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1 **Short communication**

2 **Co-encapsulation of vegetable oils with phenolic antioxidants and evaluation of their**
3 **oxidative stability under long-term storage conditions**

4

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13

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15

16 **Keywords:** oxidative stability, oil, co-encapsulation, antioxidant, protein, storage, spray-drying

17

18 **Abstract**

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

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

32

33 **1. Introduction**

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

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

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

59 Many articles have been published on developing edible oil microparticles with spray-drying for their
60 potential application in foods (Aberkane et al., 2014; Carneiro, Tonon, Grosso, & Hubinger, 2013;
61 Fioramonti, Stepanic, Tibaldo, Pavón, & Santiago, 2019; Gharsallaoui et al., 2007; Gharsallaoui et al.,
62 2010; Le Priol et al., 2019; Murali et al., 2016). However, this area of functional foods needs further
63 and continuing investigation because of the substantial increase in the demand for novel ingredients
64 with specific properties, and the awareness of the impact of food on health (Granato et al., 2020).
65 Another approach to protecting oil against oxidation is to use specific additives, such as antioxidant
66 agents (Comunian et al., 2017; Ozkan, Franco, De Marco, Xiao, & Capanoglu, 2019). Although the
67 wall material itself protects the encapsulated oil against oxidation, the addition of an antioxidant
68 improves oxidative stability. In order to combine these two approaches, the co-encapsulation of
69 vegetable oils with antioxidants can be used (Comunian et al., 2017; Sharif et al., 2017; Sun-
70 Waterhouse, Zhou, Miskelly, Wibisono, & Wadhwa, 2011; Takeungwongtrakul, Benjakul, & H-
71 kittikun, 2015). The results of these studies validate improved oxidative resistance in the oils after
72 adding antioxidants. However, oxidative stability is usually monitored for one variety of oil and during
73 a relatively short period of time (3-4 weeks), as the long-term stability of food powders is of foremost
74 importance for industrial applications. No detailed data combining the co-encapsulation of several
75 edible oils with antioxidants using spray-drying, and the monitoring of long-term oxidative stability
76 have been identified in the literature.

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

83

84 2. Materials and Methods

85

86 2.1. Materials

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

92

93 2.2. Emulsion preparation and characterization

94 Aqueous dispersion of pea protein isolate (10 g/100 g, pH 7.8) was prepared in distilled water by
95 homogenization with a high-speed disperser (Ultra-Turrax T25, IKA-Labortechnik, Staufen,
96 Germany) at 5,000 rpm for 5 min at room temperature. A small amount of pectin (0.5 g/100 g) was
97 added to the encapsulating matrix to enhance the barrier properties (Aberkane et al., 2014; Carneiro et
98 al., 2013). The required amount of PG was introduced at the end of wall material solubilization. The
99 emulsion was prepared by adding 10 g/100 mL of oil with or without α -T to an aqueous dispersion of
100 polymers. This pre-emulsion was mixed at 10,000 rpm for 5 min and then stabilized by passing
101 through a high pressure homogenization (HPH) device (Panda Plus 2000, GEA Niro Soavi, Parma,
102 Italy) operated at 400 bars for two passes. Six oil-in-water (O/W) emulsions were prepared: with pea
103 protein isolate and sunflower oil (PP/S) or flaxseed oil (PP/F) without antioxidants; with pea protein
104 isolate, sunflower oil and 0.004 g/100 g of propyl gallate (PP/S-PG1) or 0.02 g/100 g of propyl gallate
105 (PP/S-PG2) or 0.01 g/100 g of α -tocopherol (PP/S- α T); with pea protein isolate, flaxseed oil and
106 0.004 g/100 g of propyl gallate (PP/F-PG1). The concentrations of antioxidants were chosen based on
107 data from the International Food Standards ("Codex Alimentarius Commission," 2017).
108 Droplet size distributions from the emulsions obtained and mean volume diameters ($D_{4,3}$) were
109 measured using a laser diffraction instrument, the Malvern MasterSizer 2000 (Malvern Instruments

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

112

113 *2.3. Microparticle preparation and characterization*

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

121 The moisture content of the microparticles was measured gravimetrically after treating the sample in
122 an air oven at 120 °C for 6 h. The water activity was determined using a water activity meter (Aqualab
123 3TE instrument, Decagon, Pullman, WA, US) at 25 ± 2°C after 10 min of sample equilibration.
124 Microparticle morphology was evaluated using an environmental scanning electron microscope
125 (ESEM, Quanta 250 FEG, FEI Co., OR, USA). Powders were mounted on an aluminum stub, sputter-
126 coated with gold and observed at an acceleration voltage of 20 kV with different magnifications.

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

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

136

137 **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 $0.3\pm 0.1\ \mu\text{m}$,
146 corresponding to small oil droplets, and a large second population around $3.3\pm 0.2\ \mu\text{m}$, 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 $1.5\pm 0.2\ \%$ 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 $88 \pm 2\%$ (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, Sopolana, Ibargoitia, &

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

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

213 During storage at room temperature, all samples with encapsulated and the corresponding bulk oil
214 demonstrated progressive oxidation, a decrease in the oxidative stability of the oil (IP values), and a
215 decrease in the corresponding ΔIP values. For short-time storage (less than 100 days), adding PG,
216 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),
217 resulted in a remarkable increase in gains in oxidative stability, suggesting a positive impact of this
218 antioxidant on the microencapsulation process and good stability of the powders obtained. In the case
219 of sunflower oil, this effect was particularly pronounced when higher amounts of antioxidant were
220 added (PP/S – PG2 sample).

221 Based on long-term observations (more than 100 days), the Δ IP values for the three samples with
222 sunflower oil became 0 (PP/S, PP/S – PG1 and PP/S – α T). This means that the induction period (or
223 oxidative stability) of the free and encapsulated oil reached the same values and, from this moment,
224 microencapsulation had no beneficial effect on the oil's oxidative stability. The data in Table 1
225 indicate non-zero values for Δ IP for the PP/S – PG2, PP/F and PP/F-PG1 samples, even for times
226 more than or equal to 200 days. Thus, the encapsulation of flaxseed oil made it possible to enhance the
227 oxidative stability throughout the entire storage period. The positive effect of adding PG was less
228 pronounced at long times compared to short times.

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

234

235 **4. Conclusions**

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

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

253

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260

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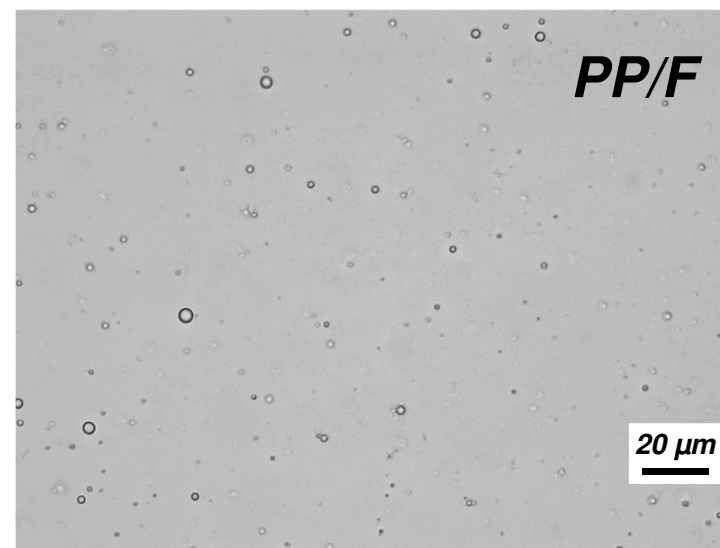
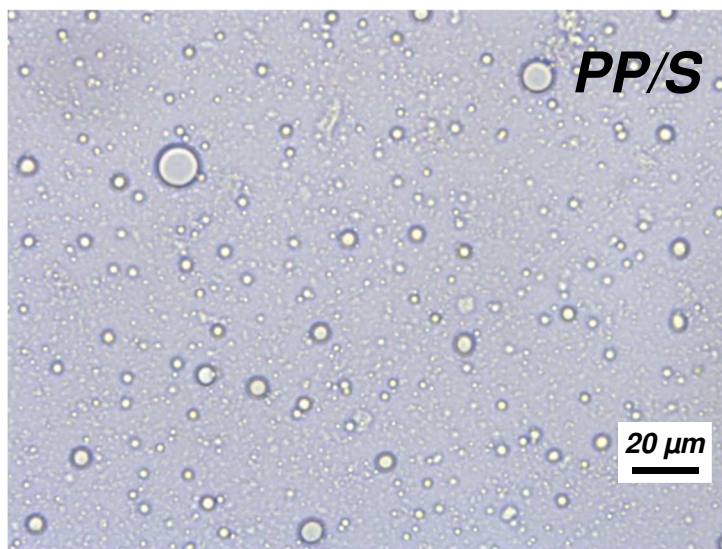
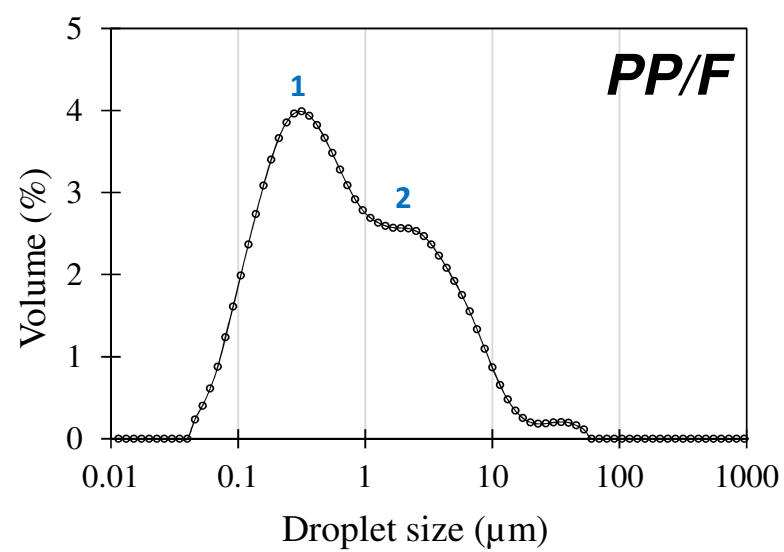
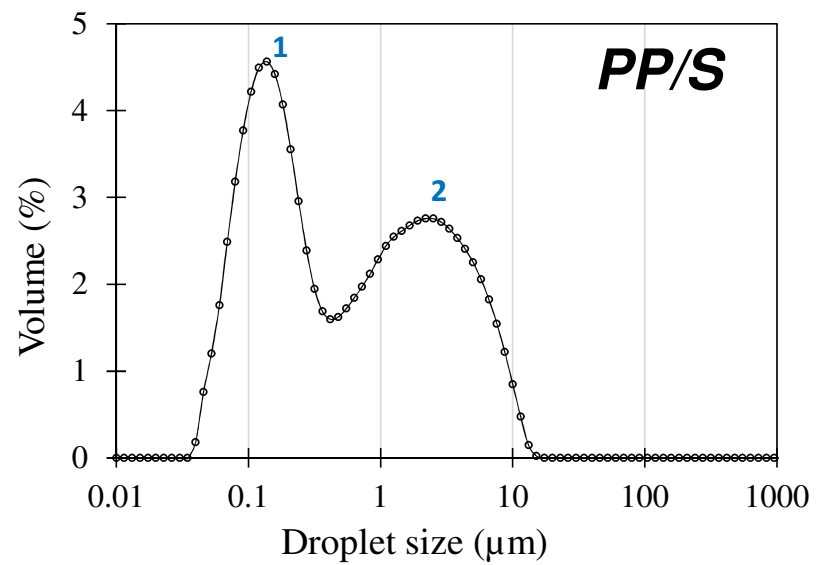
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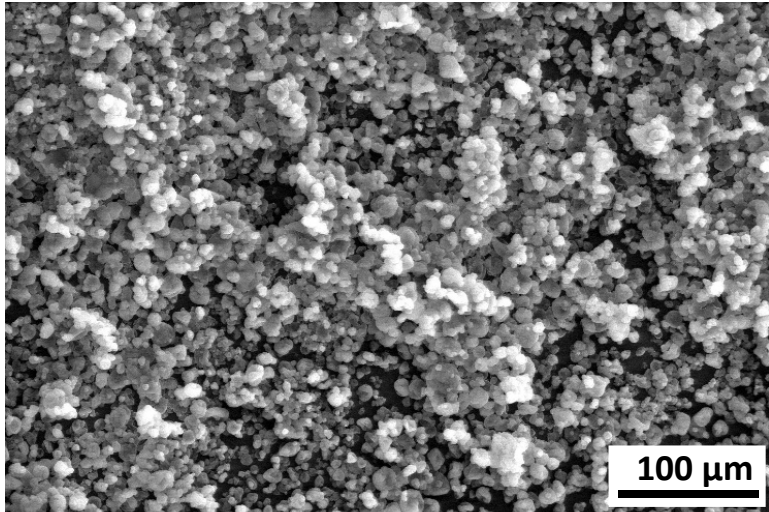
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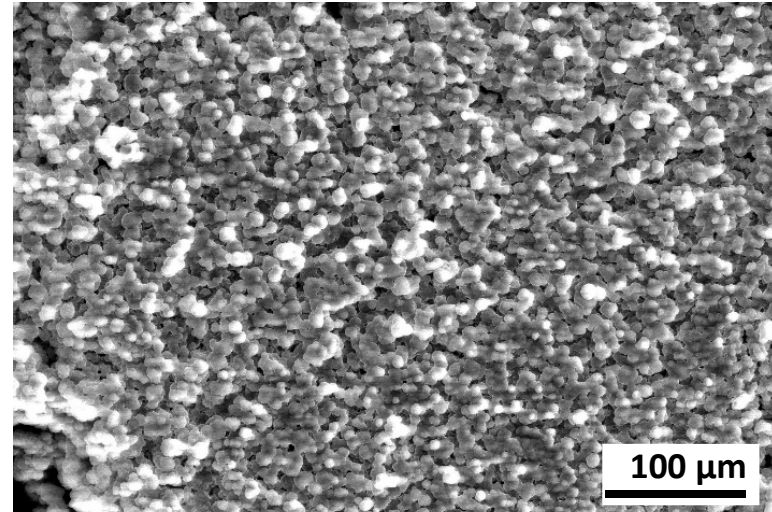
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A**B**



A



B

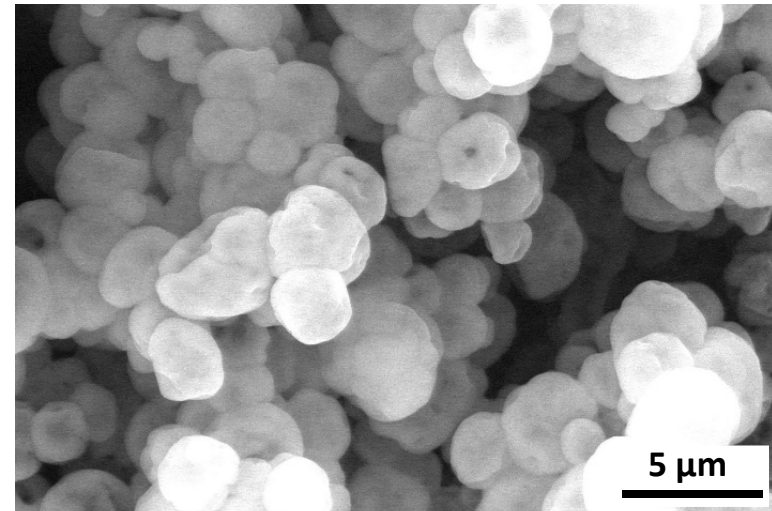
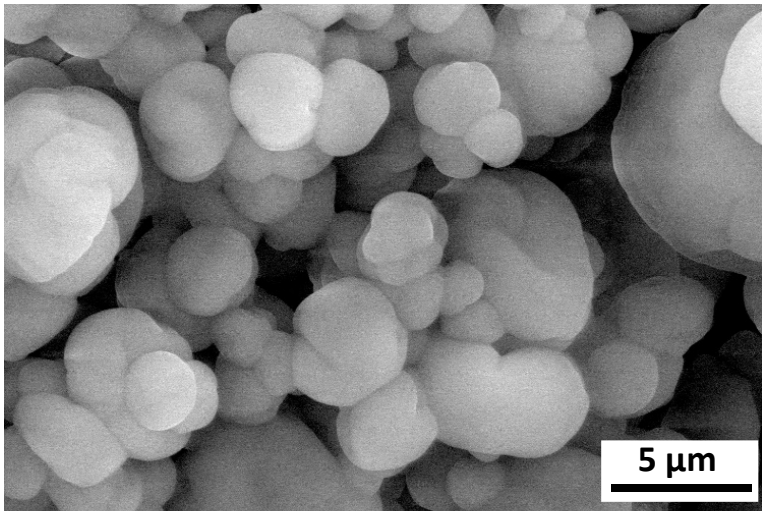


Table 1. Induction period of encapsulated oil (IP_{EO}) and corresponding bulk oil (IP_{BO}) immediately after spray-drying at t_0 , determined by Rancimat analysis, and calculated oxidative stability gain (ΔIP) for different periods of time: microparticles prepared without antioxidant (PP/S and PP/F) 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 \pm 0.1	21.4 \pm 0.3	9.0 \pm 0.4	7.3 \pm 0.3	3.5 \pm 0.4	0	0
PP/S – PG1	10.2 \pm 0.1	23.5 \pm 0.2	13.3 \pm 0.3	6.8 \pm 0.2	2.6 \pm 0.2	0	0
PP/S – PG2	10.3 \pm 0.1	28.9 \pm 0.05	17.6 \pm 0.2	13.5 \pm 0.3	8.3 \pm 0.4	3.7 \pm 0.2	0.9 \pm 0.2
PP/S – αT	10.6 \pm 0.1	17.1 \pm 0.1	6.5 \pm 0.2	4.6 \pm 0.3	2.1 \pm 0.3	0	0
PP/F	3.8 \pm 0.15	18.8 \pm 0.1	15.0 \pm 0.3	13.3 \pm 0.3	13.0 \pm 0.2	10.4 \pm 0.2	7.8 \pm 0.2
PP/F – PG1	1.4 \pm 0.05	27.1 \pm 0.1	25.7 \pm 0.2	22.5 \pm 0.3	20.4 \pm 0.4	14.4 \pm 0.2	ND