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Physicochemical characterization and oxidative stability of fish oil-loaded electrosprayed capsules: Combined use of whey protein and carbohydrates as wall materials

Pedro J. García-Moreno [a, *], Andres Pelayo [a], Sen Yu [a], María Busolo [b, c], Jose M. Lagaron [b, c], Ioannis S. Chronakis [a], Charlotte Jacobsen [a]

[a] Division of Food Technology, National Food Institute, Technical University of Denmark, Denmark
[b] Novel Materials and Nanotechnology Group, IATA-CSIC, Spain
[c] Bioinicia S.L., Spain

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ABSTRACT

The encapsulation of fish oil in electrosprayed capsules using whey protein and carbohydrates (pullulan and dextran or glucose syrup) mixtures as glassy wall materials was studied. Capsules with fish oil emulsified by using only a rotor-stator emulsification exhibited higher oxidative stability than capsules where the oil was emulsified by high-pressure homogenization. Moreover, glucose syrup capsules (with a peroxide value, PV, of 19.7 ± 4.4 meq/kg oil and a content of 1-penten-3-ol of 751.0 ± 69.8 ng/g oil) were less oxidized than dextran capsules after 21 days of storage at 20 °C (PV of 24.9 ± 0.4 meq/kg oil and 1-penten-3-ol of 1161.0 ± 222.0 ng/g oil). This finding may be attributed to differences in oxygen permeability between both types of capsules. These results indicated the potential of both combinations of whey protein, pullulan, and dextran or glucose syrup as shell materials for the encapsulation of omega-3 PUFA in nano-microcapsules obtained by electrospraying.

1. Introduction

Long chain omega-3 polyunsaturated fatty acids (PUFA) such as eicosapentaenoic (C20:5n-3) and docosahexaenoic (C22:6n-3) acids, which are mainly extracted from fish, krill or microalgae biomass, have numerous beneficial health effects on humans (Calder, 2017). Hence, and due to the low consumption of fish, krill or algae-based products by Western populations, the development of food fortified with omega-3 PUFA is still having an increasing interest for the food industry (GOED, 2015). Nevertheless, these nutritionally beneficial lipids are highly prone to oxidation (i.e. due to their high content of bis-allylic hydrogens), which limit their successful incorporation into complex food systems (e.g. containing prooxidants such as metal ions) (Jacobsen, 2015).

In this regard, encapsulation of omega-3 PUFA is an approach generally used to avoid their oxidative deterioration (i.e. formation of secondary volatile oxidation products which are responsible for undesirable off-flavours) (García Moreno et al., 2016). An emerging encapsulation technique for producing omega-3 nano-microencapsulates is electrospraying (Torres-Giner et al., 2010). Contrary to spray-drying (the most employed encapsulation technique), electrospraying can be carried out at room temperature, which should result in a better stability of thermo-sensitive bioactives (Lim, 2015). The process uses a high-voltage electrostatic field to charge the surface of a biopolymer solution droplet at the end of a capillary tube. When the surface tension of the droplet is overcome by the electric field, a charged jet is ejected from the tip of the Taylor cone (formed at the end of the capillary tube) to a grounded collector. Due to the low visco-elasticity of the biopolymer solution, the jet destabilize due to varicose instability forming fine highly charged droplets. On the way to the collector, the droplets are further disrupted due to electrostatic repulsion, which favors solvent evaporation resulting in solids particles (Ghorani and Tucker, 2015). Electrosprayed encapsulates, which present high encapsulation efficiency and large surface-to-volume ratio, are of special interest for the food industry for the encapsulation of unstable bioactive compounds

* Corresponding author.
E-mail address: pejeg@food.dtu.dk (P.J. García-Moreno).

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such as vitamins, probiotics, antioxidants and omega-3 fatty acids. Furthermore, due to their reduced size, these novel encapsulates exhibit a higher bioaccessibility than traditional capsules (Jacobsen et al., 2018).

To the best of the authors' knowledge, omega-3 fatty acids have only been encapsulated by electrospraying when using proteins such as zein, whey protein concentrate, soy protein isolate, and gelatin as shell material (Gómez-Mascaraque and López-Rubio, 2016; Moomand and Lim, 2015; Torres-Giner et al., 2010). In the authors' previous work, the potential of dextran as a biopolymer shell to produce fish oil-loaded electrosprayed capsules was reported. However, further optimization of dextran solutions was required to improve the physical stability of the emulsion as well as the oil entrapment within the capsules (García-Moreno et al., 2017a). To this end, an interesting approach to be evaluated is the combination of both carbohydrates, which usually act as filler or matrix-forming material, and proteins, which exhibit emulsifying properties and are effective film-formers (Augustin and Oliver, 2014). Dairy proteins (e.g. whey protein or casein), which also exhibit antioxidant properties (Adjonu et al., 2014), are usually combined with carbohydrates (i.e. glucose syrup, lactose, maltodextrin, starch) in order to obtain fish oil-loaded microencapsulates by spray-drying with enhanced properties (Encina et al., 2016). For instance, Aghbashlo et al. (2012) reported the production of microcapsules by spray-drying with significantly higher encapsulation efficiencies using mixtures of skim milk powder and lactose or sucrose (70% and 30%, respectively) when compared to the use of only skim milk powder. Likewise, Ramakrishnan et al. (2013) found that the replacement of part of whey protein by maltodextrin as wall materials increased the oxidative stability of fish oil-loaded microcapsules. This was attributed to lower oxygen permeability of the shell material composed of maltodextrin. Furthermore, the incorporation of high-molecular weight carbohydrates (e.g. starch, maltodextrin, dextran) also increases the glass transition temperature of the wall material, which implies that the shell material will be in glassy state in a broader range of temperature (Schutyser et al., 2012). Glassy state of the protein-carbohydrate matrix is preferred to rubbery state due to its lower free volume, which restricts diffusion of oxygen and other prooxidants (i.e. trace of metals) enhancing the oxidative stability of the encapsulates (Hu, 2016). In addition, the use of carbohydrates as encapsulating material, which are not digested in the stomach, will allow a more targeted delivery of omega-3 PUFA (e.g. in the small intestine where most absorption occurs) (Fathi et al., 2014).

In the light of the above, this work aimed at investigating the encapsulation of fish oil by electrospraying using combinations of whey protein and carbohydrates as biopolymers. Dextran and glucose syrup were selected as carbohydrates due to their appropriate properties to form electrosprayed capsules (García-Moreno et al., 2017a) and to their successful use in spray-dried capsules loaded with oils rich in omega-3 PUFA (Tamm et al., 2016), respectively. First, the influence of total concentration of biopolymers and carbohydrate to protein ratio on oil droplet size, electrospraying flow rate, and morphology of the capsules was assessed in lab scale. Secondly, the approach used to emulsify the oil (i.e. high pressure homogenization or rotor-stator emulsification) in the optimized biopolymers solution was studied. Particularly, the ability to entrap the oil and the oil distribution of capsules produced by a high-throughput electrospraying process in pilot-plant scale was investigated. Finally, the protective effect against oxidative degradation of the different encapsulating matrices used was investigated during storage of the fish oil-loaded nano-microcapsules.

2. Materials and methods

2.1. Materials

Dextran (molecular weight = 70,000 Da, dextran70) was generously provided by Pharmacosmos A/S (Holbaek, Denmark). Glucose syrup (DE38, C*Dry 1934) was kindly provided by Cargill Germany GmbH (Krefeld, Germany). Pullulan (molecular weight = 200,000 Da) was donated by Hayashibara Co., Ltd. (Okayama, Japan). Whey protein concentrate (WPC), under the commercial name of Lacprodan® DI-8090, was provided by ARLA Food Ingredients (Viby, Denmark). Citrem (citric acid ester without antioxidants) was provided from Danisco (Copenhagen, Denmark). The peroxide value (PV) of the citrem used was 2.3 ± 0.1 meq/kg oil. Commercial cod liver oil was donated by Maritex A/S, subsidiary of TINE, BA (Sortland, Norway) and stored at −40 °C until use. The fatty acid composition of the fish oil was determined by fatty acid methylation (AOCS, 1998a) followed by separation through GC (AOCS, 1998b). It was (major fatty acids only) as follows: C16:0, 9.5%; C16:1, 8.7%; C18:1, 16.3%; C20:1, 12.6%; C20:5, 9.2%; and C22:6, 11.4%. The tocopherol content of the fish oil was: α-tocopherol, 200 ± 3 μg/g oil; β-tocopherol, 5 ± 1 μg/g oil; γ-tocopherol, 96 ± 3 μg/g oil; and δ-tocopherol, 47 ± 1 μg/g oil (AOCS, 1998c). PV of the fish oil used was 0.4 ± 0.1 meq/kg oil. All other chemicals and solvents used were of analytical grade.

2.2. Preparation of biopolymer solutions containing fish oil

2.2.1. For optimization of capsules morphology in lab scale

Electrospraying solutions containing fish oil (20 wt% with respect to biopolymer), WPC (1 wt%), and carbohydrates (pullulan and dextran or glucose syrup) at different concentrations (1–5 wt% pullulan and 15 or 20 wt% dextran or 15 wt% glucose syrup) were tested in lab scale in order to optimize capsule morphology. First, WPC, pullulan, and dextran or glucose syrup were dissolved in distilled water by stirring overnight at 500 rpm. Secondly, fish oil was added slowly to the biopolymers solution during mixing at 16,000 rpm using an Ystral mixer (Ystral Gmbh, Ballrechten-Dottingen, Germany). The fish oil was added during the first minute of mixing, and the total mixing time was 3 min. Further homogenization was done on a microfluidizer (M110L Microfluidics, Newton, MA, USA) equipped with a ceramic interaction chamber (CIXC, F20Y, internal dimension 75 μm). Emulsions were homogenized at a pressure of 9000 psi, running 3 passes. Samples were used immediately after production for electrospraying processing in lab scale and for droplet size analysis.

2.2.2. For production in pilot plant

Biopolymer solutions containing fish oil for processing in pilot plant were prepared following two different approaches to emulsify the oil. In the first approach, fish oil was emulsified by using high pressure homogenization. Briefly, pullulan and dextran or glucose syrup were dissolved in distilled water under constant stirring (500 rpm) at room temperature. Fish oil was added as 10 wt% fish oil-in-water emulsion stabilized with 1 wt% WPC and 1 wt% citrem at pH 7. The homogenization process was carried out by using an Ystral mixer followed by microfluidizer (M110L Microfluidics, Newton, MA, USA) as described above. The biopolymer solutions and the fish oil-in-water emulsion were mixed under nitrogen atmosphere by using magnetic stirring (500 rpm) for 30 min at 5 °C in the dark. Finally, the resulting emulsion was passed 3 times through microfluidizer (M110L Microfluidics, Newton, MA, USA) at a pressure of 9000 psi. The resulting electrospraying solutions contained 20 wt% fish oil (with