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Influence of unadsorbed emulsifiers on the rheological properties and structure of heteroaggregate of whey protein isolate (WPI) coated droplets and flaxseed gum (FG) coated droplets

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Recent studies have shown that controlled heteroaggregation of oppositely charged lipid droplets can be used to control the rheological properties of emulsion. The effect of unadsorbed emulsifier on the microstructure and rheological properties of heteroaggregate of emulsion is not clear. Therefore, the influence of unadsorbed emulsifiers (whey protein isolate-WPI & Flaxseed gum-FG) on the microstructure and rheological properties of heteroaggregate of 40% WPI-coated droplets and 60% FG-coated droplets was studied. WPI-stabilized emulsions and FG-stabilized emulsions were centrifuged to separate the aqueous phase from the oil droplets to prepare the washed emulsions, separately. Emulsions containing mixtures of droplets with washed and unwashed WPI-emulsion and FG-emulsion were prepared, respectively. Droplet size, zeta-potential, transmission-physical stability, rheological behavior, and Cryo-SEM microstructure of the heteroaggregates were measured as a function of unwashed and washed WPI & FG emulsion. It was found that the presence of unadsorbed WPI in the aqueous phase of mixed emulsion adsorbed onto the FG-coated droplets, meanwhile, the unadsorbed FG could bind WPI-droplet and FG-droplet-WPI together forming a special three-dimensional network. Rheological properties indicated that free WPI and FG played dominated roles in the heteroaggregation of mixed emulsions. The shearing viscosity of the heteroaggregates formed by washed WPI-droplets and FG-droplets was significantly decreased compared with the unwashed mixed emulsion. Microrheological analysis showed that heteroaggregate of mixed emulsion became liquid behavior after washing compared to the solid behavior of unwashed emulsion. It indicated that unadsorbed WPI and FG dominated the physical property through a specific network structure. This study proved the effect of the continuous phase on the rheological properties of heteroaggregates and provided theoretical basis for the development of reduced-fat food.

1. Introduction

The recent increase in the number of overweight or obese individuals in many populations has become a major health issue, due to the increase in related chronic diseases such as heart disease, diabetes, and cancer (McClements, 2010a, b). In response to this problem, the food industry is developing reduced-calorie products. However, the development of high quality reduced fat products has proved to be challenging because fats play a very important role in food products such as overall appearance, flavor, texture, and biological response (Amar, Aserin, & Garti, 2004; Shchukina & Shchukin, 2012).

Heteroaggregates formed by electrostatic attraction between positive charged droplets and negative charged droplets in emulsion can be used to create novel functional materials suitable for utilization within the food, cosmetics, and pharmaceutical industries (Boon, McClements, Weiss, & Decker, 2009; Furtado, Michelon, Oliveira, & Cunha, 2016). The heteroaggregation

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approach can improve the functional properties and viscoelastic behavior of food systems (McClements, 2009). Novel textural attributes have been created by mixing β-lactoglobulin emulsion with Arabic gum emulsion under acidic (pH 4.2) conditions through electrostatic attraction leading to the semi-solid rheological properties (Klein, Aserin, Svitov, & Garti, 2010; Payet & Terentjev, 2008). Maier found that the emulsifier type greatly influence the type of heteroaggregates formation (Maier, Zeeb, & Weiss, 2014). Xu studied the unadsorbed emulsifier could protect β-carotene in emulsion (Xu, Yuan, Gao, McClements, & Decker, 2013). Although unadsorbed emulsifiers did not directly stabilize the oil droplets, they participated to the physical and chemical properties of the systems, e.g. depletion flocculation (Berton, Genot, & Ropers, 2011; Dickinson, Radford, & Golding, 2003). It was noted that unadsorbed emulsifier had interfacial bridging effect, which affected the interactions between droplets and the spatial structure of micro-aggregates (Mao & McClements, 2012). However, the effect of free unadsorbed emulsifier on the microstructure and rheological properties of micro-aggregates is not clear.

Whey protein isolate (WPI) is a typical globular protein emulsifier and normally provide stabilization against droplet aggregation by a combination of electrostatic and steric repulsion. Flaxseed gum (FG) is an anionic polysaccharide with strong interface adsorption characteristics being used as functional food emulsifier and stabilizer (Xu et al., 2017; Chen, Xu, & Wang, 2006; Xu, Aihemaiti, Cao, Teng, & Li, 2016). FG is mainly composed of xylose, arabinose, rhamnose, galactose, glucose and galacturonic acid (Oomah & Mazza, 2001). It was found that FG contained about 12.67% of the protein, which was mainly in the form of binding protein. In addition, FG contains rhamnose, which has good lipophilicity since the C_6 position of rhamnose is -CH_3 (Oomah & Mazza, 1995). The interface of FG-coated droplets in emulsion presented the electrostatic interaction and steric hindrance effect (Khalloufi, Corredig, Goff, & Alexander, 2009; Stewart & Mazza, 2000).

The purpose of the current study was to investigate the effects of free (unadsorbed) emulsifier (WPI & FG) on the formation, structure and rheological properties of micro-aggregates containing mixtures of WPI-coated droplets and FG-coated droplets. The adsorbed phase (upper layers) and free unadsorbed part (lower layers) were obtained by centrifugation of WPI emulsion and FG emulsion, respectively. The adsorbed upper layers and free unadsorbed lower layers of WPI emulsion and FG emulsion were used to study the impact of adsorbed and free WPI & FG on the hetero-aggregation, respectively. Droplet size, zeta-potential, the instability index of transmission obtained through LUMisizer, microstructure through Cryo-SEM, and micro and shearing rheological properties of the unwashed and reconstituted (washed) micro-aggregates were measured.

2. Materials and methods

2.1. Materials

Whey protein isolate (WPI) was purchased from American Davisco chemical co., LTD. The product contained 97.6% protein (dry basis), as determined by the supplier's standard proximate analysis procedures. Flaxseed gum (FG) was purchased from Xinjiang Linseed biologic technology development co., LTD. FG contained 70.92% polysaccharide, 12.67% protein, 16.31% ash, as supplied by the manufacture. Medium-chain triglyceride (MCT) oil was obtained from Lonza Inc. (Allendale, NJ, USA). The sodium azide was purchased from Sigma-Aldrich (St. Louis, MO). All other chemicals were of analytical grade.

2.2. Preparation of emulsions (as shown in Fig. 1)

2.2.1. Preparation of unwashed emulsions

WPI and FG single emulsions were prepared firstly, separately. WPI and FG were first dispersed in the 5.0 mM phosphate buffer at pH 7.0, respectively. These solutions were kept overnight to ensure complete dispersion and dissolution, while sodium azide (0.02 wt %) was added to prevent microbial growth.

Based on our previous study, WPI stabilized emulsion (1.25 wt% WPI) and FG stabilized emulsion (0.6 wt% FG) were prepared with 10 wt% medium chain triacylglycerol (MCT) oil as the dispersed phase and 90 wt% aqueous phase solution at room temperature, respectively. The two emulsions were prepared using an Ultra-Turrax at a speed of 19 000 rpm for 3 min to form coarse emulsions, which were subsequently homogenized using a M110-PS Microfluidizer processor (Microfluidics international Corp., Newton, MA) at the operational pressure of 50 MPa for three times. After preparation, the pH was adjusted to pH 3.0 using 1.0 M HCl. It was reported that the emulsifying property of WPI was improved at 90 °C, pH 3.0 (Bengochea, Peinado, & McClements, 2011). Therefore, WPI emulsion was heated at 90 °C for 30 min and then cooled to room temperature.

The unwashed heteroaggregate was prepared by a ratio of 40% WPI-coated and 60% FG-coated droplets. Our previous studies showed that WPI-coated droplets and FG-coated droplets formed heteroaggregate at pH 3.0. The rheological characteristics were obviously increased when 40% WPI-coated droplets and 60% FG-coated droplets forming heteroaggregates. All emulsions were kept overnight to ensure complete dispersion.

2.2.2. Preparation of washed emulsions

Following homogenization, the two single emulsions were divided into two parts to prepare unwashed and washed emulsions (Kellerby, Gu, McClements, & Decker, 2013). The continuous phase WPI or FG in the single WPI and FG emulsions were removed to prepare the washed emulsion, respectively. The second aliquot [emulsion with continuous phase protein (unwashed)] was stored at 4 °C until use. To remove the continuous phase proteins from the emulsion, 30 g freshly homogenized two single emulsions (WPI emulsion and FG emulsion) were placed into centrifuge tubes (50 mL) and centrifuged (60 min, 25 °C, 10 000 g) in a H/T16MM centrifuge (Hunan Herexi Instrument & Equipment Co., Ltd, China), respectively. This process separated the continuous phase (unadsorbed WPI & FG) from the dispersed phase. After centrifugation, the continuous phase was removed and replaced with an equal amount of 5.0 mM phosphate buffer at pH 3.0 to form adsorbed phase; the continuous lower phase after centrifugation was then added to the same amount of 5.0 mM phosphate buffer at pH 3.0 to form free phase. Finally, all the samples were vortexed for 2 min to disperse the emulsion droplets. This washing process (centrifugation, removal of continuous phase, and reconstitution of droplets) was repeated twice. The small quantities of unadsorbed emulsifiers and droplet could be present in the intermediate phase. The washing method has already washed nearly 95% of the unadsorbed phase (Kellerby et al., 2013; Livney, Ruimy, Ye, Zhu, & Singh, 2017; Xu et al., 2013). Following washing, the mixed system was prepared with the upper and lower layers of the two samples by the method of 2.2.1, respectively. All emulsions were kept overnight to ensure complete dispersion. In the following results part, 4:6 in all figures represented heteroaggregate with 40% WPI-coated droplets and 60% FG-coated droplets.

2.3. Measurement of zeta-potential

Zetasizer Nano-ZS90 (Malvern Instruments, Worcestershire,