, particle size, density, morphology and oxidative stability, are influenced by the type of encapsulating agent used (Jafari et al., 2008b).

Most of the works found in the literature on microencapsulation of PUFA-rich oils uses fish oil as active material (Hogan et al., 2003; Augustin et al., 2006; Serfert et al., 2009; Anwar and Kunz, 2011).

Fish oil and flaxseed oil are very rich in polyunsaturated fatty acids, but they do not have the same composition. Some works found in literature have reported the microencapsulation of fish oil containing approximately 27% (Serfert et al., 2009), 29% (Aghbashlo et al., 2012), or 33% (Drusch et al., 2009b) of omega-3 fatty acids, while the flaxseed oil contains bout 53% linolenic acid (Tonon et al., 2011). Therefore, even though they could show a similar tendency when microencapsulated, it is not possible to assure they will present the same behavior during spray drying and storage.

Very little information is available on microencapsulation of flaxseed oil (Partanen et al., 2008; Omar et al., 2009; Tonon et al., 2011) and none of the published works reported the influence of different types of wall materials on the encapsulation efficiency and oxidative stability of this oil.

The objective of this work was to evaluate the potential of maltodextrin combination with four types of wall materials (gum Arabic, whey protein concentrate and two types of modified starches), as alternative materials for microencapsulation of flaxseed oil by spray drying. The feed emulsions were characterized for stability, viscosity and droplet size, while the microcapsules were characterized for encapsulation efficiency, moisture content, particle size, bulk density, morphology and oxidative stability.

2. Material and methods

2.1. Material

Flaxseed oil (Lino Oil, Paranambi, Brazil) was used as active material with the following fatty acid composition: 5.77% 16:0, 4.57% 18:0, 21.11% 18:1, 14.30% 18:2 and 53.35% 18:3. The wall materials used were: maltodextrin MOR-REX® 1910 with 10 DE (Corn Products, Mogi Guaçu, Brazil) (MD), whey protein concentrate WPC 80® (Alibra Ingredients, Campinas, Brazil) (WPC), gum Arabic Instantgum BA® (Colloids Naturels CNI, São Paulo, Brazil) (GA) and two chemically *n*-octenyl succinic andydrid (OSAN)-modified starches: Capsul TA® (derived from Tapioca starch) and Hi-Cap 100™ (derived from waxy maize) (National Starch, São Paulo, Brazil).

2.2. Emulsion preparation

The wall materials were added to distilled water at 25 °C and the mixture was stirred until completely dissolved. The total solid concentration (wall material + oil) was fixed at 30%. Flaxseed oil was then added to the wall material solution at a concentration of 20% with respect to total solids (Ahn et al., 2008; Jafari et al., 2008a; Charve and Reineccius, 2009). Emulsions were formed using an Ultra-Turrax homogenizer MA-102 (Marconi, Piracicaba, Brazil) operating at 18,000 rpm for 5 min.

2.3. Emulsion characterization

2.3.1. Emulsion stability

Immediately after the emulsion preparation, 25 mL aliquots of each sample were transferred to graduated cylinders of 25 mL, sealed, stored at room temperature for one day, and the volume of the upper phase measured after 24 h. The stability was measured by % of separation and expressed as:

$$\%\,\text{Separation} = \left(\frac{H_1}{H_0}\right) \times 100 \quad (1)$$

Where: H_o represents the emulsion initial height and H_1 is the upper phase height.

2.3.2. Emulsion viscosity

Emulsion viscosity was measured thought the determination of steady-shear flow curves using a Physica MCR301 Rheometer (Anton Paar, Graz, Austria). Measurements were made in triplicate, using stainless steel plate-plate geometry with a diameter of 75 mm and a gap of 0.2 mm. Temperature was controlled at 25 °C by a Peltier system. Rheograms were analyzed according to empirical models and the emulsions viscosity was calculated as the relationship between shear stress and shear rate.

2.3.3. Emulsion droplet size

The droplet size distribution was measured using a laser light diffraction instrument, Mastersizer S (Malvern Instruments, Malvern, UK). A small sample was suspended in water using magnetic agitation, and the droplet size distribution was monitored during each measurement until successive readings became constant. The emulsion droplet size was expressed as D_{32}, the Sauter mean diameter.

2.4. Microencapsulation by spray drying

Spray drying process was performed in a laboratory scale spray dryer Lab Plant SD-05 (Huddersfield, England), with a nozzle atomization system with 0.5 mm diameter nozzle and main spray chamber of 500 × 215 mm. The emulsions were fed into the main chamber through a peristaltic pump and the feed flow rate was controlled by the pump rotation speed. Drying air flow rate was 73 m^3/h and compressor air pressure was 0.06 MPa. Inlet and outlet air temperature were 180 ± 2 and 110 ± 2 °C, respectively, and feed flow rate was 12 ± 2 g/min.

2.5. Powders analysis

2.5.1. Encapsulation efficiency

Encapsulation efficiency (*EE*) was determined according to the method described by Bae and Lee (2008). Fifteen milliliters of hexane were added to 1.5 g of powder in a glass jar with a lid, which was shaken by hand for the extraction of free oil, during 2 min, at room temperature. The solvent mixture was filtered through a Whatman filter paper n° 1 and the powder collected on the filter was rinsed three times with 20 mL of hexane. Then, the solvent was left to evaporate at room temperature and after at 60 °C, until constant weight. The non-encapsulated oil (surface oil) was determined by mass difference between the initial clean flask and that containing the extracted oil residue (Jafari et al., 2008b). Total oil was assumed to be equal to the initial oil, since preliminary tests revealed that all the initial oil was retained, which was expected, since flaxseed oil is not volatile. Encapsulation efficiency (EE) was calculated from Eq. (2).

$$EE = \left(\frac{TO - SO}{TO}\right) \times 100 \quad (2)$$

where *TO* is the total oil content and *SO* is the surface oil content.

2.5.2. Moisture content

Powders' moisture content was determined gravimetrically by drying in a vacuum oven at 70 °C until constant weight (AOAC, 2006).

2.5.3. Bulk density

For determination of bulk density, 2 g of powder were transferred to a 50 mL graduated cylinder. Packed bulk density was calculated from the height of powder in the cylinder after being tapped by hand on a bench 50 times from a height of 10 cm (Goula and Adamopoulos, 2004).

2.5.4. Particle size distribution

Particle mean diameter was measured using a laser light diffraction instrument, Mastersizer S (Malvern Instruments, Malvern, UK). A small sample was suspended in ethyl alcohol (99.9%) using magnetic agitation, and the particle size distribution was monitored during each measurement until successive readings became constant. The particle size was expressed as D_{43}, the volume weighted mean diameter.

2.5.5. Scanning electron microscopy (SEM)

Microcapsules were observed in a Scanning Electron Detector microscope with Energy Dispersive X-ray, SEM and EDX Leo 440i 6070 (LEO Electron Microscopy, Oxford, England) operating at 15 kV and electron beam current of 100 pA. The samples were fixed directly on door-metallic specimens (stubs) of 12 mm diameter and then subjected to metallization (sputtering) with a thin layer of gold/palladium in a Sputter Coater SC7620 polaron (VG Microtech, England) at a coverage rate of 0.51 Å/s for 180 s, with a current of 3.5 mA, 1 V and 2×10^{-2} Pa. After metallization, the samples were observed with magnifications of 4000, 5000 and 10,000×. Image acquisition was performed by the LEO software, version 3.01.

2.5.6. Oxidative stability

For the stability tests, the microcapsules were sealed in a glass vial (20 mL), stored at 45 °C in order to accelerate the oxidation process, and evaluated for oxidation by two distinct methods (peroxide value and headspace analysis) at time zero (right after drying) and over four weeks of storage.

2.5.6.1. Peroxide value. The oil extraction was performed according to Partanen et al. (2008). The peroxide value determination was carried out spectrophotometrically according to the IDF standard method 74A:1991 using the Unico 2800UV/VIS spectrophotometer (United Products & Instruments Inc., New Jersey, USA). Measurements were performed in triplicate. Hydroperoxide concentrations were determined using a Fe^{+3} standard curve with iron concentration varying from 1 to 24 μg, as described by Shantha and Decker (1994).

2.5.6.2. Headspace analysis. Headspace gas chromatography was used to determine the production of propanal and hexanal, considered as indicators of flaxseed oil oxidation (Augustin et al., 2006; Boyde et al., 1992; Jimenez et al., 2006; Drusch et al., 2007). Powder samples (1 g) of each combination were placed into an amber glass vial (20 mL) and stored under the same conditions previously described. To quantify the propanal and hexanal production, new and fresh samples were dopped with a known amount of aldehydes (purity standards known) in order to built a calibration curve. Analyses were made in a gas chromatograph type CombiPal Headspace – CTC Analytics Shimadzu – model GC-2010 (Kyoto, Japan), with a Rtx-01, 100% dimethyl polysiloxane column (30 m × 0.32 mm, 3.0 mm film). The carrier gas was helium (99.999%), used at a flow rate of 1.0 mL/min. The injector temperature was 200 °C, split mode (1:30). Finally, the detector was flame ionization and temperature used was 250 °C. Analyses of headspace were performed in triplicate.

2.6. Statistical analysis

Results were statistically analysed by Analysis of Variance, using the software Statistica® 8.0 (Statsoft Inc., Tulsa, USA). Mean analysis was performed using Duncan's procedure at $p \leqslant 0.05$.

3. Results and discussion

3.1. Emulsion characterization

The percentage of separation and the droplets mean diameter (D_{32}) observed in the emulsions produced with different types of wall materials are shown in Table 1.

The stability study revealed that most of the emulsions were kinetically stable, with exception of those prepared with WPC and maltodextrin, which showed the formation of a small separation layer and a foam phase, 24 h after its homogenization. This was unexpected, since whey proteins are well known by their good emulsifying capacity. According to Dickinson and Matsumura (1991) this result may have been caused by the unfolding of the protein molecules at the droplets surface, which would enhance protein–protein interaction leading to flocculation during emulsification and consequently reducing the emulsion stability. The unfolding of protein molecules of the oil–water interface may lead to changes in secondary and tertiary structure, and consequently exposure of their residues which would be linked (–S–S– linkages or disulphide linkages) within the native globular structure leading to the formation of intermolecular interaction at the oil–water interface and flocculating. Another hypothesis that can be considered to explain this unusual behaviour is that the stability of protein-stabilized emulsions is a function of pH and other parameters. So, depending on the emulsions' pH, the emulsifying capacity of WPC may have been lower than usual (Huynh et al., 2008), affecting the emulsion stability.

As stated before, emulsion viscosity was determined through steady-shear flow curves. Experimental data were better adjusted by the Newtonian model, according to which viscosity is constant with shear rate. The MD:Capsul mixture was the only one that presented a different rheological behaviour, being characterized as non-Newtonian (Power-law) fluid, with flow behaviour index value (n) inferior to 1 (0.830). The viscosity of emulsions produced with different wall materials combination is shown in Fig. 1.

The emulsion prepared with MD:GA showed the highest viscosity, followed by that prepared with MD:Capsul combination. Gum Arabic is generally used as a thickening agent in foodstuffs, showing a ramified structure with long chains, which can be responsible for its higher viscosity. Despite the greater difficulty of dissolution of Hi-Cap during the initial solution preparation, the emulsions prepared with this wall material and maltodextrin showed the lowest

Table 1
Characterization of emulsions prepared with different types of wall materials.

Formulation	% Separation	D_{32} (μm)
MD:Hi-Cap	–	2.11 ± 0.01^{b}
MD:WPC	16.8 ± 0.01	2.10 ± 0.02^{b}
MD:GA	–	1.73 ± 0.02^{c}
MD: Capsul	–	2.19 ± 0.03^{a}

Different letters indicate significant difference between samples at $p \leqslant 0.05$. (MD: Maltodextrin, Hi-Cap: Hi-Cap 100, WPC: Whey Protein Concentrate, GA: Gum Arabic, Capsul: Capsul TA).

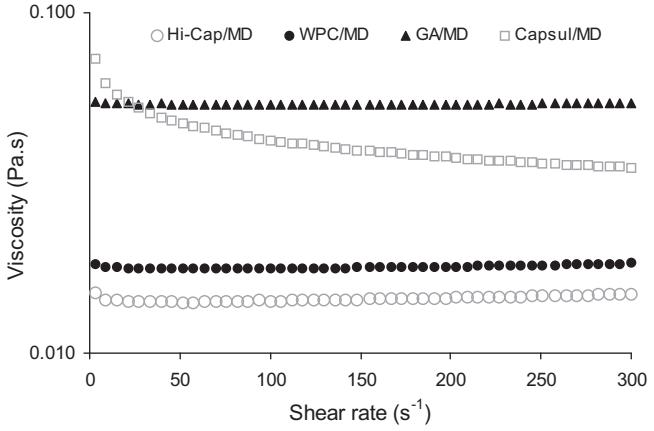

Fig. 1. Emulsions viscosity as a function of shear rate. (MD: Maltodextrin, Hi-Cap: Hi-Cap 100, WPC: Whey Protein Concentrate, GA: Gum Arabic, Capsul: Capsul TA).

viscosity values compared to other combinations. Soottitantawat et al. (2003), Fernandes et al. (2008), Bule et al. (2010) also verified that mixtures of gum Arabic and maltodextrin presented higher emulsion viscosity when compared to emulsions prepared with maltodextrin and other polymers.

The homogenization of flaxseed oil and the different wall materials combinations resulted in emulsions with droplet diameter ranging from 0.6 to 26 μm. According to Fig. 2, most of the curves presented a monomodal distribution with one peak representing a predominant size, with exception of the emulsion prepared with MD:Capsul, which showed a bimodal distribution.

The use of different wall materials had significant influence on emulsions droplet size (Table 1). The emulsion prepared with MD:Capsul had the biggest droplets when compared to the other materials, while the emulsion prepared from the MD:GA mixture showed the smallest ones. This last result can be related to the highest viscosity presented by the MD:GA emulsion, which implies in a greater resistance to droplets movement, avoiding coalescence and resulting in smaller diameters.

Although the mixture of maltodextrin and Capsul has shown higher viscosity in comparison to those produced with WPC and Hi-Cap, these last two samples showed smaller droplet mean diameters, indicating that droplets size was not affected only by the emulsion viscosity, but also by the intrinsic emulsifying properties of each type of material.

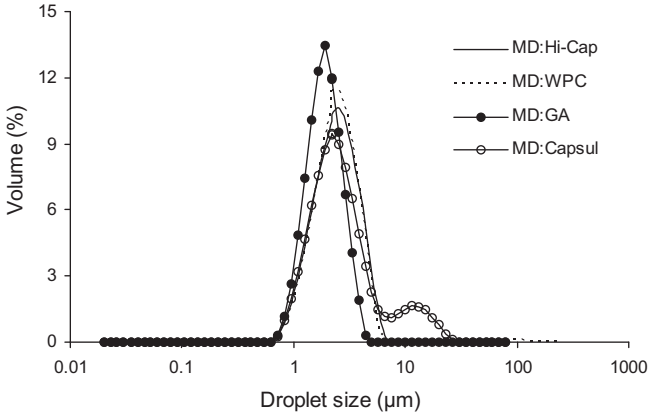

Fig. 2. Droplets size distribution of emulsions prepared with different wall materials. (MD: Maltodextrin, Hi-Cap: Hi-Cap 100, WPC: Whey Protein Concentrate, GA: Gum Arabic, Capsul: Capsul TA).

3.2. Encapsulation efficiency

According to Fig. 3, the encapsulation efficiency of samples was significantly influenced by the type of wall material used, since emulsions prepared with Hi-Cap resulted in particles with considerably lower surface oil than those prepared with the other ones. The encapsulation efficiency values varied from 62.3% to 95.7%, being the lowest value obtained for MD:WPC.

Analyzing the results, these two combinations (MD:WPC and MD:Hi-Cap) had similar rheology and droplet mean diameter characteristics. However, the emulsion containing MD:WPC showed the poorest stability, which may have influenced on the encapsulation efficiency of its resulting powders. According to Barbosa et al. (2005), the more stable the emulsion, the higher the encapsulation efficiency is, i.e., the lower the amount of nonencapsulated material on particles surface. Charve and Reineccius (2009) obtained a similar result studying the volatile retention in microcapsules prepared by spray drying, where the microencapsulated particles produced with modified starch showed higher oil retention when compared to the particles encapsulated with gum Arabic and with whey protein.

Many studies have shown that the reduction of emulsion droplets size, which generally represents an increased stability, results in greater retention of active material (Liu et al., 2001; Soottitantawat et al., 2005; Jafari et al., 2008a). In the present study, the results obtained for encapsulation efficiency could not be related to the emulsions droplet size or viscosity and the differences between them can probably be attributed to the differences between the polymer matrices formed by each one of the wall materials used, which have different retention properties and film-forming capacity.

3.3. Particle characterization

Table 2 presents the characterization of particles prepared with different wall materials. In general, samples did not show significant differences in moisture content when different wall materials were used. Only the MD:Capsul combination had a moisture content value slightly lower than the others. Hogan et al. (2001) observed moisture content values from 1% to 3% in soybean oil microencapsulated by spray-drying and these values were not affected by the type of wall material as well.

Microcapsules showed significant variation in bulk density, according to the type of wall material used. Bulk density values ranged from 0.28 (MD:WPC) to 0.40 g/cm^3 (MD:GA), being gum Arabic the material that resulted in the most dense particles. The advantage of obtaining powders with higher density is that they can be stored in large amounts into smaller containers when compared to products with lower densities. Moreover, higher bulk

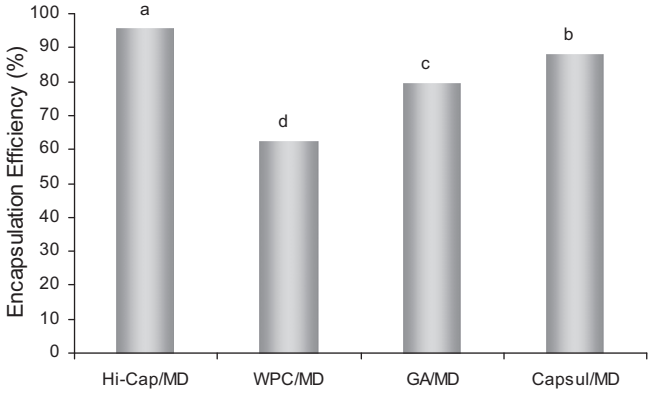

Fig. 3. Encapsulation efficiency of powders produced with different wall materials. Different letters indicate significant difference between samples at $p \leqslant 0.05$. (MD: Maltodextrin, Hi-Cap: Hi-Cap 100, WPC: Whey Protein Concentrate, GA: Gum Arabic, Capsul: Capsul TA).

Table 2
Characterization of particles prepared with different wall materials.

Formulation	% Moisture content	Bulk density (g/cm^3)	D_{43} (μm)
MD:Hi-Cap	1.65 ± 0.160^a	0.35 ± 0.027^b	19.79 ± 0.05^b
MD:WPC	1.54 ± 0.060^a	0.28 ± 0.010^c	17.98 ± 0.88^c
MD:GA	1.45 ± 0.050^a	0.40 ± 0.012^a	23.03 ± 0.31^a
MD: Capsul	1.11 ± 0.110^b	0.36 ± 0.023^b	15.32 ± 0.01^d

Different letters indicate significant difference between samples at $p \leqslant 0.05$. (MD: Maltodextrin, Hi-Cap: Hi-Cap 100, WPC: Whey Protein Concentrate, GA: Gum Arabic, Capsul: Capsul TA).

density may indicate lower amount of air occluded in the spaces between particles, which can help to prevent lipid oxidation.

Particle mean diameters varied from 17.98 to 23.03 μm. The microcapsules produced from mixtures of maltodextrin and gum Arabic showed greater size, probably due their higher emulsion viscosity. According to Masters (1991), the atomized droplet size varies directly with emulsion viscosity at a constant atomization speed. The higher the emulsion viscosity, the larger are the droplets formed during atomization, and therefore, the larger are the powdered particles obtained. This is in agreement with the results published by Hogan et al. (2001) for fish oil encapsulated using sodium caseinate and carbohydrates of varying dextrose equivalence (DE) as wall materials. Fig. 4 shows the particle size distribution of powders produced with different combinations of wall materials.

The particles exhibited a very large size range, with diameters varying from 0.02 to 160.0 μm, approximately, and showed a bimodal distribution with two distinct peaks, each one representing a predominant size. This is particularly interesting in the case of powders, once the "population" of smaller particles can penetrate into the spaces between the larger ones, thus occupying less space.

Although all the wall materials combinations have resulted in similar particle size distributions, the powders produced with the MD:WPC mixture showed a wider distribution, which means that these particles were less homogeneous. It can also be related to the lower stability of the feed emulsions produced with maltodextrin and whey protein concentrate.

3.4. Powder morphology

Fig. 5 shows the SEM microstructures (internal and external) of powders produced with different wall material combinations.

Observing the external morphology, particles showed a spherical shape and various sizes with no apparent cracks or fissures, which is an advantage, since it implies that capsules have lower permeability to gases, increasing protection and retention of the active material. Moreover, the variety in size is a typical characteristic of particles produced by spray drying. The mixtures of different wall materials influenced on microparticles morphology. This is more evident when comparing the images from the combination of MD:Hi-Cap with the others, since this mixture resulted in microspheres with smoother surface and fewer teeth or roughness. According to Ré (1998), such imperfections (teeth) are formed when there is a slow process of film formation during drying of the atomized droplets, associating the presence of surface depressions to the collapse suffered by the droplets during the initial stages of drying. Similar morphological characteristics were found by Tonon et al. (2011) and Soottitantawat et al. (2005)).

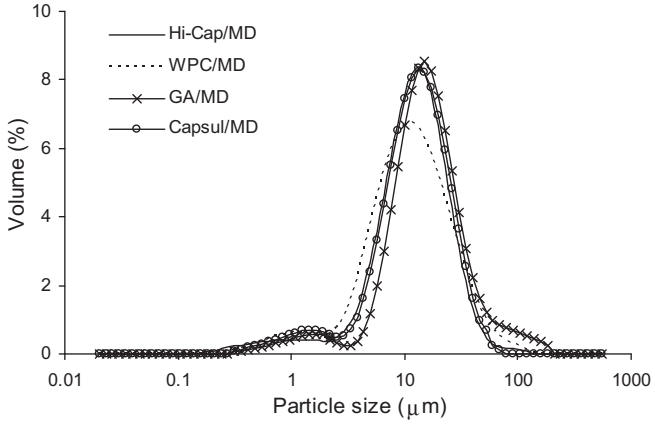

Fig. 4. Particle size distribution of powders produced with different wall materials combinations. (MD: Maltodextrin, Hi-Cap: Hi-Cap 100, WPC: Whey Protein Concentrate, GA: Gum Arabic, Capsul: Capsul TA).

Analysing the internal morphology, all microspheres were hollow and the active material was adhered to the surface as small droplets embedded in the wall materials matrix. It is another characteristic of particles obtained by spray drying. This emptiness is a result of the quick particles expansion during the final stages of drying (Jafari et al., 2008b). According to Fig. 5, the particles that showed the biggest number of droplets were obtained by the MD:Hi-Cap combination. This mixture also presented the best encapsulation efficiency (96%, approximately) which means that more active material was encapsulated and embedded in the wall material matrix, as mentioned before.

3.5. Lipid oxidation

The oxidative stability of flaxseed oil encapsulated into the different wall materials combinations was evaluated by two different methods (peroxide value and headspace gas chromatography), during four weeks of storage, at 45 °C. All the powders were in the glassy state at this temperature, since the materials used as carrier agents were expected to have glass transition temperatures higher than 45 °C. Gum Arabic was reported to show a T_g equal to 92 °C when stored at a_w of 0.11, and 62 °C when stored at a_w of 0.24 (Laine et al., 2010). García et al. (2012) found T_g values of 53 °C and 51 °C for WPC with 9.6% and 10% of moisture content, respectively. Maltodextrin 10DE had a T_g of approximately 110 °C at a_w of 0.1 (Roos, 1995). Regarding Capsul (derived from tapioca starch) and Hi-Cap (derived from waxy starch), although there is no data in the literature for these specific modified starches, Tran et al. (2007) found T_g values of 94 °C and 88–92 °C for native and modified tapioca starches with 12% of moisture content, while Yuan and Thompson (1994) showed that T_g of waxy starch was higher than 50 °C (values not reported) when it had 5.17% of moisture content.

3.5.1. Peroxide value

Peroxide value variations of flaxseed oil encapsulated with different wall materials are shown in Fig. 6. At time zero, all samples showed a low level of oxidation, ranging from 6.12 to 8.77 meq peroxide/kg oil. The samples encapsulated with MD:Hi-Cap and MD:GA presented higher peroxide concentration after one week, reaching values of 22.6 and 24.8 meq peroxide/kg oil, respectively. Samples encapsulated with Hi-Cap, GA or Capsul with maltodextrin suffered a significant increase in oxidation at the third week of storage. Between the third and fourth weeks, samples continued to oxidize and in the fourth week, MD:GA and MD:Capsul did not differ from each other.

Powders oxidative stability was strongly influenced by the wall material combination. Although the MD:WPC mixture has shown the lowest encapsulation efficiency, this combination presented the highest oil protection against oxidation, while MD:GA and MD:Capsul showed the poorest oxidative stability. Jimenez et al. (2006) encapsulated conjugated linoleic acid (CLA) using polymeric matrices as wall materials and also studied the microparticles

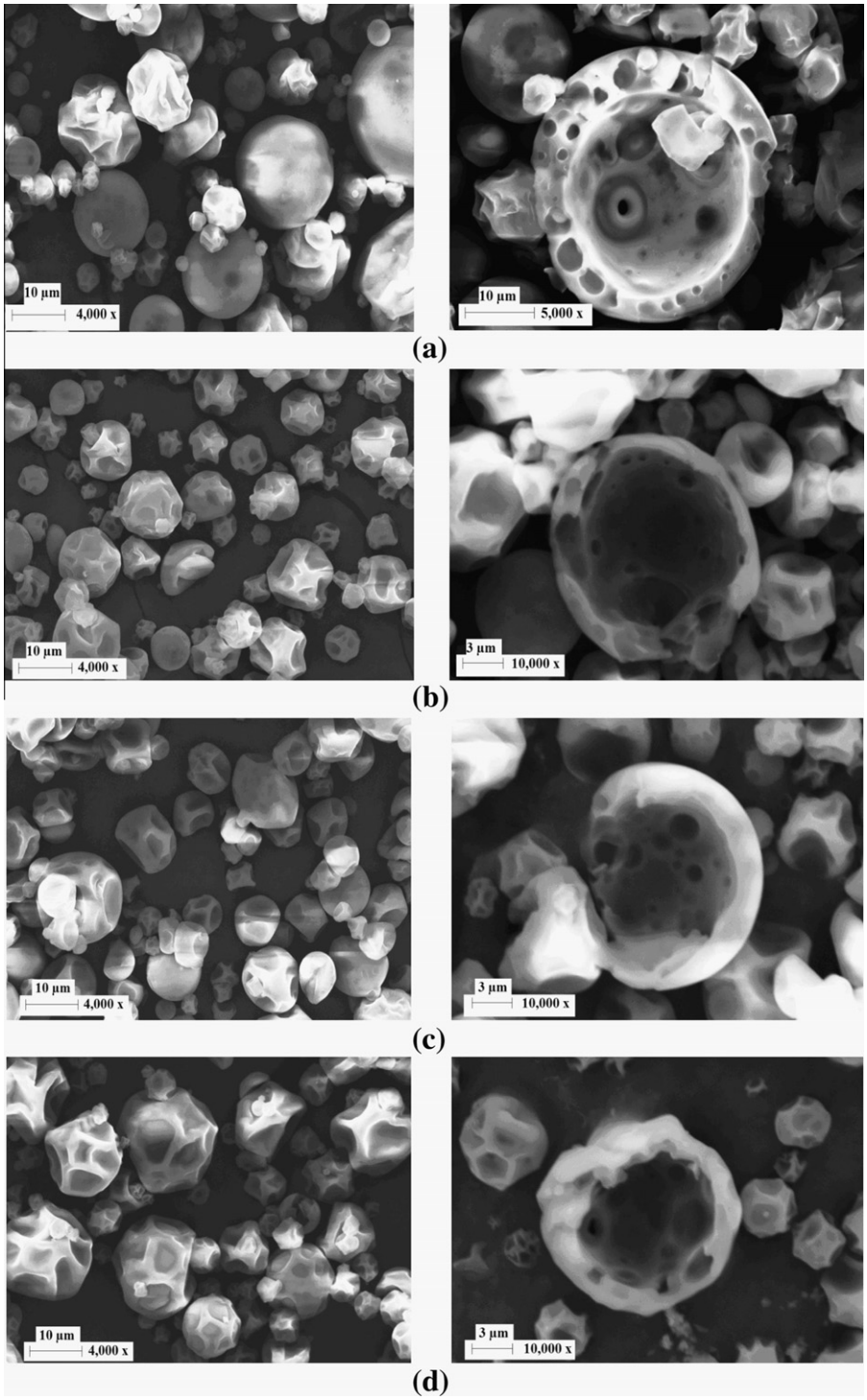

Fig. 5. External (on the left) and internal (on the right) micro structures of powders produced from different wall material combinations: (a) Maltodextrin:Hi-Cap, (b) Maltodextrin:Whey Protein Concentrate, (c) Maltodextrin:Gum Arabic and (d) Maltodextrin:Capsul.

oxidative stability by some methods, including the peroxide value. The authors used whey protein concentrate (WPC), whey protein concentrate with maltodextrin (WPC/MD) and gum arabic (GA) as wall materials, and also found that WPC was more effective in the protection against lipid oxidation than GA.

3.5.2. Headspace gas chromatography

Headspace propanal was used as the main indicator for oxidative stability of flaxseed oil. Other researches also used this aldehyde to control the oxidation of microencapsulated oils and fatty acids (Augustin et al., 2006; Jimenez et al., 2006; Drusch et al., 2007). Propanal was considered by Boyde et al. (1992) one of the most sensitive compounds to identify oxidation of fatty acids with three instaurations, such as α-linolenic acid, which corresponds to 53.28% of flaxseed oil. Hexanal was also used as an indicator of oxidation, since it is one of the more volatile products found in the linoleic acid oxidation (Jimenez et al., 2006), which is also present in the oil used in the present study (14.3%).

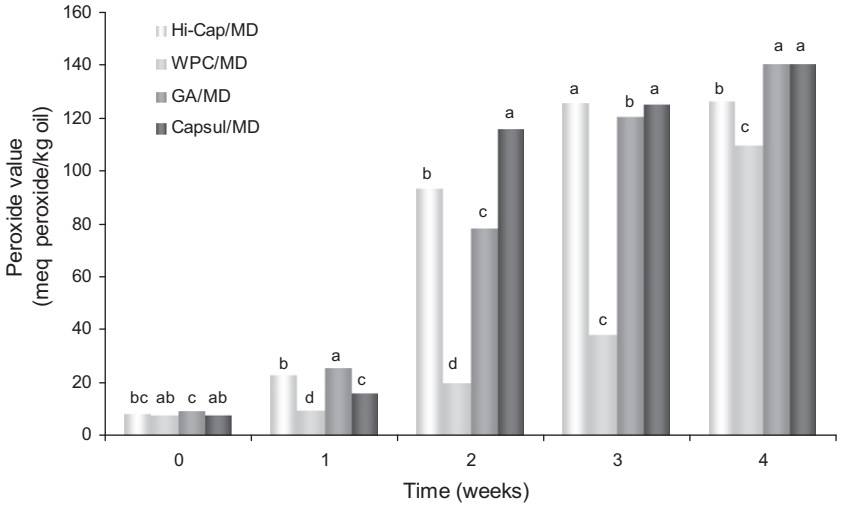

Fig. 6. Oxidative stability of encapsulated flaxseed oil evaluated by peroxide value method. Different letters indicate significant difference between samples, for each storage time, at $p \leqslant 0.05$. (MD: Maltodextrin, Hi-Cap: Hi-Cap 100, WPC: Whey Protein Concentrate, GA: Gum Arabic, Capsul: Capsul TA).

The propanal and hexanal quantification was made after the construction of a calibration curve using standards aldehydes at known concentrations and purities. The boiling points of propanal and hexanal are 49 and 130 °C and the column retention times were 6.67 and 17.79 min, respectively.

Fig. 7 shows the amounts of propanal and hexanal produced in samples along the four weeks of storage at 45 °C.

Until two weeks of storage, particles produced from MD:Hi-Cap, MD:WPC and MD:Capsul combinations remained stable to oxidation, however peaks of production of propanal in the samples of gum Arabic could be observed. The amount of propanal and hexanal produced at the beginning of storage was lower than the quantification limit of the equipment. From the second to third week, there was an increase of propanal and hexanal detection in the samples of MD:Hi-Cap, MD:GA and MD:Capsul (834.87, 659.03, 1208.99 μg propanal/g oil and 514.51, 221.25, 568.94 μg hexanal/g oil, respectively), while the mixture of MD:WPC remained stable without detection of any of the two aldehydes. In the fourth week of storage, samples of MD:GA showed a significant increase production of both aldehydes (1294.85 μg propanal/g oil and 442.85 μg hexanal/g oil), while the particles encapsulated with MD:Capsul showed a decrease in the concentration of hexanal and propanal (883.58 μg propanal/g oil and 425.25 μg hexanal/g oil). These aldehydes probably have been decomposed in the course of oxidation reaction, but additional analysis are necessary to confirm this event. The particles produced from MD:WPC combination showed no detection of these two aldehydes, along the four weeks of storage.

Jimenez et al. (2006) studied the production of hexanal during storage of microencapsulated conjugated linoleic acid (CLA) and concluded that gum Arabic was not effective in protecting these compounds against oxidation, while WPC showed the best performance. Drusch et al. (2007) evaluated the oxidative stability of fish oil microcapsules obtained by spray drying and observed a propanal production lower than 100 mmol/kg oil in samples encapsulated with proteins, while for samples encapsulated with gum Arabic, the propanal production exceeded 200 mmol/kg oil after 30 days of storage.

3.5.3. Overall remarks

Despite of the low encapsulation efficiency showed by the MD:WPC microparticles (approximately 60%), this combination of wall materials showed the greatest ability to protect the flaxseed oil against lipid oxidation at the temperature and storage time evaluated. Charve and Reineccius (2009) studied the performance of proteins (whey protein isolate and soy and sodium caseinate) and traditional materials (gum Arabic and modified starch) in the spray drying of flavours and evaluated the protection against losses during storage. According to the authors, similarly to the present work, the whey protein isolate (WPI) showed a lower retention of the active material during drying. However, they observed a more pronounced limonene oxidation in the microcapsules prepared with gum Arabic and modified starch. The authors also observed that the powders prepared with WPI have changed color (non-enzymatic browning), whereas the particles prepared with gum Arabic and modified starch have not showed this change during storage.

Augustin et al. (2006) showed that there is a relationship between the browning reactions and protection against oxidation in encapsulated oils. The authors evaluated the use of Maillard reaction products in the fish oil encapsulation and used the headspace chromatography (production of propanal) to measure the oxidative stability of the active material during four weeks of storage. As result, they observed that the level of propanal in the oil encapsulated in a protein–carbohydrate matrix was lower when they were treated at higher temperatures, indicating that fish oil oxidation was reduced when browning from the Maillard reaction was greater.

The non-enzymatic browning may be related to the presence of products known as melanoidins, which are brown pigments generated in the Maillard reaction, which have, among other properties, antioxidant capacity (Wang et al., 2011).

In addition, many studies have shown that whey proteins, as well as their hydrolysates, have antioxidant activity (Gad et al., 2011; Dryáková et al., 2010; Salami et al., 2010). So, the use of whey protein concentrate may have contributed to retard the lipid oxidation of microencapsulated flaxseed oil, being also a reason for the better oxidative stability shown by samples encapsulated with this wall material.

Another possible explanation for the differences in oxidative stability of encapsulated oils is the variation in the molecular weight of the wall materials used. According to Drusch et al. (2009a,b), the molecular weight profile of the carrier matrix is one of the key determinants for the oxidative stability of the encapsulated oils, since it affects the diffusion of small molecules such as oxygen into the particle wall. The authors observed higher

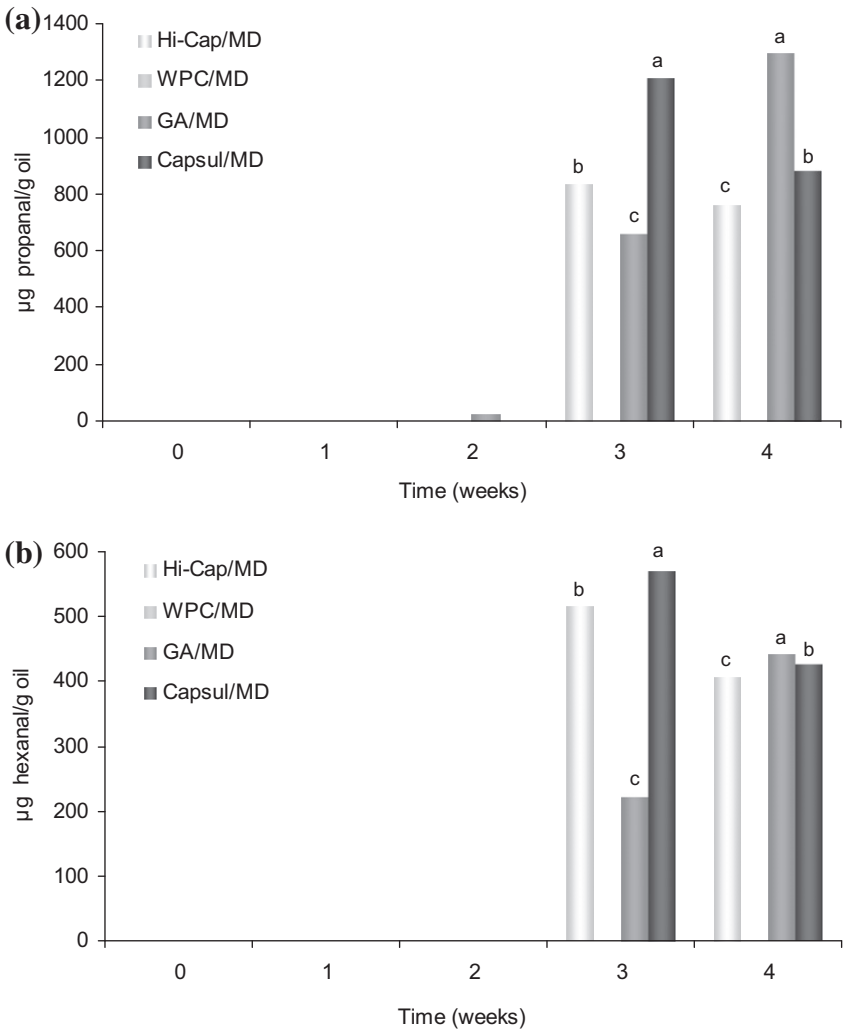

Fig. 7. Propanal (a) and hexanal (b) production during storage in powders produced from different combinations of wall materials. Different letters indicate significant difference between samples, for each storage time, at $p \leqslant 0.05$. (MD: Maltodextrin, Hi-Cap: Hi-Cap 100, WPC: Whey Protein Concentrate, GA: Gum Arabic, Capsul: Capsul TA).

hydroperoxide and propanal contents in the fish oil encapsulated with maltodextrin with DE 18, while the best oxidative stability was found in the oil encapsulated with maltodextrin DE 50, which have lower molecular weight. Desobry et al. (1999) blended different monosaccharides with maltodextrins to create carrier systems with different molecular weight profiles, in order to encapsulate β-carotene. The authors verified that the combination of monosaccharides with maltodextrin DE 4 provided a significantly higher half-life for the encapsulated β-carotene, compared to the blend of monosaccharides with maltodextrins DE 15.

4. Conclusions

In this work it was possible to evaluate the performance of different wall materials combinations in the flaxseed oil microencapsulation by spray drying. The MD:Hi-Cap combination showed the best encapsulation efficiency result. On the other hand, in the oxidative stability study, the mixture of MD:WPC performed better in protecting the active material against oxidation during storage. The oxygen diffusion though the glassy wall material matrix must be considered as one of the key factors affecting the reaction rate. According to the results, a mixture of MD, WPC and Hi-Cap could be suggested as a good wall material alternative for microencapsulation of flaxseed oil, which could result in good oxidative stability and better encapsulation efficiency.

Acknowledgments

The authors thank CAPES, FAPESP (2009/54137-1) and CNPq (474107/2010-8) for the financial support.

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