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Controlled volatile release of structured emulsions based on phytosterols crystallization

Xiao-Wei Chen [a], Jian Guo [a], Jin-Mei Wang [a], Shou-Wei Yin [a], Xiao-Quan Yang [a, b, *]

[a] Food Protein Research and Development Center, Department of Food Science and Technology, PR China
[b] State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640, PR China

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ABSTRACT

Flavor is one of the most important criteria for consumer acceptance of food products, especially for low-fat food emulsions. In this study, we prepared structured flavoring oil-in-water (O/W) emulsions based on the crystallization behavior of β-sitosterol (Sito), a functional phytosterol, in the presence of emulsifier (sodium caseinate, SC and octenylsuccinate starch, OSS), These structured emulsions improved colloidal stability during long-term storage and delayed volatiles release under real time dynamic condition. However, the equilibrium static headspace analysis did not show significant differences in the affinities of hydrophobic volatile compounds with pure constitutes of unstructured and structured emulsions. This highlighted the importance of structural properties of the O/W interface in volatile release modulation. A modified gel trapping technology (GTT) combined with polarized light microscopy (PLM) and confocal laser scanning microscope (CLSM) were applied to characterize the microstructure at the oil-water interface, and it clearly showed the formation of a novel Sito crystal/OSA starch complex interface for OSS stabilized structured emulsion. This unique interfacial microstructure might contribute to the strong retention of volatile compounds due to steric barrier and enhanced affinity to those lipophilic volatiles. The formulated flavor emulsion with controlled volatile release profile was successfully prepared by simply blending the unstructured and structured flavoring emulsions. This work provides indications for potential applications of the formulation design in flavor emulsions and phytosterols structured emulsion as novel aroma delivery systems to improve flavor perception.

1. Introduction

Aroma release has an important attribute on the sensory acceptability and hence consumers' preference of food, especially for food emulsions (e.g., yogurt, ice creams, margarines, sauces, spreads and beverages). Due to the growing problem of obesity in the world, more and more people tend to consume low-fat foods. Although consumers can be aware of health benefits of low-fat foods, poor flavor experience may be one of the factors hindering their acceptance. The improvement on flavor acceptance of low-fat food is a long-term aim of food industry, which may benefit the population by helping to reduce the overall fat intake (McClements & Demetriades, 1999). The release of volatile compounds from food matrices is mainly governed by the physicochemical characteristics of volatiles and the interactions between volatile compounds and constituents of food matrices (Guichard, 2002), but also the structural characteristics of food matrices (Chung & McClements, 2014; de Roos, 2000; Druaux & Voilley, 1997; Wang & Arntfield, 2015). Therefore, a modification of emulsion microstructure may favor or hinder the release of some volatile compounds and consequently achieve controlled, sustained or delayed release of volatiles during consumption and storage.

Volatile release from oil-in-water (O/W) emulsions involves the distribution and mass transfer of volatile compounds among the oil phase, the interface, the aqueous phase, and finally the headspace (de Roos, 2000). In O/W emulsions, due to the presence of different interfaces, the release of volatile molecules mainly not only depends on the mass transfer across the air–water interface, (Lian, Malone, Homan, & Norton, 2004), but across the oil-water interface (Seuvre, Diaz, & Voilley, 2002). The structural properties of the oil-water interface and the type of emulsifier/stabilizer were considered to influence volatile release from emulsified systems.

* Corresponding author. State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640, PR China. Tel.: +(086) 20 87114262; fax: +(086) 20 87114263.
E-mail addresses: fexqyang@scut.edu.cn, fexqyang@163.com (X.-Q. Yang).

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Modification of the O/W interface (e.g., mixed layer interface and multilayer interface) (Benjamin, Silcock, Leus, & Everett, 2012; Mao, Boiteux, Roos, & Miao, 2014; Sadovoy et al., 2013; Seuvre et al., 2002) has been used for delaying the release of volatile compounds, implying the possibility of flavor encapsulation and controlled volatile release by carefully structuring the shells of oil droplets. Sadovoy et al. (2013) prepared a multilayer flavor-containing O/W emulsion with layer-by-layer shell for retarding mass transfer of volatile molecules across the oil-water interface. On the other hand, the oil phase of emulsions, which acts as precursors, reservoir and solvents for the volatiles, plays a dominant role in the modulation of volatile release, as well as food structure and mouthfeel (Frank, Appelqvist, Piyasiri, & Delahunty, 2012). Structuring O/W emulsions with triglycerides (TAGs) and monoglycerides (MGs) was found be able to control of the volatile release for a number of binding sites. Additionally, a network formed in oil phase and around oil droplets was also able to inhibit diffusion and reduce the mobility of volatile molecules (Landy et al. 2007; Mao, Roos, & Miao, 2013; Phan et al., 2008; Paraskevopoulou, Tsoukala, & Kiosseoglou, 2009). Landy et al. (2007) found that the bulk lipid mixture of TAGs and MGs (60:40) formed a L2 phase structure, and displayed a better retention compared to the pure TAGs for aroma release, due to their specific interactions with the lipophilic aroma compounds. Unfortunately, structuring of edible oils and food-emulsions with crystalline TAGs, result in significantly higher levels of *trans* fats or saturated fatty acids (SaFAs) in food products, which linked to increased risk of cardiovascular disease (CVD) (Aro, Jaughiainen, Partanen, Salminen, & Mutanen, 1997). Phan et al. (2008) and Mao et al. (2013) prepared structured O/W emulsions based on the self-assembling behavior of MGs to modulate volatile release. In MGs structured O/W systems, the equilibrium concentration of volatiles in the headspace of MGs emulsions was significantly lower than that of unstructured emulsion. Concomitantly, delayed volatile release form these structured emulsions with low oil content was also observed. However, from a nutritional standpoint, MGs seem to deliver only limited benefits in offering a clear *trans* fats and SaFAs, if at all, compared to structuring vegetable oils by fat crystals (Flöter, E., 2012). More specifically, there are a number of low molecular weight structuring agents as an added nutritional benefit that can serve as an alternative to crystallizine in edible oils, such as dicarboxylic acids, 12-hydroxyoctadecanamides, sorbitan esters and phytosterols (Pernetti, van Malssen, Flöter, & Bot, 2007).

Phytosterols are a family of compounds consumed by the human body as part of the diet, and they have chemical structures similar to that of cholesterol. β-sitosterol (Sito) is commonly used as a cholesterol-lowering functional phytosterol and a health supplement in foods, such as margarine, vegetable oil and functional beverages (Kritchevsky & Chen, 2005). Furthermore, Sito is known to be able to form plate- and needle-like crystals of anhydrous, hemi- and monohydrates when crystallized in oil solutions or organic solvents (den Adel, Heussen, & Bot, 2010; Kawachi, Tanaka, Hirano, Igarashi, & Ooshima, 2006). Due to the presence of intermolecular hydrogen bonds, the mixtures of β-sitosterol and γ-oryzanol can self-assemble, leading to the formation of organogel with the hollow tubular microstructures and network (Bot, den Adel, & Roijers, 2008; Duffy et al., 2009). Sawalha et al. (2012) prepared organogel based water-in-oil (W/O) emulsions with mixtures of β-sitosterol and γ-oryzanol. They observed that Sito molecules self-assemble formed monohydrate crystals when bind to water molecules, which hindered the formation of tubules, and resulted in a weaker emulsion-gel. The hydroxyl groups of Sito and water molecules are hydrogen bonded to form a sheet at the bilayer interface (thickness ~ 3.6 nm), where the hydroxyl groups are periodically distributed on the crystals surface (Kawachi et al., 2006; Rossi, Sacanna, & Velikov, 2011). Due to the presence of polar groups on the crystal surface, rod-like Sito colloidal particles prepared by anti-solvent precipitation in the presence of a non-ionic surfactant (Tween 80) showed good colloidal stability and improved in *vitro* bioaccessibility (Rossi, Seijen, Melnikov, & Velikov, 2012). Sito has a high degree of surface activity due to the presence of tetracyclic fused ring skeleton (hydrophobic region) and a single hydroxyl group (polar region), which would allow them to migrate into the oil-water interface (den Adel et al., 2010; Duffy et al., 2009; Sawalha et al., 2012). Recently, Sito has been employed to stabilize Pickering emulsion gels by promoting emulsion kinetic stability with a thick steric barrier layer (Liu & Tang, 2014).

The flavor release of food emulsions is not only determined by the bulk matrix composition, but their unique microstructure formed in the meso-scale range. The aim of the present study was to fabricate the O/W flavoring emulsions with controlled volatile release profiles via Sito self-assembled microstructure. We propose protein (sodium caseinate, SC) and octenyl succinic anhydride (OSA) modified maize starches (octenylsuccinate starch, OSS) to be used as emulsifiers to constitute the O/W interface since both of them have a wide range of practical applications for flavor emulsions (Chung & McClements, 2014; McClements & Demetriades, 1999). Sito crystals structured emulsions stabilized by SC and OSS were prepared by heat homogenization. Sito formed crystalline structure in SC and OSS stabilized O/W emulsions, and volatile release was measured by gas chromatography (GC) under real-time dynamic and static studies in terms of their release rate, maximum headspace concentration, the partition coefficient and thermodynamic behavior. The knowledge obtained in this study might be useful in the development of novel foods with designable flavor profile, and thus have a good implication for designing low-fat emulsions with improved aroma perception.

2. Material and methods

2.1. Materials

β-Sitosterol (Containing 82.44% β-sitosterol, 10.02% β-sitostanol, 3.32% campesterol, and 4.21% of other minor sterols, conformed by GC analysis) was purchased from Xi'an Realin Biotechnology Co., Ltd (Xi'an, China). Sodium caseinate ($\geq$90.00% purity, SC) is product of Fonterra Group Ltd. (Auckland, New Zealand). OSA modified maize wax starch (OSS, Purity Gum 2000) was provided by Ingredion Inc. (Westchester, USA). Sunflower oil (FO) was obtained from a local supermarket (Guangzhou, China). Six volatile compounds commonly found in foods and beverages with different physicochemical properties (e.g., hydrophobic, solubility, vapor pressure, and boiling point) were purchased from Sigma Chemical Co., Ltd., China (Table S1): diacetyl (2, 3-butanedione, > 98%), hexanal (>98%), ethyl hexanoate (>99%), ethyl octanoate (>99%), linalool (>98%) and D-limonene (>97%). A model volatile stock solution was prepared by mixing of the six pure compounds and then stored at −18 °C before use. The fluorescent dye, aminofluorescein, was purchased from Sigma Chemical Co. (St. Louis, MO). Sylgard 184 curable silicone elastomer (polydimethylsiloxane, PDMS) was obtained from Dow Corning Co. (Midland, MI, USA). All other chemicals were analytical or better grade.

2.2. Preparation of Sito structured flavoring emulsions

Sodium caseinate (SC) or octenyl succinic anhydride (OSA) modified starch (OSS) was dispersed in 10 mM (pH 7.0) phosphate buffer solution (1 wt.% of final emulsion) and preheated to 85 °C. The oil phase (10 wt.%) was prepared by mixing the β-sitosterol (Sito) and sunflower oil (SO) (1:9, w/w) and then heating the