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Fabrication of viscous and paste-like materials by controlled heteroaggregation of oppositely charged lipid droplets

Yingyi Mao, David Julian McClements *

Biopolymer and Colloids Research Laboratory, Department of Food Science, University of Massachusetts, Amherst, MA 01003, United States

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ABSTRACT

This study describes the formation of materials with novel textural characteristics by controlled heteroaggregation of oppositely charged protein-coated lipid droplets. Heteroaggregation was induced by mixing a suspension of β-lactoglobulin (β-Lg)-coated lipid droplets ($\zeta = -51$ mV, $d_{43} \sim 0.35$ μm, 20 wt.%) with a suspension of lactoferrin (LF)-coated lipid droplets ($\zeta = +32$ mV, $d_{43} \sim 0.35$ μm, 20 wt.%) under conditions where the two proteins had opposite charges (pH 7). The mean particle size, flow behaviour, and shear modulus of the materials depended on positive-to-negative particle ratio (0–100%), pH (3–9), ionic strength (0–400 mM), and temperature (30–90 °C). The largest particle sizes, highest viscosities, and largest gel strengths were observed at intermediate particle ratios (40% LF:60% β-Lg), which was attributed to a strong electrostatic attraction between oppositely charged droplets (0 mM NaCl, pH 7, 25 °C). A reduction in particle aggregation, viscosity, and gel strength occurred at intermediate ionic strengths due to screening of the electrostatic attraction between oppositely charged droplets. However, increased aggregation, thickening, and gelation occurred at higher ionic strengths due to screening in electrostatic repulsion between similarly charged droplets. Thermal treatment of the samples (90 °C) promoted a substantial increase in gel strength due to protein denaturation and increased droplet attraction. This study has important implications for the utilisation of controlled particle aggregation to create novel structures in foods, cosmetics, personal care, and other products.

1. Introduction

In many developed countries there has been a rise in the percentage of the population that is either overweight or obese, which is linked to chronic diseases such as heart disease, diabetes, and cancer (Aranceta, Moreno, Moya, & Anadon, 2009; Vanamala, Tarver, & Murano, 2008). A variety of approaches are needed to tackle this problem, including education about diet and exercise, encouragement of healthier lifestyles, and increased availability of affordable and desirable reduced calorie foods. There are considerable challenges to the formulation of foods with reduced calorie contents that still maintain their desirable physicochemical and sensory attributes. For this reason consumers often choose high calorie products that taste good over low calorie alternatives that are healthier but have less desirable organoleptic properties.

For this reason, the food industry is adopting the principles of colloid science and soft matter physics to design foods with novel functional properties by controlling the characteristics and structural organisation of the building blocks they contain (McClements, Decker, Park, & Weiss, 2009; Mezzenga, Schurtenberger, Burbidge, & Michel, 2005; Schmitt & Kolodziejczyk, 2009; Ubbink, Burbidge, & Mezzenga, 2008; Ubbink & Kruger, 2006), such as lipids (e.g., triacylglycerols, surfactants, and phospholipids), biopolymers (e.g., proteins and polysaccharides) and colloidal particles (e.g., lipid droplets, fat crystals and air bubbles). In particular, there has been a focus on using structural design principles to create high quality foods with reduced calorie contents. These foods should have similar desirable sensory attributes (appearance, flavour, texture, mouthfeel, and satiety) and physical stability (shelf life) as conventional products, but should have lower calorie contents. Fat has the highest calories per unit mass of any of the major food components, and therefore it has been a primary target for reducing the overall calorie content of foods. The development of reduced fat foods has proven to be a considerable challenge to the food industry because of the multiple roles that lipid droplets play in determining the overall sensory and physicochemical properties of food products: they influence appearance due to their ability to scatter light (McClements, 2002; Velikov & Pelan, 2008); they alter flavour due to their ability to act as an organic solvent for non-polar aroma and taste molecules (De Velde, De Hoog, & Ruijschop, 2008; Guichard, 2002); they alter texture due to their influence on rheology (Arancibia, Jublot, Costell, & Bayarri, 2011); they alter perceived mouthfeel due to their interactions with saliva and oral surfaces within the mouth (Malone, Appelqvist, & Norton, 2003; van Aken, Vingerhoeds, & de Wijk,

* Corresponding author. Tel.: +1 413 545 1019.
E-mail address: mcclements@foodsci.umass.edu (D.J. McClements).

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2011); and they contribute to feelings of fullness within and between meals (satiety/satiation) (Irvine, Livingstone, & Welch, 2007).

In this study, we investigate a promising approach of creating reduced fat foods based on controlled heteroaggregation of oppositely charged lipid particles (Mao & McClements, 2011; Schmitt & Kolodziejczyk, 2009). This approach can be used to create emulsion-based products that are highly viscous or gel-like at much lower fat contents than in conventional (non-aggregated) emulsions. Previously, novel textural attributes have been created by mixing oil-in-water emulsions stabilized by a protein (β-lactoglobulin) with oil-in-water emulsions stabilized by a polysaccharide (gum arabic) under acidic (pH 4.2) conditions (Schmitt & Kolodziejczyk, 2009). At this pH, the protein-coated lipid droplets were positively charged, while the polysaccharide-coated lipid droplets were negatively charged, and hence there was an electrostatic attraction between them. This led to the formation of an aggregated network of lipid droplets that gave the resulting material formed semi-solid rheological properties. In recent studies, we have shown that material rheology and stability can be controlled in systems containing mixtures of oppositely charged protein-coated lipid droplets by manipulating the positive-to-negative particle ratio, pH, and ionic strength (Mao & McClements, 2011, 2012). The properties and behaviour of food systems created using this heteroaggregation approach can be guided by the theoretical and experimental knowledge generated for other types of colloidal dispersion (Lopez-Lopez, Schmitt, Moncho-Jorda, & Hidalgo-Alvarez, 2006, 2009).

In the present study, we focused on the formation of semi-solid (paste-like) colloidal dispersions fabricated by controlled heteroaggregation of oppositely charged protein-coated lipid droplets. These systems were prepared by mixing an emulsion containing β-lactoglobulin-coated lipid droplets with an emulsion containing lactoferrin-coated lipid droplets. These two globular proteins have different electrical charge *versus* pH profiles because of their different isoelectric points: β-lactoglobulin (β-Lg), pI ≈ 5; lactoferrin (LF) pI ≈ 8. Previously, we have shown that particle aggregation occurs when the two types of lipid droplets are oppositely charged (i.e. $pI_{B\text{-}Lg} < pH < pI_{LF}$) (Mao & McClements, 2011, 2012). For applications within the food industry it is important that these materials are fabricated entirely from food-grade ingredients (i.e., lipids and proteins) so that they are suitable for oral ingestion. We hypothesised that the rheological properties of these structures could be tailored by systematically controlling sample composition and preparation conditions. The knowledge gained from this study could be useful for the rational design of fat reduced foods for utilisation in commercial products.

2. Experimental methods

2.1. Materials

Corn oil was purchased from a commercial food supplier (Mazola, ACH Food Companies, Inc., Memphis, TN, USA). Lactoferrin powder (LOT #10408282) was supplied by DMV International (Delhi, NY, USA), and the manufacturer reported that it contained 97.7% protein and 0.12% ash. Purified β-lactoglobulin powder (BioPURE, LOT #JE-002-8-415) was supplied by Davisco Foods International (Eden Prairie, MN, USA). The manufacturer reported the composition of this powder to be 97.4% total protein, 92.5% β-lactoglobulin (β-Lg), and 2.4% ash. All solvents and reagents were of analytical grade. Double distilled water was used to make all solutions.

2.2. Formation of single-protein emulsions

Aqueous emulsifier solutions were prepared by dispersing either β-Lg powder or LF powder into double distilled water, and then stirring for at least 3 h at room temperature to ensure complete dispersion. The pH of the protein solutions was then adjusted to 7.0 using 1 M NaOH or 1 M HCl. Oil-in-water emulsions containing a single protein type were prepared by blending 20 g of corn oil and 80 g of aqueous protein solution for 2 min using a hand blender (M133/1281-0, 2 speed, Biospec Products Inc., ESGC, Switzerland) and then recirculated four-times through a two-stage homogenizer (LAB 1000, APV-Gaulin, Wilmington, MA) at a first-stage pressure of 5400 psi and a second-stage pressure of 600 psi. The β-Lg emulsion was then heated to 90 °C for 30 min to cross-link the adsorbed proteins, so as to prevent any competitive adsorption effects, i.e., exchange of proteins between lipid droplets in different types of emulsion. The LF emulsions were not heated because they are unstable to thermal treatment when heated above the thermal denaturation temperature of the proteins (Tokle, Lesmes, & McClements, 2010). All emulsions were then stored for 24 h prior to utilisation. Preliminary experiments reported elsewhere established that 0.5% β-Lg and 3% LF were suitable levels to form single-protein emulsions with relatively small droplet diameters ($d_{43} \sim 0.35$ μm) (Mao & McClements, 2011, 2012), and so these levels were used to form the mixed-protein emulsions.

2.3. Formation of mixed-protein emulsions

Initially, two single-protein emulsions stabilized by either 0.5% β-Lg or 3% LF were prepared in distilled water as described in Section 2.2. A series of mixed emulsions containing 0–20 wt.% β-Lg droplets (pH 7.0) and 20–0 wt.% LF droplets (pH 7.0) were prepared by mixing different ratios of the two emulsions together, stirring for 10 min, then allowing them to stand for 24 h prior to analysis. The resulting mixed emulsions therefore contained different mass ratios of positive-to-negative droplets (0–100%). For convenience, we designated the particle ratios in mixed emulsions in terms of the percentage of lactoferrin droplets they contained, e.g., "40% LF emulsion" means an emulsion with 40% lactoferrin-coated droplets and 60% β-Lg-coated droplets.

2.4. Influence of pH and ionic strength on the formation of mixed systems

2.4.1. pH

For each type of single emulsion, a series of samples was prepared with different pH values using either 1 M NaOH or 1 M HCl to adjust the pH of the initial samples. A mixed emulsion (40% LF) was then formed by mixing 40% of LF-emulsion with 60% of β-Lg-emulsion (mass percentage), stirring for 10 min, and then allowing them to stand overnight at ambient temperature prior to analysis.

2.4.2. Ionic strength

A 20% oil-in-water emulsion containing mixed protein-coated lipid droplets (40% LF) was formed by mixing 40% of LF-emulsion with 60% of β-Lg-emulsion (pH 7). A series of samples with different ionic strengths was then prepared by adding different amounts of crystalline sodium chloride to the emulsions and stirring to obtain final emulsions containing 0–400 mM NaCl. All samples were stored overnight at ambient temperature before analysis.

2.5. Rheological properties

The rheological behaviour of samples was measured using a dynamic shear rheometer (Kinexus Rotational Rheometer, Malvern Instruments, Malvern, U.K). A cup and bob geometry consisting of a rotating inner cylinder (diameter 25 mm) and a static outer cylinder (diameter 27.5 mm) was used in viscosity and oscillation measurements. The samples were loaded into the rheometer mea-