



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 electrospraying 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.

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1. Introduction

The development of micro-, submicro- and nanostructures from biopolymers for functional food applications is an emerging area of interest. Apart from the conventional microencapsulation techniques, such as spray drying or coacervation, electrospinning has been recently suggested to be a simple and straightforward method to generate submicron encapsulation structures for a variety of bioactive molecules (Bock, Dargaville, & Woodruff, 2012; Lopez-Rubio & Lagaron, 2012; Xie, Li, & Xia, 2008). Electrospinning is a process that produces continuous polymer fibers with diameters in the submicrometer range through the action of an external electric field imposed on a polymer solution or melt. The electrospun nanostructures morphology is affected by the solution properties (mainly by the viscosity, surface tension and conductivity of the polymer solution) and by the process parameters (voltage, flow rate of the solution, tip-to-collector distance). For certain materials, size-reduced capsules can be obtained when lowering the polymer concentration and/or increasing the tip-to-collector distance. In this case, the electrospinning process is normally referred to as “electrospraying” due to the non-continuous nature of the

structures obtained. To date, a wide variety of polymers and polymer blends have been electrospun, with synthetic polymers yielding the best results in terms of physical properties and uniformity. On the other hand, electrospinning of biopolymer solutions has been proven to be difficult due to several factors such as the polycationic nature of many biopolymers, the low chain flexibility which complicates chain entanglements (essential for fiber formation) and their generally poor solubility in organic solvents (Kriegel, Kit, McClements, & Weiss, 2009). Moreover, unlike synthetic polymers, a natural polymer derived from different sources presents widely varying properties and it has been observed that the viscosity of the solutions may vary with time due to, for instance, aqueous hydrolysis of the biopolymer (Bhattacharai & Zhang, 2007).

Electrospinning from aqueous solutions is beneficial from an environmental point of view. Furthermore, the use of water does not generate toxicity problems. On the contrary, organic solvents may be even prohibited for certain applications, such as in the case of food products (Kriegel, Kit, McClements, & Weiss, 2010). That issue further complicates the electrospinning process due to the ionization of water molecules at high voltages in an air environment, which may cause corona discharge. Besides, aqueous solutions present high surface tension values which hinder the formation of stable jets during the electrospinning. Moreover, polymers that have low aqueous solubility, low M_w polymers and polymers with rigid or globular structures that do not generate sufficient viscosity are not easily electrospun when they are in

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an aqueous solution (Nagarajan, Drew, & Mello, 2007; Stijnman, Bodnar, & Hans Tromp, 2011).

Different surfactants have been added to the electrospinning solutions for various purposes, like enzyme stabilization (Herricks et al., 2005), creation of mesoporous structures (Hong, Fan, & Zhang, 2009; Hou et al., 2009), or to make compatible hydrophilic fillers with hydrophobic matrices (Kim, Lee, & Knowles, 2006). However, more importantly, surfactants have been seen to improve the spinnability of polymer solutions, which is normally a consequence of the reduction in their surface tension (Bonino et al., 2011). To the best of our knowledge, all the studies carried out to date in this area, relate to fiber formation and it has been demonstrated that addition of surfactants reduce fiber defects, but do not promote fiber formation for solutions which are not readily spinnable (Aceituno-Medina, Lopez-Rubio, Mendoza, & Lagaron, 2013). However, the effect of surfactant addition on the sprayability or capsule formation from biopolymer solutions is unknown.

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

2. Materials and methods

2.1. Materials

A maltodextrin with a DE value of 16.5–19.5 was purchased from Sigma–Aldrich. A commercial resistant starch (derived from corn starch) with trade name Fibersol® (www.fibersol.com) manufactured by ADM/Matsutani (Iowa, USA) was used. The non-ionic surfactants, polyoxyethylene sorbitan monolaureate (Tween20) and sorbitan monolaureate (Span20), and the zwitterionic surfactant, L- α -phosphatidylcholine (lecithin) were supplied by Sigma–Aldrich. All products were used as received without further purification.

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

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

2.3. Preparation of carbohydrate-based solutions

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

2.4. Characterization of the carbohydrate-based solutions

The apparent viscosity (η_a) of the polymeric solutions at 100 s⁻¹ was determined using a rotational viscosity meter Visco Basic Plus L from Fungilab S.A. (San Feliu de Llobregat, Spain) using a Low Viscosity Adapter (LCP). The surface tension of the biopolymer solutions was measured using the Wilhemy plate method in an EasyDyne K20 tensiometer (Krüss GmbH, Hamburg, Germany). Both tests were carried out in triplicate. The conductivity of the solutions was measured using a conductivity meter XS Con6 (Lab-box, Barcelona, Spain). All measurements were made at 25 °C.

2.5. Preparation of carbohydrate-based capsules through electrospaying

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

2.6. Infrared spectroscopy

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

2.7. Scanning electron microscopy (SEM)

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

3. Results and discussion

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

Surfactants are amphiphilic molecules that readily absorb at surfaces, thereby lowering surface or interfacial tension of the medium in which they are dissolved. Moreover, above a critical concentration, the so-called critical micelle concentration, surfactants self-assemble to form a variety of colloidal structures, which have different properties from those of the dissolved surfactant monomers, e.g., solubility, surface hydrophilicity, charge density. Previous studies have demonstrated that addition of non-ionic and ionic surfactants above their critical micelle concentration to polymer solutions, significantly improved the electrospinning process generating defect-free fibers (Kriegel et al., 2009). Therefore, in this study, the first intention was to add different surfactants above their CMC to study their influence on the sprayability of low M_w carbohydrates. The CMC informs about the concentration of surfactant necessary to form a monolayer of molecules oriented at the air–water interface (Chou, Krishnamurthy, Randolph, Carpenter, &

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)		
	Span20	Tween20	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

Manning, 2005; Lin, Wang, Wang, & Wang, 2004). On the other hand, the concentration needed for the polymer–surfactant association is the critical aggregation concentration (CAC) and it is usually lower than the CMC by a factor between 1 and 10. Both the surfactant concentration and the polymer–surfactant interactions may result in changes in the rheology and conductivity of the solutions, factors which greatly affect the electrospinning/electrospraying process (Lin et al., 2004).

Initially, the surface tension for different surfactant concentrations in aqueous solution in the absence and presence of the low molecular weight carbohydrates was measured and CMC values were determined when the plateau in surface tension was obtained. Table 1 shows the CMC values for the different surfactants assayed and the concentration added in the solutions. For all the solutions tested it was observed that very low concentrations of the surfactants were needed to reach the CMC, regardless of whether the carbohydrates were present. It was also observed that CMC increased with the addition of the biopolymers probably because the surfactants were also interacting with the biopolymers in solution. It is possible that in the presence of carbohydrates, the concentration of the surfactants in the surface decreased, as part of the surfactant was bound to the carbohydrates. As a result, the amount of surfactant needed to reach the CMC increased (Chou et al., 2005). Knowing this plateau value, two different concentrations of each surfactant (5 and 30 wt.%) were added to the carbohydrate solutions, which corresponded to 28.9 mM of Span20, 8.2 mM of Tween20 and 13.2 mM of lecithin when 5% of surfactant with respect to the biopolymer weight was added; and 173.2 mM of Span20, 49.0 mM of Tween20 and 79.0 mM of lecithin when 30% of surfactant with respect to the biopolymer weight was incorporated. Please note that both concentrations were well higher than the CMC of the surfactants.

3.2. Solution properties

The physical properties of the carbohydrate–surfactant solutions are critical in the successful preparation of the electrospayed structures. Therefore, the conductivity, viscosity and surface tension of the different solutions were measured and the results are summarized in Table 2. From these data it is observed that the addition of resistant starch to water did not considerably increase the conductivity of the solvent because this material did not present any electrical charge. On the contrary, the maltodextrin-based solutions presented enhanced conductivity values. This fact could be due to maltodextrin forming charged ions when dissolved in water. From Table 2, it is also observed that addition of non-ionic surfactants to the resistant starch solutions produced a slight increase in the conductivity, probably due to the existence of polar groups in this molecule (Lin et al., 2004). However, when Span20 and Tween20 were incorporated to the maltodextrin solutions, they did not affect the conductivity, showing that the effect of these surfactants in the solution conductivity is very limited and it is only relevant when the solution presents very low conductivity. In contrast, addition of lecithin led to higher conductivity in both carbohydrate solutions. This fact was related to the zwitterionic nature of the lecithin which presents asymmetric positive and

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

3.3. Morphology of the electrospayed carbohydrates

The electrospraying of all the solutions was performed under the same processing conditions (cf. Section 2.5). Initially, the carbohydrate–aqueous solutions without surfactants were electrospayed and it was observed that although the commercial resistant starch formed spherical capsules with sizes ranging from a few nm to $\sim 2 \mu\text{m}$ with an average size of $0.6 \pm 0.3 \mu\text{m}$ (image not shown), extensive dropping occurred due to unstable electrospraying. On the other hand, it was not possible to obtain any electrospayed structure from the maltodextrin aqueous solution. These results can be explained by the physical properties of the solutions. As it was commented before, both carbohydrate solutions presented high surface tension and low viscosity values; however, resistant starch did not greatly increase the conductivity of the solution, while the addition of maltodextrin produced very high conductivity values. When the high voltage (typically in the range of 0–30 kV) is applied to the spinneret from where the solution is ejected, the surface of the fluid droplet held by its own surface tension gets electrostatically charged at the spinneret tip. Stable electrospraying or electrospinning is known to be attained when the electrostatic forces inside the droplet (arising from mutual electrostatic repulsion between the surface charges and the Coulomb force applied by the external electric field), are strong enough to overcome the surface tension of the polymer solution, forcing the ejection of the liquid jet (Zhang & Kawakami, 2010). Before the ejection of the liquid jet, and as a consequence of the mentioned electrostatic interactions, the liquid drop elongates into a conical object known as the Taylor cone. Thus, in the case of the resistant starch, the electrical conductivity of this solution was insufficient, at the voltage applied, to overcome the high surface tension and, consequently, the Taylor cone did not form and dropping of the solution occurred. In contrast, when the coulombic repulsions are too high and overcome the viscoelastic forces, less chain entanglements take place during electrospraying and, thus, very small particles or non-defined structures are obtained (Bock et al., 2012). This seemed to be the case for the maltodextrin solution, as its very high electrical conductivity completely hindered the electrospraying process.

The addition of surfactants to the carbohydrate aqueous solutions produced a decrease in surface tension which favored the formation of electrospayed structures. Fig. 1 shows the

Table 2

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

Matrix	Surfactant	Surfactant concentration (%)	Conductivity (μS)	Viscosity (cP)	Surface tension (mN/m)
Resistant starch	–	0	17 ± 1	2.0 ± 0.5	56.1 ± 1.6
	Span20	5	33 ± 1	2.3 ± 0.1	26.1 ± 0.8
		30	73 ± 2	2.5 ± 0.7	25.9 ± 0.5
	Tween20	5	35 ± 2	2.2 ± 0.6	31.0 ± 0.1
		30	136 ± 2	2.8 ± 0.1	35.4 ± 0.9
	Lecithin	5	209 ± 3	2.2 ± 0.1	29.9 ± 0.3
		30	862 ± 6	5.4 ± 0.9	27.5 ± 2.3
Maltodextrin	–	0	798 ± 1	2.2 ± 0.2	52.7 ± 4.1
	Span20	5	790 ± 1	2.2 ± 0.1	25.3 ± 0.8
		30	786 ± 2	2.4 ± 0.1	24.7 ± 0.5
	Tween20	5	802 ± 3	2.2 ± 0.5	35.1 ± 0.4
		30	843 ± 7	2.3 ± 0.2	35.0 ± 3.5
	Lecithin	5	928 ± 6	2.8 ± 0.2	32.5 ± 1.3
		30	1776 ± 8	5.3 ± 0.6	26.2 ± 0.3

SEM images and corresponding size distribution of the materials obtained from the electrospraying of the different resistant starch solutions. From Fig. 1A and B it was seen that, regardless of concentration, when Span20 was added to the resistant starch solution, three different capsule size populations were found, although the structures were smaller and more homogeneous in size when 30% of the surfactant was added. Fig. 1C and D shows that the addition of 5% of Tween20 also generated three populations with respect to the capsules diameter. However, when the concentration was increased to 30%, only two different size distributions and smaller capsules were attained. On the other hand, when lecithin was included in the solutions, only one population with respect to the capsule's diameters was seen (cf. Fig. 1E and F). Moreover, the particle size was greatly reduced when compared to capsules obtained

from the carbohydrate without surfactant. Thus, the average size in this 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. The variations observed between the different structures can be mainly attributed to the electrical conductivity of the solutions. It is known that higher conductivity leads to a decrease in size because Coulombic repulsion forces compete with the viscoelastic forces of the solution and disentangle more easily the polymer network formed during electrospraying. In other words, increasing conductivity makes it easier for the solution to be broken up into smaller droplets (Bock et al., 2012).

Regarding the maltodextrin structures, Fig. 2 shows the SEM images and corresponding size distribution of the materials obtained. It is observed that the addition of non-ionic surfactants allowed the formation of particles from a few nm to 500 nm (cf.

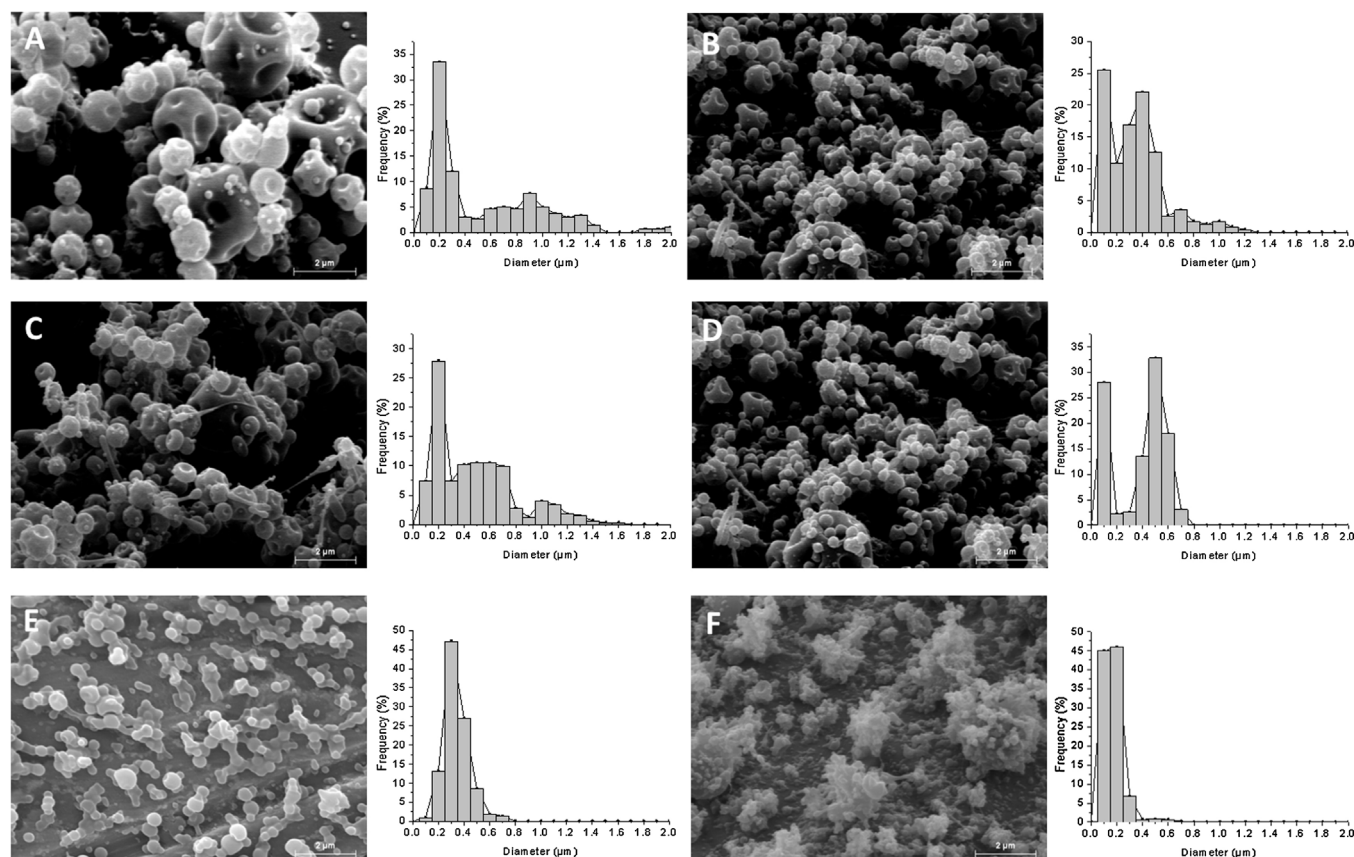


Fig. 1. Selected SEM images and their corresponding capsule size distribution of resistant starch-based structures with the different surfactants: (A) 5% Span20; (B) 30% Span20; (C) 5% Tween20; (D) 30% Tween20; (E) 5% lecithin and (F) 30% lecithin.

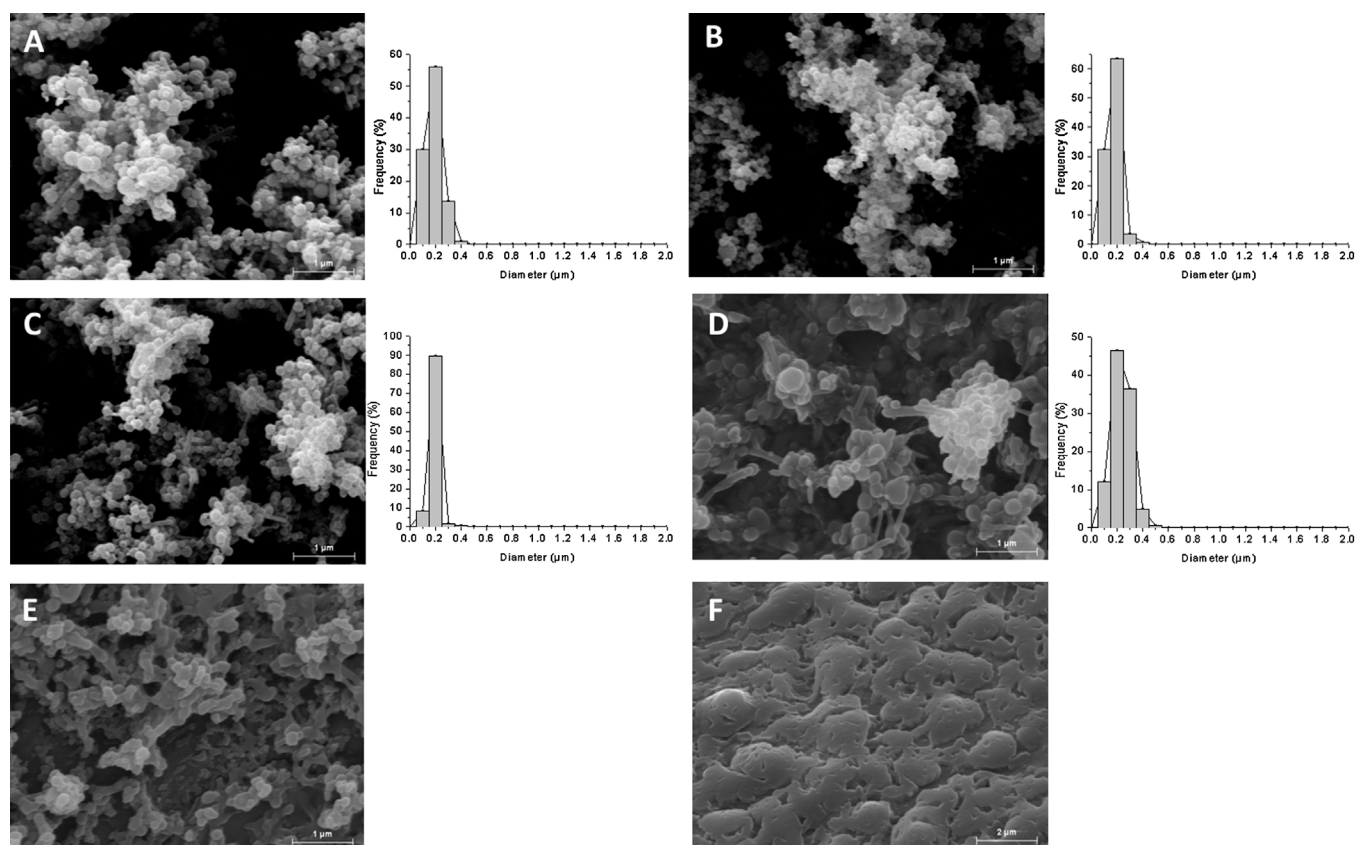


Fig. 2. Selected SEM images and their corresponding capsule size distribution of maltodextrin-based structures with different surfactants: (A) 5% Span20; (B) 30% Span20; (C) 5% Tween20; (D) 30% Tween20; (E) 5% lecithin and (F) 30% lecithin.

Fig. 2A–D). The range of size distribution was considerably narrower than for the resistant starch materials and, in most cases, more than 50% of the particles were around 200 nm in size. This fact was explained from the surface tension decrease produced by the surfactants. Viscoelastic and electrical forces must overcome the surface tension effect in order to obtain a defined structure. When surfactants were not added to the maltodextrin solution, the droplets formed on the needle tip grew until its mass was large enough to escape and electrospraying could not occur (Xu & Hanna, 2006). However, the addition of the non-ionic surfactants reduced the surface tension and, thus, a conical meniscus was formed on the needle tip. The meniscus further deformed and broke into droplets with small particle sizes and narrow size distribution due to the electrostatic force introduced by the maltodextrin. Nevertheless, when 30% of Tween20 was added to the solution, the electrical conductivity increased and different capsule morphologies were obtained, probably because the high electrical forces favored weak entanglements in the polymer (Bock et al., 2012). The addition of lecithin produced an excessive increase in the conductivity which completely hindered capsule formation.

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

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

3.4. Infrared spectra of the encapsulates

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

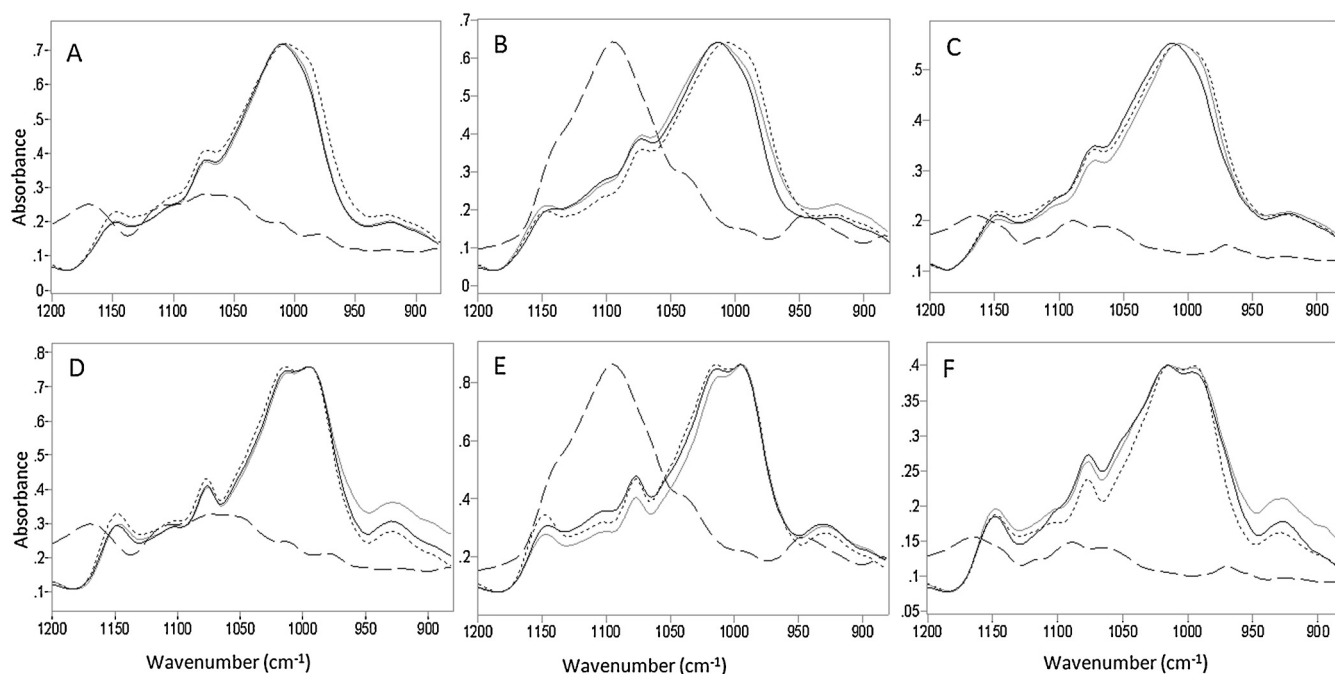


Fig. 3. ATR-FTIR spectra from 1200 to 880 cm^{-1} for the pure carbohydrate (dotted line), the surfactants (dashed line), the carbohydrate with 5% of surfactant (gray line) and with 30% of surfactant (black line) for: (A) resistant starch/Span20; (B) resistant starch/Tween20; (C) resistant starch/lecithin;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

displacements for both polymer matrices probably because it is a zwitterionic surfactant which presented a stronger interaction with the polymers (Lin et al., 2004).

Furthermore, the most characteristic band of the surfactants which was not overlapped with the carbohydrate bands was considered to determine the effect of the concentration of the surfactants in the electrosprayed material. Fig. 4 shows the capsule's

spectra from 1800 to 1600 cm^{-1} where the band corresponding to the carbonyl group, at around 1740 cm^{-1} , attributed to the surfactants was located. From the spectra, it was observed that the surfactants were incorporated in all the structures, since this peak appeared in all the materials. It is worth noting that the lecithin band showed the greatest shift when it was combined with the polymers, thus confirming the stronger interaction between the

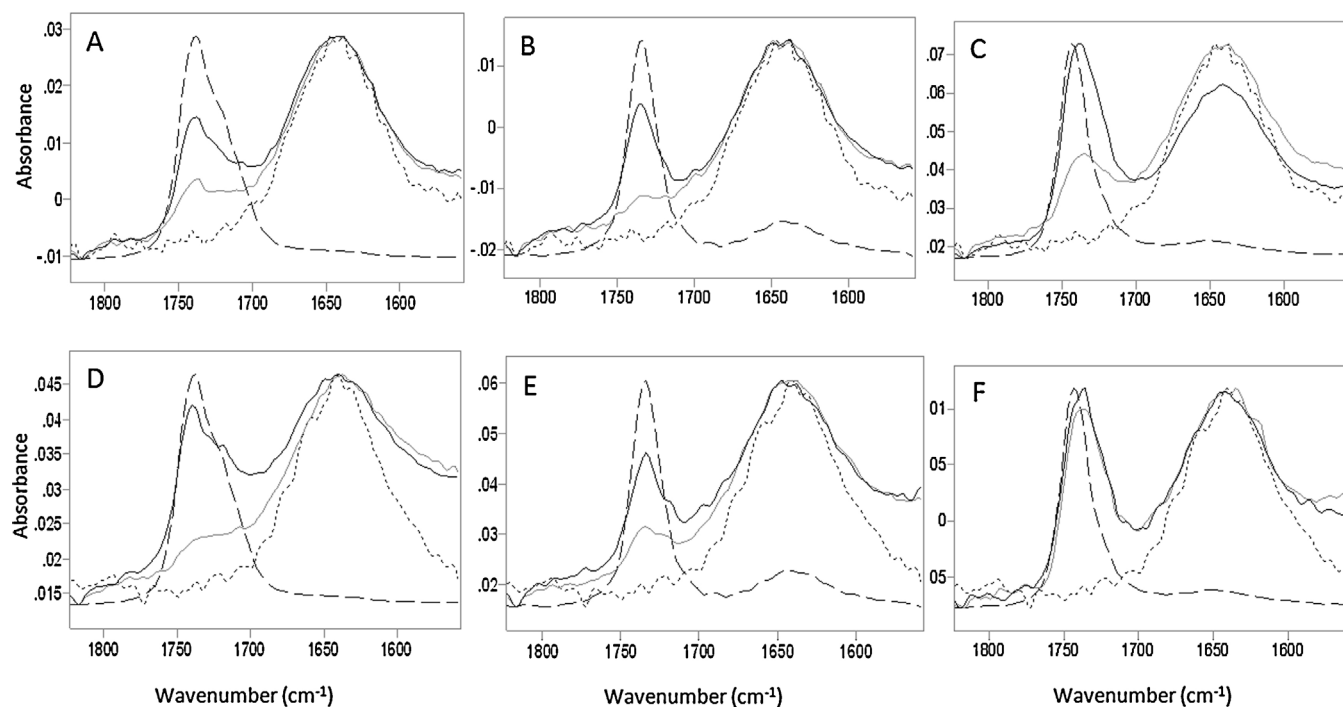


Fig. 4. ATR-FTIR spectra from 1800 to 1600 cm^{-1} for the pure carbohydrate (dotted line), the surfactants (dashed line), the carbohydrate with 5% of surfactant (gray line) and with 30% of surfactant (black line) for: (A) resistant starch/Span20; (B) resistant starch/Tween20; (C) resistant starch/lecithin;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

ionic surfactants with the polymers. Moreover, this peak could also reveal the amount of surfactant included in the initial solutions, since it was more intense with the increasing concentration of the surfactant.

4. Conclusions

In this work it is demonstrated that addition of surfactants considerably improves the electrospraying of low M_w carbohydrate aqueous polymer solutions. Specifically, ultrathin capsules made from a commercial resistant starch and a maltodextrin with Span20, Tween20 or lecithin were developed. This was mainly due to a reduction in the surface tension caused by surfactant addition, which stabilized the electrospraying process. However, it has also been shown that the type and amount of surfactant greatly influenced the morphology and size distribution of the encapsulation structures generated. In general, it can be stated that non-ionic surfactants were more suitable for the electrospraying of low M_w carbohydrate solutions, as electrically charged surfactants gave rise to fused and too small structures. FTIR results showed that the surfactants were effectively incorporated in the carbohydrate polymers and while greater molecular order and different capsule sizes were obtained from resistant starch solutions by changing the type and concentration of surfactant, only very small structures were formed from maltodextrin solutions, due to their high electrical conductivity. These results are highly interesting for the development of encapsulation structures for food-related applications where the use of aqueous solutions is mandatory.

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