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Influence of cosurfactant on the behavior of structured emulsions under simulated intestinal lipolysis conditions

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ABSTRACT

Structured emulsion-based delivery systems, fabricated from natural lipids and polymers, are finding increasing use to control the biological fate of ingested lipids within the gastrointestinal tract. The purpose of this study was to elucidate the impact of cosurfactants on the digestion behavior of structured emulsions using a simulated intestinal lipolysis model. Lipid droplets were first prepared by membrane homogenization using a globular protein (β-lactoglobulin) as the primary surfactant, and a non-ionic surfactant (Tween 20) as the cosurfactant. The structured emulsion was fabricated by mixing lipid droplets (+), alginate solution (−), and subsequently chitosan solution (+). With an outer chitosan coating, the electrical charge on the structured emulsion droplets changed from positive to negative when the pH was varied from 2 to 7.5 both in the absence and presence of cosurfactant. However, the particle size was much smaller in the presence of the cosurfactant. The rate and extent of lipid digestion under simulated intestinal lipolysis conditions were influenced by cosurfactant, interfacial structure, and digestion conditions (fasted *versus* fed). Under high calcium fed conditions (20 mM Ca^{2+}), lipid digestion was highly suppressed and delayed in delivery systems containing cosurfactant and chitosan, which was similar to the system containing alginate but no cosurfactant. This reduction in lipid digestion could be largely overcome by including cosurfactant in the delivery systems. The information obtained in this study may prove useful in designing oral delivery systems that control the digestion and release of lipids in the gastrointestinal tract.

1. Introduction

Delivery systems specifically designed to control the digestion, release and absorption of lipophilic components within the gastrointestinal (GI) tract have been developed for a variety of applications within the food and pharmaceutical industries (McClements, Decker, & Park, 2009; Porter, Trevaskis, & Charman, 2007; Porter & Wasan, 2008; Singh, Ye, & Horne, 2009). These delivery systems are used to control the release of lipophilic drugs and other bioactive components at specific locations within the GI tract, such as the mouth, stomach, small intestine, or colon (Kosaraju, 2005). Recently, a number of structural design approaches have been developed to extend the functional performance of emulsion-based delivery systems (Dickinson, 2013; Li, Kim, Park, & McClements, 2012; McClements & Li, 2010). Lipid droplets can be coated by layers of biopolymers using an electrostatic layer-by-layer deposition method to form multilayer emulsions (Caruso & Mohwald, 1999; Decher & Schlenoff, 2003; Guzey & McClements, 2006a). These biopolymer coatings can be designed to improve the stability of the encapsulated lipid droplets to environmental stresses (Aoki, Decker, & McClements, 2005; Gu, Regnier, & McClements, 2005; Guzey & McClements, 2006b; Ogawa, Decker, & McClements, 2003a, 2003b), to protect encapsulated bioactive components from chemical degradation (Djordjevic, Cercaci, Alamed, McClements, & Decker, 2007; Klinkesorn, Sophanodora, Chinachoti, McClements, & Decker, 2005), and to release encapsulated bioactive components in response to specific environmental triggers (Decher & Schelnoff, 2003). An alternative structural design approach is to embed lipid droplets within hydrogel matrices, which can be formed using various methods, such as extrusion, templating, coacervation, and thermodynamic incompatibility (Matalanis, Jones, & McClements, 2011; McClements & Li, 2010). The dimensions, permeability, and environmental responsiveness

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of the hydrogel matrices can be controlled so as to alter the digestion and release of emulsified lipids within gastrointestinal conditions (Li, Hu, & McClements, 2011; Li & McClements, 2011). A potential benefit of using structured emulsions as delivery systems is that they can be fabricated entirely from natural food-grade (GRAS) ingredients (*e.g.,* lipids, proteins, and polysaccharides) using simple processing operations (*e.g.,* homogenization and mixing).

The initial step in the preparation a structured lipid emulsions typically involves homogenizing an oil and aqueous phase together in the presence of a hydrophilic emulsifier to form a suspension of lipid droplets suspended in water (McClements, 2012). The characteristics of the lipid droplets formed depend on system composition and homogenization method. In this study, premix membrane emulsification was used to produce positively charged protein-coated lipid droplets, which were then mixed with negatively charged polysaccharides to create electrostatic complexes. Previously, we have shown that multilayer emulsions can be formed by coating anionic lipid droplets produced by membrane homogenization with cationic biopolymers, such as chitosan (Gudipati, Sandra, McClements, & Decker, 2010; Vladisavljevic & McClements, 2010). The presence of the biopolymer coating was found to alter the physical properties, chemical stability, and biological fate of the encapsulated lipids (Tokle, Lesmes, Decker, & McClements, 2012). Research into the behavior of emulsions in the gastrointestinal tract has grown recently due to the importance of understanding and controlling the biological fate of ingested lipids. The impact of the physicochemical environment of the gastrointestinal tract on the proteolysis and structural change of protein-coated lipid droplets has been studied (Maldonado-Valderrama, Terriza, Torcello-Gomez, & Cabrerizo-Vilchez, 2013; Mandalari, Mackie, Rigby, Wickham, & Mills, 2009; Singh & Sarkar, 2011). The protein coating can be broken down by proteases (pepsin, trypsin and chymotrypsin) and displaced by surface active components in the intestinal fluids (such as bile salts and phospholipids). Changes in the composition and structure of the interfacial layers coating lipid droplets may have a pronounced impact on lipid digestion. However, studies have shown that lipid droplets are readily digested in the presence of protein layers, even if they are covalently cross-linked (Sandra, Decker, & McClements, 2008). The interaction between surfactant and protein molecules in bulk solutions and at interfaces during lipid digestion have been reviewed (Wilde & Chu, 2011). Different protein interfacial coatings have been reported to have similar extents of lipid hydrolysis, which indicated that proteins did not form a barrier that compromised lipolysis (Maldonado-Valderrama et al., 2013).

To the authors' knowledge, there have been few studies investigating the influence of cosurfactants on lipid lipolysis in structured emulsions. Our previous study demonstrated that the addition of Tween 20 could modulate the electrical characteristics, microstructure and physical stability of protein-stabilized lipid droplets and their corresponding electrostatic complexes with polysaccharides (Li & McClements, 2013). Furthermore, Tween 20 addition was found to modulate lipid digestion of alginate-coated emulsified lipid droplets in a simulated gastrointestinal tract (Li & McClements, 2014). Based on our previous study, the influence of cosurfactants on the behavior of structured emulsions under simulated intestinal lipolysis conditions was further examined. The structured emulsions were fabricated by electrostatic deposition of anionic alginate and then cationic chitosan onto the surface of protein-stabilized lipid droplets. The influence of cosurfactant (Tween 20) on the physical stability, microstructure, and lipid intestinal lipolysis of the nanolaminated lipid droplets was then characterized.

2. Materials and methods

2.1. Materials

Powdered β-lactoglobulin (BLG) was obtained from Davisco Foods International (Lot # JE 002-8-415, Le Sueur, MN), USA. Tween 20 (T20) was purchased from MP Biomedicals LLC. (Lot# 1131K), USA. Corn oil was purchased from a local supermarket and used without further purification. Alginic acid (sodium salt) (Lot# 180947, viscosity of 1% alginic acid in water is 15–20 cp) and medium molecular weight chitosan powder (Lot#448877, 75–85% deacetylated, viscosity of 1 wt% chitosan in 1% acetic acid is 200–800 cp) were purchased from Sigma–Aldrich (St. Louis, MO). Lipase from porcine pancreas, Type II (L3126, triacylglycerol hydrolase E.C. 3.1.1.3, PPL), and bile extract (porcine, B8613) were purchased from Sigma–Aldrich. The supplier reported that this form of lipase (Type II) also contained amylase and protease. It has been reported that the lipase activity is 100–400 units/mg protein (using olive oil) and 30–90 units/mg protein (using triacetin) after 30 min incubation. Calcium chloride ($CaCl_2.2H_2O$) and sodium chloride (NaCl) were obtained from Fisher Scientific. Analytical grade hydrochloric acid (HCl) and sodium hydroxide (NaOH) were purchased from Sigma–Aldrich. Purified water from a Nanopure water system (Nanopure Infinity, Barnstead International, Dubuque, IA) was used for the preparation of all solutions.

2.2. Preparation of structured emulsion

The structured emulsion was fabricated according to a described method previously (Li & McClements, 2013). Briefly, the initial lipid droplets used to form the electrostatic complexes were prepared by membrane homogenization. The initial systems consisted of 20 wt% oil phase (corn oil) and 80 wt% aqueous phase (surfactant solution). The aqueous surfactant solutions contained either 5% BLG or mixture of 2% BLG/1% T20 by dissolving in 5 mM phosphate buffer (pH 7.0). One of the reasons for using a cosurfactant was to reduce the amount of protein required to form the initial emulsions. A coarse emulsion premix was initially formed by pouring the oil phase into the aqueous phase with continuous stirring. This mixture was then passed through a membrane homogenizer (MG-20-5, Kiyomoto Iron Works, Ltd., Japan). The resulting emulsion was defined as the bulk emulsion.

Structured emulsions were formed by mixing bulk emulsions containing 2 wt% lipid droplets (stabilized by BLG or BLG/T20) with aqueous solutions containing 0.4 wt% anionic alginate molecules at pH 7.0, and then adjusting to pH 3.5 to promote lipid droplet–alginate interactions. The resulted mixture was further mixed with cationic chitosan solution at pH 4.5. The final composition of the systems was 0.4 wt% oil, 0.04 wt% alginate, and 0.04 wt% chitosan, with either 0.1% BLG (no cosurfactant) or 0.04% BLG/0.02% T20 (with cosurfactant).

2.3. Influence of pH on structured emulsion stability

The aqueous suspensions of chitosan-coated structured emulsion were diluted with 5 mM buffer solutions to the same final oil concentration, and then the pH was adjusted from 2.0 to 7.5. The resulted mixtures were stirred for 30 min, and then stored at room temperature for overnight before measurement.

2.4. In vitro digestion model

The *in vitro* digestion experiment was carried out under fasted and fed conditions at 37 °C by mixing samples, phosphate buffer, and simulated intestinal fluid (SIF) (Li, Hu, & McClements, 2011).