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Encapsulation of fish oil in nanofibers by emulsion electrospinning: Physical characterization and oxidative stability

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ABSTRACT

The encapsulation of fish oil in poly(vinyl alcohol) (PVA) nanofibers by emulsion electrospinning was investigated. Independently of the emulsifier used, whey protein isolate (WPI) or fish protein hydrolysate (FPH), PVA concentration had a high influence on fiber morphology. Fibers without bead defects were only produced for solutions with 10.5% (w/w) PVA, which presented sufficient number of polymer chain entanglements. On the other hand, increasing oil load from 1.5 to 3% (w/w) resulted in fibers with larger diameters containing spindle-like enlargements interspersed. High omega-3 encapsulation efficiency (92.4 ± 2.3%) was obtained for fibers produced from 10.5% (w/w) PVA-5% (w/w) emulsion blend stabilized with WPI, resulting in an oil load capacity of 11.3 ± 0.3%. Moreover, the encapsulated oil was randomly distributed as small droplets inside the fibers. However, the electrospun fibers presented a higher content of hydroperoxides and secondary oxidation products (e.g. 1-penten-3-ol, hexanal, octanal and nonanal) compared to emulsified and unprotected fish oil.

1. Introduction

Omega-3 polyunsaturated fatty acids (PUFA), particularly eicosapentaenoic (C20:5n-3, EPA) and docosahexaenoic (C22:6n-3, DHA), have numerous beneficial health effects such as prevention of cardiovascular disease, improvement of the anti-inflammatory response and development of brain and eye retina in infants (Uauy and Valenzuela, 2000; Ward and Singh, 2005). These PUFA need to be ingested through the diet since humans have a low conversion rate of the essential α→linolenic fatty acid (ALA) to EPA and DHA (Colussi et al., 2007). As a consequence, the food industry has an increasing interest in developing omega-3 enriched foods. Accordingly, efficient strategies for protecting these highly unsaturated fatty acids against oxidation when incorporated into foods are necessary in order to avoid both the loss of nutritional value and the formation of unpleasant off-flavors. For that purpose, omega-3 delivery systems (e.g. fish oil-in-water emulsions and microencapsulated fish oil) are often employed since they can protect the oil against prooxidants in the food system by providing a physical barrier between the omega-3 oil and oxygen or prooxidants (e.g. metal ions) (Jacobsen and Nielsen, 2007). The employment of emulsified omega-3 oils is more suitable for liquid or semi-liquid foods due to handling/mixing issues. Although a higher oxidative stability was obtained when adding fish oil emulsions to milk, negative results were obtained when adding emulsified fish oil to other food systems such as yoghurt and salad dressings (Let et al., 2007). On the other hand, microencapsulated fish oil, commonly produced by spray-drying, presents in many cases a higher oxidative stability when compared to neat fish oil (Nielsen and Jacobsen, 2013). Nevertheless, the application of the resulting microcapsules is limited to dry food products (e.g. powdered infant formula) due to their poor solubility (Drusch, 2012). Furthermore, the spray-drying process requires air at high temperature (170–190 °C) which causes initial oxidation of the oil (Serfert et al., 2009). In addition, powdered product is deposited in a large amount on the outlet pipe and chamber wall during spray-drying, which reduces yield (Wan et al., 2011).

Therefore, the development of alternative omega-3 PUFA delivery systems, which are easy to disperse and which lead to improved oxidative stability of omega-3 enriched food products are

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required. In this sense, electrospinning processing is a straightforward and versatile encapsulation technique suitable for the production of nano-microfibers containing bioactive compounds (Aceituno-Medina et al., 2013; Stephansen et al., 2014). The process uses a high-voltage electro-static field to charge the surface of a polymer solution droplet formed at the end of a capillary tube. Mutual charge repulsion causes a force directly opposite to the surface tension which elongates the droplet forming a conical shape known as the Taylor cone. When the electrical forces overcome the surface tension, an electrically charged jet is ejected from the tip of the Taylor cone. On the way to the collector, the jet is stretched out due to several instabilities (e.g. whipping or bending motions) which favor the evaporation of the solvent resulting in dried fibers (Doshi and Reneker, 1995; Frenot and Chronakis, 2003). Electrospinning processing presents several advantages such as: i) it does not require heat, thus avoiding deterioration of the active compound, and ii) it results in decreased encapsulates size which allows their incorporation into food systems without affecting the sensory qualities of the product (Li et al., 2013; Weiss et al., 2012).

Recently, lipophilic compounds such as β-carotene and fish oil have successfully been entrapped into nanofibers produced by electrospinning of zein aqueous-ethanol solutions (Fernandez et al., 2009; Moomand and Lim, 2014). However, zein, which is a hydrophobic food-approved biopolymer, has a high cost which reduces its use in food applications (Kushwaha and Kawtikwar, 2013). In this context, emulsion electrospinning is a promising alternative since it allows for the encapsulation of hydrophobic compounds in low-cost hydrophilic polymers, avoiding also the use of organic solvents which are restricted in food systems (Arecchi et al., 2010). A few studies have already been reported on the encapsulation of lipophilic compounds (e.g. mineral oil, hexadecane, limonene, retinyl palmitate and *n*-butyl acetate) using this technique (Angeles et al., 2008; Arecchi et al., 2010; Camerlo et al., 2014; Gordon et al., 2015). These authors employed small-sized molecular surfactants such as Pluronic P105 (Angeles et al., 2008), Tween 20 (Arecchi et al., 2010; Camerlo et al., 2014) and Brij O10, and mixtures of Tween 80 and Span 80 (Gordon et al., 2015) as emulsifiers. Apart from the study of Angeles et al. (2008) which used polyethylene oxide (PEO), the remaining studies employed poly(vinyl) alcohol (PVA) as polymer since it has a higher thermal stability and lower cost than PEO, it is biocompatible, non-toxic, and presents sufficient amounts of chain entanglements which allow for the formation of fibers by electrospinning (Weiss et al., 2012). To the best of the authors' knowledge, no research work on the encapsulation of fish oil in nanofibers obtained by emulsion electrospinning has been previously published.

Thus, the aim of this work was to study the development of omega-3 delivery systems by emulsion electrospinning using PVA as polymer. Firstly, the effect of polymer concentration, oil load and type of emulsifier on the morphology of the fibers was evaluated. Secondly, the oxidative stability during storage of fish oil encapsulated in selected fibers was studied. Contrarily to previous works, which used low molecular weight surfactants, proteins such as whey protein isolate (WPI) and fish protein hydrolysate (FPH) were assayed as emulsifiers in this study. WPI is normally used in the food industry to stabilize oil-in-water emulsions because of its functional, bioactive and nutritional properties (Adjonu et al., 2014). Recently, FPH has also been reported as a promising alternative emulsifier leading to physical and oxidative stable fish oil-in-water emulsions (García-Moreno et al., 2016; Morales-Medina et al., 2016).

2. Materials and methods

2.1. Materials

Commercial cod liver oil was kindly provided 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 as follows (%, w/w): 9.5% palmitic acid (C16:0), 8.7% pamitoleic acid (C16:1n–7), 2.0% stearic acid (C18:0), 16.3% oleic acid (C18:1n–9), 4.8% vaccenic acid (C18:1n–7), 1.8% linoleic acid (C18:2n–6), 2.6% α-linolenic acid (C18:3n–3), 12.6% gadoleic acid (C20:1n–11), 9.2% eicosapentaenoic acid (C20:5n–3), 6.0% cetoleic acid (C22:1n–11), 11.4% docosahexaenoic acid (C22:6n–3) and 15.1% others. 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. The peroxide value (PV) of the fish oil used was 0.38 ± 0.04 meq/kg oil. Whey protein isolate (WPI), with commercial name Laprodan® DI-9224, was kindly donated by ARLA (ARLA Food Ingredients, Viby, Denmark). Fish protein hydrolysate (FPH) with a degree of hydrolysis of 4% was produced from sardine muscle using Alcalase 2.4 L (Novozymes, Bagsværd, Denmark) as described by García-Moreno et al. (2016). Three different types of poly(vinyl alcohol) (PVA) were purchased from Sigma-Aldrich (Brøndby, Denmark): a) Mowiol® 4–98 (molecular weight = 27,000 Da; degree of hydrolysis = 98–98.8%), b) Mowiol® 8–88 (molecular weight = 67,000 Da; degree of hydrolysis = 86.7–88.7%), and c) Mowiol® 18–88 (molecular weight = 130,000 Da; degree of hydrolysis = 86.7–88.7%). PVA partially saponified (130,000 Da) was kindly provided by Kuraray Europe GmbH.

2.2. Preparation of fish oil-in-water emulsion

Six different emulsions, stabilized with WPI or FPH and with fish oil content of 5, 7.5 and 10% (w/w), were produced. Aqueous phases were prepared by dissolving WPI (1%, w/w) or FPH (2%, w/w) in distilled water and the pH was adjusted to pH 2 by addition of 0.1 N HCl. Acidic pH (pH 2) led to the lowest interfacial tension for sardine hydrolysate, which may be related with increased solubility of fish protein at low pH (Morales-Medina et al., 2016). The aqueous solutions were then stirred overnight at 5 °C to allow complete rehydration of the protein. Primary homogenization was done by adding the fish oil (5, 7.5 and 10%, w/w) slowly to the aqueous phase during mixing at 16,000 rpm (Ystral mixer, Ballrechten-Dottingen, Germany). The fish oil was added during the first minute of mixing, and the total mixing time was 3 min. Secondary 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. Another emulsion (12% fish oil-in-water emulsion, w/w) stabilized with WPI was also produced only for measurement of lipid oxidation.

2.3. Preparation of fish oil-in-water emulsion-PVA solutions for electrospinning

Preliminary experiments (data not shown) indicated that adding PVA to the aqueous phase before the homogenization process led to the formation of more and larger beads in the fibers. This may be associated to a reduction in the viscosity of the solution as consequence of the homogenization process. Furthermore, adding PVA before the homogenization process also resulted in larger emulsion droplet size, which may decrease the encapsulation efficiency. The influence of the molecular weight of PVA (27, 67 and

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