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Stability control of large oil droplets by layer-by-layer deposition using polyelectrolyte dietary fibers

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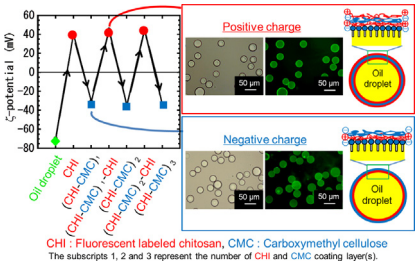
HIGHLIGHTS

- Multicoated large oil droplets could be prepared by layer-by-layer deposition using polyelectrolyte dietary fibers.
- Multicoated large oil droplets were stable even under surfactant-free condition.
- Stability against pH change was mainly determined by pK_a of outer layer coating material.

GRAPHICAL ABSTRACT



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ABSTRACT

O/W emulsion is desirable to control the stability of oil droplets for the protection of bioactive lipophilic components during the storage and their targeted release in a gastrointestinal tract. In this study, we modified the surface properties of oil droplets larger than 10 μm in size by electrostatic layer-by-layer multicoatings using polyelectrolyte dietary fibers, aiming to control their stability. Monodisperse large oil droplets were prepared by microchannel emulsification using modified-lecithin as emulsifier. Chitosan (CHI) as a cationic dietary fiber and carboxymethyl cellulose (CMC) as an anionic fiber were alternately coated onto oil droplet surface. The ζ-potential of oil droplets was alternately changed, depending on the net charge of droplets dominated by the electrostatic property of the outer fiber layer. Multicoated oil droplets did not aggregate or coalescence in an emulsifier-free aqueous medium after two weeks storage at room temperature. When CHI was modified outer layer, oil droplets were unstable at high pH value (pH > 6), due to loss of CHI charge. When CMC was outer layer, the oil droplets showed good stability to aggregation in between pH 5 and 9, but aggregated at lower pH value (pH < 5), due to loss of CMC charge. These findings indicated that large oil droplet stability can be controlled by layer-by-layer coating using food grade polyelectrolytes.

1. Introduction

Oil-in-water (O/W) emulsion is a dispersion system, in which oil droplets are finely dispersed in an aqueous medium, which has been widely used in food and pharmaceutical industries, among others. However, it is desirable to control the stability of oil droplets. For example, the protection of bioactive lipophilic components during the storage and their targeted release in a gastrointestinal tract has been investigated [1]. Therefore, way of controlling stability and targeted release of O/W emulsion is important for expanding range of utilization.

Oil droplet size, distribution of oil droplets and surface modifying were investigated as measures to control the stability and targeted release of O/W emulsions. Sub-micron size oil droplets are more stable against creaming, flocculation, coalescence and phase inversion than micrometer size droplets. In view of lipid digestion, Sub-micron size oil droplets were easily digested compared to micrometer size oil droplets so that sub-micron size oil

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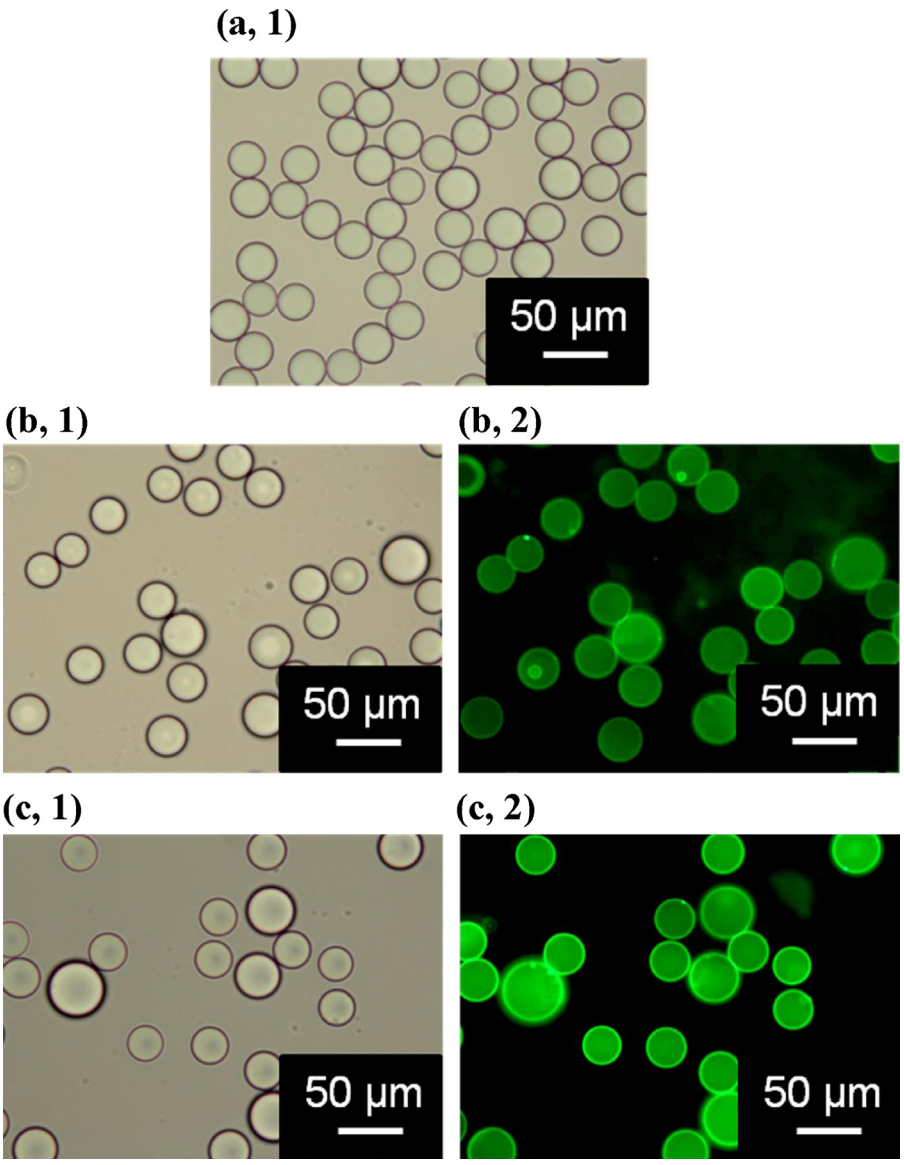

Fig. 1. Optical (1) and fluorescence (2) microscopic images of the primary emulsion (a), $(CHI\text{-}CMC)_1$ (b) and $(CHI\text{-}CMC)_3$ (c) coated oil droplets.

droplets have large specific surface area for the lipase molecules to bind [2]. Because of Ostwald ripening, polydisperse O/W emulsions are more unstable than their monodisperse counterpart. Emulsifier properties regulate stability and targeted release due to reduced interfacial tension [3], hydrophilic–lipophilc balance (HLB) [4], steric inhibition [5–7], or electrostatic repulsions [8].

Multicoating is one of the methods generally used for modification of oil droplets' surface properties. It is an effective method for controlling stability and targeted release. Multicoated emulsions are formed by layer-by-layer (LBL) deposition using electrostatic polymers onto the surfaces of oppositely charged droplets through electrostatic attraction. Electrostatic polymer coatings are formed by repeating this process a number of times using two or more oppositely charged polymers. These systems have been shown to be capable of improving the stability of lipid droplets against environmental stresses, such as thermal processing, pH changes, high salt concentrations or freezing [9].

LBL deposition is examined for applying to food emulsion. The ability of biopolymer coatings to control the stability of encapsulated oil depends on a number of factors, as follows: the type of polymers used [10–12], the number of layers deposited [13–16] and the preparation conditions used, for example ionic strength, pH, temperature, and stirring [17]. It is, therefore, possible to fabricate multilayer emulsions with different functional characteristics by controlling their composition and preparation conditions. The objective of the current research was to examine the impact of the biopolymer sequence on the properties and stability of multilayer emulsions fabricated using biopolymers (polysaccharides and protein). LBL deposition was investigated mostly for sub-micronsize O/W emulsion. From the view point of stability, micrometer size oil droplets are more unstable compared to sub-micron size oil droplets, but regarding entrapment capacity, larger oil droplets are preferable due to increased volume. Micrometer size oil droplets can be visualized by optical microscope, making it easy to evaluate the effect of multilayer deposition on droplets surface.

We therefore, aimed to determine if it is possible to increase the stability of large oil droplet larger than 10 μm size by LBL deposition using cationic chitosan and anionic carboxymethyl cellulose alternately in surfactant-free condition, and to control the stability against pH with changing the composition of outer layer and coating frequency. CHI and CMC are well known to aggregate to each other due to electrostatic interactions [18,19]. Primary O/W