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Encapsulation, protection, and release of polyunsaturated lipids using biopolymer-based hydrogel particles

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ABSTRACT

Delivery systems are needed to encapsulate polyunsaturated lipids, protect them within food products, and ensure their bioavailability within the gastrointestinal tract. Hydrogel particles assembled from food-grade biopolymers are particularly suitable for this purpose. In this study, hydrogel microspheres were fabricated by electrostatic complexation of low methoxy pectin and caseinate by decreasing the solution pH from 7 to 4.5. After hydrogel particle formation, the caseinate was enzymatically cross-linked using transglutaminase to improve the stability of the biopolymer matrix. The effect of hydrogel particle encapsulation on the physical location, chemical stability, and lipase digestibility of emulsified polyunsaturated lipids (fish oil) was investigated. The cross-linked hydrogel particles formed using this process were relatively small ($D_{43} = 4.6$ μm), negatively charged ($\zeta = -37$ mV), and evenly distributed within the system. Confocal microscopy confirmed that the fish oil droplets were trapped within casein-rich hydrogel microspheres. Encapsulation of the fish oil droplets improved their stability to lipid oxidation compared to conventional emulsions, which was attributed to a high local concentration of antioxidant protein around the emulsified lipids. The rate and extent of digestion of the encapsulated lipid droplets within a simulated small intestine were similar to those of non-encapsulated ones. These results suggest that casein-rich hydrogel microspheres may protect polyunsaturated lipids in foods and beverages, but release them after ingestion.

1. Introduction

Epidemiological, clinical, and experimental studies indicate that fish oil, which contains n − 3 polyunsaturated fatty acids (n − 3 PUFAs) such as eicosapentaenoic acid (EPA, 20:5 n − 3) and docosahexaenoic acid (DHA, 22:6, n − 3), can protect against the development of chronic diseases such as heart disease, brain disease, arthritis, and certain types of cancer (Riediger, Othman, Suh, & Moghadasian, 2009; Yashodhara et al., 2009). In the USA, where a western-style diet is predominant, the average fish intake is currently well below the recommended two to three servings per week (Kolanowski & Weissrodt, 2007). There is therefore a concerted effort to enrich various food and beverage products with n − 3 PUFA so as to improve their healthfulness. However, there are a number of challenges associated with incorporating these bioactive lipids into foods. First, PUFAs are highly non-polar molecules with low water-solubility and therefore have to be encapsulated within emulsion-based delivery systems if they are going to be introduced into aqueous-based products (Mao & McClements, 2012; McClements, 2010). Second, PUFAs are highly susceptible to chemical degradation due to lipid oxidation, which leads to a reduction in product quality and acceptability, and therefore they have to be protected against this form of chemical degradation (Drusch, Benedetti, Scampicchio, & Mannino, 2008; Jacobsen, 2008; Jacobsen, Let, Nielsen, & Meyer, 2008; Tikekar & Nitin, 2012; Waraho, McClements, & Decker, 2011). Third, it is important that PUFAs are fully absorbed within the upper gastrointestinal (GI) tract after oral ingestion so that they can demonstrate their beneficial health effects (Michalski et al., 2013). Consequently, there is a need to develop effective food-grade delivery systems to encapsulate, protect, and release PUFAs.

Filled hydrogel microspheres are examples of $O/W_1/W_2$ type structured emulsions that have potential for utilization as effective delivery systems for bioactive lipids (Norton & Frith, 2001). These systems contain lipid droplets trapped within biopolymer microspheres (W_1), which are themselves suspended within a continuous aqueous phase (W_2) (Chung, Degner, Decker, & McClements, 2013; Matalanis, Lesmes, Decker, & McClements, 2010). The internal biopolymer matrix (W_1) can be gelled to stabilize the filled hydrogel particles by changing solution conditions, such as pH, ionic composition, temperature, or enzyme addition (Norton & Frith, 2001). Previous studies in our laboratory have shown that hydrogel particles can be used to encapsulate emulsified lipids and to control their digestion within a simulated GI tract (Li, Hu, Du, Xiao, & McClements, 2011; Matalanis & McClements, 2012).

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In the present study, we fabricated filled hydrogel particles containing n − 3 PUFA droplets embedded within a dietary fiber matrix formed by complex coacervation. Complex coacervation primarily depends on the charge density, molecular structure, and concentrations of the biopolymers used. In food systems, the formation of hydrogel particles by complex coacervation is usually controlled by altering the pH or ionic strength since this modulates the electrostatic interactions that normally drive complex formation (Schmitt, Sanchez, Desobry-Banon, & Hardy, 1998; Schmitt & Turgeon, 2011). Protein–polysaccharide coacervation has been investigated for a number of potential applications in the food industry, including fat substitution, protein separation, texture modification, enzyme immobilization, and flavor encapsulation (Lutz, Aserin, Portnoy, Gottlieb, & Garti, 2009; Sperber, Schols, Stuart, Norde, & Voragen, 2009). It also provides food scientists with a relatively simple method of creating hydrogel particles that can be utilized for encapsulation of bioactive lipids, such as ω − 3 PUFAs.

In this study, we used low-methoxy (LM) amidated pectin as an anionic biopolymer and caseinate as a cationic biopolymer to form hydrogel particles. Pectin was selected because it is already widely used in the food industry as a gelling agent and it has a negative charge across a wide pH range. Caseinate was chosen because it is also a commonly used food ingredient that is positively charged at pH values below its isoelectric point (pI ≈ 4.6), and therefore can form electrostatic complexes with anionic pectin. In addition, the combination of caseinate and pectin has previously been used by our group to successfully form hydrogel particles to encapsulate lipid droplets (Matalanis et al., 2010). Nevertheless, a modified preparation method and a different anionic polysaccharide were used in the present study, which may have altered the properties and functionality of the hydrogel particles formed.

The formation of filled hydrogel particles in the present study involved a number of steps (Fig. 1). First, a fish oil-in-water emulsion was prepared at pH 7 using caseinate as an emulsifier, and then this emulsion was mixed with a caseinate solution (pH 7). The resulting droplet-biopolymer mixture was then mixed with pectin solution (pH 7) and the solution was adjusted to pH 4.5 to promote complex coacervation. Finally, the enzyme transglutaminase (Tg) was added to cross-link the caseinate and promote gelation of the hydrogel matrix. The filled hydrogel particles fabricated in this study could have advantages over conventional emulsions due to their ability to protect PUFAs from oxidation, while still maintaining high bioavailability.

2. Materials and methods

2.1. Materials

Powdered sodium caseinate was obtained from MP Biomedicals LLC (Solon, OH) and was used without further purification. As stated by the manufacturer, the protein content of the powder was 92–96%. Low methoxyl amidated pectin (Genu Pectin (Citrus), LM-104 AS-Z) was donated by CP Kelco (Lille Skensved, Denmark) and was used without further purification. The degree of esterification (DE) was approximately 27% as provided by the manufacturer. The protein cross-linking enzyme transglutaminase (Activa TI) was donated by Ajinomoto Food Ingredients (Chicago, Illinois). According to the manufacturer, the activity of this enzyme was 100 units per gram of powdered preparation. Fish oil was obtained from DSM Nutritional Products Ltd. (Basel, Switzerland). This oil contained 101 mg of EPA/g of oil, 148 mg of DHA/g oil, and a total ω − 3 PUFA content of 312 mg/g of oil.

All chemicals used, including technical grade Nile red dye (CAS #7385-67-3) and fluorescein isothiocyanate isomer I, were purchased from Sigma-Aldrich (St. Louis, MO). Double distilled water was used to prepare all solutions and emulsions.

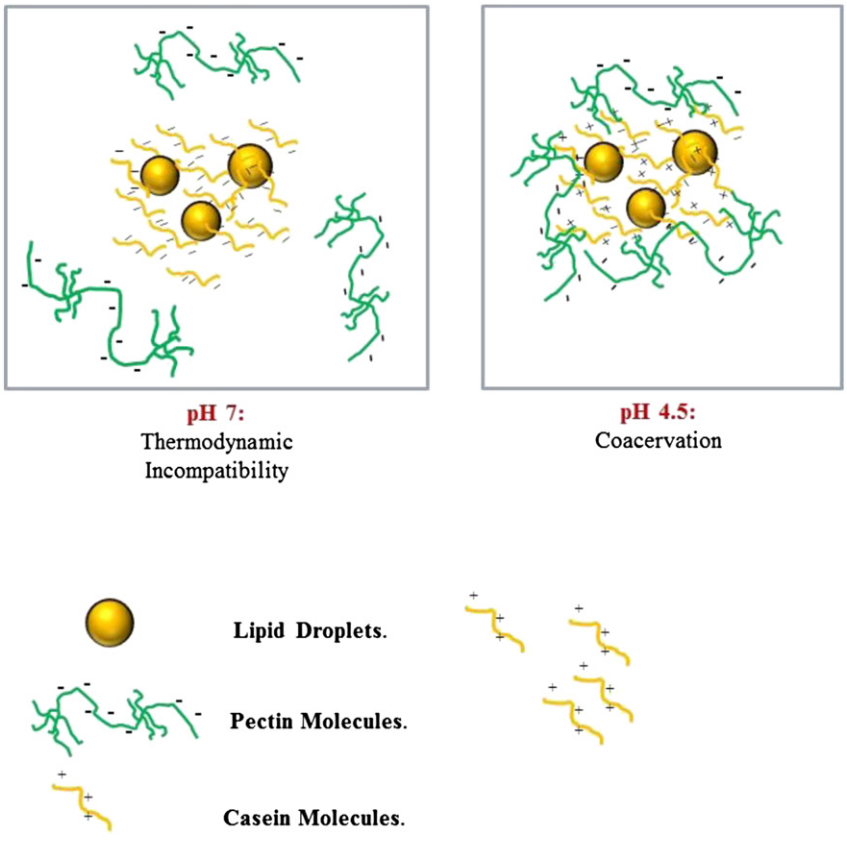

Fig. 1. Schematic diagram of preparation method for unfilled hydrogel particles, filled hydrogel particles (non-cross-linked) and filled hydrogel particles (cross-linked).