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Title: SURFACTANT-AIDED ELECTROSPRAYING OF LOW MOLECULAR WEIGHT CARBOHYDRATE POLYMERS FROM AQUEOUS SOLUTIONS

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Abstract: In this work it is demonstrated, for the first time, that it is feasible to develop, using the electro spraying technique, low molecular weight carbohydrate-based capsule morphologies from aqueous solutions through the rational use of surfactants. Two different low molecular weight carbohydrate polymers were used, a maltodextrin and a commercial resistant starch. The solution properties and subsequent high voltage sprayability was evaluated upon addition of non-ionic (Tween20, and Span20) and zwitterionic (lecithin) surfactants. The morphology and molecular organization of the structures obtained was characterized and related to the solution properties. Results showed that, while unstable jetting and dropping occurred from the pure carbohydrate solutions without surfactant, the addition of some surface active molecules above their critical micelle concentration facilitated capsule formation. Higher surfactant concentrations led to smaller and more homogeneous capsule morphologies, related to lower surface tension and higher conductivity of the solutions.

Highlights

- Electrospraying was used to develop low Mw carbohydrate-based capsules
- Surfactant addition above the CMC allowed capsule formation from aqueous solutions
- Surfactant type and concentration influenced capsule size and morphology
- Changes in capsule size upon surfactant addition were related to solution properties
- Smaller and more homogeneous capsules obtained increasing surfactant concentration

1 SURFACTANT-AIDED ELECTROSPRAYING OF LOW MOLECULAR WEIGHT

2 CARBOHYDRATE POLYMERS FROM AQUEOUS SOLUTIONS

3

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10

11

12 **Abstract**

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14 electro spraying technique, low molecular weight carbohydrate-based capsule morphologies  
15 from aqueous solutions through the rational use of surfactants. Two different low molecular  
16 weight carbohydrate polymers were used, a maltodextrin and a commercial resistant starch.  
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21 the pure carbohydrate solutions without surfactant, the addition of some surface active  
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26 **Keywords:** Electro spraying, electro spinning, encapsulation, surfactant, aqueous solution,  
27 carbohydrate

## 28 1. Introduction

29 The development of micro-, submicro- and nanostructures from biopolymers for functional  
30 food applications is an emerging area of interest. Apart from the conventional  
31 microencapsulation techniques, such as spray drying or coacervation, electrospinning has  
32 been recently suggested to be a simple and straightforward method to generate submicron  
33 encapsulation structures for a variety of bioactive molecules (Xie, Li & Xia, 2008; Lopez-Rubio  
34 & Lagaron, 2012; Bock, Dargaville, & Woodruff, 2012). Electrospinning is a process that  
35 produces continuous polymer fibers with diameters in the submicrometer range through the  
36 action of an external electric field imposed on a polymer solution or melt. The electrospun  
37 nanostructures morphology is affected by the solution properties (mainly by the viscosity,  
38 surface tension and conductivity of the polymer solution) and by the process parameters  
39 (voltage, flow rate of the solution, tip-to-collector distance). For certain materials, size-reduced  
40 capsules can be obtained when lowering the polymer concentration and/or increasing the tip-  
41 to-collector distance. In this case, the electrospinning process is normally referred to as  
42 “electrospraying” due to the non-continuous nature of the structures obtained. To date, a  
43 wide variety of polymers and polymer blends have been electrospun, with synthetic polymers  
44 yielding the best results in terms of physical properties and uniformity. On the other hand,  
45 electrospinning of biopolymer solutions has been proven to be difficult due to several factors  
46 such as the polycationic nature of many biopolymers, the low chain flexibility which  
47 complicates chain entanglements (essential for fiber formation) and their generally poor  
48 solubility in organic solvents (Kriegel, Kit, McClements, & Weiss, 2009). Moreover, unlike  
49 synthetic polymers, a natural polymer derived from different sources presents widely varying  
50 properties and it has been observed that the viscosity of the solutions may vary with time due  
51 to, for instance, aqueous hydrolysis of the biopolymer (Bhattarai & Zhang, 2007).

52 Electrospinning from aqueous solutions is beneficial from an environmental point of view.  
53 Furthermore, the use of water does not generate toxicity problems. On the contrary, organic

54 solvents may be even prohibited for certain applications, such as in the case of food products  
55 (Kriegel, Kit, McClements, & Weiss, 2010). That issue further complicates the electrospinning  
56 process due to the ionization of water molecules at high voltages in an air environment, which  
57 may cause corona discharge. Besides, aqueous solutions present high surface tension values  
58 which hinder the formation of stable jets during the electrospinning. Moreover, polymers that  
59 have low aqueous solubility, low  $M_w$  polymers and polymers with rigid or globular structures  
60 that do not generate sufficient viscosity are not easily electrospun when they are in an  
61 aqueous solution (Nagarajan, Drew, & Mello, 2007; Stijnman, Bodnar & Tromp, 2011).  
62 Different surfactants have been added to the electrospinning solutions for various purposes,  
63 like enzyme stabilization (Herricks et al., 2005), creation of mesoporous structures (Hong, Fan,  
64 & Zhang, 2009; Hou et al., 2009), or to make compatible hydrophilic fillers with hydrophobic  
65 matrices (Kim, Lee, & Knowles, 2006). However, more importantly, surfactants have been seen  
66 to improve the spinnability of polymer solutions, which is normally a consequence of the  
67 reduction in their surface tension (Bonino et al., 2011). To the best of our knowledge, all the  
68 studies carried out to date in this area, relate to fiber formation and it has been demonstrated  
69 that addition of surfactants reduce fiber defects, but do not promote fiber formation for  
70 solutions which are not readily spinnable (Aceituno-Medina, Lopez-Rubio, Mendoza, &  
71 Lagaron, 2013). However, the effect of surfactant addition on the sprayability or capsule  
72 formation from biopolymer solutions is unknown.

73 In this study, we hypothesize that addition of surfactants to aqueous biopolymer solutions may  
74 prove to be a convenient **method** to produce encapsulation structures by modulating the  
75 electrospaying conditions. To test this hypothesis, various surfactants (a zwitterionic and two  
76 nonionic surfactants) were added to two different low molecular weight carbohydrate polymer  
77 solutions. Solutions were subjected to electrospaying and the influence of surfactant type and  
78 charge on solution properties and on the morphology of the submicron structures generated  
79 were evaluated.

80

81 **2. Materials and Methods**

82 2.1 Materials

83 A maltodextrin with a DE value of 16.5-19.5 was purchased from Sigma Aldrich. A commercial  
84 resistant starch (derived from corn starch) with trade name Fibersol® ([www.fibersol.com](http://www.fibersol.com))  
85 manufactured by ADM/Matsutani (Iowa, USA) was used. The non-ionic surfactants,  
86 polyoxyethylene sorbitan monolaurate (Tween20) and sorbitan monolaurate (Span20), and  
87 the zwitterionic surfactant, L- $\alpha$ -phosphatidylcholine (lecithin) were supplied by Sigma-Aldrich.  
88 All products were used as received without further purification.

89

90 2.2 Determination of the critical micelle concentrations (CMC) for each surfactant by plate  
91 tensiometry

92 The CMC of surfactants in the absence and presence of the low molecular weight carbohydrate  
93 polymers was determined by measuring the surface tension as a function of surfactant  
94 concentration through a digital tensiometer (model EasyDyne K20, Krüss GmbH, Hamburg,  
95 Germany) using the Wilhemy plate method. An amount of 30 g of each test solution was  
96 poured into an 80 mm diameter glass beaker. The glass had been previously rinsed with  
97 absolute ethanol and deionized and distilled water and then dried at 70°C to remove any  
98 surface-active material. All measurements were done in triplicate after equilibrating the  
99 solutions at 25°C.

100

101 2.3 Preparation of carbohydrate-based solutions

102 Carbohydrate-based solutions were prepared by dissolving a 20 wt.-% of the materials in  
103 distilled water through gentle stirring at room temperature. Different concentrations of the  
104 various surfactants (0, 5, and 30 wt.-% with respect to the biopolymer weight) were added to  
105 the solutions.

106

107 2.4 Characterization of the carbohydrate-based solutions

108 The apparent viscosity ( $\eta_a$ ) of the polymeric solutions at  $100 \text{ s}^{-1}$  was determined using a  
109 rotational viscosity meter Visco Basic Plus L from Fungilab S.A. (San Feliu de Llobregat, Spain)  
110 using a Low Viscosity Adapter (LCP). The surface tension of the biopolymer solutions was  
111 measured using the Wilhemy plate method in an EasyDyne K20 tensiometer (Krüss GmbH,  
112 Hamburg, Germany). Both tests were carried out in triplicate. The conductivity of the solutions  
113 was measured using a conductivity meter XS Con6 (Labbox, Barcelona, Spain). All  
114 measurements were made at  $25^\circ\text{C}$ .

115

116 2.5 Preparation of carbohydrate-based capsules through electrospraying

117 The electrospraying apparatus, equipped with a variable high-voltage 0-30 kV power supply,  
118 was a single needle Fluidnatek<sup>®</sup> basic setup from Bioinicia S.L. (Valencia, Spain). The syringe  
119 containing the carbohydrate solutions was placed horizontally to the collector. The distance  
120 between the needle and the collector was set at 10 cm. The experimental setup was housed in  
121 a laminar flow safety cabinet. The electrosprayed capsules were obtained using a voltage of 9  
122 kV and a flow rate of 0.15 mL/h.

123

124 2.6 Infrared spectroscopy

125 Attenuated total reflectance infrared spectroscopy (ATR-FTIR) experiments were performed in  
126 a controlled chamber at  $21^\circ\text{C}$  and 40% RH coupling the ATR accessory GoldenGate of Specac  
127 Ltd. (Orpington, UK) to a Bruker (Rheinstetten, Germany) FTIR Tensor 37 equipment. All the  
128 spectra were collected within the wavenumber range of  $4000\text{--}600 \text{ cm}^{-1}$  by averaging 15 scans  
129 at  $4 \text{ cm}^{-1}$  resolution. Analysis of the spectral data was performed by using Grams/AI 7.02  
130 (Galactic Industries, Salem, NH, USA) software.

131

132 2.7 Scanning electron microscopy (SEM)



133 SEM was conducted on a Hitachi microscope (Hitachi S-4100) at an accelerating voltage of 10  
134 KV and a working distance of 15 mm. The electro sprayed capsules were sputtered with a gold-  
135 palladium mixture under vacuum before their morphology was examined using SEM. Capsule  
136 diameters of the electro sprayed materials were measured by means of the Adobe Photoshop  
137 CS3 extended software from the SEM micrographs in their original magnification.

138

139

140 **3. Results and Discussion**

141 3.1 Critical micelle concentration (CMC) of the different surfactants

142 Surfactants are amphiphilic molecules that readily adsorb at surfaces, thereby lowering surface  
143 or interfacial tension of the medium in which they are dissolved. Moreover, above a critical  
144 concentration, the so-called critical micelle concentration, surfactants self-assemble to form a  
145 variety of colloidal structures, which have different properties from those of the dissolved  
146 surfactant monomers, e.g., solubility, surface hydrophilicity, charge density. Previous studies  
147 have demonstrated that addition of non-ionic and ionic surfactants above their critical micelle  
148 concentration to polymer solutions, significantly improved the electrospinning process  
149 generating defect-free fibers (Kriegel et al., 2009). Therefore, in this study, the first intention  
150 was to add different surfactants above their CMC to study their influence on the sprayability of  
151 low  $M_w$  carbohydrates. The CMC informs about the concentration of surfactant necessary to  
152 form a monolayer of molecules oriented at the air-water interface (Lin, Wang, Wang & Wang,  
153 2004; Chou, Krishnamurthy, Randolph, Carpenter & Manning, 2005). On the other hand, the  
154 concentration needed for the polymer-surfactant association is the critical aggregation  
155 concentration (CAC) and it is usually lower than the CMC by a factor between 1 and 10. Both  
156 the surfactant concentration and the polymer-surfactant interactions may result in changes in  
157 the rheology and conductivity of the solutions, factors which greatly affect the  
158 electrospinning/ electrospraying process (Lin et al. 2004).

159 Initially, the surface tension for different surfactant concentrations in aqueous solution in the  
160 absence and presence of the low molecular weight carbohydrates was measured and CMC  
161 values were determined when the plateau in surface tension was obtained. Table 1 shows the  
162 CMC values for the different surfactants assayed and the concentration added in the solutions.  
163 For all the solutions tested it was observed that very low concentrations of the surfactants  
164 were needed to reach the CMC, regardless of whether the carbohydrates were present. It was  
165 also observed that CMC increased with the addition of the biopolymers probably because the

166 surfactants were also interacting with the biopolymers in solution. It is possible that in the  
167 presence of carbohydrates, the concentration of the surfactants in the surface decreased, as  
168 part of the surfactant was bound to the carbohydrates. As a result, the amount of surfactant  
169 needed to reach the CMC increased (Chou et al., 2005). Knowing this plateau value, two  
170 different concentrations of each surfactant (5 and 30 wt.%) were added to the carbohydrate  
171 solutions, which corresponded to 28.9 mM of Span20, 8.2 mM of Tween20 and 13.2 mM of  
172 lecithin when 5% of surfactant with respect to the biopolymer weight was added; and 173.2  
173 mM of Span 20, 49.0 mM of Tween 20 and 79.0 mM of lecithin when 30% of surfactant with  
174 respect to the biopolymer weight was incorporated. Please note that both concentrations  
175 were well **higher than** the CMC of the surfactants.

176

177 **INSERT TABLE 1 ABOUT HERE**

178

### 179 3.2 Solution properties

180 The physical properties of the carbohydrate-surfactant solutions are critical in the successful  
181 preparation of the electrosprayed structures. Therefore, the conductivity, viscosity and surface  
182 tension of the different solutions were measured and the results are summarized in Table 2.

183 From these data it is observed that the addition of resistant starch to water did not  
184 considerably increase the conductivity of the solvent because this material did not present any  
185 electrical charge. On the contrary, the maltodextrin-based solutions presented enhanced  
186 conductivity values. This fact could be due to maltodextrin forming charged ions when  
187 dissolved in water. From Table 2, it is also observed that addition of non-ionic surfactants to  
188 the resistant starch solutions produced a slight increase in the conductivity, probably due to  
189 the existence of polar groups in this molecule (Lin et al. 2004). However, when Span20 and  
190 Tween20 were incorporated to the maltodextrin solutions, they did not affect the conductivity,  
191 showing that the effect of these surfactants in the solution conductivity is very limited and it is

192 only relevant when the solution presents very low conductivity. In contrast, addition of lecithin  
193 led to higher conductivity in both carbohydrate solutions. This fact was related to the  
194 zwitterionic nature of the lecithin which presents asymmetric positive and negative electric  
195 charges. These charges were dissociated in aqueous solution and thus, led to an increase of  
196 the electrical conductivity (Hunley, England & Long, 2010). Concerning the viscosity, it was  
197 seen that very low values were obtained regardless the absence or presence of the  
198 surfactants. These results were expected, since the low molecular weight carbohydrates used  
199 in this study would require greater concentrations to achieve comparable solution viscosities  
200 to high molecular weight polymers. In particular, the addition of Span20 and Tween20 hardly  
201 increased the viscosity values. However, addition of lecithin increased the solutions viscosity  
202 from ca. 2 to 5 cP, probably because the interactions between the carbohydrates and the ionic  
203 surfactant were stronger than those with the non-ionic surfactants. Nevertheless, low viscosity  
204 values are needed for electrospraying, since higher viscosity favors the formation of fibers  
205 instead of spherical capsules (beads) (Fong, Chun & Reneker, 1999). Finally, Table 2 shows the  
206 surface tension of the different solutions assayed. It was observed that surface tension values  
207 of surfactant-free solutions were over 50 mN/m, due to the high surface tension of water,  
208 which was the solvent used in the solutions. Addition of the different surfactants led to a  
209 decrease in surface tension, reaching the plateau values obtained for the CMC of the different  
210 surfactants. In general, it can be stated that increasing the surfactant concentration led to  
211 greater conductivity and viscosity values.

212

213 **INSERT TABLE 2 ABOUT HERE**

214

### 215 3.3 Morphology of the electrosprayed carbohydrates

216 The electrospraying of all the solutions was performed under the same processing conditions  
217 (cf. section 2.5). Initially, the carbohydrate-aqueous solutions without surfactants were

218 electrospayed and it was observed that although the commercial resistant starch formed  
219 spherical capsules with sizes ranging from a few nm to  $\sim 2 \mu\text{m}$  with an average size of  $0.6 \pm 0.3$   
220  $\mu\text{m}$  (image not shown), extensive dropping occurred due to unstable electrospaying. On the  
221 other hand, it was not possible to obtain any electrospayed structure from the maltodextrin  
222 aqueous solution. These results can be explained by the physical properties of the solutions. As  
223 it was commented before, both carbohydrate solutions presented high surface tension and  
224 low viscosity values; however, resistant starch did not greatly increase the conductivity of the  
225 solution, while the addition of maltodextrin produced very high conductivity values. **When the**  
226 **high voltage (typically in the range of 0–30 kV) is applied to the spinneret from where the**  
227 **solution is ejected, the surface of the fluid droplet held by its own surface tension gets**  
228 **electrostatically charged at the spinneret tip.** Stable electrospaying or electrospinning is  
229 known to be attained when **the electrostatic forces inside the droplet (arising from mutual**  
230 **electrostatic repulsion between the surface charges and the Coulomb force applied by the**  
231 **external electric field), are** strong enough to overcome the surface tension **of the polymer**  
232 **solution, forcing the ejection of the liquid jet** (Zhang & Kawakami, 2010). **Before the ejection of**  
233 **the liquid jet, and as a consequence of the mentioned electrostatic interactions, the liquid**  
234 **drop elongates into a conical object known as the Taylor cone.** Thus, in the case of the  
235 resistant starch, **the electrical conductivity of this solution was insufficient, at the voltage**  
236 **applied, to overcome the high surface tension and, consequently, the Taylor cone did not form**  
237 **and dropping of the solution occurred.** In contrast, when the **coulombic repulsions are too high**  
238 **and** overcome the viscoelastic forces, less chain entanglements take place during  
239 electrospaying and, thus, very small particles or non-defined structures are obtained (Bock et  
240 al., 2012). **This seemed to be the case for the maltodextrin solution, as its very high electrical**  
241 **conductivity completely hindered the electrospaying process.**  
242 The addition of surfactants to the carbohydrate aqueous solutions produced a decrease in  
243 surface tension which favored the formation of electrospayed structures. Figure 1 shows the

244 SEM images and corresponding size distribution of the materials obtained from the  
245 electro spraying of the different resistant starch solutions. From Figures 1A and 1B it was seen  
246 that, regardless of concentration, when Span20 was added to the resistant starch solution,  
247 three different capsule size populations were found, although the structures were smaller and  
248 more homogeneous in size when 30% of the surfactant was added. Figures 1C and 1D show  
249 that the addition of 5% of Tween20 also generated three populations with respect to the  
250 capsules diameter. However, when the concentration was increased to 30%, only two different  
251 size distributions and smaller capsules were attained. On the other hand, when lecithin was  
252 included in the solutions, only one population with respect to the capsule's diameters was  
253 seen (cf. Figures 1E and 1F). Moreover, the particle size was greatly reduced when compared  
254 to capsules obtained from the carbohydrate without surfactant. Thus, the average size in this  
255 case was  $0.3 \pm 0.1 \mu\text{m}$  and  $0.2 \pm 0.1 \mu\text{m}$  when 5% and 30% of lecithin was added respectively.  
256 The variations observed between the different structures can be mainly attributed to the  
257 electrical conductivity of the solutions. It is known that higher conductivity leads to a decrease  
258 in size because Coulombic repulsion forces compete with the viscoelastic forces of the solution  
259 and disentangle more easily the polymer network formed during electro spraying. In other  
260 words, increasing conductivity makes it easier for the solution to be broken up into smaller  
261 droplets (Gañan-Calvo, Davila & Barrero, 1997; Bock et al., 2012).

262

263 **INSERT FIGURE 1 ABOUT HERE**

264

265 Regarding the maltodextrin structures, Figure 2 shows the SEM images and corresponding size  
266 distribution of the materials obtained. It is observed that the addition of non-ionic surfactants  
267 allowed the formation of particles from a few nm to 500 nm (cf. Figures 2A to 2D). The range  
268 of size distribution was considerably narrower than for the resistant starch materials and, in  
269 most cases, more than 50% of the particles were around 200 nm in size. This fact was

270 explained from the surface tension decrease produced by the surfactants. Viscoelastic and  
271 electrical forces must overcome the surface tension effect in order to obtain a defined  
272 structure. When surfactants were not added to the maltodextrin solution, the droplets formed  
273 on the needle tip grew until its mass was large enough to escape and electrospaying could not  
274 occur (Xu & Hanna, 2006). However, the addition of the non-ionic surfactants reduced the  
275 surface tension and, thus, a conical meniscus was formed on the needle tip. The meniscus  
276 further deformed and broke into droplets with small particle sizes and narrow size distribution  
277 due to the electrostatic force introduced by the maltodextrin. Nevertheless, when 30% of  
278 Tween20 was added to the solution, the electrical conductivity increased and different capsule  
279 morphologies were obtained, probably because the high electrical forces favored weak  
280 entanglements in the polymer (Bock et al., 2012). The addition of lecithin produced an  
281 excessive increase in the conductivity which completely hindered capsule formation.

282

283 **INSERT FIGURE 2 ABOUT HERE**

284

285 It is interesting to note that, apart from the capsular morphology generated, addition of  
286 surfactants also led to needle-like morphologies in both carbohydrate matrices, thus  
287 confirming that addition of these amphiphilic molecules, which decreased the surface tension  
288 of the aqueous solutions, considerably enhanced chain entanglements.

289 In general, from the morphology of the structures obtained, it can be stated that non-ionic  
290 surfactants are more suitable for generating encapsulation structures from low molecular  
291 weight carbohydrate polymers, and that the size and size distribution can be modified by the  
292 type and amount of surfactant added.

293

294 3.4 Infrared spectra of the encapsulates

295 ATR-FTIR analyses were done in order to characterize the molecular organization of the  
296 structures attained, as well as to confirm the presence of the surfactants in the carbohydrate  
297 structures. In first place, the region from 800 to 1200  $\text{cm}^{-1}$  was analyzed for all the materials  
298 obtained. This area presents the characteristic vibrational bands of the carbohydrates,  
299 corresponding to the stretching vibrations of C-O and C-C groups, and the bending vibration of  
300 C-O-H (Wolkers, Oliver, Tablin, & Crowe, 2004; Kacurakova & Mathlouthi, 1996). From Figure 3  
301 it was observed that when surfactants were added to the resistant starch, these bands were  
302 shifted by approximately 2-6  $\text{cm}^{-1}$  suggesting that there was a chemical interaction between  
303 the carbohydrate and the surfactants. Specifically, the most noted shift was observed for the  
304 band which arose at 1006  $\text{cm}^{-1}$  in the resistant starch (cf. Figures 3A to 3C). This band was  
305 shifted towards higher wavenumbers in the surfactant/polymer capsules, which could mean  
306 stronger hydrogen bonding due to the interaction of the carbohydrate with the surfactants  
307 (Wolkers et al., 2004). It is interesting to note that greater band shifts were related to smaller  
308 capsule mean diameters, which may be probably explained by the greater specific surface  
309 present in the material containing smaller capsules. Moreover, in this specific carbohydrate  
310 polymer, i.e. the resistant starch, a clear change in band shape was also observed in the  
311 spectral range 950-1050  $\text{cm}^{-1}$ , which also resulted in narrower bands in the encapsulates  
312 containing the surfactants, indicating that surfactant addition led to greater molecular order.  
313 On the contrary, for the maltodextrin structures (Figures 3E to 3F), the characteristic  
314 carbohydrate bands hardly shifted with the incorporation of the surfactants, indicating that  
315 their interaction with the polymer may be less intense than in the previous case. Nevertheless,  
316 it was seen that lecithin produced the greatest band displacements for both polymer matrices  
317 probably because it is a zwitterionic surfactant which presented a stronger interaction with the  
318 polymers (Lin et al. 2004).

319

320 **INSERT FIGURE 3 ABOUT HERE**



321

322 Furthermore, the most characteristic band of the surfactants which was not overlapped with  
323 the carbohydrate bands was considered to determine the effect of the concentration of the  
324 surfactants in the electrosprayed material. Figure 4 shows the capsule's spectra from 1800 to  
325  $1600\text{ cm}^{-1}$  where the band corresponding to the carbonyl group, at around  $1740\text{ cm}^{-1}$ ,  
326 attributed to the surfactants was located. From the spectra, it was observed that the  
327 surfactants were incorporated in all the structures, since this peak appeared in all the  
328 materials. It is worth noting that the lecithin band showed the greatest shift when it was  
329 combined with the polymers, thus confirming the stronger interaction between the ionic  
330 surfactants with the polymers. Moreover, this peak could also reveal the amount of surfactant  
331 included in the initial solutions, since it was more intense with the increasing concentration of  
332 the surfactant.

333

334 **INSERT FIGURE 4 ABOUT HERE**

335

#### 336 **4. Conclusions**

337 In this work it is demonstrated that addition of surfactants considerably improves the  
338 electrospraying of low Mw carbohydrate aqueous polymer solutions. Specifically, ultrathin  
339 capsules made from a commercial resistant starch and a maltodextrin with Span20, Tween20  
340 or lecithin were developed. This was mainly due to a reduction in the surface tension caused  
341 by surfactant addition, which stabilized the electrospraying process. However, it has also been  
342 shown that the type and amount of surfactant greatly influenced the morphology and size  
343 distribution of the encapsulation structures generated. In general, it can be stated that non-  
344 ionic surfactants were more suitable for the electrospraying of low Mw carbohydrate  
345 solutions, as electrically charged surfactants gave rise to fused and too small structures. FTIR  
346 results showed that the surfactants were effectively incorporated in the carbohydrate

347 polymers and while greater molecular order and different capsule sizes were obtained from  
348 resistant starch solutions by changing the type and concentration of surfactant, only very small  
349 structures were formed from maltodextrin solutions, due to their high electrical conductivity.  
350 These results are highly interesting for the development of encapsulation structures for food-  
351 related applications where the use of aqueous solutions is mandatory.

352

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359

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**Table 1.** Critical micelle concentration (CMC) of the different surfactants in aqueous solution in absence and presence of the carbohydrates.

Carbohydrate (wt-%)	CMC of surfactant (mM)		
	Span 20	Tween 20	Lecithin
Aqueous solution	0.04	0.01	0.12
Resistant starch 20%	0.1	0.03	0.16
Maltodextrin 20%	0.1	0.05	0.16

**Table 2.** Conductivity, viscosity and surface tension of the carbohydrate-surfactant solutions.

Matrix	Surfactant	Surfactant concentration (%)	Conductivity ( $\mu\text{S}$ )	Viscosity (cP)	Surface Tension (mN/m)
Resistant starch	-	0	$17 \pm 1$	$2.0 \pm 0.5$	$56.1 \pm 1.6$
	Span 20	5	$33 \pm 1$	$2.3 \pm 0.1$	$26.1 \pm 0.8$
		30	$73 \pm 2$	$2.5 \pm 0.7$	$25.9 \pm 0.5$
	Tween 20	5	$35 \pm 2$	$2.2 \pm 0.6$	$31.0 \pm 0.1$
		30	$136 \pm 2$	$2.8 \pm 0.1$	$35.4 \pm 0.9$
	Lecithin	5	$209 \pm 3$	$2.2 \pm 0.1$	$29.9 \pm 0.3$
		30	$862 \pm 6$	$5.4 \pm 0.9$	$27.5 \pm 2.3$
	Maltodextrin	-	0	$798 \pm 1$	$2.2 \pm 0.2$
Span 20		5	$790 \pm 1$	$2.2 \pm 0.1$	$25.3 \pm 0.8$
		30	$786 \pm 2$	$2.4 \pm 0.1$	$24.7 \pm 0.5$
Tween 20		5	$802 \pm 3$	$2.2 \pm 0.5$	$35.1 \pm 0.4$
		30	$843 \pm 7$	$2.3 \pm 0.2$	$35.0 \pm 3.5$
Lecithin		5	$928 \pm 6$	$2.8 \pm 0.2$	$32.5 \pm 1.3$
		30	$1776 \pm 8$	$5.3 \pm 0.6$	$26.2 \pm 0.3$

**FIGURE CAPTIONS**

**Figure 1.** Selected SEM images and their corresponding capsule size distribution of resistant starch-based structures with the different surfactants: A) 5% Span20; B) 30% Span20; C) 5% Tween20; D) 30% Tween20; E) 5% lecithin and F) 30% lecithin.

**Figure 2.** Selected SEM images and their corresponding capsule size distribution of maltodextrin-based structures with different surfactants: A) 5% Span20; B) 30% Span20; C) 5% Tween20; D) 30% Tween20; E) 5% lecithin and F) 30% lecithin.

**Figure 3.** ATR-FTIR spectra from 1200 to 880  $\text{cm}^{-1}$  for the pure carbohydrate (dotted line), the surfactants (dashed line), the carbohydrate with 5% of surfactant (grey line) and with 30% of surfactant (black line) for: (A) resistant starch/Span20; (B) resistant starch/Tween20; (C) resistant starch/lecithin; (D) maltodextrin/Span20; (E) maltodextrin/Tween20; and (F) maltodextrin/lecithin.

**Figure 4.** ATR-FTIR spectra from 1600 to 1800  $\text{cm}^{-1}$  for the pure carbohydrate (dotted line), the surfactants (dashed line), the carbohydrate with 5% of surfactant (grey line) and with 30% of surfactant (black line) for: (A) resistant starch/Span20; (B) resistant starch/Tween20; (C) resistant starch/lecithin; (D) maltodextrin/Span20; (E) maltodextrin/Tween20; and (F) maltodextrin/lecithin (F).



Figure 1\_reviewed  
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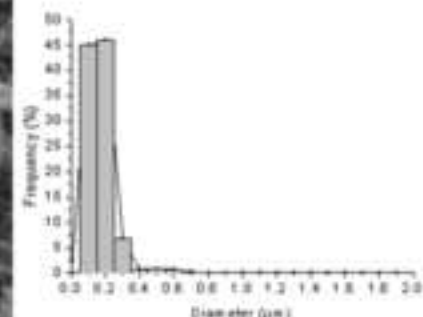
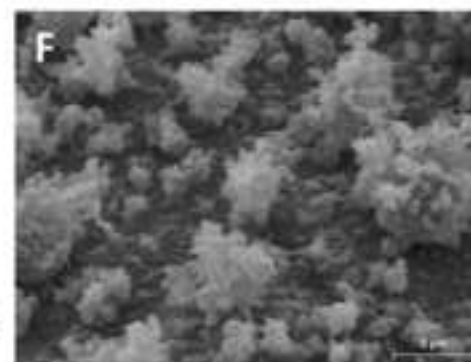
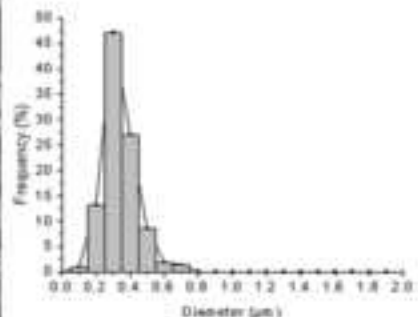
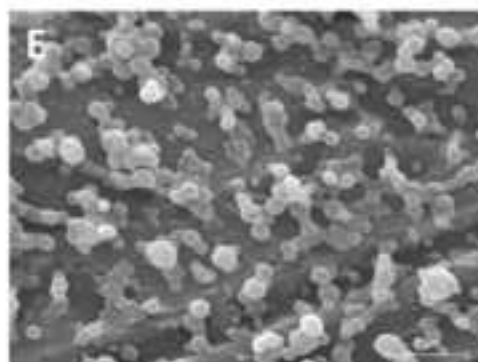
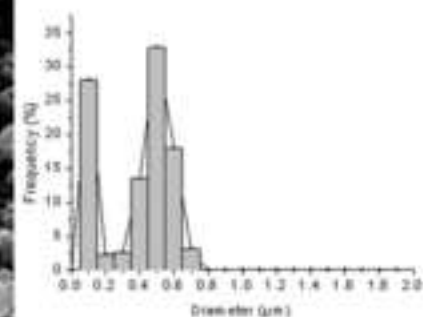
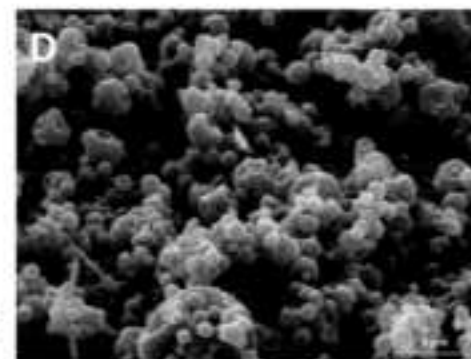
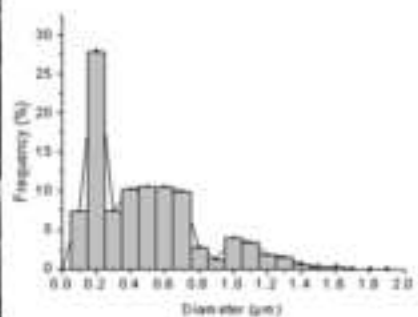
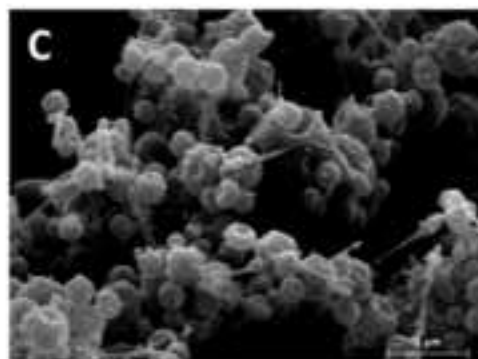
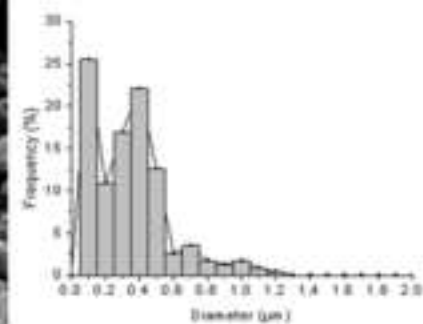
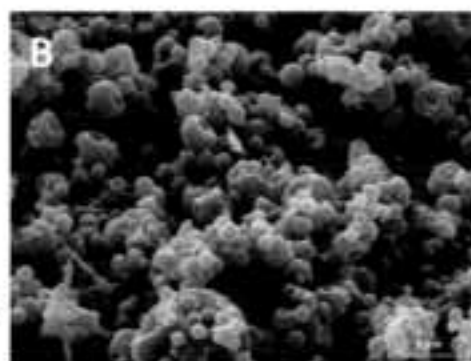
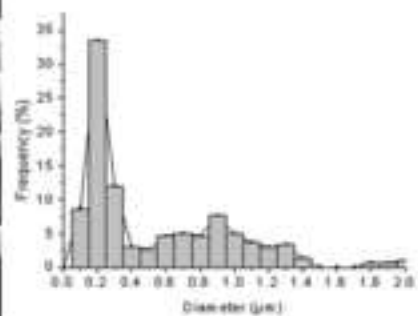
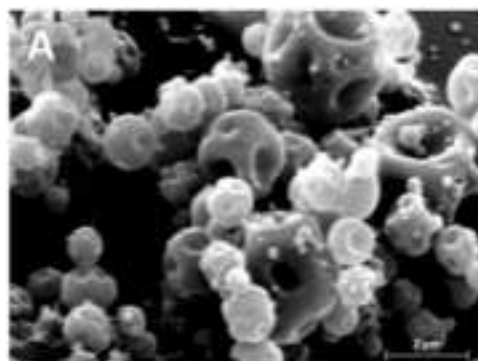
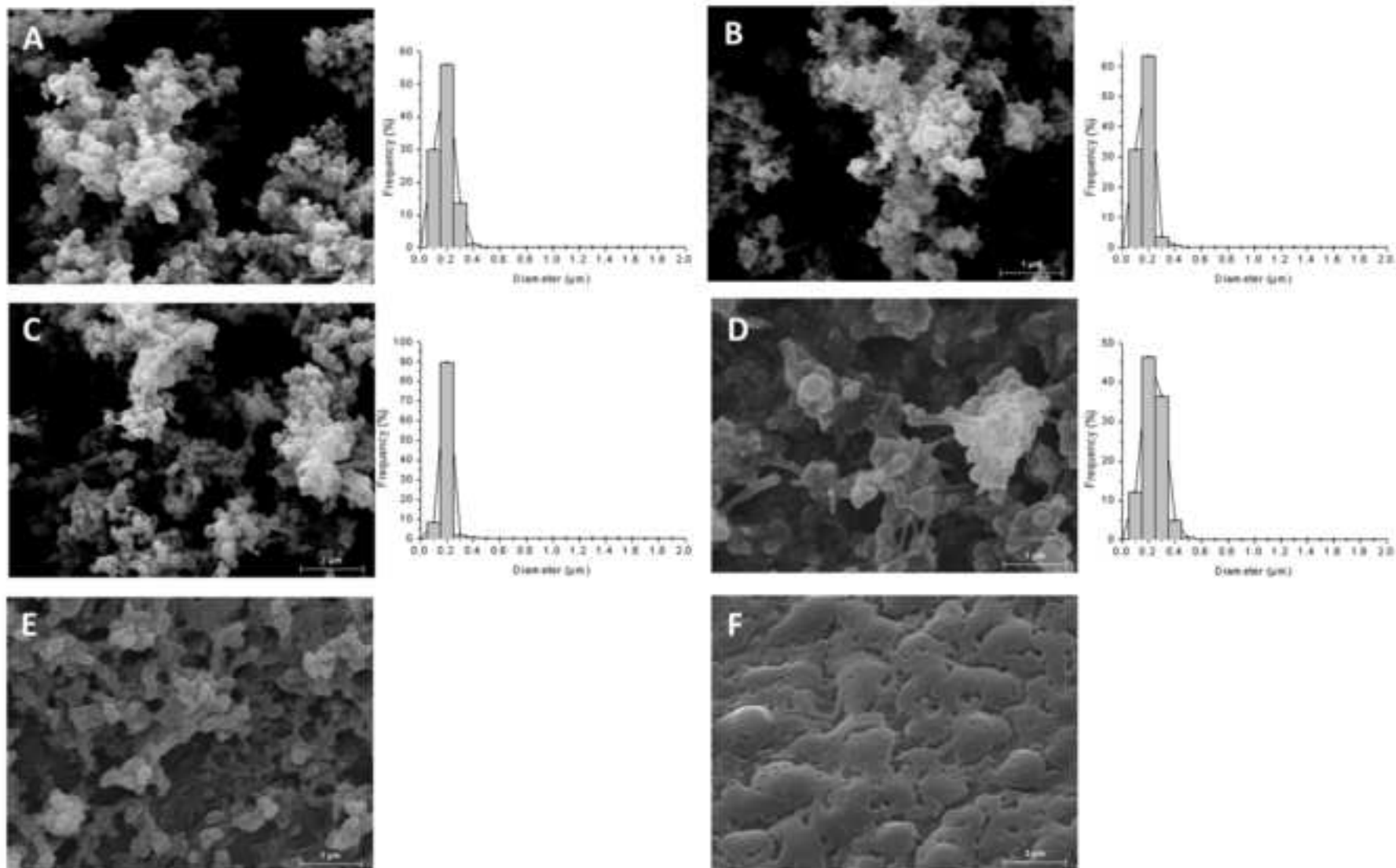


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**Figure 3**  
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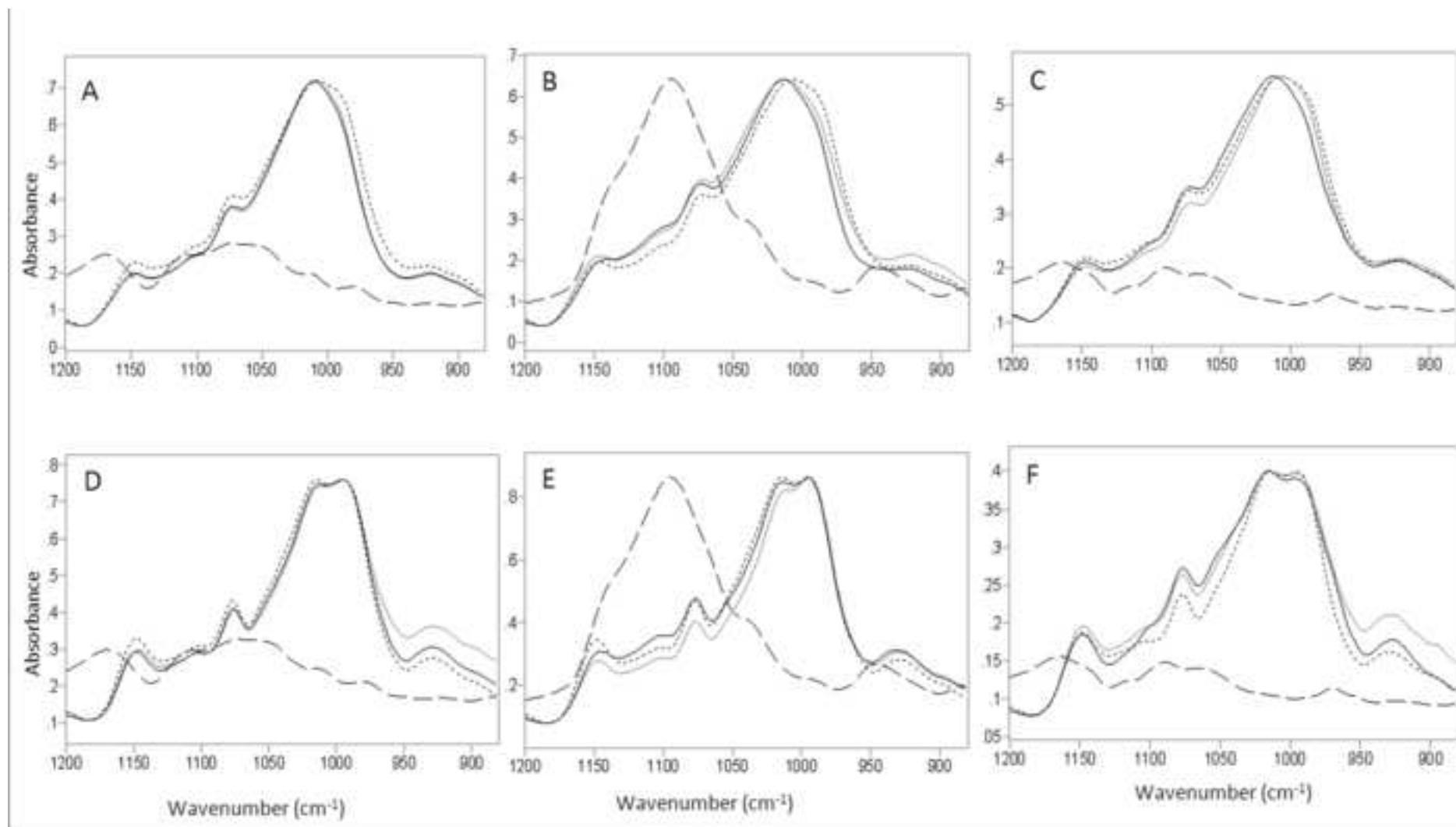


Figure 4  
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