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# 1 **Emulsifying properties of food by-products: valorizing apple** 2 **pomace and oat bran**

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7  
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## 9 10 **Graphical Abstract**

## 11 12 **Abstract**

13 The potential emulsifying properties of two food byproducts, apple pomace and oat bran, were  
14 investigated to assess if their insoluble and soluble contents can stabilize oil in water emulsions. If so,  
15 this would mean that such raw, unpurified and complex materials could be used whole, with no  
16 additional processing and/or solvents added to separate and purify the desired fractions. If the two  
17 byproducts only need to be dried and micronized, the environmental impact would be considerably  
18 reduced. Rapeseed, jojoba and myrtilol oils were used to assess feasibility for both food and cosmetic  
19 applications. Dynamic rheological measurements, droplet size distribution, backscattered light, light  
20 and confocal microscopy showed that apple powder has better emulsifying potential, especially in  
21 myrtilol and rapeseed oil. The action of the insoluble fibers maintained the stability of the emulsions  
22 through Pickering mechanism and/or network formation in the continuous phase, probably favored by  
23 stabilization of proteins and pectins in the soluble fraction. Such raw materials can thus be a renewable  
24 source of stabilizing agents with useful functional properties such as gel behavior and stability against  
25 coalescence.

## 26 27 **Key words**

1

28 Unpurified raw materials, emulsions, solid particles, functional properties, stability mechanisms

29

## 30 **1. Introduction**

31 Management of wastes and byproducts is of great interest to the food industry, since exploiting them  
32 can provide added value in addition to environmental benefits. Many authors already evaluated how  
33 byproducts originating from fruits [1] vegetables or cereals [2] can be processed to obtain functional  
34 fractions such as insoluble fibers from sugar beet [3, 4] cherry [5], peach [6] or orange [7], but also  
35 proteins, starches or polyphenols. However, all these approaches require added energy to extract,  
36 fractionate, purify, homogenize, mix, filter, dry, or freeze-dry the components of interest. Solvents,  
37 and alkaline or acid conditions may also be required to retrieve fibers, for example [5, 8, 9].  
38 Considering that one of the main objectives is reducing impacts on the environment, one may question  
39 whether these strategies are best suited for the purpose. To achieve the environmental goal in addition  
40 to the expected added value, a possible alternative strategy is minimal processing, i.e. focusing on  
41 functionality more than on purity, using a shorter fractionation process [10]. Using these ingredients  
42 could help reduce product processing, even if the byproducts themselves are more complex, maybe  
43 more variable. The concept has already been promoted for food by several researchers in a holistic  
44 approach [11], the NOVA classification [12] or the “wholism” movement [13]. The complexity of the  
45 raw materials could be an advantage in the formulation of food or cosmetics when several  
46 functionalities are needed as texturizers, emulsifiers, foaming agents, color (or the reverse, no color  
47 other than white, for cosmetic creams for instance). Working with a raw material with several  
48 functionalities could be an asset, especially if the source material is also biodegradable, biocompatible  
49 and consistent with a clean-labelling approach.

50 In this context, the aim of the present study was to investigate the emulsifying properties of two food  
51 byproducts: apple pomace from *Pyrus Malus* and oat bran from *Avena Sativa*. The two byproducts  
52 were only dried and micronized to obtain powders, with no further fractionation or purification, and no  
53 use of solvents. The potential of the insoluble and soluble fractions had to be evaluated at the same  
54 time. Oil in water emulsions were studied using the plant powders as only additive, to compare three  
55 different oils used in the food or cosmetic industries, rapeseed, myrtilol and jojoba oil. The droplet

56 sizes, the rheological properties and the stability of the emulsions were assessed. Finally, the  
57 underlying mechanisms are discussed regarding the importance of insoluble fibers compared to the  
58 other native components, proteins, pectins and starch.

59

## 60 **2. Materials & Methods**

### 61 2.1 Characterization of the raw materials

62 The plant powders used were micronized apple pomace (*Pyrus Malus*) or oat bran (*Avena Sativa*),  
63 kindly provided by JRS (Rosenberg, Germany) as ultra-fine fruit or cereal fibers from VITACEL® CS  
64 5 brand. The physical-chemical characterization of the two powders was completed by other  
65 measurements. First, the Brix of the aqueous phase of the dispersion of 9% powder was measured with  
66 a refractometer (Pocket PAL-1, ATAGO, Tokyo, Japan), with three replicates for each powder. Water  
67 content was measured by drying 5 g of powder in an oven at 105 °C for 10 h. Three replicates were  
68 also made for the two powders. The characteristics are summarized in Table 1.

69

**Table 1: Physical-chemical characteristics of apple and oat powder**

<b>Measured characteristics</b>	<b>Apple powder</b>	<b>Oat powder</b>
Water content (% wt/wt)	15.3 ± 0.06	3.9 ± 0.02
Brix degree (°)	4.2 ± 0.01	0.4 ± 0.01
<b>Technical characteristics</b>		
Protein content (% wt/wt)	5.2	2.7
Starch content (% wt/wt)	0.9	2.1
Pectin present	Yes	No

70

71 Three commercial oils were used in the present study: rapeseed oil (0.916 g.cm<sup>-3</sup> at 20 °C, 58 mPa.s at  
72 20 °C) (purchased at a local retail outlet), myritol 318 (0.948 g.cm<sup>-3</sup> at 20 °C, 23 mPa.s at 20 °C) (AMI  
73 chimie, Tauxigny, France), and jojoba liquid wax (Aroma zone, France) (0.870 g.cm<sup>-3</sup> at 20 °C, 37  
74 mPa.s at 20 °C). In the article, they will all be called oils, according to their commercial names, even if  
75 rapeseed and myritol are both composed of triglycerides while jojoba is composed of a blend of  
76 different fatty acid esters. MilliQ ultra-pure water was used to create the oil in water emulsions.

77

78           2.2 Dispersion and emulsification processes

79   The plant powders were dispersed in distilled water or in oil, using a Polytron rotor-stator (PTG 30/2,  
80   Kinematica AG, Switzerland) at 10, 000 rpm for 2 min at room temperature. The reference particle  
81   load was set at 100 mg of powder.g<sup>-1</sup> of oil, corresponding to 4.8% wt/wt. This value is commonly  
82   cited in the literature on food, for starch, for example. Emulsification was carried out using the same  
83   Polytron rotor-stator device at 10, 000 rpm for 3 min at room temperature, by adding the oil in the  
84   aqueous dispersion all at once or the reverse, i.e. adding water to oil. The final emulsion was 50/50  
85   (wt/wt) oil in water. Emulsions were immediately sampled for the following tests.

86

87           2.3 Flow curve measurements

88   Apparent viscosity ( $\eta$ , Pa.s) of the emulsions was measured using a MCR 301 rheometer (Anton Paar,  
89   Graz, Austria) with a striated plate-plate geometry (5 cm diameter, gap of 1 mm, using a solvent trap  
90   to avoid any change in water content). The temperature was set at 25 °C and controlled with a Peltier  
91   plate. The shear rate explored ranged from 0.1 s<sup>-1</sup> to 100 s<sup>-1</sup>. Experimental data were fitted by a power  
92   law equation giving the shear-thinning index. All measurements were made in triplicate. For oat  
93   emulsions that showed some draining, all the rheological measurements were performed on the upper  
94   emulsified phase.

95

96           2.4 Viscoelastic properties

97   The storage  $G'$  (Pa) and loss  $G''$  (Pa) moduli were determined at 25 °C (Peltier plane) using a MCR  
98   301 rheometer (Anton Paar, Graz, Austria) with a striated plate-plate geometry (5 cm diameter, 1 mm  
99   gap, using a solvent trap to avoid any change in water content). A frequency sweep was carried out  
100   from 100 to 0.1 Hz, with a 0.2 % strain, taken from the viscoelastic linear domain of all samples. All  
101   measurements were made in triplicate.

102

103           2.5 Particle size distribution

104   Particle size distribution was measured using a Mastersizer 2000 analyzer (Malvern Instruments,  
105   Worcestershire, UK). Measurements were made using a liquid cell at room temperature (RI = 1.545,

106 RI dispersant 1.33, Ab 0.1) on emulsions 10-fold diluted with distilled water. Particle size distribution  
107 is expressed as volume of particles (%) =  $f(\text{size } (\mu\text{m}))$ . Three repetitions were performed for each  
108 sample at day 0 (the day the emulsion was produced) and one week later at day 8.

109

## 110 2.6 Microscopy

111 Dispersions and emulsions were observed under a light microscope (MZ6, Leica, Germany). Five  
112 snapshots per sample were taken at 20-fold magnification. Confocal scanning electron microscopy  
113 (CLSM) was performed using a TCS SP8 AOBS reversed microscope (Leica, Germany), equipped  
114 with a helium-neon laser (458 nm excitation wavelength) and an argon laser (633 nm excitation  
115 wavelength). The emulsions were double stained with DyLight 488 nm ((Thermo Fisher Scientific,  
116 USA) for proteins, which appear in green, and Bodipy 665/676 nm for fat (Invitrogen, USA), which  
117 appear in red. Two samples were taken from each emulsion and 5 images were taken of each sample.  
118 Representative images were selected to illustrate the microstructure of the emulsions.

119

## 120 2.7 Emulsion stability over time

121 Emulsions were sampled in test tubes (diameter 1 cm), filled to a height of 6.5 mm. Transmitted and  
122 backscattered light was measured using a Turbiscan® device (Formulaction, Toulouse, France). The  
123 emulsions were monitored for one or two weeks to determine if coalescence and/or creaming remained  
124 stable.

125

# 126 3. Results & Discussion

## 127 3.1 Comparison of apple and oat bran powders

128 The ability of the two plant powders to stabilize rapeseed oil in water emulsions was compared based  
129 on changes in several indicators over time. First, the oil droplet size distribution, then backscattered  
130 light were used to assess stability against coalescence and gravity dependent phenomena, such as  
131 creaming or sedimentation. Storage and loss moduli were studied to determine the structure of the  
132 emulsions.

133

134 **Figure 1: Microstructure profiles of 50% wt oil in water emulsions made with apple or oat powder with 100 mg of**  
135 **powder.g<sup>-1</sup> of oil: light microscopy images at (a) day 0 for apple, (b) day 0 for oat, (c) day 0 for apple magnification x3,**  
136 **(d) day 15 for apple and (e) day 15 for oat with scale bars (a, b, d, e) = 100 μm and scale bar (c) = 300 μm; (f) size**  
137 **distribution profile of apple (dots) and oat (triangles) at day 0 (black symbols) and Day 15 (empty symbols). Average**  
138 **values, n = 3.**  
139

140 Three size classes are shown in Figure 1f: 1) a few particles ca. 1 μm in diameter could be very small  
141 droplets stabilized by the soluble components of the powders (proteins, intrinsic surfactants, pectins);  
142 2) a second particle population ca. 6 μm in diameter, which is the size of the powder particles  
143 measured after dispersion that could correspond to insoluble particles in excess; 3) the third most  
144 common particles were bigger, around 30 μm in diameter for apple and 45 μm for oat at d0, this  
145 population corresponded to the oil droplets. These hypothetical sizes were consistent with light  
146 microscopy observations, in which the main diameter of the oil droplets were bigger in oat emulsions  
147 than in apple emulsions at day 0. High polydispersity among the sizes of the oil droplets was observed  
148 in the two types of emulsion. The close up (Fig 1.c) shows some thin particles around the droplets (the  
149 example given is an apple emulsion but the same phenomenon was also visible with the oat powder).  
150 In the present study, the oil droplets are clearly bigger than those usually obtained with surfactants or  
151 proteins, which would be more consistent with the first classes around 1 μm listed above. However,  
152 their size is comparable with the average sizes obtained in Pickering emulsions made with plant  
153 particles such as starches, with particles ranging from 0.360 to 10 μm (raw starch and nanoparticles)  
154 and oil droplets ranging from 10 to 100 μm [14, 15, 16, 17]. This order of magnitude is also reported  
155 in studies using cellulose particles, such as cocoa, where a fraction of fibers around 2 μm stabilized the  
156 oil droplets with an average diameter of 10 μm [18], or milled cellulose particles with diameters  
157 ranging from 40 to 670 nm that give the droplets an average diameter of 40 to 60 μm [19]. The present  
158 size distribution profile is also close to the one obtained for oil in water emulsions made with  
159 microfibrillated cellulose from mangosteen rind [9]. Therefore, it is probable that the apple and oat  
160 insoluble particles of the present study were able to stabilize the emulsions through Pickering  
161 mechanism. However, this was a very challenging hypothesis to confirm on its own since 1) the

162 soluble elements also played a role and 2) the particles created a network that can entrap the oil  
163 droplets, as will be showed on Fig.3.

164 Between day 0 and day 15, emulsions made with apple powder displayed a significantly increasing  
165 average diameter, from 30 to 45  $\mu\text{m}$  with time, while the size distributions of emulsions made with oat  
166 powder remained more stable (the average diameter increased from 45 to 50  $\mu\text{m}$  at the main peak).

167 This is confirmed by the microscopy image (fig 1d and fig 1e) showing bigger droplets in the apple  
168 emulsion at D15 than at D0, pointing to more marked coalescence phenomena in emulsions stabilized  
169 with apple powder. In addition to the insoluble particles, the soluble components (such as protein)

170 also contributed some stabilizing properties to the overall size distribution profile. This was  
171 qualitatively confirmed by using the supernatant obtained after centrifuging apple and oat dispersions  
172 containing the same amount of powder to test whether or not it could stabilize an emulsion of its own.

173 The results showed that even if the emulsions were much less stable than their “soluble + insoluble  
174 content” counterparts, they could still be created using the supernatants only, and that apple produced  
175 bigger droplets than oats (data not shown). Therefore, the soluble elements did exhibit some

176 stabilizing potential, even though a real difference was observed when the whole powders were used.  
177 It is possible that the water soluble components of the apple powder (more important considering the  
178 Brix level) were responsible for the droplets present at day 0, that were not stable with time, thus

179 shifting the average diameter of the droplets towards bigger sizes, with the main peak corresponding to  
180 droplets stabilized by particles (actual Pickering effect) and/or entrapped in the solid particles network  
181 (see Fig.3). It thus appears that oat powder is a better protector against coalescence than apple powder

182 even if both of them displayed the same average size for oil droplets after two weeks of storage. One  
183 possible explanation is that the starch fraction of this powder reinforces the interfacial steric barrier  
184 already formed by the cellulose particles

185 The macroscopic stability of the emulsions was monitored using Turbiscan®, which made it possible  
186 to record backscattered light along the height of the solution over time (Figure 2).

187

188 **Figure 2: a) Changes in the backscattered light profile with time (day 0 in black and day 15 in grey) for 50%wt**  
189 **oil/water emulsions made with apple (left) or oat powder (right) with 100 mg of powder.g<sup>-1</sup> of oil; b) and c) photos of**  
190 **the apple emulsions at day 0 and day 15; d) and e) photos of the oat emulsions at Day 0 and Day 15.**

191

192 The intensity of backscattered light of the apple and oat emulsions was very similar at day 0, with an  
193 average value of 64% along the tube and this value did not change much between day 0 and day 15.  
194 The signal for apple emulsions decreased slightly corresponding to the slight coalescence that occurred  
195 between day 0 and day 15, in good agreement with the particle size distributions. For oat emulsions,  
196 the change over time was more distinct, with a decrease in the backscattered light intensity at the  
197 bottom of the tube at day 15 (0.3 cm in height), from initially 64% down to 20% to 30%. This resulted  
198 in more translucency at the bottom of the tube, and can be explained by some draining of the  
199 continuous phase from the emulsion, leading to the concentration of the oil droplets in the upper  
200 phase. The backscattering signal of the upper phase remained unchanged as no significant coalescence  
201 was observed. Monitoring of the backscattered light produced the same results as visual observations  
202 of a larger volume of emulsions (100 mL), as shown in Fig. 2b-e. The draining phenomenon in the oat  
203 emulsion was very clear at day 15 (Fig. 2e), when the bottom of the cup was translucent (water phase).  
204 Regarding the rheological properties, dynamic measurements showed that a gel was created in both  
205 apple and oat emulsions, since the storage modulus  $G'$  was always higher than the loss modulus  $G''$   
206 and independent of the frequency over two decade in the apple emulsions, from day 0 to day 15.  
207 (Figure 3).

208

209 **Figure 3: Dynamic rheological profiles for 50% wt rapeseed oil/ water emulsions made with apple (left) or oat powder**  
210 **(right) with 100 mg of powder.g<sup>-1</sup> of oil, at day 0 (black) and day 15 (grey) - storage modulus  $G'$  (full symbols) and loss**  
211 **modulus  $G''$  (empty symbols). Average values, n = 3. All tests were carried out on the emulsions, i.e. whole sample for**  
212 **apple and upper phase for oat, without the slightly drainage**  
213

214 This viscoelastic behavior is common in emulsions, especially in the present case where 50% of oil is  
215 dispersed in 50% of water, reaching a closely packed system. However, the plateau value of  $G'$  at low  
216 frequency was almost 5 times higher for apple emulsions than for oat ones, with  $49.2 \pm 3.2$  Pa versus  
217  $10.7 \pm 3.9$  Pa, respectively. The order of magnitude of  $G'$  is consistent or slightly lower than the  
218 values obtained in several studies in which plant fibers were used to stabilize emulsions, ranging from  
219 10 to 100 Pa for mangosteen rind microfibrillated cellulose [9] and from 50 to 200 Pa for cherry fibers  
220 [5]. The present emulsions displayed different behaviors over time, since in oat emulsions, both  $G'$   
221 and  $G''$  values increased from respectively 10 to 225 Pa and from 3 to 30 Pa in 15 days. This increase

222 may be due to the fact that at day 15 we took the samples from the upper phase of the cups, i.e. from  
223 the concentrated emulsion (Fig 2e). Even though the concentration phenomenon was not very  
224 important, *i.e.* 5.2% concentration based on the calculation of the heights in Fig. 2a for oats, it could  
225 still have a major impact on the dynamic rheology measurements of highly concentrated emulsion.  
226 Tangent  $\delta$  (ratio  $G''/G'$ ) decreased from 0.3 to 0.1, highlighting a gel structure. In contrast, in the  
227 apple emulsions the storage and loss moduli remained very close between day 0 and day 15,  
228 underlining the stability of the gel structure. More information on the difference in behavior between  
229 apple and oat emulsions was acquired by analyzing the behaviors of powders dispersed in water with  
230 no added oil. The concentration was set at 10% wt, which is twice the concentration of the particles in  
231 the previously described emulsions, in order to match the volume of the particle fraction in the 50%  
232 water that can be found in these emulsions. Then, after the same preparation protocol as for the  
233 emulsions (using the rotor-stator twice), oscillatory measurements were performed on the apple and  
234 oat dispersions. At day 0,  $G'$  was higher than  $G''$  in both dispersions, with  $2.2 \pm 1.5$  Pa for apple and  
235  $0.16 \pm 0.04$  Pa for oat and  $G'$  was independent of the frequency for a week. Even if these values are  
236 low, especially for oat, and the variation coefficient was high, it still highlighted (weak) gel properties.  
237 At day 1, sedimentation was already clear in the oat powder suspension. The same phenomenon  
238 occurred in the apple powder, but only became visible at day 3. No measurements were possible in  
239 either case at these times. This experiment showed that the particles in the apple powder, perhaps in  
240 combination with the soluble elements, were able to create a network able to persist for at least 24 h.  
241 This allowed the validation that solid particles of the present study were able to connect to each other  
242 even without fat droplets. This reinforces the elements in favor of a network created by the particles  
243 around the fat droplets as a probable mechanism in the stabilization of the emulsions by oat and  
244 especially apple powder. This can come in combination with the ability of the solid particle to adsorb  
245 at the interface, but we were not able to decorelate these two phenomena in order to further prioritize  
246 them.

247 Regarding rheological properties, apple powder displayed a higher stabilizing potential than oat  
248 powder, since the network created during emulsification remained unchanged over time. A mixed

249 network of particle-stabilized oil droplets and powder particles may have been created. It is therefore  
250 logical that creaming did not occur in the apple emulsions.

251 The flow profiles of the emulsions were also recorded at different shear rates. Both emulsions were  
252 very shear-thinning systems, with apparent viscosity at  $50\text{ s}^{-1}$  of  $400 \pm 40\text{ mPa}\cdot\text{s}$  and a shear-thinning  
253 index of 0.38 for apple, compared with  $170 \pm 50\text{ mPa}\cdot\text{s}$  and 0.51 for oat, at day 0. Apple-stabilized  
254 emulsion displayed higher shear thinning behavior thereby highlighting the difference in structure.

255  
256 Apple powder therefore had the best stabilizing potential against draining. It also resulted in stronger  
257 gels ( $G'$  5 times higher in the apple emulsion than in the oat emulsion at day 0). Oat powder appeared  
258 to better avoid coalescence and the emulsions were also lighter in color than the brownish apple  
259 emulsions. In both cases, the emulsifying properties of the powders are based on their insoluble  
260 content, which was absolutely necessary in order to achieve a good stability and a network formation,  
261 since the soluble elements (including proteins) were not sufficient for stabilizing the 50/50% oil in  
262 water emulsions. We can also hypothesize that solid particles can adsorb at the interface, which would  
263 produce Pickering emulsions. What we know for sure is that they were responsible for the creation of  
264 a network with and around the oil droplets. However, soluble elements are also involved in the  
265 stabilizing potential, probably through some native proteins (especially in apple powder with 5.2%  
266 wt/wt), but also thanks to the pectins in the apple powder and maybe some solubilized starch polymers  
267 in the oat powder.

268

### 269 3.2 Effect of the type of oil on emulsion stability

270 Rapeseed oil is a good candidate to evaluate the potential of the plant powders for food applications.  
271 However, given the 50% oil ratio, it did not seem overly realistic to consider only food products.  
272 Therefore, using apple powder, two other oils commonly used for cosmetics were studied: myrtil oil  
273 (which, like rapeseed oil, is mainly composed of triglycerides) and jojoba oil. The size distribution  
274 profiles were measured at day 0 and day 9 to compare how the type of oil would affect our previous  
275 results (Figure 4)

276

277 **Figure 4: Size distribution profiles for 50% wt oil/water emulsions made with apple powder with 100 mg of powder.g<sup>-1</sup>**  
278 **of oil, at day 0 (left) and day 9 (right) for 3 oils: rapeseed (◇), jojoba (◆) and myritol (◆). Average values, n = 3.**  
279

280 At day 0, jojoba oil droplets had a smaller average diameter than that of rapeseed oil (20 μm) and  
281 myritol (30 μm), whose profiles were very similar. Nine days later, jojoba emulsions underwent strong  
282 coalescence, with a large peak appearing at around 160 μm in the size distribution profile. When  
283 rapeseed oil or myritol was used, the change over time led to an increase in a first peak around 6 μm,  
284 corresponding to the solid particles, while the oil droplets remained consistent with previous results,  
285 *i.e.* some coalescence occurred with the average diameter of the droplets increasing from 30 to 45 μm  
286 for rapeseed oil and from 30 to and 52 μm for myritol. The results for myritol and rapeseed oil were  
287 very close, probably because they are both mainly composed of triglycerides. These results are in  
288 agreement with those comparing miglyol, paraffin and shea nut oil used at 56% for Pickering  
289 emulsions stabilized with quinoa starch, since the average diameter of the oil droplets ranged from 43  
290 to 73 μm depending on the type of oil [20]. Therefore, the type of oil has a marked impact on the  
291 stability of the emulsions stabilized with both apple and oat powder.

292 Regarding dynamic rheological properties, emulsions made from jojoba oil also differed from those  
293 made from rapeseed oil and myritol, which were very close (Figure 5).

294

295 **Figure 5: Dynamic rheological profiles for 50%wt oil/water emulsions made with apple powder with 100 mg of**  
296 **powder.g<sup>-1</sup> of oil for the three types of oil, at day 0 (●) and day 9 (●) for 3 oils - storage modulus G' (full circles) and**  
297 **loss modulus G'' (empty circles). Average values, n = 4, n = 4 and n = 3.**  
298

299 At day 0, the plateau values of the storage modulus G' were 1.7 times lower for emulsions made with  
300 jojoba oil than emulsions made with myritol and rapeseed oil, with respectively  $28.7 \pm 4.9$ ,  $47.3 \pm 10.7$   
301 and  $49.2 \pm 3.2$  Pa. The loss moduli were all lower than the storage ones, showing that the three  
302 emulsions made with apple powder displayed gel-like behavior, even if the behavior was less marked  
303 with jojoba oil than with myritol and rapeseed oil. Moreover, G' was independent of the frequency for  
304 at least two decades with all three oils. There was no marked change in any of the three emulsions  
305 over time, particularly with myritol. The rapeseed oil values did not change significantly between day

306 0 and day 9. The increase was significant in jojoba oil, with  $G' = 40.5 \pm 1.9$  Pa at day 9 versus  $25.3 \pm$   
307  $4.4$  Pa at day 0. This result could be due to the difficulty involved in collecting representative samples  
308 of these emulsions that were less stable over time as evidenced by the droplets sizes (Fig. 4), even if  
309 the very low standard deviations ( $n = 4$ , two samples taken from two different emulsions) suggest  
310 good reproducibility.

311 Based on the changes in the size of the oil droplets over time and the rheological properties of the  
312 emulsion, it can be reasonably hypothesized that in our experimental conditions, jojoba oil is not a  
313 good candidate to obtain stable systems. This was confirmed visually, since a thin layer of oil  
314 appeared at the surface of jojoba emulsions after a week of storage. Conversely, both rapeseed and  
315 myritol can be used satisfactorily, at the same time confirming the potential of the apple powder as a  
316 stabilizing agent for both food and cosmetic applications.

317

### 318 3.3 Optimization of emulsion stability: dispersion in oil

319 Both apple and oat powders are mainly composed of hydrophilic units: cellulose particles,  
320 carbohydrates, proteins, pectins or starch, etc. Therefore, trying to disperse the powders in water was  
321 the first obvious choice, and is widely used in the literature to make Pickering emulsions with food  
322 grade particles. However, we wondered if dispersion was also possible in oil, and what would the  
323 effect would be on the resulted emulsions. We thus applied the same process as previously, using the  
324 same ingredients, except that the powders were dispersed in oil. The example of myritol and apple  
325 powder was chosen to illustrate the results. The size distribution of the emulsions obtained after  
326 dispersing in the two media are displayed in Figure 6.

327

328 **Figure 6: Size distribution profiles for 50% wt oil/water emulsions made with apple powder with 100 mg of powder.g-**  
329 **<sup>1</sup> of myritol, at day 0 (●), day 3 (●) and day 9 (○) when apple powder was dispersed in myritol (left) and in water**  
330 **(right). Average values, n = 3.**

331

332 At day 0, the size profiles of the two emulsions were close, even though the main peak was narrower  
333 with a dispersion in oil ( $\sim 30 \mu\text{m}$ ), the size of the oil droplets thus appeared to be less polydispersed  
334 and more homogeneous. More surprisingly, the size distribution profile did not change over time when  
335 the apple powder was dispersed in oil. It was as if the droplets were better protected against

336 coalescence in this case, compared to dispersion of the powder in water, in which there was an  
337 increase in the main peak, as described above. When apple powder was dispersed in myritol rather  
338 than in water, the main difference is that the water soluble elements remain organized around the solid  
339 particles and were unable to proceed to the continuous phase and hence to participate to the  
340 emulsifying process.

341 When the dispersions were examined under a light microscope, the apple powder in oil appeared to be  
342 a continuous layer, whereas in water, some clusters were visible, suggesting that dispersing the  
343 powder in myritol avoided aggregation. It could also be due to swelling of the particles, but this was  
344 not our primary hypothesis since the droplets created after emulsification all displayed the same  
345 average size of 30  $\mu\text{m}$  whatever the original dispersion medium, in which case the droplets stabilized  
346 with solid particles would not be subject to coalescence in either case, and in the case of dispersion in  
347 water, the shift from 30 to 45  $\mu\text{m}$  (or 52  $\mu\text{m}$  at day 9) could be attributed to the coalescence of droplets  
348 stabilized by water soluble elements, as discussed above. It would also explain why the main peak was  
349 narrower for oil dispersion than for water dispersion, since only one main type of droplet was created.  
350 The impact of the dispersion medium on the emulsions was also tested with respect to their rheological  
351 properties, using dynamic measurements (Figure 7).

352

353 **Figure 7: Dynamic rheological profiles for 50%wt oil/water emulsions made with apple powder with 100 mg of**  
354 **powder.g<sup>-1</sup> of myritol, at day 0 (●), and day 9 (●) when apple powder was dispersed in water (left) and in oil (right) -**  
355 **storage modulus G' (full symbols) and loss modulus G'' (empty symbols). Average values, n = 3.**  
356

357

358 At day 0, no significant difference was observed in the viscoelastic profiles of the emulsions made  
359 from apple powder dispersed in water or in oil (Figure 7). They both exhibited gel characteristics with  
360  $G' > G''$  and independent to the frequency over two decades. After one week, the gel characteristics  
361 were still present, with no significant difference between the dispersion media. Visually, the texture of  
362 the emulsions was also very similar.

363 Finally, we wondered if changing the dispersion medium would change the emulsion from an oil-in-  
364 water to a water-in-oil emulsion. Confocal laser scanning microscopy was used to make sure the  
365 systems were comparable, since it can specifically distinguish stained fat from proteins (Figure 8).

366

367 **Figure 8: Confocal microscopy images of 50% wt oil in water emulsions made with apple powder and 100 mg of**  
368 **powder.g<sup>-1</sup> of myritol at day 0, originating from dispersion of powder in water (top row) or in oil (bottom row). Double**  
369 **staining: proteins in green and fat in red. Magnifications x10 (scale bar = 100 μm) and x40 (scale bar = 200 μm).**  
370

371 Based on these images, the type of emulsion, *i.e.* oil in water, remained unchanged whether the  
372 powder was previously dispersing the powder in water or in myritol. Two magnifications were used to  
373 characterize the microstructure of the emulsions. At x10 magnification, the closely packed network  
374 was clearly visible, with the oil droplets in red dispersed in a green matrix. Images of the emulsion  
375 obtained by dispersing the powder in water had to be taken closer to the lamella due to a higher  
376 extinction of the signal with depth. This may explain some big pools of fat compared to dispersion in  
377 oil. However, no other significant difference between the two dispersion modes was found. At x40  
378 magnification, a green background was clearly visible, probably due to the proteins solubilized in the  
379 continuous water phase (5.2% of the powder for apple), in which black holes were embedded (fat  
380 droplets and air bubbles). We decided to display only the green probe in order to focus on the particles  
381 that were clearly visible in these close up images. Indeed, some dark objects were visible around the  
382 spherical oil droplets (white arrows in Figure 8). These objects did not have a specific shape, although  
383 some appeared to be elongated. What appeared more clearly is that they were connected to each other  
384 and also connected the droplets to each other, thereby creating a network, as presumed after  
385 rheological measurements.

386

#### 387 **4. Conclusion**

388 The two food byproducts studied (apple pomace from *Pyrus Malus* and oat bran from *Avena Sativa*)  
389 were found to have very useful emulsifying properties, especially when used with myritol and  
390 rapeseed oil, while jojoba oil led to less stable emulsions. Both powder-stabilized emulsions sustained  
391 gel behaviors over a period of two weeks. No creaming was observed. Emulsions made with oat  
392 powder were less stable with respect to draining, which is why apple powder is a better candidate than  
393 oat powder as natural stabilizer, even if the brown color could cause a problem for cosmetic  
394 applications for example. Slight coalescence occurred between day 0 and day 3, after which the size

395 distribution of the droplets remained constant until day 15. This could be due to changes in the  
396 droplets stabilized by the water soluble fraction. The emulsions were very easily optimized by  
397 dispersing the powder in oil instead of water, prior to emulsification. The slight coalescence observed  
398 between day 0 and day 3 no longer occurred. The innovative potential of these powders relies on their  
399 biosourcing, the minimal processing used during their manufacture (drying and micronization, no  
400 purification or fractionation and no solvent used). Therefore, the insoluble and soluble fractions were  
401 complementary. Since less purified raw materials are the key to more responsible formulation of  
402 bioproducts, in the future, it would be interesting to assess the variability of these materials and to test  
403 scaling up such applications. It would also be interesting to see how such complex powders interact  
404 with the other ingredients commonly found in food or cosmetic products.

405

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409

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Apple powder

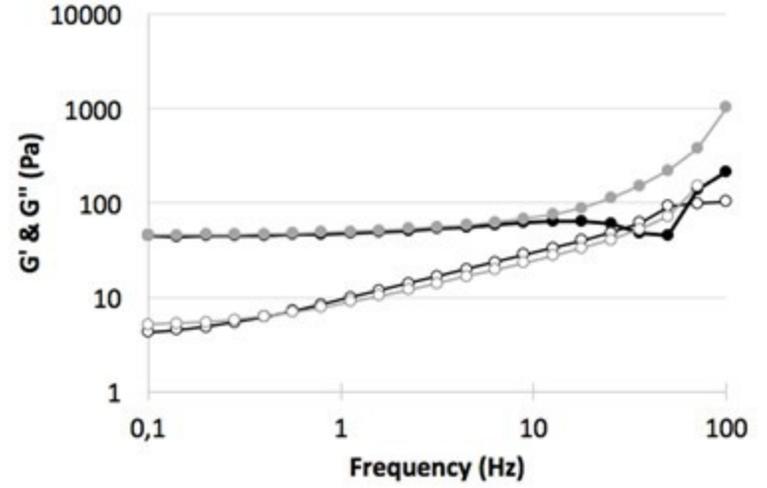
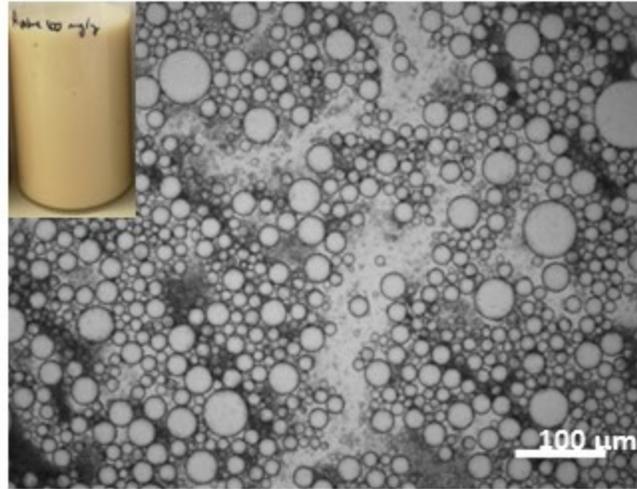
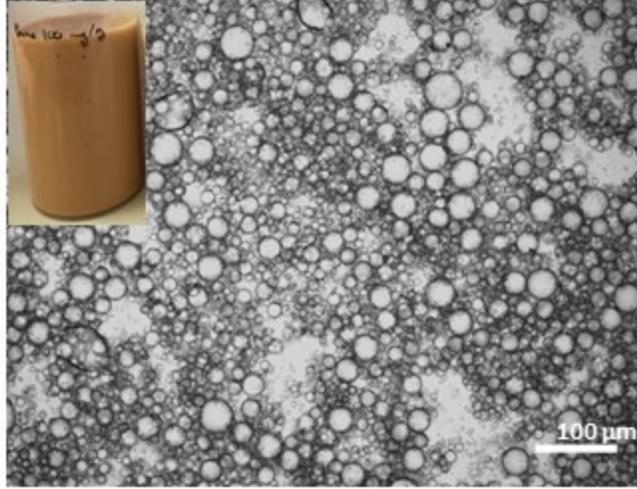


Water

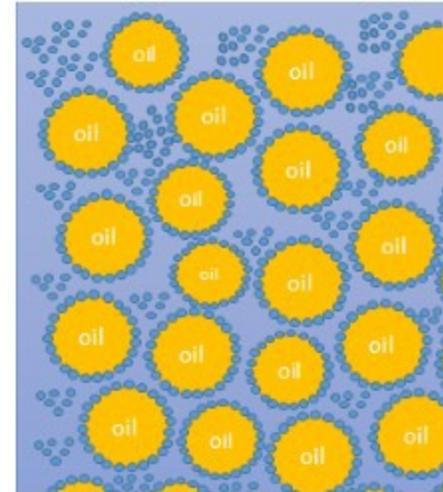
oil



Oat powder



Gel like structure?



Oat or apple particles