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Development and characterization of spray-dried chia oil microcapsules using by-products from chia as wall material

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ABSTRACT

This research deals with the characteristics of spray-dried chia oil microcapsules formulated with different wall materials, including new encapsulant agents from chia seed (protein rich fraction, PRF; chia mucilage, Muc). The performance of six different wall materials combinations was studied: sodium caseinate and lactose (NaCas + L), NaCas and maltodextrin (NaCas + Mx), PRF and Mx (PRF + Mx), and each of the previous three with the addition of Muc. The particle size, rheology, and stability of the parent emulsions were analyzed. The characterization of the powders obtained by spray-drying the parent emulsions was carried out by their moisture content, water activity, microencapsulation efficiency, glass transition temperature, morphology, oxidative stability, and dispersibility. Emulsions were reconstituted from the powders at different storage times and analyzed by their particle size and stability. The encapsulation efficiencies were NaCas + L + Muc (96.23 ± 0.40%) ~NaCas + L (95.20 ± 0.42%) > NaCas + Mx + Muc (86.65 ± 0.27%) > NaCas + Mx (71.26 ± 0.06%) > PRF + Mx (57.74 ± 3.49%) ~PRF + Mx + Muc (53.37 ± 0.99%). The addition of Muc significantly improved the ME% in microcapsules with NaCas + Mx. The induction time values (t_i) of NaCas + L, PRF + Mx and NaCas + Mx systems were about two, three, and five times higher than that of chia bulk oil, respectively. Thus, the studied wall materials were efficient to protect chia seed oil against the oxidation process.

1. Introduction

Nowadays, consumers are making food choices based on the effects that the diet has on their health. Some bioactive lipids, such as ω-3 fatty acids (ω-3 FAs) are the most efficient compounds for improving cardiovascular protection. The use of nutraceutical and functional foods containing ω-3 polyunsaturated fatty acids (ω-3 PUFAs) has become a topic of great interest due to their favorable effects on the health of the world population [1]. The α-linolenic acid (ALA) and the linoleic acid (LNA) are the metabolic precursors of other ω-3 and ω-6 FAs by a combination of elongation and desaturation reactions. These compounds are essential because they cannot be synthesized de novo and consequently should be present in the diet. Several studies reported that these two families of FAs compete for the same metabolic enzymes. Because the diet of Western countries has a marked deficit of ω-3 FAs, health authorities of these countries are promoting the intake of foods with this type of FAs and an adequate ω-3/ω-6 FA ratio [2].

Chia (*Salvia hispanica* L.) is a vegetable source of oil with a high PUFAs content recording >60% of ALA and about 20% of LNA. The ω-3/ω-6 FA ratio of this oil ranges from 3.18 to 4.18, showing values markedly higher than those of most vegetable oils. Chia seed oil also presents a moderate content of bioactive components, such as tocopherols (mainly γ-tocopherol), polyphenols (chlorogenic and caffeic acids, myricetin, quercetin, and kaempferol), carotenoids and phospholipids [3]. The oil extraction residue (meal) is constituted by proteins, soluble and insoluble fibers and antioxidants (polyphenols). Dry fractionation of the residual flour yields two fractions, a fiber-enriched fraction (FRF) and a protein-enriched fraction (PRF), both with high functionality [4]. Chia seeds also contain 5–6% mucilage (gum), which is part of the soluble dietary fiber [5]. This mucilage has high water retention and a great potential as a thickener in foods [6]. Recently, Ullah, Nadeem, Khalique, Imran, Mehmood, Javid and Hussain [7] have reviewed the great nutritional and therapeutic potential of chia. Thus, the different by-products from chia seeds constitute an alternative source of bioactive components to include in foods with high nutritional value.

Although the FA composition of chia oil is responsible for granting it beneficial qualities for human health, the high amount of PUFAs determines its low oxidative stability. Consequently, developing strategies aimed to improve its oxidative stability is relevant.

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Encapsulation constitutes a system to stabilize ingredients with high ω-3 content. It is a technique which entraps components within a matrix and isolates them from the surrounding environment [8]. The food industry commonly uses spray drying for microencapsulation because of its low cost and wide availability. The first step in this process is to design a formulation for obtaining microcapsules with high microencapsulation efficiency and oxidative stability in the ω-3 rich oil core, both characteristics closely related to the composition of the wall material [9]. The selection of the encapsulant material is a determining point in developing microcapsules. Few materials have the appropriate characteristics to be used as the wall of microcapsules produced by spray drying [10]. For this reason, the industry is interested in the search for new materials to be used as a wall. The most commonly used include low molecular weight carbohydrates, natural gums, proteins, gelatin, and waxes between others. Carbohydrates are suitable encapsulating agents since they possess good solubility and low viscosity at high solid content. However, they exhibit poor interfacial properties which are important to obtain high microencapsulation efficiency [9,11]. For this reason, carbohydrates usually must be used in conjunction with other materials such as proteins or gums. The amphiphilic character and the emulsifying properties of proteins offer the necessary characteristics to encapsulate different oils [9]. Food gums possess the ability to form films and stabilize emulsions which are properties required for materials used in microencapsulation.

Many authors have studied the microencapsulation of unsaturated FA-rich oils, and recently some research works using chia oil have been reported [12–19]. However, none of the published studies on the microencapsulation of chia oil by spray-drying have used chia protein rich fraction (PRF) and chia mucilage (Muc) as wall materials. Based on our previous studies [13,18], this research was performed to study also whether PRF and Muc, by-products with high nutritional value, can be used to microencapsulate chia oil. In this way, the food industry could realize an integral use of the chia seed.

The objective of this work was to characterize spray-dried chia oil microcapsules formulated with different wall material compositions, including by-products from chia seeds.

2. Materials and methods

2.1. Materials

Nutracéutica Sturla S.R.L. (Argentina) provided the chia cold-pressed oil, stored under refrigeration and darkness until use. The fatty acid composition of the oil determined by GC analysis [13] was the following: 16:0 7.2%, 18:0 3.8%, 18:1 5.2%, 18:2 19.1% and 18:3 64.7%.

Sodium caseinate (NaCas) from bovine milk was purchased from Sigma Chemical Company (St. Louis, MO), D-lactose (L) monohydrate from Anedra (Argentina) and maltodextrin (Mx) Globe 019150 DE 13–17% from Productos de Maíz S.A. (Argentina). All reagents were analytical grade.

Chia mucilage (Muc) was obtained using the method proposed by Segura-Campos, Ciau-Solís, Rosado-Rubio, Chel-Guerrero and Betancur-Ancona [20] with some modifications. Briefly, whole chia seeds were soaked in water (1:20 wt/v) for 30 min at 50 °C with constant stirring. Then, the seeds with the mucilage were frozen at −20 °C for 12 h and later freeze-dried (−40 °C, 0.133 bar, 72 h) (Labconco freeze dryer, Freezone 18, USA). Once dried, the mucilage was separated from the seeds on a sieve using mesh N° 20 ASTM (0.849 mm) and 25 ASTM (0.710 mm) in three periods of 15 min.

The protein rich fraction (PRF) was obtained by dry processing the defatted chia flour [4]. Briefly, 500 g of flour was sifted using a Tyler 100 mesh (140 mm screen) for 20 min and a Ro-Tap agitation system. The PRF was passed through the mesh and stored for later use.

The Muc and PRF proximate compositions were analyzed according to AOAC standard procedures [21]. The moisture, ash, protein, fat and fiber content of the chia mucilage was 10.8 ± 0.5%, 8.9 ± 0.1%, 9.1 ± 0.1%, 3.9 ± 0.1% and 13.6% ± 0.1, respectively, whereas the nitrogen-free extract was 53.7%. The composition of the PRF was the following: moisture 8.4 ± 0.1%, ash 8.4 ± 0.1%, protein 43.0 ± 0.2%, fat 0.7 ± 0.1%, fiber 14.1 ± 0.4% and nitrogen-free extract 25.4%.

2.2. Formulation and preparation of chia oil-in-water (O/W) emulsions

Six oil-in-water (O/W) emulsions (30% wt/wt total solids containing 10% wt/wt chia oil) with different aqueous phase compositions were prepared as detailed below: NaCas + L (10% wt/wt sodium caseinate, 10% wt/wt lactose), NaCas + Mx (10% wt/wt sodium caseinate, 10% wt/wt maltodextrin), PRF + Mx (2% wt/wt chia protein rich fraction, 18% wt/wt maltodextrin), NaCas + L + Muc (10% wt/wt sodium caseinate, 9.8% wt/wt lactose, 0.2 wt/wt chia mucilage), NaCas + Mx + Muc (10% wt/wt sodium caseinate, 9.8% wt/wt maltodextrin, 0.2 wt/wt chia mucilage) and PRF + Mx + Muc (2% wt/wt chia protein rich fraction, 17.8% wt/wt maltodextrin, 0.2 wt/wt chia mucilage).

Prior to emulsification, a dispersion of NaCas was obtained by dissolving it in deionized water by constantly stirring at 50 °C for 3 h. Then this dispersion was stored overnight at 4 °C to achieve complete dissolution of this polymer. After that, L or Mx was added to the NaCas dispersion while stirring at 25 °C.

In PRF-aqueous phases, PRF was dissolved in deionized water by mixing at 25 °C for 1 h and then the Mx was added.

In the aqueous phases with Muc, before its incorporation, the dried mucilage was dispersed in deionized water at 60 °C, stirring for 1 h and left overnight at 4 °C to ensure its complete rehydration.

Emulsions were prepared homogenizing the chia seed oil with the corresponding aqueous phase using first an Ultra-Turrax T25 (Janke & Kunkel GmbH, Staufen, Germany) operated at 10,000 rpm for 60 s, and subsequently a high-pressure valve homogenizer (Panda 2 K, GEA NiroSoavi, Parma, Italy) at a pressure level of 600 bar, 4 cycles. Nisine (12.5 mg/kg) and potassium sorbate (1000 mg/kg) were used as food grade preservatives.

2.3. Characterization of parent O/W emulsions

2.3.1. Particle size distribution and mean diameter

Particle size distribution and Sauter (D [2, 3]) mean diameter of particles were determined by laser diffraction using a Malvern Mastersizer 2000E analyzer (Malvern Instruments, Ltd., Worcestershire, UK) [13,22]. For measurements, samples were suspended directly in a dispersion system (Hydro 2000MU) with distilled water at 2000 rpm reaching an obscuration of ~18%. The particle absorption index employed was 0.001 and the refractive indices used were 1.47 and 1.33 which correspond to the dispersed and the continuous phase, respectively.

2.3.2. Rheology

The viscosity of emulsions was determined at 25 ± 0.2 °C using a controlled stress oscillatory rheometer (Haake RS600, Karlsruhe, Germany) with a plate-plate sensor system and 1.0 mm gap between plates. A logarithmic increasing shear rate with a continuous ramp from 1 to 500 s^{-1} in 2 min was applied [23].

The dependence of emulsion viscosity with shear rate was investigated using the power law empirical model (Eq. (1)):

$$\tau = k(\dot{\gamma})^n \quad (1)$$

where τ = shear stress (Pa), k = consistency index (Pa s^n), $\dot{\gamma}$ = shear rate (s^{-1}), n = flow behavior index.

2.3.3. Parent emulsion stability

Parent emulsion stability was investigated by measurements of dispersed light according to Cabezas, Madoery, Diehl and Tomás [24], using a Vertical Scan Analyzer Quick Scan (Coulter Corp., Miami, FL, USA).

2.4. Preparation of microcapsules by spray-drying

The emulsions were spray-dried using a laboratory scale Büchi spray-dryer (Mini Spray dryer B-191, BuchiLabortechnik, Flawil, Switzerland) equipped with an air atomizing nozzle (0.5 mm diameter). The drying air inlet/outlet temperature was 170/90 °C, the drying air flow rate was 500 L/h and the feed flow rate 10 mL/min. These selected conditions were based on previous studies about microencapsulation of chia oil [13].

2.5. Storage of microcapsules

Approximately 10 g of encapsulated oil and 10 g of bulk oil were placed into glass Petri dishes (95 mm × 15 mm) and glass beaker (50 mL), respectively. Samples were kept open to allow contact with air and stored in a chamber with saturated $MgCl_2$ solution (relative humidity, RH = 33%) at 20 ± 2 °C in the dark.

2.6. Characterization of chia oil powders

2.6.1. Moisture content

The moisture content of the powders (2 g) was determined gravimetrically by vacuum oven-drying at 70 °C and 29 in Hg for 24 h [13,25].

2.6.2. Water activity (a_w)

The a_w of the powders was measured using Aqua-Lab Water Activity Meter, Series 3, Decagon Devices Inc., USA at 25.0 ± 0.5 °C.

2.6.3. Microencapsulation efficiency

The non-encapsulated oil fraction named surface oil was determined using the method of Aberkane, Roudaut and Saurel [26]. The total oil was analyzed by the Rosse-Gottlieb method [27].

Microencapsulation efficiency (ME%) was obtained from Eq. (2):

$$ME\% = \left(\frac{\text{Total oil} - \text{Surface oil}}{\text{Total oil}}\right) \times 100 \quad (2)$$

2.6.4. Glass transition

A Differential Scanning Calorimetry (DSC) study using a Q 100 calorimeter (TA Instruments, Newcastle, USA) was carried out to analyze the glass transition temperature of microcapsules. Samples of dried powder (~10 mg) were sealed in an aluminum pan and scanned at a constant heating rate β = 10 °C/min from 2 to 100 °C. Data were analyzed using TA Universal Analysis 2000 program v. 4.2E (TA Instruments, New Castle, USA) [28].

2.6.5. Scanning electron microscopy (SEM)

Scanning electron microscopy allowed studying the morphology of the microcapsules. Powders adhered to a cover slip were protected with Au/Pd film and examined under high vacuum, 5 kV, by SEM (MA10 Carl Zeiss SMT Ltd., Cambridge, UK).

2.6.6. Accelerated oxidation by Rancimat

Accelerated oxidation tests for bulk and microencapsulated oil were carried out using a Rancimat model 743 (Metrohm AG, Herisau, Switzerland). About 3 g of chia oil, or 1.5 g of microcapsules, were heated under an air flow rate of 20 L/h at 98 °C [29].

2.6.7. Dispersibility

The dispersibility of the powders was studied using laser diffraction according to the method of Klinkesorn, Sophanodora, Chinachoti, McClements and Decker [30]. The sample (~0.3 mg of powder/mL of distilled water) was added to the chamber of the instrument (Malvern Instruments, Worcestershire, UK) at a stirring speed of 2000 rpm, recording the obscuration every 10 s for 5 min.

2.6.8. Particle size distribution, mean diameter and physical stability of reconstituted emulsions

The reconstituted emulsions were studied as described in Sections 2.3.1 and 2.3.3. For this purpose, the powders were dissolved in distilled water up to 10 g solids/100 g emulsion at room temperature (~25 °C) under constant magnetic stirring for 30 min [30].

2.7. Statistical analysis

Experimental results were analyzed by ANOVA ($p \le 0.05$) using the Statgraphics Centurion XV·II software for Windows (Statpoint Technologies, Warrenton, VA, USA). Multiple comparisons of the means were carried out by Tukey's test ($p \le 0.05$).

3. Results and discussion

A total of six different microcapsule systems were evaluated, including combinations of sodium caseinate and lactose (NaCas + L), sodium caseinate and maltodextrin (NaCas + Mx), chia protein rich fraction and maltodextrin (PRF + Mx), and each of the previous three with the addition of chia mucilage (NaCas + L + Muc, NaCas+Mx + Muc, PRF + Mx + Muc).

3.1. Characterization of parent O/W emulsion

Many authors have reported the influence of emulsion characteristics on the microencapsulation efficiency (ME%) and the final physicochemical properties of the powders [31–33]. The surface diameters of particles D [2,3] ranged between 0.215 and 0.267 μm for emulsions with NaCas, whereas the particle sizes corresponding to systems with PRF were significantly ($p \le 0.05$) higher, indicating that it was difficult for this last emulsifier agent to create a surface area (Table 1). These differences would be related to the amount of chia PRF available in the aqueous phase, which would not be enough to fully cover the surface of the oil droplets and stabilize them. Besides, the higher hydrophobicity and structural flexibility and the lower surface tension of NaCas in comparison with chia globulin proteins (the main component of PRF) make that NaCas has a better emulsifier capacity, resulting in smaller droplets [34].

The particle size distribution curves also show these differences between the different parent emulsions, being unimodal for NaCas + L and NaCas + L + Muc, bimodal for NaCas + Mx and NaCas + Mx + Muc and trimodal with a displacement to larger droplet sizes for systems with PRF (Fig. 1a).

The smaller ($p \le 0.05$) droplet sizes recorded for the PRF + Mx + Muc emulsions relative to the PRF + Mx systems could be related to the presence of the mucilage associated protein. Apparently, these proteins would contribute to the surface activity of these systems. Different authors [35,36] also reported about the enhancement of the surface activity of gums due to the presence of protein traces.

The rheological data were fit to the power law, recording determination coefficient values (R^2) higher than 0.98. The parent emulsions formulated with NaCas presented values of $n < 1$, indicating shear-thinning behavior (Fig. 2). The consistent coefficients (k) for a shear rate range of 1–500 s^{-1} were $k = 0.234$ Pa s^n (NaCas + L), 0.537 Pa s^n (NaCas + Mx), 1.007 Pa s^n(NaCas + L + Muc), and 3.905 Pa s^n (NaCas + Mx + Muc). On the other hand, emulsions with PRF presented a Newtonian behavior (n~1).The viscosity values at 100 s^{-1} (η_{100}), a typical shear rate for food processes, were 0.124, 0.173, 0.007, 0.261, 0.464 and 0.015 Pa s for the NaCas + L, NaCas + Mx, PRF + Mx, NaCas + L + Muc, NaCas + Mx + Muc, PRF + Mx + Muc emulsions, respectively. Thus, systems with NaCas recorded much higher values ($p \le 0.05$) of this parameter compared to the PRF-stabilized emulsions. The viscosity of the parent emulsion plays an important role to take into account since it is closely related to the microencapsulation efficiency. Increasing this parameter

Table 1
Particle size (D [2, 3]) of O/W parent and reconstituted emulsions from microcapsules with different wall materials stored at 20 ± 2 °C, 33% relative humidity (RH).

Wall material	D [2, 3] (μm)			
	Parent emulsion	Reconstituted emulsion		
		Storage time (d)		
		15	30	45
NaCas + L	0.250 ± 0.007^{aA}	0.252 ± 0.003^{aA}	0.257 ± 0.001^{aA}	0.272 ± 0.007^{abA}
NaCas + Mx	0.267 ± 0.018^{aA}	0.312 ± 0.041^{aA}	0.321 ± 0.115^{aA}	0.361 ± 0.031^{abA}
PRF + Mx	6.974 ± 0.237^{cA}	6.739 ± 0.262^{cA}	6.569 ± 0.037^{cA}	6.103 ± 0.003^{cA}
NaCas + L + Muc	0.215 ± 0.001^{aA}	0.221 ± 0.003^{aAB}	0.225 ± 0.005^{aAB}	0.241 ± 0.011^{aB}
NaCas + Mx + Muc	0.233 ± 0.005^{aA}	0.261 ± 0.001^{aB}	0.292 ± 0.040^{aB}	0.442 ± 0.169^{bC}
PRF + Mx + Muc	7.443 ± 0.778^{bA}	7.725 ± 0.311^{bA}	6.090 ± 0.019^{bA}	6.949 ± 0.001^{dA}

Mean values standard deviation ($n = 2$). Different small letters in each column indicate differences at $p \leq 0.05$ between wall materials for each storage time, according to the Tukey (HSD) test.
Different capital letters in each row indicate differences at $p \leq 0.05$ between storage times for each wall material, according to the Tukey (HSD) test.

to a certain extent will decrease the internal circulation and the oscillation of the droplets, which is related to higher oil retention [31].

On the other hand, the η_{100} increased when maltodextrin was used instead of lactose, and in systems with the addition of chia mucilage. The significant ($p \leq 0.05$) effect of chia mucilage on the emulsion viscosity would be related to the 4-O-methyl glucuronic acid substituent present in its structure which forms an inter-molecular network in an aqueous medium [16,34].

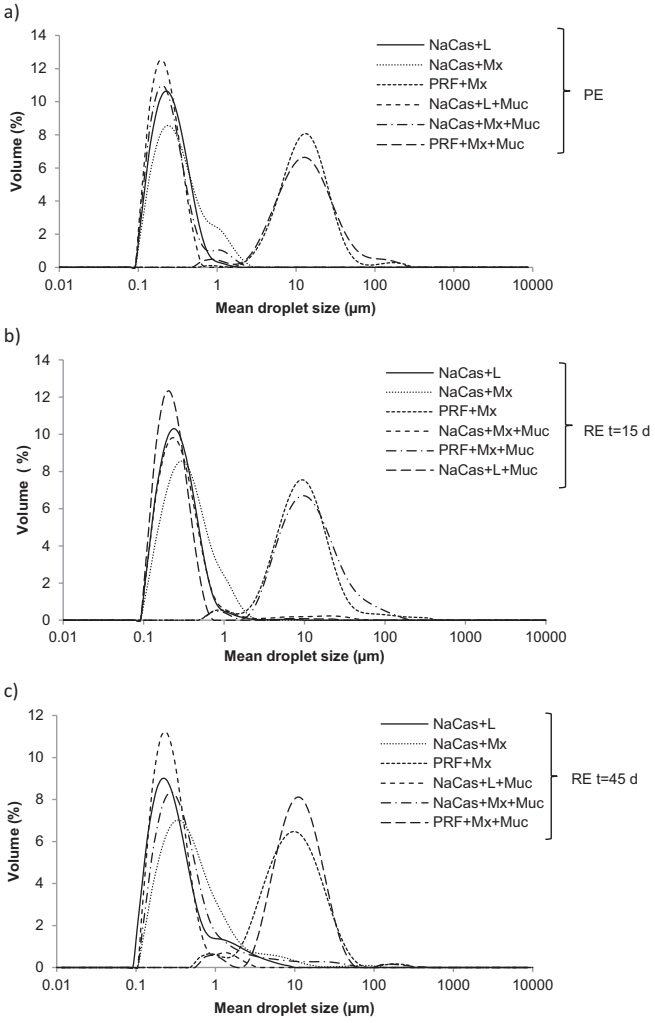

Fig. 1. Volume particle size distribution of: (a) parent emulsion (PE), (b–c) reconstituted emulsion (RE) from powder stored at 20 ± 2 °C and 33% RH for 15 and 45 d, respectively.

A Vertical Analyzer Quick Scan was used to measure the physical stability of the emulsions. This parameter is important to know the time in which the emulsion is stable to be able to be dried. Besides, the initial physical stability of the emulsion influences the microencapsulation efficiency, being both positively correlated [31]. Systems with NaCas exhibited a high physical stability after 360 h of preparation, whereas those with PRF recorded a clarification process at the bottom of the measuring tube after 120 h (data not shown). This behavior could be related to the high viscosity of NaCas-systems, which slows down the free mobility of the droplets and the degree of particle interactions. Hence, stability is improved [34].

3.2. Characterization of chia oil powders and reconstituted emulsions

Table 2 lists the physicochemical properties of the microcapsules containing chia seed oil. The moisture content and the a_w of the powders were 2.72–4.40 g/100 g (d.b.) and 0.334–0.478, respectively, values that were within those recommended for food powders [15,37]. There were no significant differences ($p > 0.05$) between the treatments for these parameters. These results are coincident with Hogan, McNamee, O'Riordan and O'Sullivan [33] and Ixtaina, Julio, Wagner, Nolasco and Tomás [13] who found that moisture content was unaffected by the type of wall material or core/wall ratio.

Regarding the glass transition temperature (T_g), it ranged between 40.56 and 50.19 °C, showing no significant differences ($p > 0.05$) between the wall materials studied (Table 2). This parameter is important to know because it is related to maintaining the powder quality during storage. Thus, a storage temperature above the T_g would produce

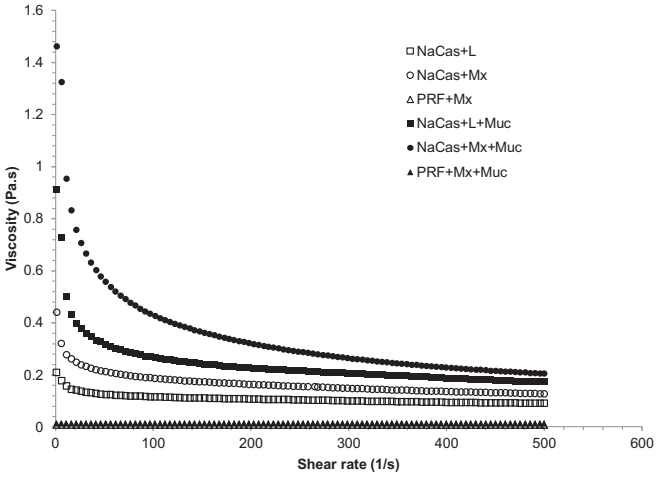

Fig. 2. Effect of wall material on rheological properties of parent emulsions containing chia seed oil.

Table 2
Physicochemical properties of the microcapsules containing chia oil.

Property	Encapsulant matrix					
	NaCas + L	NaCas + Mx	PRF + Mx	NaCas + L + Muc	NaCas + Mx + Muc	PRF + Mx + Muc
Moisture content (%, d.b.)	4.40 ± 0.42[a]	4.04 ± 0.64[a]	3.66 ± 0.10[a]	2.72 ± 0.08[a]	3.92 ± 0.58[a]	3.50 ± 0.69[a]
$a_{w\ 25°C}$	0.412 ± 0.013[a]	0.383 ± 0.010[a]	0.478 ± 0.027[a]	0.334 ± 0.001[a]	0.367 ± 0.082[a]	0.370 ± 0.012[a]
Glass transition temperature (Tg) (°C)	40.82 ± 8.27[a]	40.56 ± 0.54[a]	47.39 ± 5.64[a]	45.84 ± 0.28[a]	50.19 ± 1.62[a]	46.44 ± 0.48[a]
Free oil (%, d.b.)	1.60 ± 0.14[a]	9.58 ± 0.02[c]	14.08 ± 1.16[d]	1.16 ± 0.24[a]	4.45 ± 0.09[b]	15.63 ± 0.45[d]
Microencapsulation efficiency (%)	95.20 ± 0.42[d]	71.26 ± 0.06[b]	57.74 ± 3.49[a]	96.23 ± 0.40[d]	86.65 ± 0.27[c]	53.37 ± 0.99[a]
Induction time (h)	5.01 ± 0.08[a]	13.75 ± 0.03[c]	7.51 ± 0.11[b]	6.51 ± 0.18[ab]	13.90 ± 1.11[c]	7.66 ± 0.11[b]

Mean values ± standard deviation ($n = 2$). Different letters in each row indicate differences at $p \leq 0.05$ between wall materials, according to the Tukey (HSD) test.

changes in the powders structure (crystallization) and deteriorating consequences such as an increase in the rate of oxidation due to an enhance in diffusivity of oxygen through the matrix [38].

The ME% reflects the free oil on the particle surface. Chia oil encapsulated with NaCas+L (with or without mucilage) exhibited the highest ME% (95.20–96.23%), followed by NaCas + Mx + Muc > NaCas + Mx > PRF + Mx~PRF + Mx + Muc (Table 2). The ME% difference between the NaCas + L and NaCas + Mx wall material combinations was also found by Calvo, Hernández, Lozano and González-Gómez [39]. The positive effect of lactose could be related to the formation of a continuous glass phase of lactose in which the protein chains are dispersed, resulting in high ME% values [13].

The ME% values found in systems with PRF (53.37–57.74%) were similar to those of González, Martínez, Paredes, León and Ribotta [17] for chia oil microencapsulated using isolated soy proteins and maltodextrin. On the other hand, the ME% values of PRF-systems were lower than those of NaCas-systems. These differences could be due to the larger particle size, the lower viscosity, and the lower physical stability of the PRF-parent emulsions in comparison with the NaCas ones (Figs. 1 and 2, Table 1) which would be related to the greater particle size, the lower viscosity and the physical stability of the respective parent emulsions. Some authors have shown that the ME% of oils improves with decreasing emulsion droplet size and increasing physical stability [40,41]. According to Jafari, Assadpoor, He and Bhandari [31] the high free oil on the particles from emulsions with large droplets could be due to the rupture of them during atomization. After the rupture, the droplets would be devoid of wall material around them, so producing an inefficient microencapsulation. These authors also reported that it is important to decrease the emulsion size until ~1 μm, below which there was no evidence that the ME% improves. In our study, the systems with the highest ME% corresponding to NaCas-systems had particle sizes <1 μm. In addition, an inversely significant correlation was found between the particle size of the parent emulsion and ME% (D [3, 4] vs. ME% $r = -0.88$; $p = 0.0002$; D [2,3] vs. ME% $r = -0.86$; $p = 0.0003$).

Regarding the mucilage addition, it improved the ME% in the case of NaCas + Mx systems. As previously discussed in Section 3.1., this effect could associate with a significant increase in the viscosity of this system due to the addition of chia mucilage as a thickener agent, which would contribute to a greater physical stability of the parent emulsions during the spray-drying process [31].

Fig. 3 presents the SEM micrographs of the powders with the different wall materials showing particles of various sizes, which range from 2 to 14 μm. Surface analysis of the microcapsules revealed that most them were approximately spherical with continuous walls and no apparent fissures or cracks. Moreover, some of the particles presented concave and shriveled surfaces, which is typical of microcapsules produced by spray drying [41]. It is possible to observe some differences between microcapsules formulated with NaCas and those with PRF. Thus, powders containing PRF + Mx and PRF + Mx + Muc as wall materials appeared agglomerated, possibly due to the presence of surface oil (Fig. 3c, f). In contrast, powders prepared using NaCas + L, NaCas + L + Muc, NaCas + Mx and NaCas + Mx + Muc (Fig. 3a–b, d–e) presented discrete particles with both smooth and wrinkled surfaces.

The effect of the different wall systems on the oxidation stability of microencapsulated chia oil was analyzed by Rancimat test. The oxidative stability of the chia oil was effectively enhanced by spray-drying microencapsulation since all systems presented higher induction times (t_i) than those corresponding to bulk chia oil ($t_i = 2.46 \pm 0.07$) (Table 2). Overall, our results showed that the oxidative stability was not related to the ME% of the spray dried microcapsules. It is supported by the fact that NaCas+L and NaCas + L + Muc systems presented the highest ME% values, but the lowest oxidative stability. Different authors reported that the oxidative deterioration of microencapsulated oils cannot be explained only by the ME% [22,42,43]. Another possible explanation is related to the variation in the molecular weight of the wall materials used. Chung, Sanguansri and Augustin [42] found a correlation between molecular weight and oxidative stability for NaCas-based fish oil microcapsules with modified starch as co-encapsulant. Thus, the lower oxidative stability of systems with lactose compared with those with maltodextrin may be related to the lower structural stability of the microcapsules afforded by the lower molecular weight of lactose, which allowed higher access of oxygen to the oils, resulting in less protection against oxidation.

Microcapsules with PRF + Mx presented lower t_i values (7.51–7.66 h) than those of NaCas + Mx and NaCas + Mx + Muc systems, but higher than NaCas + L. In this sense, the caffeic and chlorogenic acids and other phenolic compounds with antioxidant activity associated with the chia PRF could contribute to protecting microencapsulated chia oil [3,44].

The laser diffraction technique was used to obtain information about the ability of microcapsules to be redispersed in water, which is an important property for practical application. The powder dispersibility was measured by changes in the obscuration as a function of time, since this parameter is sensitive to the total amount of material dispersed in the fluid [30]. Samples analyzed at t = 15 d (data not shown) recorded a steeply increase in the obscuration with the agitation time up to ~1.5–2.0 min, after which it reached a constant value. This result is similar to that of Ixtaina, Julio, Wagner, Nolasco and Tomás [13] for chia seed oil microencapsulated with NaCas and L at different operating conditions. Overall, the fast increase in obscuration indicated that most of the powder particles dissolve relatively quickly (<2 min). The order for time required to reach the constant obscuration value was NaCas + L + Muc > NaCas + L > NaCas + Mx + Muc > NaCas + Mx > PRF + Mx + Muc > PRF + Mx. As can be seen, systems with mucilage required a little more time to be dispersed than the corresponding system without it, which could be attributed to a lower solubility of microcapsules with mucilage as a component of the wall material. The evolution of obscuration as a function of stirring time for microcapsules stored for 30 d was similar to those for 15 d (data not shown). This fact suggests that the microcapsules maintained their ability to disperse in water after storage at 20 ± 2 °C and 33% RH.

Emulsions were reconstituted in water from the microcapsules (RE) at different storage times and then it was studied the respective particle sizes (Table 1). In a similar way to parent emulsions, the particle size of RE presented differences between the different systems, with the PRF-based microcapsules recording the highest D [2,3] values. No significant differences ($p > 0.05$) were recorded between RE and parent

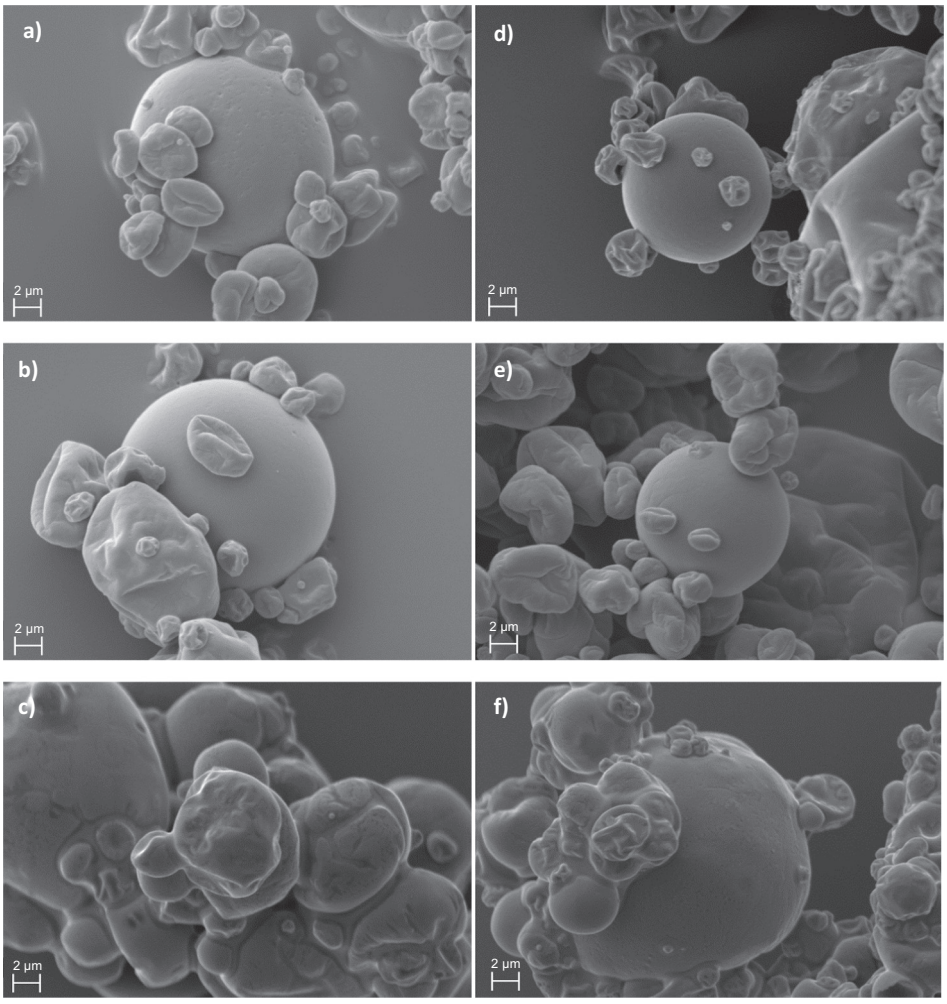

Fig. 3. Micrographs of the outer morphology of chia oil microcapsules obtained with different wall materials: a) NaCas + L; b) NaCas + Mx; c) PRF + Mx; d) NaCas + L + Muc; e) NaCas+Mx + Muc; f) PRF + Mx + Muc.

emulsions in NaCas-based systems without chia mucilage. However, RE from NaCas + Mx + Muc and NaCas + L + Muc presented higher particle size values than the parent emulsions after 15 and 45 d of powder storage, respectively. This fact could be related to a lower solubility of microcapsules with mucilage compared to those without it. In spite of these differences, the D [2,3] remained at a low level during the storage (D [2, 3] <0.500 μm).

The particle distribution of RE compared to that of the parent emulsion can provide information about the stability of oil droplets during the drying process [33]. In our study, the particle size distribution of the emulsions reconstituted after 15 d of storage (Fig. 1b) was rather similar to those of the corresponding parent emulsions (Fig. 1a), being uni or bi modal for NaCas-based systems and trimodal with larger droplet sizes for PRF-based emulsions. After 45 d of powder storage, RE with NaCas presented a wider range of droplet size, indicating the formation of some large particles (flocculated/coalesced droplets) (Fig. 1c).

The physical stability of the RE was examined over the 30 days after their reconstitution through the optical characterization method with a Vertical Scan Analyzer (Quick Scan). The backscattering (BS) profiles of the RE from NaCas + L, NaCas + Mx, and PRF + Mx microcapsules are shown in Fig. 4a, b, and c, respectively. Immediately after the reconstitution (t = 0), all RE were stable, since the particle distribution was homogeneous along the tube. Regarding the stability of the RE, NaCas-based systems showed a high physical stability with no significant ($p > 0.05$)

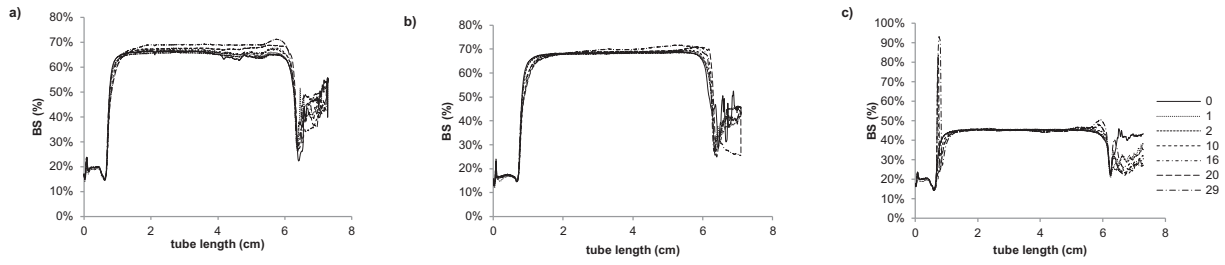

Fig. 4. Backscattering profiles of reconstituted emulsions (10 g solids/100 g) evaluated by the Vertical Analyzer Quick Scan. Data reported as a function of time (~0.05–29 d) and sample height of emulsions (~0–6 cm): a) NaCas + L; b) NaCas + Mx; c) PRF + Mx.

changes in BS profiles during their storage (Fig. 4a, b). In contrast, RE with PRF destabilized after 15 d of storage, visualized by a clear zone at the bottom of the sample tube (Fig. 4). As mentioned above and in a similar way to parent emulsions, the D [2,3] of the reconstituted emulsions with PRF was higher than the other ones, which promote the destabilization process.

RE from microcapsules with chia mucilage presented similar BS profiles as those corresponding to the systems without mucilage (data not shown).

4. Conclusions

In the present study, new encapsulant agents from chia seed (protein rich fraction and mucilage) in combination with materials commonly employed as a wall (sodium caseinate, lactose, or maltodextrin) were used to microencapsulate chia oil by spray-drying. Results showed that developed powders exhibited relatively low moisture content and water activity (a_w), spherical shaped particles without any cracks or fissures and rapid water dispersibility (~1.5–2.0 min). In all cases, the oxidative stability of microencapsulated chia oil was significantly higher than that of bulk chia oil. The NaCas+L systems (with and without chia mucilage) presented the highest microencapsulation efficiency for spray-drying chia seed oil. However, NaCas + Mx and NaCas + Mx + Muc recorded the highest oxidative stability in the Rancimat test. The addition of chia mucilage significantly improved the ME% for systems with NaCas + Mx, achieving values >85%. Although the microcapsules with PRF showed lower ME% levels compared to those with NaCas, they had a higher oxidative stability than NaCas + L system. In this sense, the t_i recorded for PRF-Mx systems were three times higher than that of chia bulk oil, indicating that this wall material was efficient to delay chia seed oil oxidation. Supplementary research is needed to study the application of PRF using other combinations of wall materials and different microencapsulation techniques to improve the ME%.

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Conflict of interest

The authors declare no conflict of interest.

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