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Development and Characterization of Functional O/W Emulsions with Chia Seed (*Salvia hispanica* L.) by-Products †

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Abstract: Physicochemical properties of O/W emulsions containing functional ingredients (high ω-3 fatty acid content, protein, and soluble fiber) from chia seeds with different protein–carbohydrate combinations (sodium caseinate-lactose, sodium caseinate-maltodextrin, and chia protein-rich fraction-maltodextrin) and chia mucilage were studied. Sodium caseinate with lactose or maltodextrin produced O/W emulsions with small droplet size, high uniformity in droplet size distribution, negatively charged droplets (pH 6.5), pseudoplastic behavior, and high physical stability. Emulsions with chia protein-rich fraction presented wider droplet size distribution and higher $D_{3,2}$ values than the previous ones, recording a Newtonian behavior. The addition of chia mucilage affected the rheological characteristics of emulsions.

Keywords: chia by-products; chia mucilage; O/W emulsions; ω-3 fatty acids; chia protein-rich fractions

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1. Introduction

The demand for functional foods with multiple health benefits has increased in recent years due to the new trend towards a healthy lifestyle. Functional foods are designed to supply basic nutrients as well as to reduce the risk of some diseases. Advances in food technology resulting in new components, products, processes, and packaging have provided more opportunities for value-added products.

Nowadays, interest in the substitution of synthetic emulsifiers and stabilizers by others of natural origin, such as vegetal polysaccharides and proteins, has grown. The industry generates residual cake with a high fiber and protein content after the extraction of chia oil from the seeds. These by-products are mainly used for animal feed with limited economic and social impacts. Thus, an alternative to adding value to these by-products would be the application of technologies to develop functional food that including them.

A chia protein-rich fraction containing 64.9% of globulins, 20.2% of glutelins, 10.9% of albumins, and 4.0% of prolamins was studied by Sandoval-Oliveros and Paredes-López [1]. This protein-rich fraction presented high contents of glutamic acid, arginine, and aspartic acid, which are important for the proper functioning of the immune system and the prevention of cardiovascular diseases. Besides, chia seed contains between 5 and 6% of mucilage, a tetrapolysaccharide of high molecular weight mainly composed of D-xylose, D-mannose, D-arabinose, D-glucose, and galacturonic and glucuronic acids [2,3]. The intake of chia mucilage as dietary fiber source was associated with numerous health benefits, including the reduction of the risk of coronary heart disease, diabetes, obesity, and different types of cancer [4].

This work deals with the development and characterization of oil-in-water (O/W) emulsions with chia oil, evaluating the influence of different combinations of proteins–carbohydrates and the application of chia by-products (mucilage, protein-rich fraction) on the physicochemical properties of these systems.

2. Materials and Methods

2.1. Material

Chia oil ($C_{16:0}$ 9.27%; $C_{18:0}$ 3.41%; $C_{18:1}$ 9.37%; $C_{18:2}$ 17.58%; $C_{18:3}$ 59.02%; $C_{20:0}$ 1.36%) was provided by SDA S.A. (Argentina). Casein sodium from bovine milk was purchased from Sigma Chemical Company (St. Louis, MO), the Maltodextrin DE 13–17% was obtained from Productos de Maíz S.A. (Argentina) and the D-lactose monohydrate from Anedra (Argentina). All reagents used were of analytical grade.

Chia protein-rich fraction with 43.0 of protein, 0.7 of fat, 8.4 of moisture, 14.1 of fiber, 8.4 of ash, and 25.4% of nitrogen-free extract was obtained by a dry processing of defatted chia flour according to Vázquez-Ovando et al. [5]. Chia mucilage was obtained from whole chia seeds according to Segura-Campos et al. [6] method with some modifications. The proximal composition of chia mucilage was 10.7, 8.9, 9.1, 3.9, 13.6, and 53.8% of moisture, ash, protein, fat, fiber, and nitrogen-free extract, respectively.

2.2. Methods

2.2.1. Preparation of Emulsions

Oil-in-water (O/W) emulsions were prepared mixing 10% (*wt*/*wt*) of chia oil and 90% (*wt*/*wt*) of aqueous phase with different compositions (Table 1) using a rotor–stator system Ultraturrax T-25 (Janke and Kunkel GmbH, Staufen, Germany) at 9500 rpm, 1 min. Then, in a second homogenization stage, the samples were passed four times through a high-pressure homogenizer (Panda 2 K, GEA NiroSoavi, Parma, Italy) at 600 bar. Nisine 0.0012% (*wt*/*wt*) and potassium sorbate 0.1% (*wt*/*wt*) were added to the emulsions to prevent microbial growth. Emulsions were stored at 4 ± 1 °C and protected from light for 15 days.

2.2.2. Droplet Size

The droplet size distribution and the De Sauter ($D_{3.2}$) mean diameter were obtained using a laser diffraction Malvern Mastersizer 2000E particle size analyzer (Malvern Mastersizer 2000E, Malvern Instruments Ltd., Worcestershire, UK) in a range of 0.1–1000 μm.

2.2.3. ζ-potential

The ζ-potential was determined using a Zeta Potential Analyzer (Brookhaven 90Plus/Bi-MAS, USA) instrument at room temperature according to Julio et al. [7]. The ζ-potential range was set from −100 to 50 mV. For each determination, 50 mg of emulsion was dispersed in 100 mL of milli-Q water.

Table 1. Composition of chia oil-in-water (O/W) emulsions.

Sample	Chia Oil	Aqueous Phase Composition % *wt*/*wt*				
		Chia Protein-Rich Fraction	**Sodium Caseinate**	**Lactose**	**Malodextrin**	**Chia Mucilage**
CL	10	-	10	10	-	-
CM	10	-	10	-	10	-
PM	10	10	-	-	10	-
CL + Mg	10	-	10	10	-	0.2
CM + Mg	10	-	10	-	10	0.2
PM + Mg	10	10	-	-	10	0.2

Chia protein-rich fraction (P), sodium caseinate (C), lactose (L), maltodextrin (M), and chia mucilage (Mg).

2.2.4. Rheological Properties

Rheological measurements were performed using a Haake RS600 controlled stress oscillatory rheometer (Haake, Germany) with a coarse plate–plate sensor system at 25 ± 1 °C. The samples were subjected to a logarithmic increasing of shear rate from 1 to 500 s^{-1} in 2 min, followed by a steady shear at 500 s^{-1} for 1 min, and finally a decreasing shear rate from 500 to 1 s^{-1} in 2 min [8].

2.2.5. Emulsion Stability

Physical stability of emulsions was determined by measurements of dispersed light using a Vertical Scan Analyzer Quick Scan (Coulter Corp., Miami, FL, USA) according to Pan et al. [9]. The emulsions were transferred to cylindrical glass tubes and periodically measured during 15 days.

3. Results and Discussion

The droplet size distribution (DSD) of chia O/W emulsions with sodium caseinate presented DSD curves with a mono (CL) or bimodal (CM) shape. On the other hand, emulsions prepared with chia protein-rich fraction exhibited wider and trimodal DSD with a shift towards larger droplet sizes. Additionally, systems with chia mucilage addition presented similar DSD curves shape but shifted to lower particle sizes, which was especially noticeable for emulsions with the protein-rich fraction.

The protein–carbohydrate combination had a significant effect ($p \leq 0.05$) on the $D_{3.2}$ diameter of emulsions droplets. At the initial time, emulsions with sodium caseinate presented droplet sizes between 0.22 and 0.27 μm and Span values from 1.07 to 1.46, exhibiting a high degree of uniformity. Emulsions containing the protein-rich fraction presented droplet sizes of ~9.86 μm and Span values from 2.23 to 2.65 due to the presence of bigger particle populations. The larger drop size of the emulsions of chia protein-rich fractions could be due to their lower level of protein available under the conditions of the chemical environment. Thus, when the emulsifying agent is not enough to fully stabilize the droplet interface, larger particles may be formed during homogenization [10,11]. Additionally, since sodium caseinate (protein with structural flexibility) is more effective to reduce the interfacial tension at the interface than chia proteins, which are mainly constituted by globular proteins [1], it is expected that it plays a major role as an emulsifier. Besides, a smaller ($p \leq 0.05$) droplet size for PM + Mg emulsions (7.44 μm) in comparison with PM systems (9.86 μm) was observed. This fact could be due to the increase of viscosity in systems with mucilage, which reduces the movement of the oil droplets, their collision, and coalescence.

The surface droplet charge at pH 6.5 was negative for all O/W emulsions, probably due to the ionized groups of the proteins at pH above the isoelectric point (pI) (Figure 1). The electric charge of the emulsion droplets stabilized with sodium caseinate was −35 and −31 mV for CL and CM, respectively, while those coated by the chia protein-rich fraction resulted in ~−23 mV. The more negative charge in droplets of protein-rich fraction systems could be due to the presence of anionic functional groups present in the chia protein structure, mainly related to glutamic and aspartic acids. Besides, the net charge of oil droplets became less ($p \leq 0.05$) negative when chia mucilage was added into the emulsions, possibly related to the charge suppression caused by electrostatic associations between polypeptide chains and charged groups of the chia mucilage.

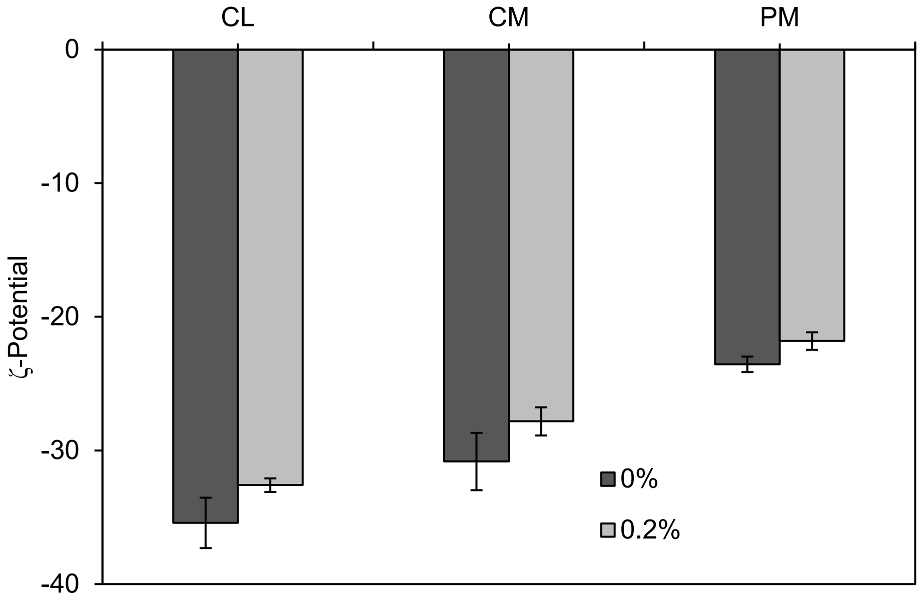

Figure 1. ζ-potential values of chia O/W emulsions at pH 6.5.

Regarding rheological properties, emulsions were affected by the proteins–carbohydrates combination used and the addition of chia mucilage. The experimental data, corresponding to rheological measurements, was fitted to the power-law model, and n (flow behavior index) and K (consistency coefficient) parameters were calculated. Differences in the flow behavior of the different O/W emulsions were evidenced (Figure 2). Systems with sodium caseinate recorded values of $n < 1$, exhibiting pseudo-plasticity on different levels. In this sense, emulsions with maltodextrin had greater pseudoplastic behavior than lactose ones. On the other hand, emulsions with the chia protein-rich fraction presented a Newtonian behavior ($n \sim 1$) (Figure 2).

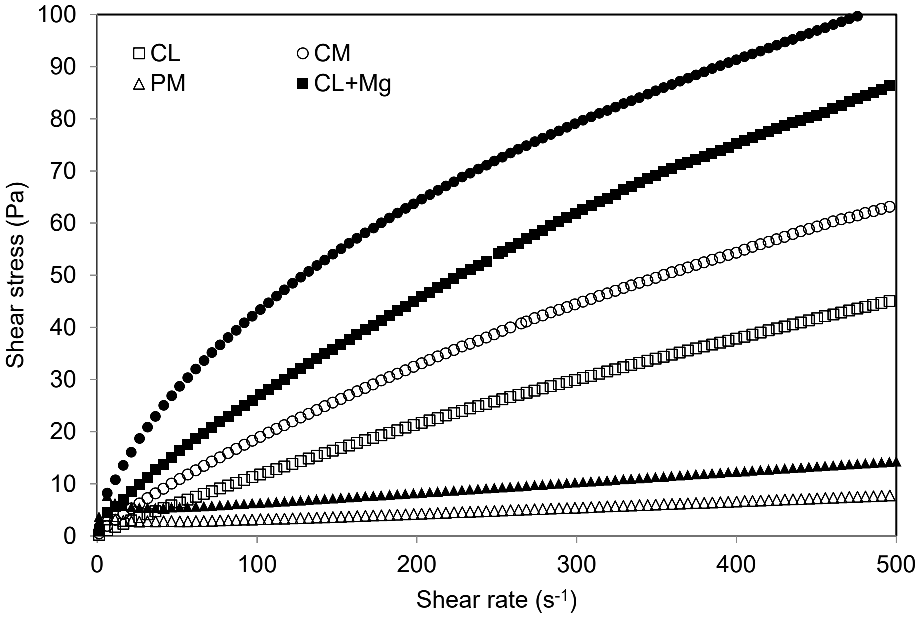

Figure 2. Flow curves of chia O/W emulsions. Average values ($n = 3$).

The apparent viscosity of emulsions at 100 s^{-1} (η_{100}), typical of food processes such as flow through pipes, agitation, and chewing [12], was also calculated. In this sense, systems with the chia protein-rich fraction had lower η_{100} values ($p \leq 0.05$) than emulsions stabilized with sodium caseinate. This fact could be related to a significant amount of nonadsorbed sodium caseinate in the continuous phase, which would lead to the formation of aggregates and a transient network structure with an enhancement in the viscosity [7]. Furthermore, there was an increase ($p \leq 0.05$) in the viscosity of emulsions with sodium caseinate containing chia mucilage. Similar results were reported by Timilsena et al. [3], who attributed the high viscosity of the chia mucilage solutions to the presence of 4-O-methyl-glucuronic acid and the intermolecular chain networks formation in aqueous media.

The physical stability of each emulsion was examined through its optical characterization during 15 days. The backscattering (BS) profiles evolution, as a function of the sample height (10–20 and 40–50 mm) and the storage time, for the different systems, are presented in Figure 3. Emulsions with sodium caseinate had high physical stability, causing their BS profiles to remain unchanged during the entire storage period (Figure 3a,b). This behavior could be due to the high viscosity level and small particle size of these systems, which reduce the droplet mobility and therefore its upward movement according to Stokes's law. In contrast, emulsions prepared with the chia protein-rich fraction recorded clarification at the bottom of the sample tube at day 5 of storage (Figure 3a,b). This creaming occurrence would be caused by higher mobility and interaction of the oil droplets as a result of weak viscous forces in the aqueous phase of these systems. Emulsions with the chia mucilage addition presented similar BS profiles to those without this by-product.

(**a**)

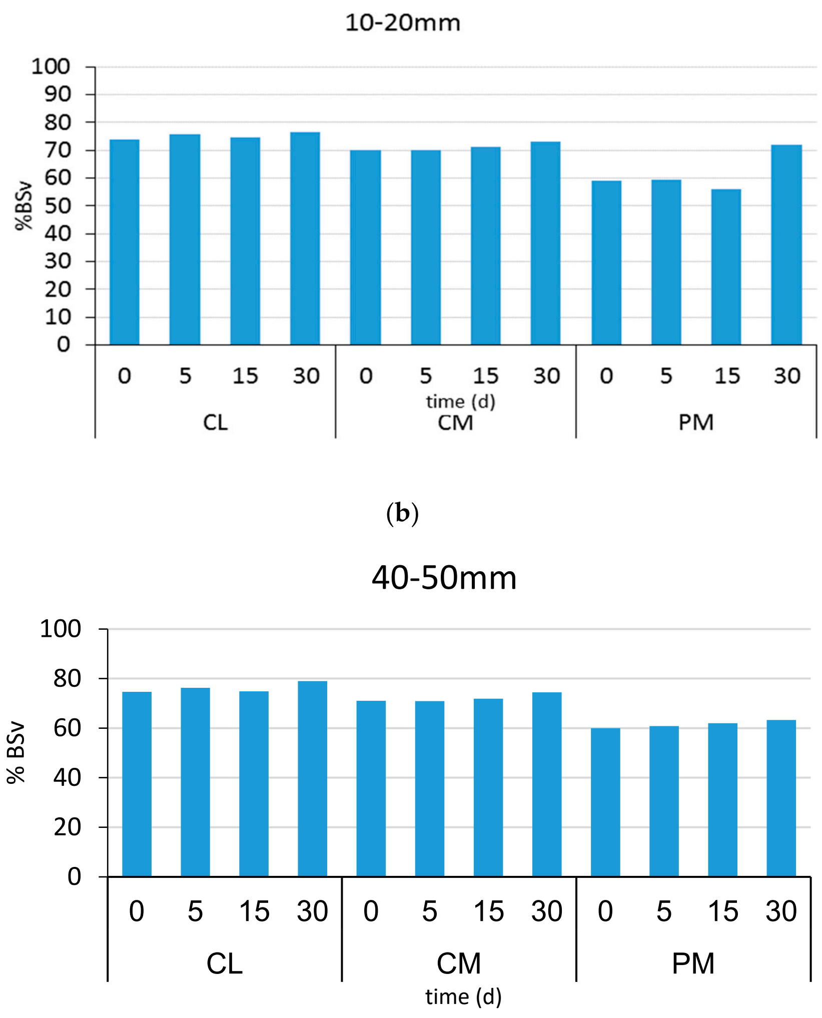

Figure 3. Backscattering profiles vs. sample tube height: (**a**) 10–20 mm and (**b**) 40–50 mm. Average values ($n = 2$). Std. deviation < 5%.

4. Conclusions

O/W emulsions proved to be suitable systems to deliver and protect chia seed by-products. All protein–carbohydrate combinations used for emulsions preparation led to the improvement of the oxidative stability of chia oil.

Chia mucilage addition had a significant effect on the rheological properties of the emulsions. Systems containing chia mucilage recorded higher viscosity and global stability due to the reduction of the oil droplets movement. Thus, chia mucilage exhibited a potential role as a thickening agent.

The obtained information could be applied to design and develop O/W emulsions as delivery systems of ω-3 fatty acids and other by-products from chia seed, allowing the revaluation of these novel ingredients.

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