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Influence of morphology and polymorphic transformation of fat crystals on the freeze-thaw stability of mayonnaise-type oil-in-water emulsions

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ABSTRACT

This study examined the destabilization of an oil-in-water (O/W) emulsion by freeze-thawing with a focus on the influence of the morphology and polymorph of fat crystals. For a model of food emulsion, this study used a mayonnaise-type O/W emulsion containing 70 wt% canola oil (canola emulsion) or soybean oil (soybean emulsion) stored at −15, −20, and −30 °C. The freeze-thaw stabilities of the emulsions were evaluated by measuring the upper oil layer after freeze-thawing. The soybean emulsion kept at −20 °C had the highest stability; the other emulsions were destabilized during 6 h of storage. Crystallization in the emulsions was determined using differential scanning calorimetry (DSC), time variation of temperature, X-ray diffraction measurement, and polarized light microscopy. DSC thermograms indicated that crystallization in emulsions occurred first in the high-melting fraction of oil, followed by water and, last, in the low-melting fraction of oil during cooling to −40 °C. In the canola emulsion, the amount of fat crystals derived from the low-melting fraction of oil increased during storage at all temperatures, resulting in partial coalescence. The soybean emulsion was expected to be destabilized by polymorphic transformation (sub-α to β′ and β) of fat crystals derived from the high-melting fraction during storage at −15 and −20 °C. However, the soybean emulsion did not exhibit polymorphic transformation stored at −30 °C, and the amount of fat crystals did not increase during freezing; thus, it was destabilized via a different mechanism.

1. Introduction

Oil-in-water (O/W) emulsions, in which oil droplets are dispersed in a water phase, are thermodynamically unstable systems. Many food O/W emulsions (e.g., mayonnaise, sauces, and beverages) are frozen to improve their shelf life (Degner et al., 2013; Magnusson, Rosén, & Nilsson, 2011; Márquez, Salvatore, Otero, Wagner, & Palazolo, 2015) or are commercially supplied as frozen foods. However, most O/W emulsions are easily destabilized after freeze-thawing because of the crystallization of fats and water in emulsions (Degner, Chung, Schlegel, Hutkins, & McClements, 2014; Ghosh & Coupland, 2008). Several mechanisms have been proposed to explain how destabilization occurs via freeze-thawing. Water crystallization is widely accepted as a cause of freeze-thaw destabilization. The formation of ice crystals in an emulsion results in the following: flocculation of oil droplets, increase of ion strength, and pH variation in the unfrozen aqueous phase (Komatsu, Okada, & Handa, 1997; Thanasukarn, Pongsawatmanit, & McClements, 2004). These changes in the emulsion increase droplet-droplet contact. In addition, the ice crystals become larger due to recrystallization during storage, resulting in interfacial membrane disruption (Fioramonti, Arzeni, Pilosof, Rubiolo, & Santiago, 2015). Moreover, emulsifiers that adsorb to the droplet interface may be damaged by water crystallization because emulsifiers lose their functionality with dehydration, e.g., cold denaturation of proteins (Davey, Zabik, & Dawson, 1969; Xiong, 1997). Redistribution of emulsifiers to oil droplets and ice surfaces removes emulsifiers from the droplet surface, promoting deterioration of the emulsion (Hillgren, Lindgren, & Aldén, 2002). When an O/W emulsion is stored at low temperatures, it is destabilized by fat crystallization. In partial coalescence, fat crystals nucleate and grow in oil droplets during cooling. The growing fat crystals then penetrate into the other oil droplets connecting them (Boode, Walstra, & de Groot-Mostert, 1993; Palanuwech & Coupland, 2003; Vanapalli, Palanuwech, & Coupland, 2002a, 2002b). The partially coalesced droplets collapse and form larger droplets when they are heated. Polymorphism, morphology, and location of fat crystals also affect the stability of an O/W emulsion (Rousseau, 2000). The polymorph and crystal morphology depend on various factors, including the chemical structure of the fat, the cooling rate, temperature cycling, the application of shear force, droplet size distribution, and the type of emulsifier used to stabilize the emulsion droplets (Boode, Bisperink, & Walstra, 1991; McClements, 1999; Walstra, 1967). Boode et al. (1991) found that larger or oriented fat crystals at the oil/water interface make the emulsion more sensitive to partial coalescence. Arima, Ueji, Ueno, Ogawa, and Sato (2007) studied the

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relationship between polymorphism and the stability of an O/W emulsion. They found that the palm mid fraction in water emulsion was destabilized because of a polymorphic transition from α to β′. However, the influence of fat crystals (their location, orientation, morphology, and polymorph forms in oil droplets) on the freeze-thaw stability of O/W emulsions has not been clarified.

Mayonnaise is a mixture of egg, vinegar, and oil, and is a widely consumed O/W emulsion throughout the world. Mayonnaise typically contains 70 to 80% fat that is stabilized with egg yolk as an emulsifying agent (Depree & Savage, 2001). Recently, the freeze-thaw stability of a mayonnaise-type emulsion has been studied. Magnusson et al. (2011) reported that the composition and crystallization of fats significantly affect the freeze-thaw stability of a mayonnaise-type emulsion. Miyagawa, Ogawa, Nakagawa, and Adachi (2016) obtained similar results. These studies used differential scanning calorimetry (DSC) to investigate the crystallization of fats; the effects of the amount and growth of fat crystals were also analyzed. However, the destabilization mechanism of a mayonnaise-type emulsion remains unclear.

The purpose of the present study was to analyze destabilization by freeze-thawing, focusing on the influence of the crystallization of fats by observing the polymorph, particle microstructure, and location of fat crystals in oil droplets during freezing. In this study, our food model emulsion was a mayonnaise-type O/W emulsion. To simplify the system, the model O/W emulsion did not contain salt or artificial emulsifiers for the freeze-thaw experiments. The influence of the fatty acid composition (canola oil is composed mainly of oleic acid and soybean oil is composed mainly of linoleic acid) and the storage temperatures (−15 °C, −20 °C, and −30 °C) on the crystallization of fats and the freeze-thaw stability were also analyzed.

2. Materials and methods

2.1. Materials

Canola oil (Nisshin OilliO Group, Ltd.), soybean oil (Junko, Inc.), vinegar, and egg were obtained from a local supermarket. Silver iodide (99.0% purity) was purchased from Sigma-Aldrich Co. (St. Louis, MO, USA).

2.2. Preparation of mayonnaise-type O/W emulsions

A mayonnaise-type O/W emulsion was preparing composed of 70 wt% canola oil or soybean oil, 15 wt% vinegar, and 15 wt% egg yolk. First, the egg yolk and half of the vinegar were stirred in glassware at 1000 rpm (BLh1200, Shinto Scientific, Japan) for 2 min. Canola oil or soybean oil was then added dropwise at a rate of 0.1 mL s^{-1} (MP-3, Tokyo Rikakikai, Japan) to the mixture with stirring at 1000 rpm. Finally, the residual vinegar was added to the mixture, and the mixture was stirred at 1000 rpm for 2 min. The total mass of the mayonnaise-type emulsion was 70 g. The coarse emulsion was further homogenized at 13,600 rpm (Ultra-Turrax T25 Digital, IKA, Germany) for 3 min to obtain a fine emulsion. The droplet size and the distribution of the obtained emulsion were measured using a laser particle-size analyzer (Shimadzu, SALD-2000J, Japan). The average droplet size of the coarse emulsion was 12 ± 3 μm, and that of the fine emulsion was 3.2 ± 0.3 μm. Emulsions were stored in a refrigerator and used within one month.

2.3. Differential scanning calorimetry

The thermal behaviors of the emulsions were investigated using DSC (Thermo Plus 8240, Rigaku, Japan). Samples (20 mg) were sealed in an aluminum pan; thermograms were taken from 0 to −40 °C, held for 10 min, and then heated to 10 °C at a rate of 2 °C min^{-1}. Al_2O_3 was the reference material. The crystallization temperature was determined from the onset temperature of peaks, and the melting point was determined from the peak top temperature on the thermograms. The melting

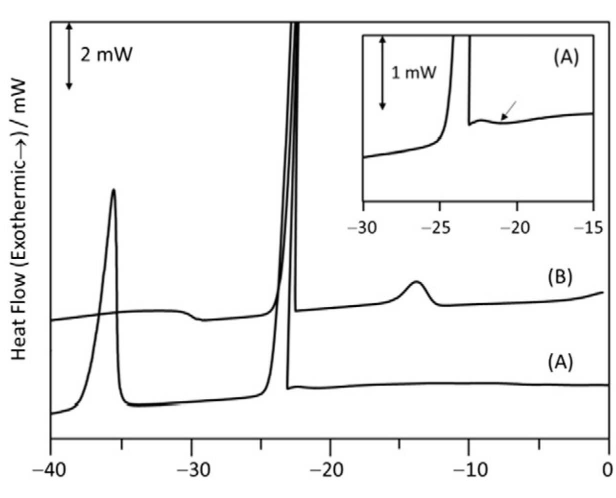

Fig. 1. DSC thermograms of (A) canola emulsion and (B) soybean emulsion during cooling at a rate of 2 °C min^{-1}. Insert presents magnified thermograms of (A) from −15 to −30 °C.

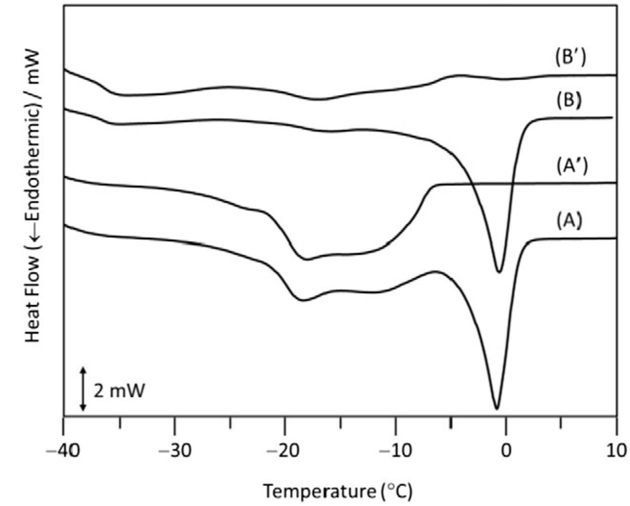

Fig. 2. DSC thermograms of (A) canola emulsion, (A′) canola oil, (B) soybean emulsion, and (B′) soybean oil during heating at a rate of 2 °C min^{-1}.

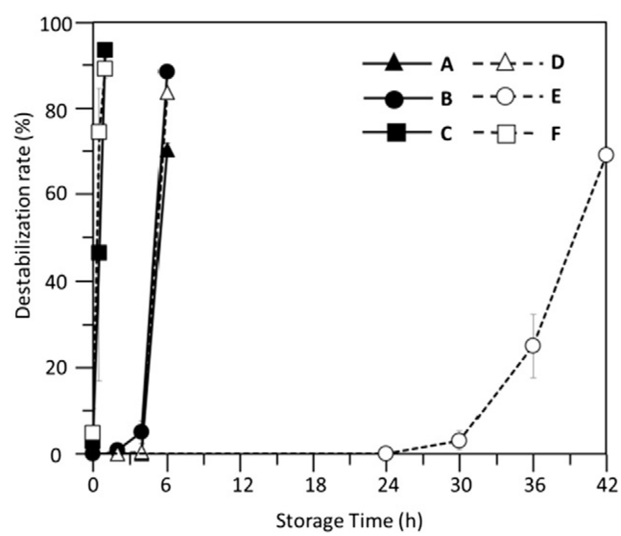

Fig. 3. Destabilization rate in the emulsions during storage from 0 to 42 h. (A) −15 °C, (B) −20 °C, and (C) −30 °C of canola emulsions. (D) −15 °C, (E) −20 °C, and (F) −30 °C of soybean emulsions. Error bars are S.D. ($n = 4$).