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Modification of emulsion properties by heteroaggregation of oppositely charged starch-coated and protein-coated fat droplets

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ABSTRACT

The manuscript describes the formation and characterization of emulsions formed by controlled heteroaggregation of oppositely charged fat droplets coated by either cationic whey protein isolate (WPI) or anionic modified starch (MS). Heteroaggregation was induced by mixing two the oppositely charged 20 wt% oil-in-water emulsions together ($d_{43} \approx 380$ nm) at pH 3.5. The mean particle diameter, electrical charge, and micro-structure of the heteroaggregates formed were measured as a function of negative-to positive particle ratio (0–100%) and pH (2.5–6.5). WPI-coated fat droplets were positive below pH 5.5 and negative above this value, while MS-coated fat droplets were negatively charged across the entire pH range. Upon mixing the two types of fat droplets together we found that the largest aggregates and highest viscosity occurred at a particle ratio of 70% MS and 30% WPI, which was attributed to strong electrostatic attraction between the oppositely charged droplets. The heteroaggregates partly dissociated at certain pH values, which was attributed to weakening of the electrostatic attraction between the different droplets. Heteroaggregates formed by oppositely charged fat droplets may be useful for creating specific food structures that lead to desirable physicochemical properties, such as enhanced viscosity at low fat content.

1. Introduction

The high hedonic rating of many commercial food products is related to their relatively high fat contents, *e.g.*, mayonnaises, sauces, dressings, and desserts (Drewnowski, 1997a, 1997b). However, fat has a higher caloric value and a weaker satiety/satiation effect (on a per weight basis) than other major food nutrients (Blundell et al., 2005; Cooling & Blundell, 1998), which may lead to passive overconsumption and an increase in overweight and obesity (Micha & Mozaffarian, 2010). The development of reduced fat foods is therefore a major goal of many food scientists (Nehir El & Simsek, 2012; Rogers, 2009). Unfortunately, it is difficult to remove fats from fatty foods without adversely affecting their desirable quality attributes. Fats play an important role in determining the appearance, texture, and flavor of foods, and when they are removed many of the desirable qualities are lost (McClements & Demetriades, 1998). The food industry is therefore searching for effective strategies to reduce the fat content of foods, without adversely altering the desirable quality attributes. Various fat-reduction strategies have been developed, including the use of indigestible fats, reduced calorie fats, thickening agents, and colloidal particles (Williams & Buttriss, 2006).

One approach that we have recently studied in our laboratory is the utilization of *heteroaggregation* of oppositely charged fat droplets to create highly viscous or paste like materials with reduced fat contents (Mao & McClements, 2011, 2012a, 2012b, 2012c). Heteroaggregation is defined as the aggregation of dissimilar particles, which may differ in their size, shape, charge, chemical composition, or other properties (Lopez-Lopez, Schmitt, Moncho-Jorda, & Hidalgo-Alvarez, 2006; Yates, Franks, Biggs, & Jameson, 2005). This approach has been widely used in non-food science applications for a variety of reasons, such as controlling the rheological properties of ceramics (Piechowiak et al., 2012), creating ion exchange columns (Han, Daniels, Sudol, Dimonie, & Klein, 2013), removing colloidal particles from solutions (Findlay, Thompson, & Tipping, 1996), and encapsulating and targeting biomolecules (Lemmers, Sprakel, Voets, van der Gucht, & Stuart, 2010; McParlane et al., 2012; Ohsugi, Furukawa, Kakugo, Osada, & Gong, 2006; Spruijt et al., 2011). Our previous studies have shown that heteroaggregates can be formed from food ingredients by mixing two emulsions together containing oppositely charged protein-coated fat droplets (Mao & McClements, 2011, 2012a). Previously, we used lactoferrin (LF) and β-lactoglobulin (β-Lg) at neutral pH to create droplets with different charges, since LF has an isoelectric

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point around 8 and is therefore positive, whereas β-Lg has an isoelectric point around 5 and is therefore negative (Mao & McClements, 2011). However, LF and β-Lg are highly purified proteins that are too expensive for widespread use as functional ingredients in many foods. It is therefore important to identify alternative emulsifiers that are more suitable for commercial application in the food industry. Previous researchers have shown that novel textural attributes could be created in model foods by mixing an emulsion containing β-lactoglobulin-coated fat droplets with one containing gum arabic-coated fat droplets under acidic (pH 4.2) conditions (Schmitt & Kolodziejczyk, 2009). In this study, we investigated the possibility of using whey protein isolate (WPI) and modified starch (MS) as two food-grade emulsifiers with different electrical characteristics to induce heteroaggregation in mixed emulsions.

Whey protein isolate is a mixture of surface-active globular proteins normally isolated from diary milk, such as β-lactoglobulin, α-lactalbumin and bovine serum albumin (Hu, McClements, & Decker, 2003). WPI-coated droplets are positively charged below the isoelectric point of the adsorbed globular proteins (pI ≈ 5), but negatively charged above this value (Demetriades, Coupland, & McClements, 1997). Modified starch is formed by covalently attaching non-polar (octenyl succinic anhydride) groups to hydrophilic starch molecules to form an amphiphilic molecule that can adsorb to oil-water interfaces and stabilize emulsions (McClements, Decker, & Weiss, 2007; Trubiano, 1995). MS-coated fat droplets have been shown to be negatively charged over a wide pH range due to the presence of anionic groups on the MS backbone (Charoen et al., 2011). At pH values below the isoelectric point of WPI, one would expect heteroaggregation to occur between the anionic MS-coated droplets and the cationic WPI-coated droplets. We hypothesized that these economical food-grade emulsifiers may be suitable for producing novel desirable characteristics in reduced-fat products through the heteroaggregation process.

2. Experimental methods

2.1. Materials

Corn oil was purchased from a commercial food supplier (Mazola, ACH Food Companies, Inc., Memphis, TN). Powdered whey protein isolate (97.7 wt% protein) was supplied by Davisco Foods Intl. (Eden Prairie, MN, U.S.A.). Powdered OSA-modified starch (PURITY GUM™ Ultra) was supplied by the National Starch LLC (Bridgewater, N.J., U.S.A.). Glacial acetic acid, sodium acetate, and sodium azide were purchased from Sigma–Aldrich (Sigma Chemical Co., St. Louis, MO) or Fisher Scientific (Pittsburgh, PA). All other chemicals were purchased from Sigma–Aldrich (St Louis, MO). Double distilled water was used to prepare all solutions.

2.2. Emulsion preparation

2.2.1. Preparation of Single-droplet Type Emulsions:

Aqueous emulsifier solutions were prepared by dispersing either WPI (1 wt%) or MS (4 wt%) powder into acetic acid buffer (10 mM, 0.02% sodium azide, pH 7) and then stirring for 3 h at room temperature to ensure complete dispersion. These emulsifier levels were selected based on previous studies that have shown that emulsions with relatively small droplet diameters can be produced (Charoen et al., 2011). The pH of the aqueous emulsifier solutions was then adjusted to pH 3.5 using 1 M HCl, which led to the formation of clear solutions. Oil-in-water emulsions were prepared by homogenizing 20 wt% oil phase with 80 wt% aqueous phase at ambient temperature. Coarse emulsions were formed using a hand blender (M133/1281-0, 2 speed, Biospec Products Inc., ESGC, Switzerland) for 2 min at level 2. These emulsions were then passed 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. All emulsions were stored for 24 h prior to utilization. The diameters of the WPI- and MS-stabilized emulsions produced were similar: $d_{43} \approx 0.37$ μm.

2.2.2. Preparation of Mixed-droplet Type Emulsions:

Initially, two series of emulsions stabilized by either 1% WPI or 4% MS were prepared in acetic acid buffer (pH 3.5). Mixed emulsions containing a total of 10 wt% oil were prepared by mixing the two single emulsions together (each also containing 10 wt% oil), stirring for 10 min, and then storing them for 24 h before analysis. This resulted in mixed emulsions containing different amounts of WPI-coated droplets (0–10 wt%) and MS-coated droplets (10–0 wt%). After these steps, the mixed emulsions contained different mass ratios of negative-to-positive particles, *i.e.*, MS-coated-to-WPI-coated oil droplets. For convenience, we used the notation"70% MS" to refer to mixtures containing 70 wt% MS-stabilized emulsion and 30% wt% WPI-stabilized emulsion.

2.3. Influence of pH on emulsion stability

The influence of pH on the electrical charge, stability, and rheology of WPI-emulsions, MS-emulsions, and mixed-emulsions (70% MS) were examined. Emulsions were adjusted to a particular pH value (pH 2.5–6.5) using either 1 M HCl or 1 M NaOH, and then stored overnight prior to analysis.

2.4. Particle characterization

2.4.1. Particle Size:

The particle size distribution of the emulsions was measured using a laser diffraction particle size analyzer (Mastersizer 2000; Malvern Instruments, Ltd., Worcestershire, UK). To avoid multiple scattering effects the emulsions were diluted to a droplet concentration of approximately 0.005 wt% using pH-adjusted water at the same pH as the sample. The emulsions were stirred continuously throughout the measurements to ensure they were homogenous. Measurements are reported as the volume-weighted mean diameter: $d_{4,3} = \sum d_i n_i^4 / \sum d_i n_i^3$, where n_i is the number of droplets of diameter d_i.

It should be noted that particle size measurements made by static light scattering on highly flocculated emulsions should be treated with caution. First, the theory (Mie theory) used to interpret light scattering data assumes that the scattering particles are homogeneous spheres with well-defined refractive indices. In practice, flocs are non-spherical and non-homogeneous particles, with ill-defined refractive indices. Second, the process of dilution and stirring may have altered the dimensions and structural organization of the flocs. Consequently, the reported particle sizes should only be treated as an indication of strong droplet association rather than a measure of the actual size of any aggregates present in the original non-diluted samples.

2.4.2. Particle Charge:

The ζ-potential of the particles in the emulsions was determined using a particle electrophoresis instrument (Zetasizer Nano ZS series, Malvern Instruments, Worcestershire, UK). Emulsions were diluted to a droplet concentration of approximately 0.001 wt% using pH-adjusted water to avoid multiple scattering effects. After loading the samples into the instrument they were equilibrated for about 120 s before particle charge data was collected over 20 continuous readings.