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High hydrostatic pressure induced changes on palm stearin emulsions

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ABSTRACT

Emulsions are thermodynamically unstable systems formed through blending of two immiscible fluids. Recent studies have shown that High Hydrostatic Pressure (HHP) can initiate or accelerate lipid crystallization in emulsions. In this study, the effect of HHP on lipid crystallization was examined. Emulsion samples were prepared with palm stearin (PS) as the oil phase and sodium caseinate (SC) as the emulsifier and they were pressurized at 100 and 500 MPa at 10, 20 and 40 °C for 15 min. In order to determine the crystal structure of the emulsions, differential scanning calorimeter (DSC) was used and the change in the crystal morphology during 28 day-storage at 4 °C was observed. Nuclear Magnetic Resonance Relaxometry (NMR) experiments were also conducted and transverse relaxation time (T_2) and self-diffusion coefficient (SDC) values showed a trend to follow polymorphic changes of lipid crystals. Results showed that pressure and storage time both had significant effects ($p < 0.05$) on the crystal structures of emulsions.

1. Introduction

Emulsions make significant contribution to control physical properties, flavors and stability in food systems (Whittinghill et al., 2000). They are thermodynamically unstable systems which contain two immiscible liquids, generally oil and water, and one liquid disperses as small droplets (dispersed phase) in the other liquid (continuous phase). Emulsions have different destabilization mechanisms but the most common ones are creaming, flocculation and coalescence (Palanuwech and Coupland, 2003; McClements, 2005; Tadros, 2013). Creaming is caused by density differences between continuous and dispersed phases and denser layer is formed at the bottom of the emulsions. Therefore, it may increase the rate of other destabilization mechanisms' occurrence (Tadros, 2013). Flocculation is a process in which droplets come together and form a three-dimensional structure but in this structure, droplets maintain their integrity. Flocculation also causes significant changes in emulsions' physicochemical and sensorial properties like texture, viscosity, shelf life and appearance (McClements, 2005). Coalescence is similar with flocculation regarding droplet gathering but in this mechanism droplets merge with each other and do not maintain their integrity. Coalescence also causes an increase in the creaming rate due to bigger sizes of droplets (McClements, 2005; Ritzoulis, 2013).

Some emulsions may have more complex structures because they contain totally or partially crystallized phases (dispersed and/or continuous phases) (Palanuwech and Coupland, 2003). In oil-in-water emulsion, fat crystals in oil droplets may initiate destabilization mechanisms via partial coalescence. Fat crystals in a droplet can interfere with crystals of another droplet and make a link between these two droplets. However, each droplet can preserve their integrity through their internal crystal structures' mechanical strength. When an emulsion is heated, fat crystals melt, droplets' integrity are lost and they finally merge with each other which triggers the coalescence (Boode and Walstra, 1993; Dickinson and McClements, 1995; Vanapalli et al., 2002; Palanuwech and Coupland, 2003; McClements, 2005). Partial coalescence rate depends on particle size and volume fraction of dispersed phase, emulsifier type and concentration, solid fat content and crystal structure (Dickinson and McClements, 1995; Palanuwech and Coupland, 2003; McClements, 2005).

Lipid crystallization consists of three steps namely; supercooling, nucleation and crystal growth. Oil can preserve its liquid phase for sometime below its crystallization temperature. The time

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span until the first crystal nuclei can be observed is named as supercooling. Nucleation is the step where crystal nuclei are formed all over the system (Coupland, 2002). After nucleation, crystals start to grow around each nuclei and this step is called crystal growth. However, lipids can form different crystal structures that are called polymorphs. Polymorphs are generally classified in three forms, α, β′ and β-crystals but some fats have more polymorphic structures. Lipids first crystallize into α and β' forms (which are less stable), and then turn to denser β-crystals (Coupland, 2002; Zulkurnain et al., 2016a). Initial crystal structure and the rate of polymorphic change may be affected by internal (triglyceride content, structure, molecular interactions, etc.) and external (temperature-time applications, mechanical mixing, etc.) factors (McClements, 2005).

Palm stearin (PS) is the highly saturated solid part of palm oil and produced by fractionation process. PS contains different types of triacylglycerol with different ratios so melting temperatures of PS can vary. The polymorphism of PS cannot be fully understood due to this different composition (Sonoda et al., 2004).

Sodium caseinate (SC) is a protein obtained from casein, a milk protein, by means of acid-coagulation with sodium hydroxide. It is an amphiphilic molecule and provides a strong stability against steric and electrostatic repulsions between emulsion droplets. SC is used in food industry in a wide range of products as emulsifier because of its emulsification, water-binding, fat-binding, thickening, gelation and whipping properties.

Nuclear Magnetic Resonance (NMR) relaxometry is used as a non-destructive method to analyze the interior composition of complex food systems (Greiff et al., 2014). It may provide characterization of such systems via proton relaxation experiments by measuring transverse relaxation time (T_2) (also known as spin-spin relaxation time). T_2 measurement is a good tool not only to reveal the internal compositions of foods, in this case emulsions, since each organic material possesses a distinct relaxation time characteristic (Barrabino et al., 2014; Zhang et al., 2016), but also to characterize the degree of water-surrounding network interactions within a system. Self-diffusion coefficient (SDC) -characterizing the mobility of water molecules within food materials-is also measured to support the T_2 results (Salami et al., 2013).

In literature, there are some studies investigating the effects of HHP on crystal polymorphism by NMR measurements but they mainly focus on NMR spectroscopy experiments, free induction decay (FID) of sole crystals and transverse relaxation of sole crystal components (Bouteille et al., 2013; Mazzanti et al., 2008; Nadakatti, 1999; Van Duynhoven et al., 2002). To the best of our knowledge the effect of HHP on lipid crystallization in emulsions is quite a new area of interest and has not been explored extensively despite limited number of studies with conflicting observations in the literature. Oh and Swanson (2006), claimed that crystallization rate of cocoa oil emulsions was not affected ($p > 0.05$) and only their polymorphic structure could be slightly changed by the HHP treatment up to 600 MPa. On the other hand, Blümer and Mäder (2005) and Ferstl et al. (2011) reported that HHP treatment (at 200–750 MPa and 4–48 °C for 5–30 min) could be used to modulate the microstructure of crystalline lipid droplets. High pressure values (300–600 MPa) caused substantial reduction in lipid volume (17–30%) (Rostocki et al., 2013) due to weak Van der Waals interactions that were easily overcame by pressure treatments (Zulkurnain et al., 2016b). HHP is more effective on saturated fatty acids than unsaturated ones, consequently leading to faster crystallization of saturated fatty acids. Application of HHP decreases the specific surface energy needed for crystallization thus, induces crystal nucleation in an energy efficient way and affects the polymorphism of such crystals (Zulkurnain et al., 2016b).

The objective of this study is to i) observe and track the effect of HHP treatment on the crystal structure of an emulsion produced with PS as disperse phase and SC as emulsifier, by NMR relaxometry method, ii) provide transverse relaxation profile for the whole emulsion system and iii) supply information on the overall crystallization process and mechanisms taking place within the emulsion system. NMR relaxometry was proposed as an alternative method to understand polymorphic changes of lipid crystals due to HHP treatment and during storage period.

2. Materials and methods

2.1. Materials

Palm stearin (PS) (fully hydrogenated palm stearin with a min 55 °C melting point) was donated by Cargill Turkey (Bursa, Turkey). Casein sodium salt (C8654) was purchased from Sigma-Aldrich (St. Louis, Missouri, USA).

2.2. Emulsion preparation

Hot homogenization technique was used for emulsion preparation (Yucel et al., 2013). Sodium caseinate solution (2 wt %) was prepared with double distilled water, stirred overnight and heated up to 80 °C for 1 h. Palm stearin was incubated at 70 °C for 30 min to ensure that all crystal structures were melt. Palm stearin and sodium caseinate solution were mixed with a ratio of 1:9 (w/w) by using T18 digital ULTRA TURRAX® (IKA, Staufen, Germany) with a speed of 1000 rpm for 30 s. This coarse emulsion was passed 3 times through M-110Y Microfluidizer® (Microfluidics Corporation, MA, USA) at 100 MPa at 60-65 °C. The hot samples were stored at 45 °C (i.e., above crystallization temperature of PS droplets) for less than 1 h in water bath until HHP treatment.

2.3. High hydrostatic pressure (HHP) treatment

HHP applications were performed with type-760.0118 high hydrostatic equipment (SITEC, Zurich, Switzerland). The equipment consists of a pressurization chamber, two end closures, a means for restraining the end closures, a pressure pump, a hydraulic unit and a temperature control device. Pressure transmitting medium was a mixture of water and glycol. The liquid was heated prior to pressurization to the desired temperature by an electrical heating system surrounding the chamber. Pressurization chamber has 24 mm internal diameter, 153 mm length and 100 mL capacity. The rate of pressure increase and pressure release was approximately 5–10 s for the designed system. Pressurization time reported in this study did not include the pressure increase and release times.

Prepared emulsions were pressurized in 2 mL sterile cryotubes (Biosigma Srl, CLEARLINE®, CryoGen®Tubes) at two different pressure (100 and 500 MPa) and three different temperatures (10, 20 and 40 °C) for 15 min. HHP treatments were carried out at temperatures defined according to preliminary differential scanning calorimetry (DSC) experiments (Fig. 1 (Sevdin et al., 2017)) to define roughly the approximate melting and crystallization temperatures 40 °C was selected as the point where no crystal formation occur, 20 °C as the point that crystal formation depending on the temperature was completed and 10 °C as a low reference temperature. Pressure levels were selected to be one low and one high level as 100 and 500 MPa. Pressure application time was constant and relatively longer than general HHP applications to remove the effect of time on the crystal formation. At the end of the processing time, samples were held at room temperature until the analyses were completed. They were then stored at refrigeration temperature (4 °C) for 28 days.

Following HHP application, abbreviations were implemented

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