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Short communication

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Abstract

The aim of this study is to evaluate the feasibility of edible oils co-encapsulation with antioxidants in a natural protein matrix obtained using the spray-drying method, and to demonstrate the long-term stability of microparticles. Sunflower and flaxseed oils were encapsulated in pea protein isolate (PP) with a hydrophilic antioxidant, propyl gallate (PG), and a lipophilic antioxidant, α-tocopherol (α-T). Samples with encapsulated oil and the corresponding unencapsulated oil were then stored at 25°C for up to 10 months (300 days) to monitor the long-term oxidative stability. The results demonstrated that microencapsulation, the addition of antioxidants, as well as the nature of the oil all affected the oxidative stability of oils. The addition of PG made it possible the increase in oil stability during the total storage period, whereas α-T had a pro-oxidant effect and induced the decrease in oil resistivity to

oxidation. The positive effect of PG was more pronounced for short storage times ($t < 100$ days). Flaxseed oil, which is more sensitive to oxidation, showed slower oxidation kinetic after encapsulation compared to sunflower oil. The proposed encapsulation method may be an efficient approach for enhancing oxidative stability of edible oils for functional food powders.

1. Introduction

A growing consumer trend towards sustainable and safe vegetable-based diets is having a strong impact on the food industry. The production of new healthy, functional, and natural ingredients is one of the major challenges (Helkar, Sahoo, & Patil, 2016). Vegetable oil is a main source of essential fatty acids and an indispensable component of the human diet. The main functional compounds responsible for the health benefits of vegetable oils are polyunsaturated fatty acids (PUFAs) (Borsonelo & Galduróz, 2008; Huerta-Yépez, Tirado-Rodriguez, & Hankinson, 2016; Singh, 2005). PUFAs need to be provided by diet, as they cannot be produced by the human body. One significant problem associated with oils rich in PUFAs is their high susceptibility to oxidative deterioration, followed by the formation of hydroperoxides with undesirable taste and flavors (Aberkane, Roudaut, & Saurel, 2014). The health-benefit properties of PUFAs remain underused in formulated dry food products because of their susceptibility to oxidation. Developing food powders that are stable during storage and that contain edible oils is a fast-growing area in the food industry. Additionally, there are significant difficulties in food processing when incorporating oils into different formulations because of their poor miscibility in aqueous systems.

Microencapsulation is a well-known approach that makes it possible to overcome these issues. This technology enables the unstable oily compounds to transform into free-flowing and stable powders, reduces oxygen access and provides good protection for the oil against oxidation. Spray-drying is an efficient, fast and inexpensive industrial method, which is mostly used for the microencapsulation of food ingredients (Gharsallaoui, Roudaut, Chambin, Voilley, & Saurel, 2007). An important step in the microencapsulation process is selecting the wall material, which can be capable of forming a protective barrier to inhibit and delay oil oxidation. Due to their various functionalities, such as emulsifying, film-forming, fat-adsorbing and water binding properties, natural proteins appear to be

very suitable wall-forming materials for encapsulation by spray-drying (Di Giorgio, Salgado, & Mauri, 2019; Gharsallaoui, Saurel, Chambin, & Voilley, 2012; Le Priol et al., 2019; Alla Nesterenko, Alric, Silvestre, & Durrieu, 2013; A. Nesterenko, Alric, Violleau, Silvestre, & Durrieu, 2013).

Many articles have been published on developing edible oil microparticles with spray-drying for their potential application in foods (Aberkane et al., 2014; Carneiro, Tonon, Grosso, & Hubinger, 2013; Fioramonti, Stepanic, Tibaldo, Pavón, & Santiago, 2019; Gharsallaoui et al., 2007; Gharsallaoui et al., 2010; Le Priol et al., 2019; Murali et al., 2016). However, this area of functional foods needs further and continuing investigation because of the substantial increase in the demand for novel ingredients with specific properties, and the awareness of the impact of food on health (Granato et al., 2020). Another approach to protecting oil against oxidation is to use specific additives, such as antioxidant agents (Comunian et al., 2017; Ozkan, Franco, De Marco, Xiao, & Capanoglu, 2019). Although the wall material itself protects the encapsulated oil against oxidation, the addition of an antioxidant improves oxidative stability. In order to combine these two approaches, the co-encapsulation of vegetable oils with antioxidants can be used (Comunian et al., 2017; Sharif et al., 2017; Sun-Waterhouse, Zhou, Miskelly, Wibisono, & Wadhwa, 2011; Takeungwongtrakul, Benjakul, & H-kittikun, 2015). The results of these studies validate improved oxidative resistance in the oils after adding antioxidants. However, oxidative stability is usually monitored for one variety of oil and during a relatively short period of time (3-4 weeks), as the long-term stability of food powders is of foremost importance for industrial applications. No detailed data combining the co-encapsulation of several edible oils with antioxidants using spray-drying, and the monitoring of long-term oxidative stability have been identified in the literature.

The aims of the present article are to compare the oxidative stability of two encapsulated edible oils under long-term storage conditions, and to study the effect on the kinetics of oxidation of adding polyphenolic antioxidants. The analysis focused on the characteristic properties of oil-in-water emulsions stabilized with pea protein isolate and corresponding spray-dried microparticles. The oxidative stability of encapsulated oils and the corresponding bulk oil was determined using the Rancimat method over a 300-day storage period at 25°C.

2. Materials and Methods

2.1. Materials

Sunflower oil was supplied by the company SAS PIVERT (Compiègne, France), organic virgin flaxseed oil (cold pressure extracted) was purchased from the French market (Bio Planète) and stored at room temperature. Commercial pea protein isolate (75 g/100 g of protein) was purchased from MyProtein (Cheshire, UK), α-tocopherol (α-T, purity ≥ 95.5%) and propyl gallate (PG, purity ≥ 98%) were purchased from Sigma-Aldrich (France).

2.2. Emulsion preparation and characterization

Aqueous dispersion of pea protein isolate (10 g/100 g, pH 7.8) was prepared in distilled water by homogenization with a high-speed disperser (Ultra-Turrax T25, IKA-Labortechnik, Staufen, Germany) at 5,000 rpm for 5 min at room temperature. A small amount of pectin (0.5 g/100 g) was added to the encapsulating matrix to enhance the barrier properties (Aberkane et al., 2014; Carneiro et al., 2013). The required amount of PG was introduced at the end of wall material solubilization. The emulsion was prepared by adding 10 g/100 mL of oil with or without α-T to an aqueous dispersion of polymers. This pre-emulsion was mixed at 10,000 rpm for 5 min and then stabilized by passing through a high pressure homogenization (HPH) device (Panda Plus 2000, GEA Niro Soavi, Parma, Italy) operated at 400 bars for two passes. Six oil-in-water (O/W) emulsions were prepared: with pea protein isolate and sunflower oil (PP/S) or flaxseed oil (PP/F) without antioxidants; with pea protein isolate, sunflower oil and 0.004 g/100 g of propyl gallate (PP/S-PG1) or 0.02 g/100 g of propyl gallate (PP/S-PG2) or 0.01 g/100 g of α-tocopherol (PP/S-αT); with pea protein isolate, flaxseed oil and 0.004 g/100 g of propyl gallate (PP/F-PG1). The concentrations of antioxidants were chosen based on data from the International Food Standards ("Codex Alimentarius Commission," 2017).

Droplet size distributions from the emulsions obtained and mean volume diameters ($D_{4,3}$) were measured using a laser diffraction instrument, the Malvern MasterSizer 2000 (Malvern Instruments

Ltd, Malvern, Worcestershire, UK). Emulsion morphology was observed with optical microscopy using a Leica DM2700M optical microscope (Leica Microsystems, Wetzlar, Germany).

2.3. Microparticle preparation and characterization

Fresh emulsions were subjected to drying using a laboratory scale spray-dryer (Büchi B-290, Büchi Labortechnik, Flawil, Switzerland). Emulsion was fed into the main chamber through a nozzle with a diameter of 0.7 mm, feed flow rate was 9 mL/min and hot air flow rate was 670 L/h (100% of aspiration). Air inlet and outlet temperature was 160°C and 90±2°C respectively. The powders obtained were collected and stored in darkness at 25°C. The unencapsulated oils used for the corresponding emulsion preparation were stored in the same conditions. Samples of microparticles were named as the corresponding O/W emulsions.

The moisture content of the microparticles was measured gravimetrically after treating the sample in an air oven at 120 °C for 6 h. The water activity was determined using a water activity meter (Aqualab 3TE instrument, Decagon, Pullman, WA, US) at 25 ± 2°C after 10 min of sample equilibration. Microparticle morphology was evaluated using an environmental scanning electron microscope (ESEM, Quanta 250 FEG, FEI Co., OR, USA). Powders were mounted on an aluminum stub, sputter-coated with gold and observed at an acceleration voltage of 20 kV with different magnifications.

The oxidative stability of the dried microparticles and corresponding unencapsulated pure oils at different periods of time was analyzed using the Rancimat apparatus (892 Rancimat METROHM, Switzerland) at 100°C and an air flow rate of 10 L/h. 2 g of powder or crude oil was used for each assay. The induction period (IP) of the samples was used to characterize the oxidative stability. The gain in oxidative stability was calculated as: $\Delta IP\ (h) = IP_{EO} - IP_{BO}$, where IP_{EO} is the induction period of encapsulated oil and IP_{BO} is the induction period of the corresponding bulk oil. The higher the ΔIP value, the more stable the encapsulated oil against oxidation compared to the bulk oil.

All of the characterization measurements of the emulsions and microparticles were performed in triplicate.

3. Results and Discussion

138

139 *3.1. Characterizing the O/W emulsions and dried microparticles*

140 Different characterizations of the emulsions and spray-dried powders are reported for the PP/S and
141 PP/F samples, as the amount of antioxidant added was very low and did not alter emulsion droplet
142 size, microparticle water content, or morphology.

143 To control the good dispersion of the oil in protein solution prior to the spray-drying step, O/W
144 emulsion morphology and droplet size were analyzed (Fig. 1). It was observed that droplet size
145 distribution for both O/W emulsions was bimodal with a first population around 0.3±0.1 µm,
146 corresponding to small oil droplets, and a large second population around 3.3±0.2µm, corresponding
147 to larger or coalesced droplets and insoluble protein residuals. As shown in the optical microscopy
148 images, the emulsions obtained with the HPH treatment were composed of a homogeneous dispersion
149 of oil droplets stabilized by protein chains.

150 Moisture content, representing the total amount of water in powder, and water activity, characterizing
151 the amount of associated water, are critical parameters for evaluating food powder stability during
152 storage (Nielsen, 2010; Velasco, Dobarganes, & Márquez-Ruiz, 2003). PP/S and PP/F microparticles
153 were characterized by the similar moisture content of 1.5±0.2 % and water activity of 0.12±0.02. This
154 indicates that the samples could be considered as microbiologically stable (Quek, Chok, & Swedlund,
155 2007) and acceptable for spray-dried food formulations (Schuck, Dolivet, Méjean, & Jeantet, 2008).
156 The morphology of spray-dried microparticles has a significant influence on the efficiency of active
157 core protection and stability of powder (Gharsallaoui et al., 2007; Ozkan et al., 2019; Reineccius,
158 2004). Fig. 2 shows the scanning electron micrographs of the PP/S and PP/F spray-dried emulsions.
159 As can be seen, the microparticles produced exhibited a completely smooth and continuous surface
160 structure without visible pores or fissures. These characteristics are important for providing a high
161 degree of retention and protection for the core substance, and low permeability to gases. The
162 formation of certain agglomerated particles was visible, which is often observed in the encapsulation
163 of oils with plant proteins using the spray-drying method (Le Priol et al., 2019; Locali Pereira,
164 Gonçalves Cattelan, & Nicoletti, 2019; Moser, Ferreira, & Nicoletti, 2019). The results of previous
165 study (Le Priol et al., 2019) demonstrated that the emulsion stability index (24h after preparation) and

166 the apparent viscosity of the PP/S emulsion were, respectively, 100% and 3.3 mPa.s, which satisfies
167 the conditions necessary for proper and efficient encapsulation with spray-drying.
168 To conclude, the PP/S and PP/F samples showed similar characteristics, indicating that the protocol
169 used, the nature of the vegetable oil had no notable influence on the O/W emulsion and microparticle
170 structural properties.
171
172 *3.2. Oxidative stability of encapsulated oils during storage*
173 Evaluating the oxidative stability of oily compounds in food formulations is of great importance for
174 both food quality and safety. Of the different methods making it possible to measure the oxidative
175 stability of vegetable and animal oily products, the Rancimat test has several advantages: it is rapid,
176 easy to use and has good reproducibility (Farhoosh & Hoseini-Yazdi, 2014). It has been shown that
177 Rancimat results have a high correlation with other methods, such as differential scanning calorimetry
178 (DSC) or electron spin resonance (ESR) spectroscopy, and have led to similar experimental results
179 (Farhoosh, Niazmand, Rezaei, & Sarabi, 2008). Based on this method, the induction period (IP),
180 corresponding to the time required for oil deterioration, was measured.
181 Oxidation of encapsulated oil and the corresponding bulk oil was monitored during storage over 10
182 months (300 days) using the Rancimat method. Data obtained from these experiments are shown in
183 Table 1. At t_0, the time immediately after microparticle preparation, all samples of encapsulated oils
184 demonstrated a significant increase in oxidative stability compared to unencapsulated oil. These
185 results confirm the efficacy of the microencapsulation process for protecting oil and delaying its
186 oxidation. The amount of oil retention in the pea protein matrix (or the efficiency of encapsulation) is
187 88 ± 2% (see previous study (Le Priol et al., 2019)). Coating wall material prevents the diffusion of
188 small molecules, such as oxygen, into the microparticle and enhances the oxidative stability of the
189 encapsulated oil. Surprisingly, two antioxidants had an antagonistic effect on the oxidative resistance
190 of the encapsulated sunflower oil. It should be noted that adding PG promoted the increase in IP
191 values compared to the PP/S sample (from 21.4 to 28.9 h), whereas adding α-T led to decrease in IP
192 values (from 21.4 to 17.1 h). A few recent reports have described the pro-oxidant effect of α-T,
193 confirmed by the accelerated oxidation of bulk soybean (Martin-Rubio, Sopelana, Ibargoitia, &

Guillén, 2018) and flaxseed (Mohanan, Nickerson, & Ghosh, 2018) oils. The phenomena observed are generally in agreement with previous findings reported in the literature, e.g. the microencapsulation of oils with natural polymers increased their oxidative stability and the co-encapsulation of oils with antioxidants made it possible to obtain supplementary gains in oil stability over a short-term storage period (30 days) (Comunian et al., 2017; Sharif et al., 2017; Sun-Waterhouse et al., 2011; Takeungwongtrakul et al., 2015).

The innovative nature of this study consists in comparing the oxidative stability of two encapsulated edible oils in long-term storage conditions, which to our knowledge, has not been reported before. The results showed that microparticles with flaxseed oil presented a much slower rate of oil oxidation compared to samples with sunflower oil prepared under the same conditions. For example, at t_0, the gain in oxidative stability, ΔIP, for encapsulated sunflower oil (PP/S) and flaxseed oil (PP/F) was 9.0 and 15.0 h respectively. This difference was even more pronounced for PP/S – PG1 and PP/F – PG1 samples. As the physicochemical and structural properties of the PP/S and PP/F samples were similar, this significant difference in the degree of oxidation could be attributed to the fatty acid profiles of the oils. The dominant fatty acid in sunflower oil is linoleic acid (LA, C18:2, omega-6), whereas the main constituent of linseed oil is α-linolenic acid (ALA, C18:3, omega-3) (Dubois, Breton, Linder, Fanni, & Parmentier, 2007). The higher number of unsaturations make oil more sensitive to oxidation. It therefore seems that for the same wall material, the degree of protection from encapsulation increased for oils with higher sensitivity to oxidation.

During storage at room temperature, all samples with encapsulated and the corresponding bulk oil demonstrated progressive oxidation, a decrease in the oxidative stability of the oil (IP values), and a decrease in the corresponding ΔIP values. For short-time storage (less than 100 days), adding PG, even at a very low level (0.004 g/100 g for PP/S-PG1 and PP/F-PG1, 0.02 g/100 g for PP/S-PG2), resulted in a remarkable increase in gains in oxidative stability, suggesting a positive impact of this antioxidant on the microencapsulation process and good stability of the powders obtained. In the case of sunflower oil, this effect was particularly pronounced when higher amounts of antioxidant were added (PP/S – PG2 sample).

Based on long-term observations (more than 100 days), the ΔIP values for the three samples with sunflower oil became 0 (PP/S, PP/S – PG1 and PP/S – αT). This means that the induction period (or oxidative stability) of the free and encapsulated oil reached the same values and, from this moment, microencapsulation had no beneficial effect on the oil's oxidative stability. The data in Table 1 indicate non-zero values for ΔIP for the PP/S – PG2, PP/F and PP/F-PG1 samples, even for times more than or equal to 200 days. Thus, the encapsulation of flaxseed oil made it possible to enhance the oxidative stability throughout the entire storage period. The positive effect of adding PG was less pronounced at long times compared to short times.

In summary, the oxidation rate of encapsulated edible oils is highly dependent on the oil's nature and the presence of antioxidants. The combined effect of microencapsulation and the addition of appropriate antioxidant could be effective in delaying the oil's oxidation, even after long-term storage of the powder. The procedure proposed makes it possible to efficiently prevent the oxidation related to the rancidity of oils and seems to be particularly appropriate for very sensitive oils rich in PUFAs.

4. Conclusions

In this work, the performance of pea protein isolate for microencapsulation of PUFA-rich oils with spray-drying, with or without the use of phenolic antioxidants, was evaluated. Emulsions and microparticles obtained with flaxseed and sunflower oil showed similar characteristics, in terms of size distribution and morphology. However, significant differences were observed in the oxidative stability of microparticles produced. During the entire storage period, microencapsulation was more efficient for enhancing the oxidative stability of flaxseed oil compared to sunflower oil, which could be linked to fatty acid composition. Furthermore, the co-encapsulation of oxidizable oil with phenolic antioxidants showed that PG played its antioxidant role, improving the oxidative stability of the oil. On the contrary, co-encapsulation with α-T had the opposite pro-oxidant effect and reduced the stability of the oil. The use of appropriate antioxidant could significantly increase the oxidative stability of encapsulated oil. The positive effect on oxidative stability of adding PG was particularly pronounced over a short time (less than 100 days). The role played by PG was nevertheless still visible up to 300 days of storage.

This study proposes a feasible approach for protecting vegetable oil from oxidation during storage in PUFA-enriched food powders. Future research will focus on screening a larger number of antioxidants, and identifying more efficient compounds for preventing the oxidation of edible oils during their shelf-life.

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References

Aberkane, L., Roudaut, G., & Saurel, R. (2014). Encapsulation and Oxidative Stability of PUFA-Rich Oil Microencapsulated by Spray Drying Using Pea Protein and Pectin. *Food and Bioprocess Technology, 7*(5), 1505-1517. doi: https://doi.org/10.1007/s11947-013-1202-9

Borsonelo, E. C., & Galduróz, J. C. F. (2008). The role of polyunsaturated fatty acids (PUFAs) in development, aging and substance abuse disorders: Review and propositions. *Prostaglandins, Leukotrienes and Essential Fatty Acids, 78*(4), 237-245. doi: https://doi.org/10.1016/j.plefa.2008.03.005

Carneiro, H. C. F., Tonon, R. V., Grosso, C. R. F., & Hubinger, M. D. (2013). Encapsulation efficiency and oxidative stability of flaxseed oil microencapsulated by spray drying using different combinations of wall materials. *Journal of Food Engineering, 115*(4), 443-451. doi: https://doi.org/10.1016/j.jfoodeng.2012.03.033

Codex Alimentarius Commission, CAC40, Food safety and quality standards, 40th Session, Geneva, Switzerland, 17-22 July 2017 (2017).

Comunian, T. A., Ravanfar, R., de Castro, I. A., Dando, R., Favaro-Trindade, C. S., & Abbaspourrad, A. (2017). Improving oxidative stability of echium oil emulsions fabricated by Microfluidics: Effect of ionic gelation and phenolic compounds. *Food Chemistry, 233*, 125-134. doi: https://doi.org/10.1016/j.foodchem.2017.04.085

Di Giorgio, L., Salgado, P. R., & Mauri, A. N. (2019). Encapsulation of fish oil in soybean protein particles by emulsification and spray drying. *Food Hydrocolloids, 87*, 891-901. doi: https://doi.org/10.1016/j.foodhyd.2018.09.024

Dubois, V., Breton, S., Linder, M., Fanni, J., & Parmentier, M. (2007). Fatty acid profiles of 80 vegetable oils with regard to their nutritional potential. *European Journal of Lipid Science and Technology, 109*(7), 710-732. doi: https://doi.org/10.1002/ejlt.200700040

Farhoosh, R., & Hoseini-Yazdi, S.-Z. (2014). Evolution of Oxidative Values during Kinetic Studies on Olive Oil Oxidation in the Rancimat Test. *Journal of the American Oil Chemists' Society, 91*(2), 281-293. doi: https://doi.org/10.1007/s11746-013-2368-z

Farhoosh, R., Niazmand, R., Rezaei, M., & Sarabi, M. (2008). Kinetic parameter determination of vegetable oil oxidation under Rancimat test conditions. *European Journal of Lipid Science and Technology, 110*(6), 587-592. doi: https://doi.org/10.1002/ejlt.200800004

Fioramonti, S. A., Stepanic, E. M., Tibaldo, A. M., Pavón, Y. L., & Santiago, L. G. (2019). Spray dried flaxseed oil powdered microcapsules obtained using milk whey proteins-alginate double layer emulsions. *Food Research International, 119*, 931-940. doi: https://doi.org/10.1016/j.foodres.2018.10.079

Gharsallaoui, A., Roudaut, G., Chambin, O., Voilley, A., & Saurel, R. (2007). Applications of spray-drying in microencapsulation of food ingredients: An overview. *Food Research International, 40*(9), 1107-1121. doi: https://doi.org/10.1016/j.foodres.2007.07.004

Gharsallaoui, A., Saurel, R., Chambin, O., Cases, E., Voilley, A., & Cayot, P. (2010). Utilisation of pectin coating to enhance spray-dry stability of pea protein-stabilised oil-in-water emulsions. *Food Chemistry, 122*(2), 447-454. doi: https://doi.org/10.1016/j.foodchem.2009.04.017

Gharsallaoui, A., Saurel, R., Chambin, O., & Voilley, A. (2012). Pea (Pisum sativum, L.) Protein Isolate Stabilized Emulsions: A Novel System for Microencapsulation of Lipophilic Ingredients by Spray Drying. *Food and Bioprocess Technology, 5*(6), 2211-2221. doi: https://doi.org/10.1007/s11947-010-0497-z

Granato, D., Barba, F. J., Bursać Kovačević, D., Lorenzo, J. M., Cruz, A. G., & Putnik, P. (2020). Functional Foods: Product Development, Technological Trends, Efficacy Testing, and Safety. *Annual Review of Food Science and Technology, 11*(1), 93-118. doi: https://doi.org/10.1146/annurev-food-032519-051708

Helkar, P. B., Sahoo, A., & Patil, N. J. (2016). Review: Food Industry By-Products used as a Functional Food Ingredients. *International Journal of Waste Resources, 6*, 1-6. doi: https://doi.org/10.4172/2252-5211.1000248

Huerta-Yépez, S., Tirado-Rodriguez, A. B., & Hankinson, O. (2016). Role of diets rich in omega-3 and omega-6 in the development of cancer. *Boletín Médico del Hospital Infantil de México, 73*(6), 446-456. doi: https://doi.org/10.1016/j.bmhimx.2016.11.001

Le Priol, L., Dagmey, A., Morandat, S., Saleh, K., El Kirat, K., & Nesterenko, A. (2019). Comparative study of plant protein extracts as wall materials for the improvement of the oxidative stability of sunflower oil by microencapsulation. *Food Hydrocolloids, 95*, 105-115. doi: https://doi.org/10.1016/j.foodhyd.2019.04.026

Locali Pereira, A. R., Gonçalves Cattelan, M., & Nicoletti, V. R. (2019). Microencapsulation of pink pepper essential oil: Properties of spray-dried pectin/SPI double-layer versus SPI single-layer stabilized emulsions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 581*, 123806. doi: https://doi.org/10.1016/j.colsurfa.2019.123806

Martin-Rubio, A. S., Sopelana, P., Ibargoitia, M. L., & Guillén, M. D. (2018). Prooxidant effect of α-tocopherol on soybean oil. Global monitoring of its oxidation process under accelerated storage conditions by 1H nuclear magnetic resonance. *Food Chemistry, 245*, 312-323. doi: https://doi.org/10.1016/j.foodchem.2017.10.098

Mohanan, A., Nickerson, M. T., & Ghosh, S. (2018). Oxidative stability of flaxseed oil: Effect of hydrophilic, hydrophobic and intermediate polarity antioxidants. *Food Chemistry, 266*, 524-533. doi: https://doi.org/10.1016/j.foodchem.2018.05.117

Moser, P., Ferreira, S., & Nicoletti, V. R. (2019). Buriti oil microencapsulation in chickpea protein-pectin matrix as affected by spray drying parameters. *Food and Bioproducts Processing, 117*, 183-193. doi: https://doi.org/10.1016/j.fbp.2019.07.009

Murali, S., Kar, A., Patel, A., Kumar, J., Mohapatra, D., & Dash, S. K. (2016). Encapsulation of rice bran oil in tapioca starch-soya protein isolate complex using spray drying. *Indian Journal of Agricultural Sciences, 86*, 984-991.

Nesterenko, A., Alric, I., Silvestre, F., & Durrieu, V. (2013). Vegetable proteins in microencapsulation: A review of recent interventions and their effectiveness. *Industrial Crops and Products, 42*, 469-479. doi: https://doi.org/10.1016/j.indcrop.2012.06.035

Nesterenko, A., Alric, I., Violleau, F., Silvestre, F., & Durrieu, V. (2013). A new way of valorizing biomaterials: The use of sunflower protein for α-tocopherol microencapsulation. *Food Research International, 53*(1), 115-124. doi: https://doi.org/10.1016/j.foodres.2013.04.020

Nielsen, S. S. (2010). Introduction to Food Analysis. In S. S. Nielsen (Ed.), *Food Analysis* (pp. 3-14). Boston, MA: Springer US.

Ozkan, G., Franco, P., De Marco, I., Xiao, J., & Capanoglu, E. (2019). A review of microencapsulation methods for food antioxidants: Principles, advantages, drawbacks and applications. *Food Chemistry, 272*, 494-506. doi: https://doi.org/10.1016/j.foodchem.2018.07.205

Quek, S. Y., Chok, N. K., & Swedlund, P. (2007). The physicochemical properties of spray-dried watermelon powders. *Chemical Engineering and Processing: Process Intensification, 46*(5), 386-392. doi: https://doi.org/10.1016/j.cep.2006.06.020

Reineccius, G. A. (2004). The Spray Drying of Food Flavors. *Drying Technology, 22*(6), 1289-1324. doi: https://doi.org/10.1081/DRT-120038731

Schuck, P., Dolivet, A., Méjean, S., & Jeantet, R. (2008). Relative humidity of outlet air: the key parameter to optimize moisture content and water activity of dairy powders. *Dairy Science & Technology, 88*(1), 45-52. doi: https://doi.org/10.1051/dst:2007007

Sharif, H. R., Goff, H. D., Majeed, H., Shamoon, M., Liu, F., Nsor-Atindana, J., . . . Zhong, F. (2017). Physicochemical properties of β-carotene and eugenol co-encapsulated flax seed oil powders using OSA starches as wall material. *Food Hydrocolloids, 73*, 274-283. doi: https://doi.org/10.1016/j.foodhyd.2017.07.002

Singh, M. (2005). Essential fatty acids, DHA and human brain. *The Indian Journal of Pediatrics, 72*(3), 239-242. doi: https://doi.org/10.1007/BF02859265

Sun-Waterhouse, D., Zhou, J., Miskelly, G. M., Wibisono, R., & Wadhwa, S. S. (2011). Stability of encapsulated olive oil in the presence of caffeic acid. *Food Chemistry, 126*(3), 1049-1056. doi: https://doi.org/10.1016/j.foodchem.2010.11.124

Takeungwongtrakul, S., Benjakul, S., & H-kittikun, A. (2015). Wall materials and the presence of antioxidants influence encapsulation efficiency and oxidative stability of micro-encapsulated shrimp oil. *European Journal of Lipid Science and Technology, 117*(4), 450-459. doi: https://doi.org/10.1002/ejlt.201400235

Velasco, J., Dobarganes, C., & Márquez-Ruiz, G. (2003). Variables affecting lipid oxidation in dried microencapsulated oils. *Grasas y Aceites; Vol 54, No 3 (2003)DO - 10.3989/gya.2003.v54.i3.246*. doi: http://grasasyaceites.revistas.csic.es/index.php/grasasyaceites/article/view/246

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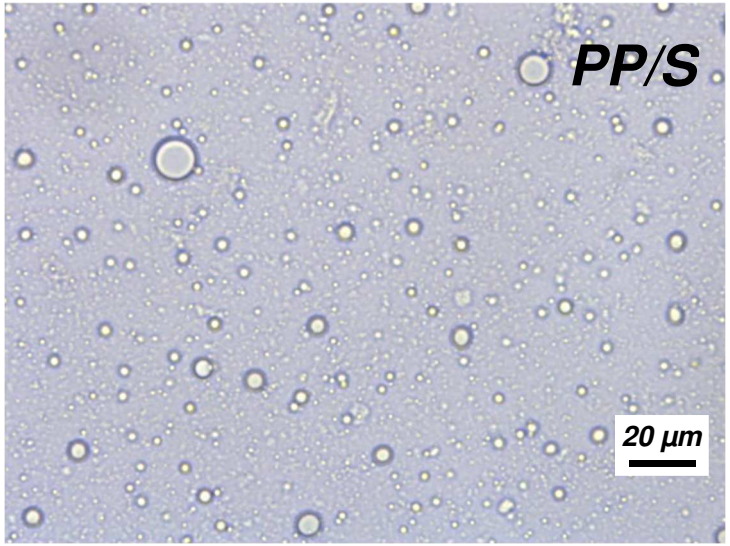
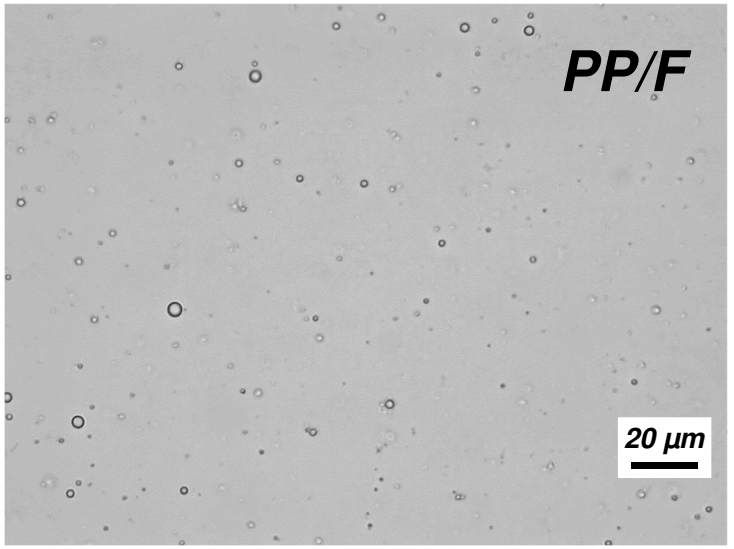

PP/S
20 µm


PP/F
20 µm

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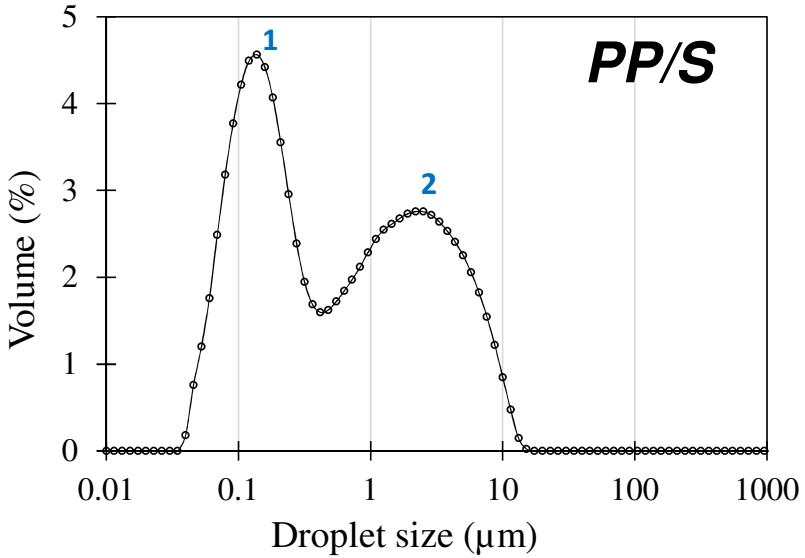
PP/S
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2
Volume (%)
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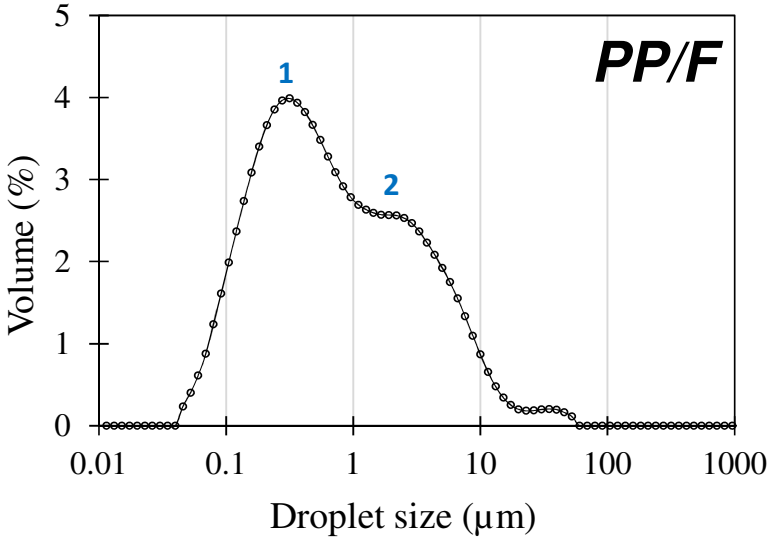
1
2
3
4
5
0.01
0.1
1
10
100
1000
Droplet size (µm)


PP/F
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Volume (%)
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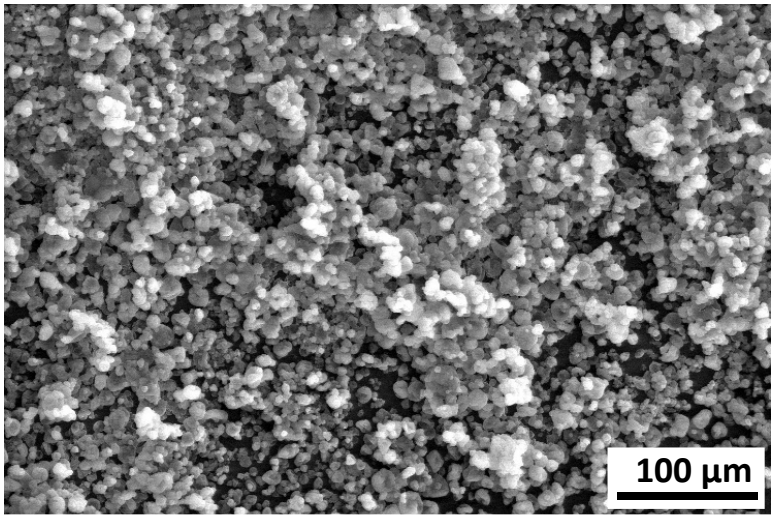

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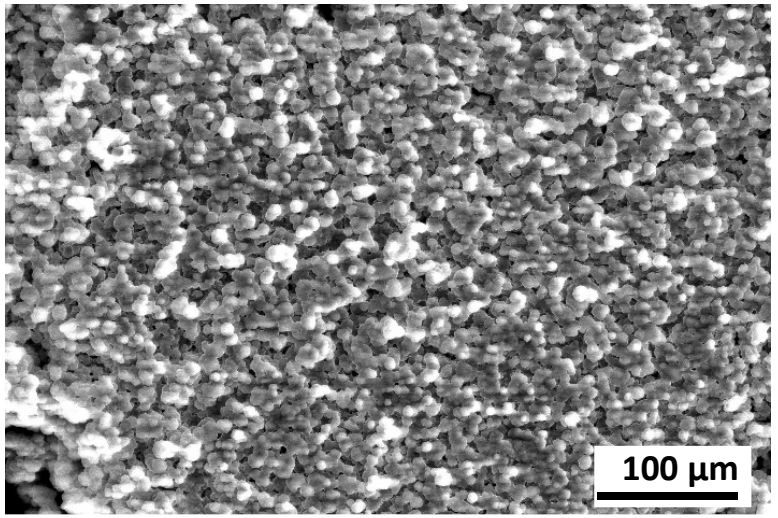

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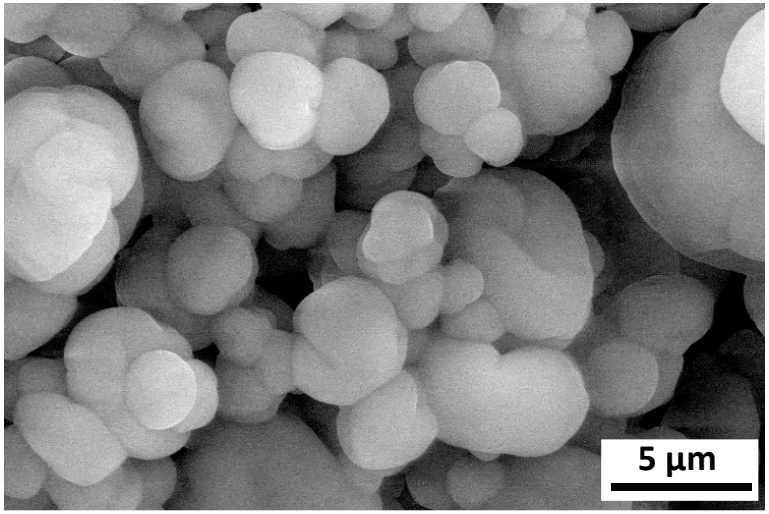

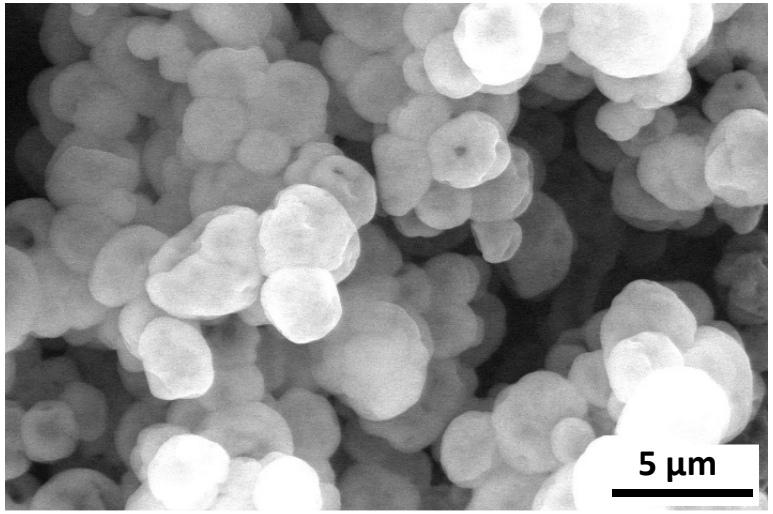

Table 1. Induction period of encapsulated oil (IP_{EO}) and corresponding bulk oil (IP_{BO}) immediately after spray-drying at t_0, determined by Rancimat analysis, and calculated oxidative stability gain (ΔIP) for different periods of time: microparticles prepared without antioxidant (PP/S and PP/F) and with addition of propyl gallate (PP/S-PG1, PP/S-PG2 and PP/F-PG1) or α-tocopherol (PP/S-αT).

Sample	**IP_{BO} (h)**	**IP_{EO} (h)**	**Oxidative stability gain, ΔIP (h)**				
	t_0	**t_0**	**t_0**	**50 days**	**100 days**	**200 days**	**300 days**
PP/S	12.4±0.1	21.4±0.3	9.0±0.4	7.3±0.3	3.5±0.4	0	0
PP/S – PG1	10.2±0.1	23.5±0.2	13.3±0.3	6.8±0.2	2.6±0.2	0	0
PP/S – PG2	10.3±0.1	28.9±0.05	17.6±0.2	13.5±0.3	8.3±0.4	3.7±0.2	0.9±0.2
PP/S – αT	10.6±0.1	17.1±0.1	6.5±0.2	4.6±0.3	2.1±0.3	0	0
PP/F	3.8±0.15	18.8±0.1	15.0±0.3	13.3±0.3	13.0±0.2	10.4±0.2	7.8±0.2
PP/F – PG1	1.4±0.05	27.1±0.1	25.7±0.2	22.5±0.3	20.4±0.4	14.4±0.2	ND