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Electrospinning vs. electrospraying: a comparative assessment of the two techniques for orange essential oil encapsulation

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ABSTRACT

The aim of this study was to encapsulate orange essential oil (OEO) in zein polymer by the electrospinning/electrospraying techniques. OEO at concentrations of 30, 40 and 50% (w/w), was incorporated into 10 and 20% (w/v) zein polymer solutions, for the formation of the capsules and fibers, respectively. The polymer solutions were evaluated for zeta potential. The fibers and capsules were electrospinning/electosprayed and evaluated by efficiency of encapsulation (EE%), loading capacity (LC%), morphology, size distribution and infrared spectrum. Zeta potential proportionately increased with increasing concentration of the OEO. The fibers had higher EE values (77–89%) than capsules (16-20%). The higher OEO concentration showed a higher EE for both products (capsules and fibers) and improved fiber morphology. The electrospinning process was more efficient than electrospraying for OEO encapsulation using zein as a polymeric matrix, showing that this technique is suitable for encapsulation of essential oils.

KEYWORDS: capsules; electrospinning; electrospray; fibers; orange essential oil.

INTRODUCTION

Citrus essential oils are widely reported in literature due to its applications as natural conservative in foods (Bora *et al*., 2020; Kringel *et al.*, 2020). Several studies had provided results that proved the antibacterial and antioxidant potential of Citrus essential oils (Evangelho, *et al.*, 2019b; Araújo *et al.*, 2020; Kringel *et al.*, 2020; Kringel *et al.*, 2021), hypothesizing it as an alternative for the development of safer products using natural ingredients. Moreover, during processing of orange juice, large amounts of by-products are generated; the orange peel is the main one, which may represent up to 50-65% of the total weight (Mahmoud *et al.*, 2016). Therefore, the exploration of by-products from the processing of citrus fruits and their application in food is a promising field (Mahato *et al.*, 2018). In addition, among the genus *Citrus*, the Valencia variety *Citrus sinensis* is the main orange variety produced in Brazil, which is the main producer and exporter of orange essential oils (Gonçalves *et al.*, 2018).

Despite its promising use, citrus essential oils are highly volatile and easily degraded by external factors leading to the formation of unpleasant taste or odor and affecting their biological activity (Kringel *et al.*, 2017). The encapsulation can protect against degradation, caused mainly by high temperatures, UV light and oxidation, besides extending the action of their bioactive principle (Biduski *et al.*, 2019). However, the majorities of encapsulation techniques involve high temperatures or requires a large amount of organic solvents which leads to degradation of active compounds as well as toxicity concerns (Niu *et al.*, 2020).

Among several encapsulation methods, the electrospinning/electrospray techniques have gained interest due to several advantages such as higher bioavailability, bioaccessibility, controlled bioactive release of encapsulated compounds (Ricaurte *et al.* 2020). This technique has the following advantages: works under mild ambient conditions (does not involve high temperatures or pressures), high encapsulation efficiencies and obtaining smaller particle sizes than in the conventional mechanical atomizers (Fonseca *et al.*, 2020; Krumreich *et al.*, 2019).

Polysaccharides and proteins have great potential as encapsulating materials for food applications due to their abundance, low cost, chemical diversity, and biological activities. However, some challenges in electrospraying/electrospinning processing of proteins are reported, such as high surface tension hindering the formation of stable Taylor cone; low chain flexibility, and/or globular structure; polyelectrolytic nature of polypeptide chains and low molecular weight which leads to limited chain entanglement (Lim, Mendes & Chronakis, 2019).

Molecular weight is considered a determining factor for the electrohydrodynamic process, and its increase promotes the entanglement of the polymeric chain, resulting in the stabilization of the polymeric jet and therefore, producing continuous fibers (electrospinning). On the other hand, excessive entanglement of the chains promoted by polymer solutions with low molecular weight can result in high shear stress resulting in capsules formation (electrospraying) (Niu *et al.*, 2020).

Some methods for encapsulation of orange essential oil, including inclusion complex with commercial cyclodextrin have been proposed by our research group (Kringel *et al.*, 2017) and cyclodextrins from germinated wheat starch (Kringel *et*

al., 2019) and recently, anti-solvent precipitation method using zein as polymer matrix (Kringel *et al.*, 2020), which proved to be a great wall material for this purpose. However, there are currently no published studies focusing on the comparison of these two techniques (electrospinning x electrospraying) for essential oil encapsulation.

The use and application of both, electrospinning and electrospraying, techniques are well described in the literature. Zein (supplementary material) has been widely studied in electrospinning process either single or combined by another polymer for encapsulation of essential oil. As an example, Niu *et al.*, (2020) evaluated the combination of zein and ethyl cellulose (EC) to encapsulate cinnamon essential oil. The authors reported the formation of beaded fibers due to the low zein content, which was improved by EC addition; consequently, smooth surface and uniform structures were formed. Moreover, Leena *et al.*, (2020) studied zein as single coat material for resveratrol encapsulation via electrospinning and reported bead free nanofibers with ribbon-like morphology with an encapsulation efficiency range of 78 to 97%. On the contrary, electrospraying of zein has allowed the formation of spherical and smoothed particles with an encapsulation efficiency range of 38 to 68% (Jayan *et al.*, 2019). Miguel *et al.*, (2019) have reported an encapsulation efficiency of 83% of fish oil loaded in zein capsule via electrospraying. The inconsistency of reported result for zein in electrospinning/electrospray process may be due to the different conditions applied by researchers preventing for a suitable comparison of techniques. Therefore, the understanding of polymer behavior in both electrospinning/electrospray processes is essential to identify the proper technique to be applied. In this sense, the aim of this study was to encapsulate OEO by electrospinning and electrospraying techniques.

MATERIALS AND METHODS

MATERIALS

Oranges of Valencia variety [*Citrus sinensis* (L.) Osbeck] were collected in 2019, located in the southern Rio Grande do Sul, in the city of Pelotas, Brazil. Zein prolamine was purchased from Sigma-Aldrich (grade Z3625; St. Louis, MO, USA). Anhydrous ethanol was supplied by Commercial Alcohols (Brampton, ON, Canada). All other chemicals used were of analytical grade.

EXTRACTION OF ORANGE ESSENTIAL OIL

For the orange essential oil extraction process, the peels of oranges were frozen and crushed, aiming to increase the contact surface, which results in a higher yield of the process. The essential oil was obtained by hydrodistillation technique using Clevenger apparatus according to methodology described by Kringel *et al.* (2017). In a flask with a capacity of 2 L was added 300 g of crushed orange peel and 1 L of distilled water for extraction of the orange essential oil. The flask was then connected to Clevenger apparatus and heated at boiling temperature by a heating mantle during 3 h. The orange essential oil was stored at -20 ± 2 °C in an amber glass bottle until analysis.

CHEMICAL COMPOSITION AND VOLATILE COMPOUNDS OF OEO

Orange essential oil constituents were identified and the relative composition of the oil was determined by gas chromatography followed by mass spectrometry (GC–MS) following the methodology proposed by Kringel *et al.* (2017). Analyses were carried out using a gas chromatograph equipped with a flame ionization detector (GC-FID; Varian 3400CX, Palo Alto, Calif., U.S.A.). A 1 µL aliquot of OEO diluted in hexane was injected in split mode 1:20, at an injector temperature of 250°C and an electron ionization energy of 70 eV. Analysis were measured in mass analyzer with a scan range of 35 to 350 m/z. Starting at 40 °C, the oven temperature was increased at 4 °C/min to 80 °C, then to 230 °C by at 10 °C/min and kept under isothermal conditions for 2 min. The identification of constituents was based on a comparison of their mass spectra and relative retention indices (RI) against the National Institute of Standards and Technology (NIST) Library. Carrier gas was nitrogen (constant flow 1 mL/min, 99.999% purity). The percentage of each compound was calculated from the peak area in relation to the total area of all peaks.

The volatile compounds were determined using the static headspace by gas chromatography (SH-GC) method. Approximately 40 mg of OEO was used in a 20 mL glass vial, according to methodology described by Kringel *et al.* (2017). The vials were sealed with a silicone/PTFE septum and subjected to a water bath at 30 ± 0.1 °C for 30 min, in order to establish the equilibrium time. Then, 1 mL of headspace was sampled using a gas-tight syringe (SGE, Australia) and injected into the GC-FID injection port. The analysis conditions and the identification of the compounds were performed as described above for determination of chemical composition by GC/MS.

PREPARATION OF ZEIN POLYMER SOLUTION

Polymer solutions of zein were used to produce fibers by electrospinning and capsules by electrospraying techniques. Polymer solutions were prepared under the same conditions, however in two different zein concentrations: using 20% (w/v) zein for fiber formation and 10% (w/v) zein for capsule. The zein powder was dissolved in ethanol solution (70%, v/v, ethanol in water) with the aid of a magnetic stirrer. Subsequently, 30, 40 or 50% (w/w) of OEO was added to the polymer solutions and stirred for 15 min in the dark at 21 ± 2 °C. The concentrations of zein and OEO were determined based on preliminary tests.

DETERMINATION OF ZETA POTENTIAL

The zeta potential was obtained by a dynamic light scattering technique (DLS) using equipment Zetasizer Nano Series (Malvern Instruments, Worcestershire, UK). The polymers solutions were diluted 100 times with ethanol 70% and measured at 25 °C (Biduski *et al.*, 2019).

ELECTROSPRAYING AND ELECTROSPINNING PROCESS

For both techniques, the polymer solutions loaded in a 6 mL plastic syringe pumped (Model 780100; Kd Scientific Inc., Holliston, MA, USA) were electrospinning/electrosprayed with a feed rate of 0.8 mL/h controlled by an

infusion pump (Model 780100; Kd Scientific Inc., Holliston, MA, USA). The spinneret was connected to the positive electrode of a direct current (DC) power supply (Model ES30R-5 W/DM; Gamma High Voltage Research, Ormond Beach, FL, USA). Electrospinning/electrosprayed capsules and fibers were collected on a circular stainless steel collector plate (25 cm of diameter) covered with aluminum foil. The collector–spinneret tip distance was fixed at 20 cm and the voltage applied was 20 kV. The entire electrospun setup was housed within an environmental test chamber (Model MLR-350; SANYO Electric Co., Ltd., Ora-Gun, GU, Japan), maintained at 21 ± 2 °C. The processing time was performed until the all solution contained in the syringe was spinned (7.5 h). The process parameters were determined based on preliminary tests and according to methodology described by Moomand and Lim (2015), with some modifications.

LOADING CAPACITY AND ENCAPSULATION EFFICIENCY

The loading capacity (LC%) and the encapsulation efficiency (EE%) were measured according to Moomand and Lim (2014) by measuring the essential oil present on the surface (nonentrapped), with some modifications. The essential oil in surface was removed by washing an amount of the capsules and fibers with hexane. The absorbance of the liquid (hexane + surface essential oil) was determined by spectrophotometer at 285 nm. The LC and EE were calculated by equations 1 and 2, where A is the total theoretical amount of essential oil added (30, 40, and 50% w/w; OEO/zein), B is amount of free essential oil (mL) in collection solution, and C is the weight of the material (capsules and fibers, in grams).

$$LC = \frac{(A-B)}{C} x100 \quad (1)$$

$$EE = \frac{(A-B)}{A} x100 \quad (2)$$

MORPHOLOGY AND DIAMETER DISTRIBUTION OF THE ELECTROSPINNING/ELECTROSPRAYED CAPSULES AND FIBERS

The morphology of the capsules and fibers was evaluated using a scanning electron microscope (SEM) (Model S-570; Hitachi High Technologies Corp., Tokyo, Japan) at an accelerating voltage of 10 kV. The samples were sputtered-coated with gold using a vacuum metallizer. The mean diameter and diameter distribution of the capsules and ultrafine fibers were evaluated from the SEM images, measuring about 50 fibers, through the ImageJ software (2015 version, USA). (Evangelho *et al.*, 2019a).

FOURIER TRANSFORM INFRARED SPECTROSCOPY ANALYSIS

Infrared spectra of capsules and fibers were collected by using an Fourier transform infrared (FTIR) spectrometer (model IRPrestige-21; Shimadzu Corp., Kyoto, Japan) equipped with an attenuated total reflectance (ATR) accessory (Pike Technologies, Madison, WI, USA). Samples were scanned from 600 to 4000 cm^{-1} at

4 cm^{-1} resolution. An average of 40 scans was taken for each spectrum (Biduski *et al.*, 2019).

STATISTICAL ANALYSIS

Analytical determinations were performed in triplicate and standard deviations were reported. Means were compared by Tukey's test at 5% level of significance by analysis of variance (ANOVA).

RESULTS AND DISCUSSION

CHEMICAL COMPOSITION AND VOLATILE COMPOUNDS OF OEO

The components of the OEO identified by GC/MS and the volatile compounds identified by SH/GC are listed in Table 1. Limonene was identified as the major component of OEO (95.9%), followed by β-myrcene (1.9%), β-linalol (0.96%), α-pinene (0.51%), cis-cimene (0.43%), 4-thujene (0.29%), and α-terpineol (0.05%), totaling 7 compounds identified by GC/MS. Static headspace by gas chromatography (SH-GC) method allowed the identification of 5 volatile compounds of the OEO: limonene (96.7%), β-myrcene (2.05%), β-linalol (0.42%), cis-cimene (0.49%) and 4-thujene (0.29%). α-pinene and α-terpineol were not identified by this method.

Table 1. Chemical composition and volatile compounds of OEO from peels of Valencia variety Citrus *sinensis* (L.) Osbeck.

Compounds	Chemical composition[a] (%)	Volatile compounds[b] (%)
Limonene	95.9	96.7
β-myrcene	1.9	2.05
β-linalol	0.96	0.42
α-pinene	0.51	Nd
cis-cimene	0.43	0.49
4-thujene	0.29	0.29
α-terpineol	0.05	Nd

NOTE: [a]=Essential oil composition determined by GC/MS; [b]= Volatiles composition determined using Static headspace by gas chromatography (SH-GC) method. Nd= not detected.

Limonene is widely used in food industry since it presents a wide spectrum of antimicrobial, antioxidant, therapeutic, and chemotherapeutic properties (Lan *et al.*, 2019, Melendez-Rodriguez *et al.*, 2019, Rezaeinia *et al.*, 2019). Besides, limonene is also classified as generally recognized as safe (GRAS) (Alehosseini, Jafari and Tabarestani, 2021). Similar results were obtained in a study by Razzaghi *et al.* (2019) who reported that orange essential oil is composed mainly of monoterpenes with D-limonene being the major constituent, representing about 94%. This statement is in agreement with El Sawi *et al.* (2019) who isolated the essential oils from peels of three citrus species, among them *Citrus sinensis*, similar to specie used in this study and also mentioned that monoterpenes hydrocarbons group represents the main class of *Citrus sinensis* peel essential oil.

The headspace vapor phase of the orange essential oil is composed almost exclusively by the more volatile monoterpenes, the hydrocarbons (González-Mas *et al.*, 2019) accounting for >98% of the total composition of the essential oil. Similar results were reported by Simas *et al.* (2017) for fruit peel essential oils of four citrus species. Regarding the volatile composition, limonene was the most abundant compound identified, comprising more than 96% of the total oil composition.

ZETA POTENTIAL

The zeta potential values of the capsules and fibers solutions are showed in Fig. 1 (a) and (b), respectively. Zeta potential values are useful for evaluating the electrostatic interaction forces among the particles and therefore can be used as an indicator of the colloidal stability of suspension and consequently of tendency of particle aggregation (Biduski *et al.*, 2019). For both samples solutions (capsules and fibers) the behaviour observed is the same, the zeta potential proportionately increased with increasing concentration of the orange essential oil. The zeta potential was slightly greater for fibers than for capsules, in all the essential oil concentrations studied. The increase in zeta potential value suggests a greater interaction between guest molecule and zein (Liang *et al.*, 2018). According to Gagliardi *et al.* (2018) the increase in the polymer concentration may result in the formation of non-covalent binding between the molecules of the compound or the modulation of the protein conformation, altering the surface charges. Therefore, initially negative surface charges become positives when the polymer concentration was increased, with consequent change of zeta potential values.

Zeta potential values higher than ±30 mV indicate highly charged of negative or positive particles, which physically stabilizes dispersions due to electrostatic repulsion, and zeta potential below ±30 mV, indicating a tendency for particle aggregation due to insufficient levels of polymer to reach the complete saturation of the particle surfaces (Davidov-Pardo, Joye, & McClements, 2015). Thus, the charges on the polymer solution must be high enough to overcome the surface tension of the solution, which has the effect of decreasing the surface area per unit mass of a fluid. Therefore, when there is used a low concentration of polymer and consequently there is a high concentration of free solvent molecules, increased the tendency of these solvent molecules to congregate acquiring a spherical shape (capsules) (Lim, Mendes and Chronakis, 2019).

LOADING CAPACITY AND ENCAPSULATION EFFICIENCY

The loading capacity (%) and encapsulation efficiency (%) of the capsules and fibers loaded of OEO are shown in Figure 2 (a) and (b), respectively. The encapsulation efficiency of OEO in zein capsules ranged from 16.08 to 20.09%; while in zein fibers ranged from 76.58 to 89.24%. Loading capacity and encapsulation efficiency were significantly higher on fibers than capsules. This result shows a significant influence on the increase in the concentration of zein in these parameters.

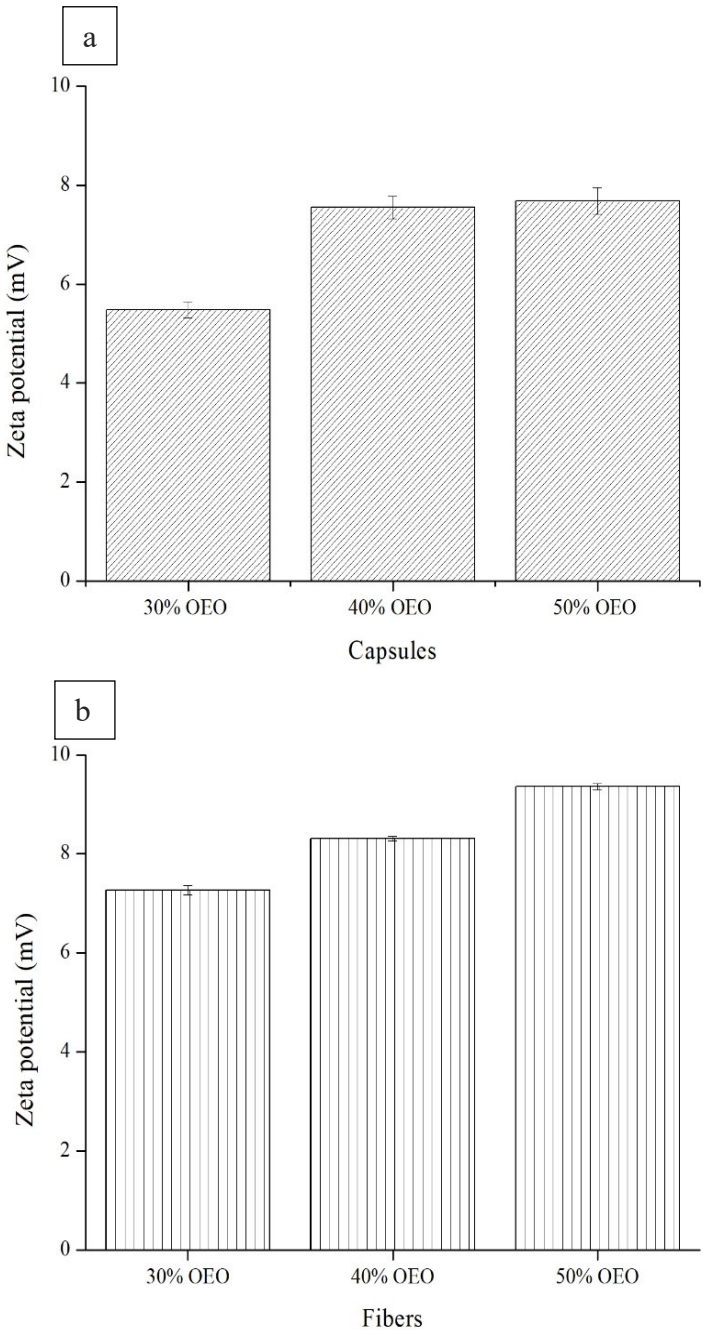

Figure 1. Zeta potential of the zein capsules (a) and fibers (b) solutions with OEO in concentrations of 30%, 40% and 50% (w/w).
NOTE**:** *Each value is the mean of three experiments. Mean ±standard deviation. Different letters differ significantly by Tukey test ($p<0.05$)**.**

This finding suggests that electrosprinning is more efficient for orange essential oil encapsulation compared to electrospraying. The inefficient orange essential oil encapsulation within capsules can be due to ease of vapor diffusion through relatively reduced polymer content used for the formation of capsules compared to the zein concentration used for the fibers (Yao *et al.* 2016). The same behavior was observed by Liang *et al.* (2017) for encapsulation of epigallocatechin

gallate, where the encapsulation efficiency increased proportionally with the increase of zein concentration.

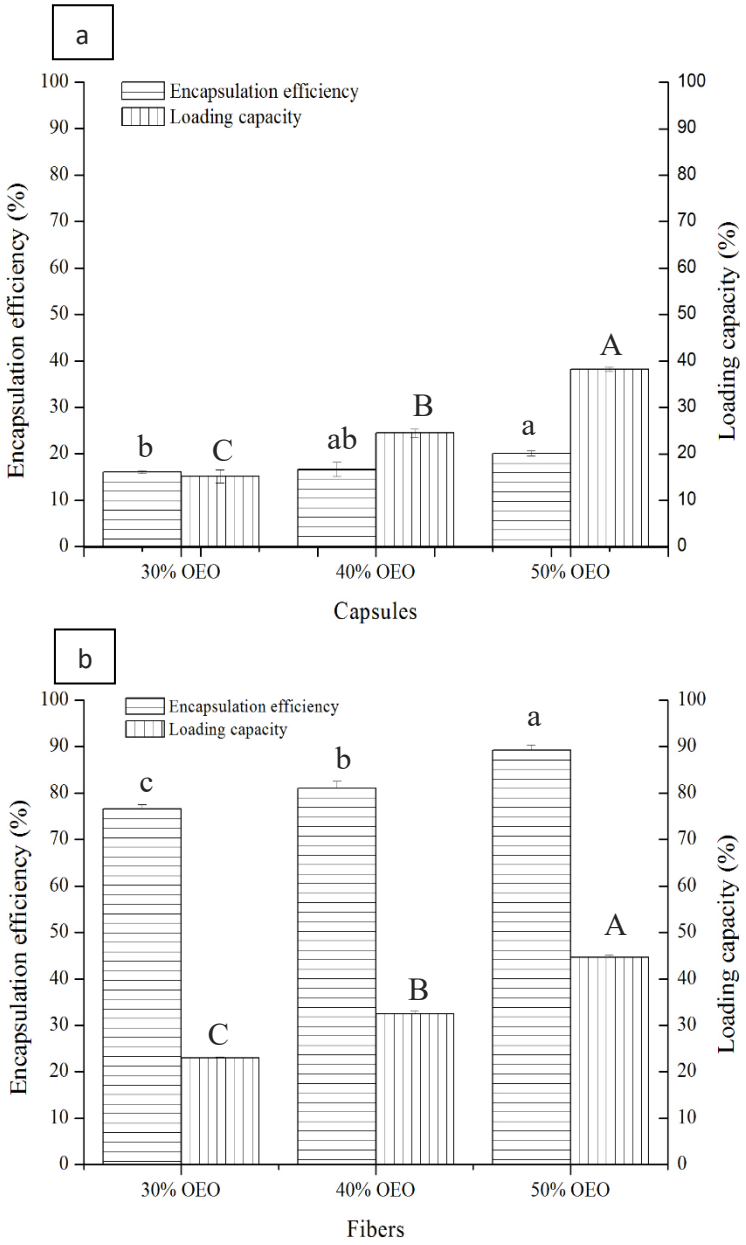

Figure 2. Encapsulation efficiency (%) and loading capacity (%) of the capsules (a) and fibers (b) with OEO in concentrations of 30%, 40% and 50% (w/w).
NOTE: *Each value is the mean of three experiments. Mean ±standard deviation. Different letters, lowercase for EE and uppercase for LC, differ significantly by Tukey test ($p<0.05$)

The increased in zein concentration (electrospinning process) promotes an increase in solution viscosity, leading to a fast drying of the crust in the spinning process, which consequently results in higher retention of OEO. The increase in encapsulation efficiency and loading capacity can be related to the improvement of system stability, i.e., increase in zeta potential. According to Zhang *et al.*, (2020),

increase of zeta potential indicates the improvement of system stability. On the other hand, in the electrospraying process, where a lower concentration of zein is used and consequently a lower solution viscosity is obtained, the time for solvent evaporation is longer, favouring the volatility of OEO until capsule formation (Rajabi *et al.*, 2015). The encapsulation efficiency achieved in this study using electrospinning technique was greater than those reported for OEO using emulsification and coacervation methods, where encapsulation efficiencies range from 40 to 88% (Velmurugan *et al.*, 2017; Ghasemi *et al.*, 2017). This result probably is due to the process conditions used during encapsulation, whereas the electrospinning does not involve severe temperature, pressure and chemical conditions, besides the solvent is evaporated quickly. Thus, the essential oils are protected from volatilization and degradation during encapsulation process (Khoshakhlagh *et al.*, 2017).

Regarding essential oil concentration, in both capsules and fibers, it was possible to observe a significant increase in the values of LC and EE with an increase of OEO concentration. This behaviour can be due to the high capacity of zein as a hydrophobic carrier, loading compounds such as essential oils. The presence of apolar amino acids in zein structure enables hydrophobic interactions with constituents of the essential oil (Krumreich *et al.* 2019). Karim *et al.* (2021) produced zein nanofibers containing cinnamic aldehyde by electrospinning and obtained similar behaviours for EE and LC. Dehcheshmeh and Fathi (2019) encapsulated saffron extract in zein nanofibers by electrospinning and also observed an increase in EE and LC with increased concentration of saffron extract. According to Kringel *et al.* (2017) the affinity between guest and host molecules is influenced by chemical composition, molecular size and structure of the essential oil.

MORPHOLOGY AND DIAMETER DISTRIBUTION

The morphology and size distribution of the capsules (electrosprayed) and fibers (electrospinning) loaded with different concentrations of OEO are presented in Fig. 3 and Fig. 4, respectively. For the capsules in all orange essential oil concentrations studied were observed “shrunken” particles, with wrinkles or dimples (Figure 3a, 3c and 3e). According to Gomez-Estaca *et al.* (2012) this shape of zein particles could be due to an increase in droplet size along with rapid evaporation of the solvent, forming a semi-solid skin of polymer at the surface, that after drying collapses and forms shrunken particles.

Fibers produced with 30 and 50% orange essential oil (Fig. 4a and 4e, respectively) had discontinuous morphology and presence of beads, while the fibers with 40% orange essential oil (Fig. 4c) showed more homogeneous morphology with only a few beads noticed. The OEO concentration had a significant effect on fibers morphologies.

The essential oil addition can promote the reduction of electrical conductivity, leading to a reduction of the elongation of polymer jet by the applied voltage and resulting in the tendency of beads formation and an increase in diameter of fibers. This increase of diameter of fibers generally promotes a higher entrapment of essential oil (Vafania *et al.*, 2019). This statement was confirmed by the higher encapsulation efficiency observed in fibers with 50% of orange essential oil (Figure 2b).

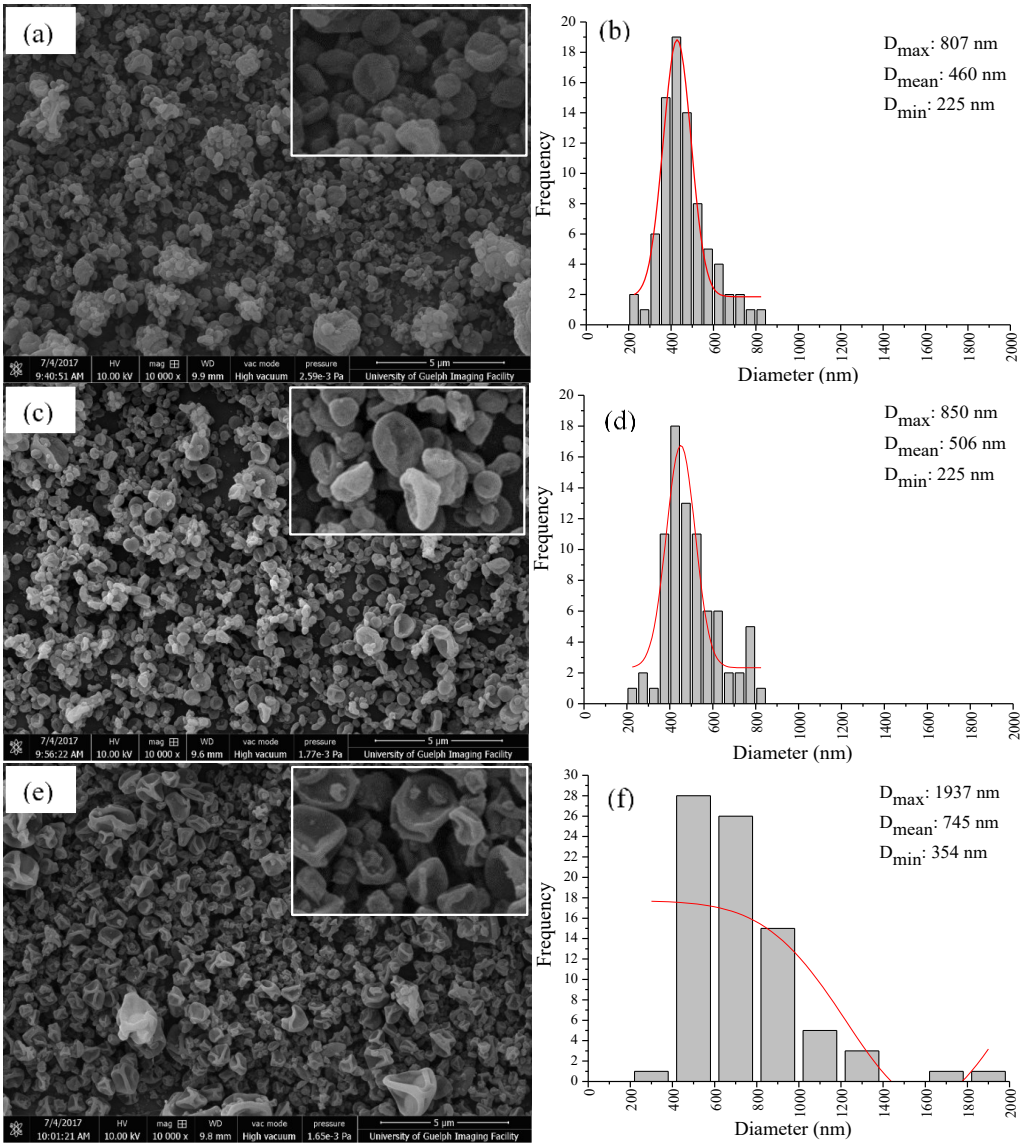

Figure 3. Morphology and size distribution of capsules loaded with OEO in concentrations of 30% (a and b), 40% (c and d) and 50% (e and f); *Note*: concentrations in 10% (w/v) zein for capsule.

The mean diameter of capsules ranged from 460 nm to 745 nm, while the fiber ranged from 107 nm to 166 nm. With increased OEO concentration, higher diameter values were observed in the capsules and fibers. This could be explained due to the fiber thickness which is proportional to the concentration of solids present in the fiber solution. Krumreich *et al.* (2019) reported the same behavior in their study, evaluating the encapsulation of avocado oil in zein fibers; however, the authors found a mean fiber diameter higher than that found in the present study (from 264 to 663 nm).

The differences in the morphologies and size distributions also can be related to polymer concentration. Moomand and Lim (2014) noticed that lower polymer concentration (10% w/w) produced electrosprayed zein aggregates, while higher polymer concentration (20% w/w) resulted in smooth fibers. This may imply that

zein is more suitable for orange essential oil encapsulation in fibers than in capsules.

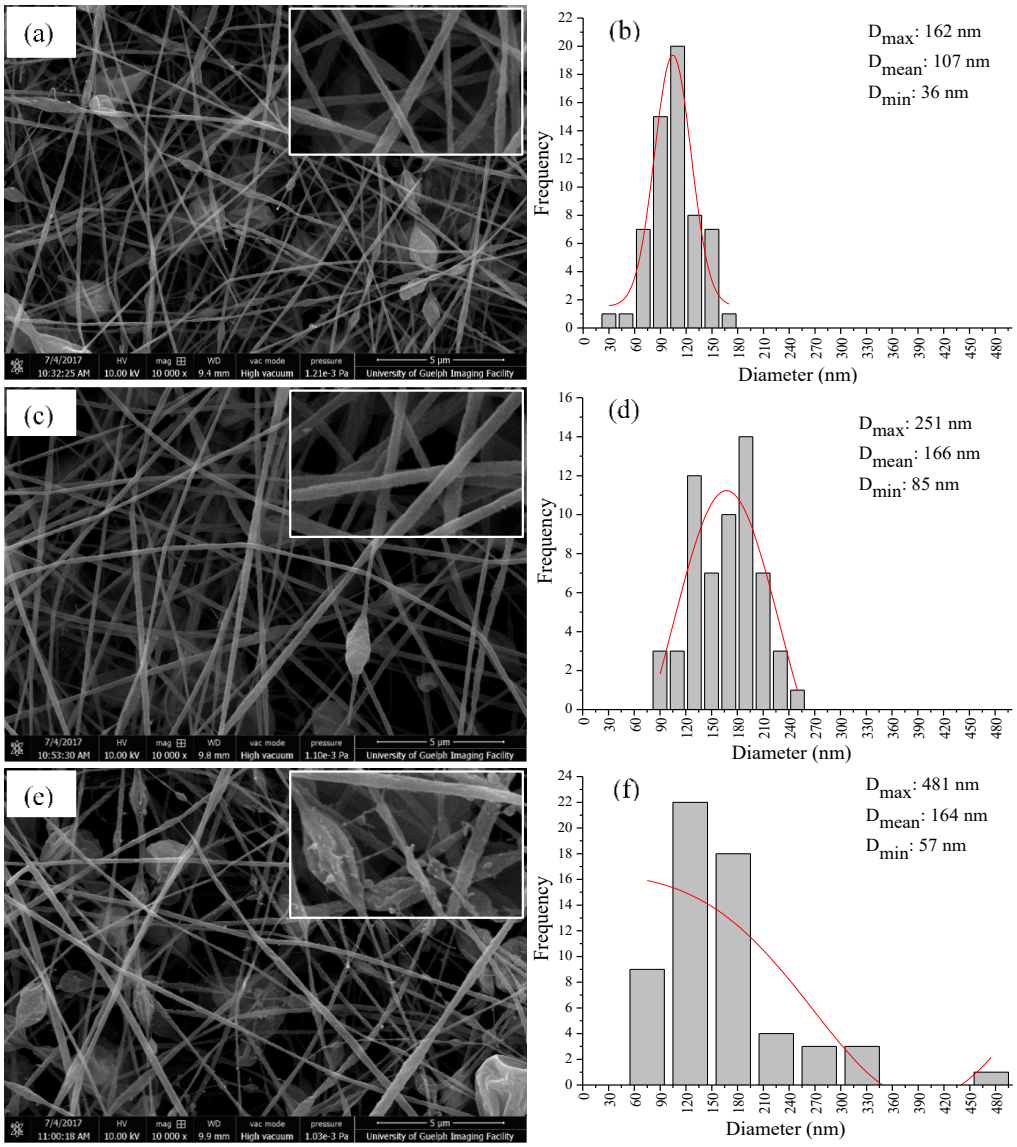

Figure 4. Morphology and size distribution of fibers loaded with OEO in concentrations of 30% (a and b), 40% (c and d) and 50% (e and f); *Note*: concentrations in 20% (w/v) zein for fiber.

FOURIER TRANSFORM INFRARED SPECTROSCOPY ANALYSIS

The spectra of the FTIR analysis of OEO and capsules and fiber are shown in Fig. 5. The interactions between the encapsulated compound (OEO) and wall material (zein) are crucial for stability of products formed (capsules or fibers). The spectra of the zein had characteristic peaks at 1645 and 1446 cm^{-1} attributed to –C=O bond of amide I and –C–N bond of amide II, respectively. The bands in the region from 3288 to 2920 cm^{-1} refer to an O-H stretch superimposed on the N–H stretch and asymmetric and symmetric C-H single bond in relation to the free fatty acid derivatives present in the zein (Evangelho *et al.*, 2019a).

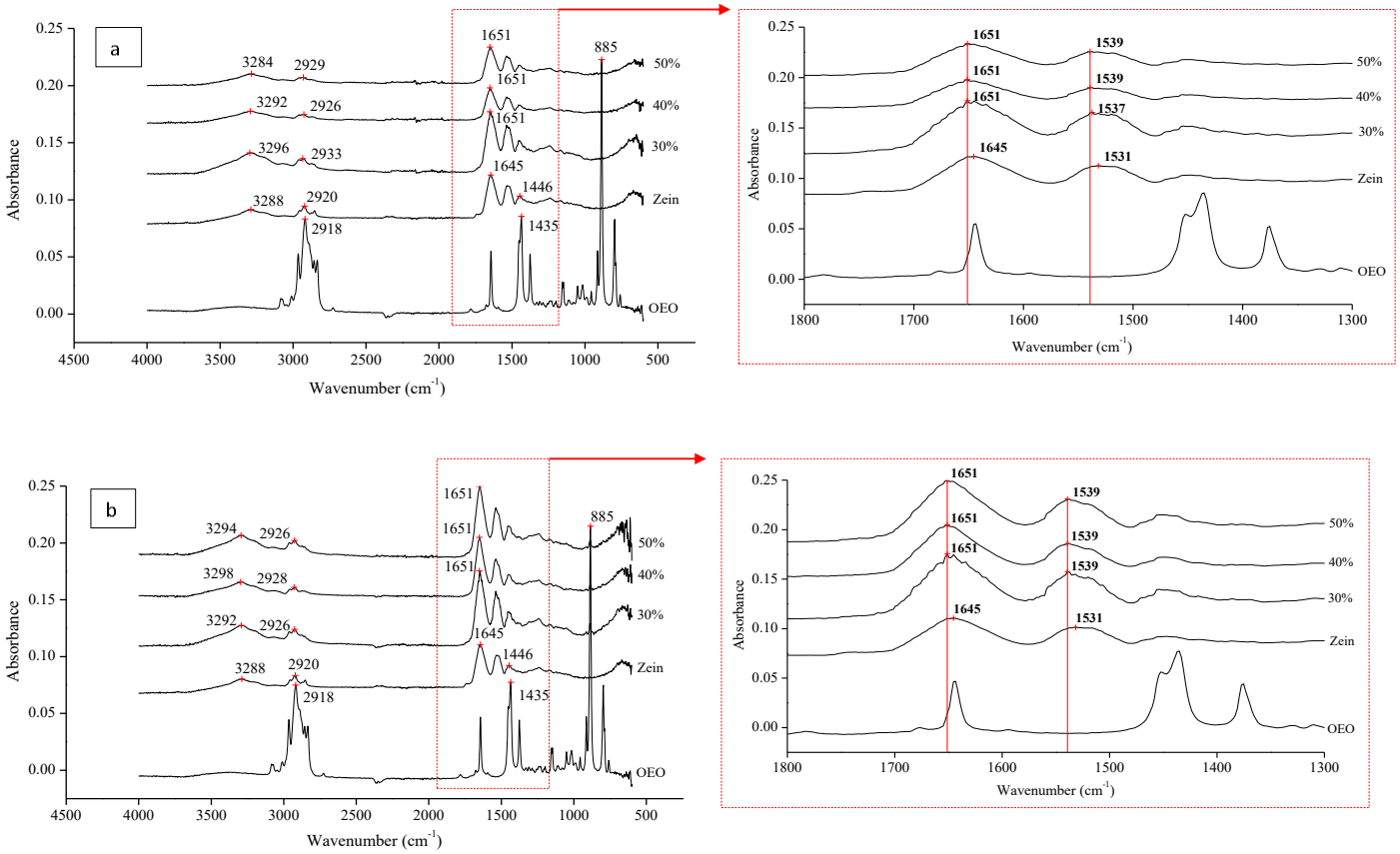

Figure 5. FT-IR spectra of OEO; zein; capsules (a) and fibers (b) loaded with OEO in concentrations of 30%, 40%, 50% (w/w).

The FTIR spectra of pure OEO exposed the existence of functional groups at ~2918 cm^{-1}, 1435 cm^{-1}, and 885 cm^{-1} and, corresponding to alkane group due to the methyl C-H asymmetrical stretch, carbonyl C=O stretching vibration, aromatic ring stretch (C=C), presence of terpenoid components (C-O) and C-H stretch, respectively (Bounaas *et al.*, 2018; Hasani *et al.*, 2018; Velmurugan *et al.*, 2017).

Regarding to capsules and fibers, all of the characteristic peaks of the OEO disappeared from the spectra of all samples, independent of the OEO concentrations tested (30, 40 and 50% of OEO). Liu *et al.* (2018) also noted the absence of the characteristic peaks of the Tamoxifen Citrate (TAM) from the spectra of the electrosprayed particles compared to the spectra of pure TAM. The authors attributed this to the possible interactions among the constituents of the particles.

Besides that, both capsules and fibers at OEO concentrations of 30%, 40%, and 50% (w/w) present only slight differences in the peaks for the pure zein capsules or fibers (with 0% of OEO). These differences can be attributed to the characteristic absorbances of the –C=O (since 1651 cm^{-1} to 16645 cm^{-1}) and –C–N (since 1539 cm^{-1} to 1531 cm^{-1}) groups in zein fibers slightly shifted, in all OEO concentrations, suggesting the formation of hydrogen bonds between zein and OEO molecules, which suggest the compatibility between these components. Evangelho *et al.*

(2019a) also found this behavior in zein capsules with folic acid, when observed a displacement in the amide I and II bands, compared to the pure zein capsules. Additionally, in the capsules spectra (Fig. 5a) also was noted the disappearance of the characteristic O-H stretch band, between 3000–3600 cm^{-1}, which also suggests the formation of hydrogen interactions between zein and OEO.

Considering the insolubility of zein in water, future studies on its controlled release having as a trigger the change in moisture content of packaged fresh produce would be interesting. The excess of water molecules could precipitate the zein and weaken the interaction between zein and guest molecules in the outer environment. Therefore, the moisture-triggered release could be interesting for release of the OEO contained in the zein capsules and fibers. This hypothesis suggests that zein capsules and fibers containing OEO might have potential application in developing moisture controlled active packaging materials, they can be administered for delivery and release of OEO bioactive, protection of sensorially, protection of volatile compounds.

CONCLUSIONS

Polymer solutions of zein were not suitable to form capsules for loading of OEO by electrospraying technique. OEO was successfully encapsulated into zein electrospinning fibers and increasing OEO concentration resulted in higher encapsulation efficiency (89.24%); moreover, zein fibers loaded with the intermediate concentration of OEO (40%; w/w) presented more uniform morphology, with less beads and with a smooth surface. The interactions between zein and OEO were evidenced by Fourier transform infrared-Attenuated Total Reflection (FTIR-ATR) analysis.

Despite low encapsulation efficiency showed in this study, electrosprayed capsules had a greater diameter which may be ideal for more protection of loaded oils; however, further studies are needed to prove this relationship.

Therefore, considering mainly the high encapsulation efficiency, we conclude that electrospinning are more suitable technique for encapsulation of OEO using zein as polymer. Zein fibers loaded essential oils and prepared by electrospinning present promising characteristics for application in food packaging. However, complementary studies are needed to assess release over storage or specific application conditions.

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Electrospinning vs. electrospraying: avaliação comparativa de duas técnicas para encapsulamento de óleo essencial de laranja

RESUMO

O objetivo deste estudo foi encapsular o óleo essencial de laranja (OEO) em polímero zeína pelas técnicas de *electrospinning/electrospraying*. OEO nas concentrações de 30, 40 e 50% (p / p), foi incorporado em soluções de polímero zeína a 10 e 20% (p / v), para a formação das cápsulas e fibras, respectivamente. As soluções de polímero foram avaliadas quanto ao potencial zeta. As fibras e cápsulas foram submetidas a *electrospinning*/*electosprayed* e avaliadas quanto à eficiência de encapsulação (EE%), capacidade de carga (LC%), morfologia, distribuição de tamanhos e espectro infravermelho. O potencial Zeta aumentou proporcionalmente com o aumento da concentração de OEO. As fibras apresentaram valores de EE mais elevados (77–89%) do que as cápsulas (16-20%). A maior concentração de OEO apresentou maior EE para ambos os produtos (cápsulas e fibras) e melhorou a morfologia da fibra. O processo de *electrospinning* foi mais eficiente do que *electrospraying* para encapsulamento OEO utilizando zeína como matriz polimérica, mostrando que esta técnica é adequada para encapsulamento de óleos essenciais.

PALAVRAS-CHAVE: cápsulas; *electrospinning*; *electrospray;* fibras; óleo essencial de laranja.

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