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Effect of maltodextrins on the stability and release of volatile compounds of oil-in-water emulsions subjected to freeze–thaw treatment

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ABSTRACT

Whey protein stabilized O/W emulsions with and without maltodextrins were subjected to three cycles of freeze-thawing, and changes in particle size, creaming index (CI), free oil (oiling off), microstructures, and volatile release behavior were evaluated. After freeze-thawing, emulsions without maltodextrins experienced extensive droplet aggregation, and considerable level of creaming and oiling off were observed. Differential scanning calorimetry suggested that emulsion destabilization was mainly due to water crystallization. Among the three maltodextrins tested, maltodextrin with a dextrose equivalent (DE) value of 6 (DE 6) has the highest molecular weight and it offered the emulsion the least change in droplet size, CI and oiling off after the temperature processing. When volatile compounds were incorporated into the emulsions, the presence of maltodextrins modified their release behavior before and after freeze-thawing. Most volatiles had lower air-emulsion partition coefficients ($K_{A/E}$) in emulsions containing maltodextrins, and the $K_{A/E}$ decreased with the increase of DE value of maltodextrins for some volatiles. In the emulsion without maltodextrins, freeze–thaw treatment resulted in lower release of propanol, pentanone, heptanone and higher release of diacetyl and hexanal in comparison to the release from controls without freeze-thawing. In emulsions with maltodextrins, no significant difference was found in the release of propanol, pentanone, heptanone between freeze-thawed emulsions and the untreated emulsion ($p > 0.05$).

1. Introduction

Food emulsions are often subjected to freezing, either to improve the shelf life of the food (e.g., slow microbial growth, inhibit some chemical reactions), or to produce certain types of food (e.g., ice creams, frozen cocktails). Moreover, low temperature treatment is beneficial to maintain the nutritional value of the bioactives incorporated and the volatile characteristics of the food emulsions.

Food emulsions are thermodynamically unstable. When frozen emulsions are thawed, different types of destabilization take place, which largely alter the functionality of the emulsions (McClements, 2005). A typical freeze-thawing destabilized O/W emulsion tends to separate into three layers: an upper layer of free oil, an intermediate coagulated creamy layer and a lower turbid aqueous layer (Cramp, Docking, Ghosh, & Coupland, 2004). The destabilization is mainly induced by fat crystallization or ice formation (and growth). Fat crystallization triggers emulsion destabilization via a mechanism called “partial coalescence”, in which a fat crystal from one droplet penetrates into the liquid oil region of a neighboring droplet, and droplet aggregates are thus formed. When subjected to thawing, the droplets in the aggregates tend to merge and the individual interfacial film disappears, resulting in droplet coalescence and subsequent phase separation (Ghosh & Coupland, 2008). When the water phase of an emulsion is frozen and then thawed, extensive aggregation and oiling off have been reported (Ghosh & Coupland, 2008). With the presence of many ice crystals, oil droplets are forced much closer and penetration of ice crystals into oil droplets leads to the rupture of interfacial membrane (Saito et al., 1999). Moreover, the lower level of liquid water in the frozen emulsion results in increased ionic strength, which could screen electrostatic repulsion between droplets and promote

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flocculation. Water crystallization can also lead to protein denaturation and emulsifier oversaturation (Carvajal, MacDonald, & Lanier, 1999), which then induce phase separation. Other studies revealed that emulsifiers can adsorb onto the surface of ice crystals, thereby reducing the effective concentration of emulsifiers covering oil droplets (Hillgren, Lindgren, & Aldén, 2002). Although emulsion destabilization is desirable for the production of ice cream, butter, etc., higher emulsion stability is essential to guarantee high quality food in most situations. Emulsions are widely used as delivery systems for bioactive compounds (McClements, 2010), and an intact emulsion could be essential to better deliver bioactives and maintain their functionality. Once destabilization takes place, the bioactives in the oil droplets are no longer protected by the interfacial film and exposed to adverse environment.

In the food industry, sugars/polyols, e.g., maltose, sucrose, sorbitol, are widely added as cryoprotectants to improve freeze–thaw stability of food emulsions (Gu, Decker, & McClements, 2007; Saito et al., 1999). It is generally recognized that the presence of sugars can decrease the freezing temperature of water, and increase the amount of unfrozen water available to disperse the oil droplets (Thanasukarn, Pongsawatmanit, & McClements, 2004). Harrigan, Madden, and Cullis (1990) suggested that the sugars may behave as a spacing matrix between droplets, thus behaving as barrier to inhibit droplet merging. In concentrated sugar solution, the emulsion droplets do not come into close contact with each other in the unfrozen glassy solution between ice crystals (Miyajima, Tomita, & Nakagaki, 1986). It was also reported that maltose was able to interact with the phospholipid at the interface, thus forming an interfacial film with stronger mechanical properties against droplet coalescence. In this case, multilayer emulsions made from protein-polysaccharide complexes are more resistant to freeze-thawing (Guzey & McClements, 2006). For most protein-stabilized emulsions, sugars protect proteins from freeze-denaturation, thereby increasing emulsion stability (Carvajal et al., 1999; McClements, 2005). Levine and Slade (1988, 1989) proposed that sugars could reduce water mobility, which led to higher glass transition temperature of the water phase, possibly higher than the storage temperature. In this situation, the unfrozen liquid in the water phase is in the glassy state, and diffusion limited processes are significantly halted.

Most sugars impart an additional sweet taste to the food, which is not acceptable for certain applications. Therefore, efforts have been made to obtain nonsweet additives with a cryoprotective effect similar to that of sugars. Literature studies indicated that maltodextrins could be potential substitutes (Carvajal et al., 1999). Maltodextrins (MDs) are generally produced from starch by partial hydrolysis, consisting of D-glucose units connected in chains of variable length. MDs are mostly flavorless, and can be easily digested and adsorbed (Chronakis, 1998). Moreover, MDs (when gelled) can be used as fat replacer to reduce fat content while maintaining desirable textural properties (Loret, Meunier, Frith, & Fryer, 2004). It was also reported that MDs were able to prevent protein degradation during freezing. In a protein stabilized emulsion, the addition of maltodextrin reduced droplet aggregation after freeze–thaw cycling (Mun, Cho, Decker, & McClements, 2008).

Although extensive studies have been carried out on the freeze–thaw stability of emulsions stabilized by different emulsifiers/polymers, and some sugars/polyols were tested (Degner, Chung, Schlegel, Hutkins, & McClements, 2014) as cryoprotectants, the roles of maltodextrins on emulsion stability were not well elucidated. On the other hand, the presence of cryoprotectants could largely affect the delivery functionality of the emulsions, which also require further experimental work. In the current study, volatile compounds were incorporated in O/W emulsion systems with the addition of different maltodextrins. The main objective of the current study was to understand the effect of maltodextrins (with different dextrose equivalent value, DE) on the physicochemical properties and volatile characteristics of O/W emulsions subjected to freeze-thawing.

2. Materials and methods

2.1. Materials

Glucidex 6 (maltodextrin DE 6, MD 6), Glucidex12 (maltodextrin DE 12, MD 12), and Glucidex 21 (maltodextrin DE 21, MD 21) were kindly offered by Roquette Freres (Lestrem, France). WPI (BiPro), which contained 71% β-lactoglobulin and 12% α-lactalbumin, was bought from Davisco Food International (Le Sueur, MN, USA). Sunflower oil was purchased from a local supermarket and used without further purification. 1-propanol (>99.5% purity), diacetyl (butane-2, 3-dione, > 99.5% purity), 2-pentanone (>99% purity), hexanal (>99% purity), 2-heptanone (>99% purity), Sundan III, Nile red, and Fast Green were all products of Sigma–Aldrich (St. Louis, MO, USA). It should be noted that maltodextrins are normally defined as having a DE value <20, and corn syrup solid are defined as have a DE value ≥20. In this paper, the term “maltodexrin” was also used for glucidex 21 (MD 21) for an easier understanding and discussion of the results.

2.2. Emulsion preparation

WPI suspension was prepared by dispersing the powdered WPI in phosphate buffer (5 mM, pH 7.0 ± 0.1) and the mixture was stirred overnight to ensure complete dissolution. Sodium azide (0.01% w/w) was added to inhibit microbial growth. Oil-in-water emulsions were prepared by mixing the WPI (1% w/w in the final emulsion) suspensions and sunflower oil (20% w/w) at 10, 000 rpm for 1 min using an Ultra -Turrax (IKA, Staufen, Germany) and followed by high pressure homogenization (M110-EH Microfluidizer, Microfluidics International Corp., Newton, MA, USA) at 50 MPa for three passes. The emulsions were immediately cooled to room temperature (~23 °C) with tap water. Maltodextrin (10% w/w) was then added into the emulsions and stirred using a magnetic stirrer (IKA) until completely dissolved.

2.3. Freeze–thaw treatment

Emulsions were stored in plastic tubes at −20 °C for 16 h in a temperature-controlled refrigerator, and then thawed at 25 °C for 6 h in a water bath. This cycling was repeated three times, and physicochemical characterization of the emulsions was performed after each cycle. As a control, emulsions kept at 25 °C were also analyzed.

2.4. Particle size analysis

The particle size of the emulsions was determined using a Mastersizer 3000 laser diffraction instrument (Malvern Instruments Ltd., Malvern, UK). Emulsions were diluted in deionized water in the sample dispersion unit. For the measurement, laser obscuration level was set at ~6%, and particle (oil) and dispersant (water) refractive index were chosen as 1.46 and 1.33, respectively. From particle size distributions, the surface-weighted mean diameter (d_{32}) and volume-weighted mean diameter (d_{43}) were reported, both expressed in micrometer. It should be noted that d_{43} is more sensitive to the presence of large particles (e.g., droplet aggregations), while d_{32} is more sensitive to the presence of small particles (McClements, 2005).