



# Influence of interfacial adsorption of glyceryl monostearate and proteins on fat crystallization behavior and stability of whipped-frozen emulsions

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## ABSTRACT

The effect of interfacial competitive adsorption of glyceryl monostearate (GMS) with proteins and GMS-fat (anhydrous milk fat; coconut oil) interactions on the fat crystallization behavior and stability of whipped-frozen emulsions were investigated. The results indicated GMS retarded the nucleation of emulsified anhydrous milk fat, but accelerated crystal growth. A contrasting outcome was elicited by emulsified coconut oil. Increasing GMS concentration strengthened and weakened the structural networking within anhydrous milk fat and coconut oil emulsions, respectively, which was evidenced by the oscillatory rheology results. Anhydrous milk fat whipped-frozen emulsions were characterized by increased partial coalescence degree with increasing GMS concentration. However, lower partial destabilization index and insignificant effect of GMS was found in coconut oil systems. Confocal laser scanning micrographs revealed that big clumps of fat globules were present at air bubble surfaces in anhydrous milk fat whipped-frozen emulsions, while only some individual fat globules were observed in coconut oil systems.

## 1. Introduction

Many food products occur in the form of oil-in-water emulsions in which an oil phase is dispersed into a continuous aqueous phase. From a thermodynamical point of view, these emulsions are unstable systems due to the unfavorable contact between fat droplets and molecules in the aqueous phase. Various types of instability mechanisms such as Ostwald ripening, creaming, flocculation and coalescence affect the shelf life of commercially available products (Fredrick, Walstra, & Dewettinck, 2010). However, in some emulsion food systems such as ice cream, partial coalescence is required to achieve the desired structure development during its production. This contributes to the physicochemical properties and sensory perception of the final food products (Fredrick et al., 2013). The susceptibility of the fat globules towards partial coalescence depends on the property of the adsorbed layer such as composition, thickness and viscoelasticity at the oil/water interface. Furthermore, fat crystallization is of high importance for partial coalescence of emulsions (Cheng et al., 2016). The coexistence of protein and emulsifier at the fat globule interface not only influences the protein surface coverage and the thickness of the adsorbed layer, but also

fat crystallization behavior and solid fat content (Goibier, Lecomte, Leal-Calderon, & Faure, 2017).

In oil-in-water (O/W) emulsions stabilized by proteins, both steric and electrostatic repulsion are abundant. Thus, the extent of partial coalescence is less for globules stabilized by proteins when compared with those stabilized by small-molecule surfactants because proteins exhibit stronger steric repulsion compared to most small-molecule surfactants. Especially for the ice cream emulsions, the protein amount tends to be 4% (w/w) which is much more than that required to cover the surface area of the fat droplets (10–14% fat) created by homogenization. Secondly, proteins tend to form a thicker and a more viscoelastic membrane at the oil/water interface (Fredrick et al., 2010). This layer of adsorbed proteins prevent the close contact of globules necessary for partial coalescence to occur which is elucidated by the low levels of fat destabilization index found in ice creams containing no emulsifier (Segall & Goff, 2002). However, the presence of emulsifiers at lipid globule interfaces can decrease the strength of the adsorbed protein interfaces significantly and induces destabilization of the fat droplets. Emulsifiers can access the protein stabilized interface via small gaps in the entangled protein layer. This results to surface

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pressure and formation of emulsifier-rich domains at the interface. The protein layer collapses and then displaced by emulsifiers from the interface at sufficiently high surface pressure (Munk, Erichsen, & Andersen, 2014).

Fat crystals are essential in the microstructure formation of ice cream and determine the physical and sensory properties. Crystallization of the fat droplets occurs when applying a certain degree of supercooling. Crystals nucleate and start to grow. The resulting solid fat content (SFC), the morphology and size of the crystals and their internal arrangement during manufacture will greatly affect the partial destabilization of the fat globules. The emulsifier would interact with fat upon adsorption and alter fat crystallization property. Numerous investigation have reported the effect of fat characteristics and fat-emulsifier interaction on the physicochemical properties and stability of O/W emulsions or ice cream (Bazmi, Duquenois, & Relkin, 2007; Bugeat et al., 2011; Granger, Barey, Combe, Veschambre, & Cansell, 2003; Granger, Barey, Veschambre, & Cansell, 2005; Méndez-Velasco & Goff, 2009; Méndez-Velasco & Goff, 2011, 2012). In the previous study, it was found that increasing the unsaturated fatty acid content in milk fat can affect the crystallization property of milk triacylglycerols and their functional property (Bugeat et al., 2011). Fat type and fat-emulsifier interaction can influence the particle size, protein load, viscosity and solid fat content of emulsions based on milk proteins-glycerol ester mixtures (Granger et al., 2003). Pertaining to the effect of emulsifier on fat crystallization property, most studies focused on their influence on solid fat content, crystallization behavior, thermal behavior and polymorphism in bulk fat (Domingues, Silva, Da Ribeiro, & Chih, 2016; Ipsen, 2013; Maruyama, 2016). Concerning the effect of surfactants in emulsions, most of the studies dealt with their propensity to displace proteins (Fuller et al., 2015; Jiang et al., 2018; Jiang, Weiqin, Xiong, & Yuanfa, 2019), oil/water interfacial properties (Jiang et al., 2018; Kim, Bot, Vries, Golding, & Pelan, 2013) and their templating effect on fat crystallization (Awad & Sato, 2001; Jiang et al., 2019; Sakamoto et al., 2004). There is a paucity of information relating to fat crystallization kinetic (especially crystal growth) in ice cream. Moreover, due to the small volume of fat (usually 10–14%) and size of fat droplets in ice cream emulsions, some technical analytical methods are unsuitable to acquire additional information about fat globules such as polarized optical microscope which was used to observe the morphology of fat crystals. Hence, the analysis of fat crystallization kinetic in ice cream emulsions can provide some useful information about fat nucleation and crystal growth, which is closely related to destabilization of fat globules and property of final products.

The present study compared two solid fats having different fatty acids and saturated levels and their interactions with different concentrations of glyceryl monostearate, as well as interfacial competitive adsorption of glyceryl monostearate with proteins for their roles in the formation and stabilization of milk oil-in-water ice cream emulsions. In order to better understand the relationship between adsorbed interfacial layer, fat crystallization behavior and emulsion stability during aeration process, the particle size, protein surface load, rheology properties, fat crystallization behavior, crystallization kinetics and microstructure of whipped-frozen emulsions were examined. This study will provide insight on how to control and improve partial coalescence in ice cream emulsions containing different types of fat and different concentrations of glyceryl monostearate.

## 2. Materials and methods

### 2.1. Materials

Coconut oil (CO, 43.9 g/100 g C12:0, 22.7 g/100 g C14:0, 10.9 g/100 g C16:0) was purchased from the local market. Anhydrous milk fat (AMF, 99.9% anhydrous, 9.8 g/100 g C14:0, 32.7 g/100 g C16:0, 12.8 g/100 g C18:0, 27.6 g/100 g C18:1n9t), skimmed milk powder (SMP, 33.4% protein content), carboxymethylcellulose, and glyceryl

monostearate (GMS, 2.24 g/100 g C14:0, 96.37 g/100 g C18:0, 0.75 g/100 g C20:0) were kindly supplied by the China Mengniu Dairy (Inner Mongolia, China). The Hydrophile-Lipophile Balance (HLB) value of GMS was 4.0. Fluorescein isothiocyanate (FITC) and Nile red were obtained from Sigma-Aldrich Chemical Co. Ltd. (St. Louis, USA).

### 2.2. Preparation of ice cream emulsions

Ice cream emulsions were prepared based on (all in weight proportion) 10% fat, 4% protein, 14% sucrose, 0.25% carboxymethylcellulose and different concentrations of GMS (0–0.40%). All of the ingredients except AMF or CO, were dry blended and mixed with water at 55 °C. The melted fat was slowly added with shear emulsifying mixer and mixed for 10 min to obtain a coarse emulsion. Pre-emulsions were pasteurized at 65 °C for 30 min and homogenized with a two-stage single-piston homogenizer using 20 MPa pressure on the first stage and 4 MPa on the second stage. The freshly prepared ice cream emulsions were cooled to 4 °C overnight. Following the ageing step, the emulsions were whipped and frozen in a scraped-surface continuous ice cream freezer (IC6308C, Petrus Ltd., Beijing, China) for 50 min. The whipped-frozen emulsions were stored at −18 °C before analysis.

### 2.3. Fat globule size and fat destabilization

The average particle diameter ( $D_{4,3}$ ) was determined by laser scattering using a Malvern Mastersizer 2000 (Malvern Instruments Ltd, Worcestershire, UK). The refractive indices of fat and water were 1.47 and 1.33, respectively, with an absorbance of 0.001 and an obscuration value in the range of 10–20%. The globule size distribution was measured by a polydisperse analysis mode. The pumping speed was 2000 rpm. Before measurement, the emulsions or the melted whipped emulsions were diluted with distilled water or with 1% sodium dodecylsulfate (SDS) solution at a ratio of 1:100. Partial coalescence and flocculation degree in the emulsions was discriminated by using SDS solution. Flocculation degree (FD) was measured to describe the tendency to droplet flocculation regardless of droplet coalescence/partial coalescence (Cheng et al., 2016). FD was calculated from the following equation:

$$FD(\%) = \frac{D_{4,3}(\text{water}) - D_{4,3}(\text{SDS})}{D_{4,3}(\text{SDS})} \times 100 \quad (1)$$

$D_{4,3}(\text{water})$  and  $D_{4,3}(\text{SDS})$  are the volume-weighted diameters, measured in water and SDS solution, respectively.

Partial coalescence degree (PCD) as a measure of another type of fat aggregation, was defined by the following equation:

$$PCD(\%) = \frac{D_{4,3}(\text{SDS})_{\text{WE}} - D_{4,3}(\text{SDS})_{\text{E}}}{D_{4,3}(\text{SDS})_{\text{E}}} \times 100 \quad (2)$$

where  $D_{4,3}(\text{SDS})_{\text{E}}$  and  $D_{4,3}(\text{SDS})_{\text{WE}}$  are the volume-weighted diameters measured in the presence of SDS solution for freshly prepared emulsions and whipped-frozen emulsions, respectively.

### 2.4. Protein surface coverage

Aged ice cream emulsions were centrifuged at 15,000g for 60 min at 30 °C. The cream layers that formed on the top of the tubes were carefully removed, weighted and subjected to protein and fat determinations (Relkin & Sourdet, 2005). The surface protein load was expressed in  $\text{mg} \cdot \text{m}^{-2}$  of fat globule surface. Specific surface area was measured using a particle size analyzer (MasterSizer 2000).

### 2.5. Differential scanning calorimetry (DSC)

Crystallization and melting behavior of the bulk fat and its emulsified fat globules in non-isothermal mode was monitored by a

differential scanning calorimeter (DSC1 STARE System, Mettler-Toledo, Schwerzenbach, Switzerland). Samples were heated from 25 to 50 °C and held for 5 min to eliminate thermal history, cooled to −10 °C (emulsions) or −40 °C (bulk fat) and reheated to 50 °C. Cooling and heating rates of 5 °C min<sup>−1</sup> were used in the experiment. Crystallization and melting behavior of fat in bulk and emulsified phase was calculated from the following calorimetric parameters: temperature of initial crystallization ( $T_{c-onset}$ , °C; signal of first heat flow release), temperature of final crystallization ( $T_{c-endset}$ , °C; completion of crystallization process), temperature of final melting ( $T_{m-endset}$ , °C; melting completion temperature upon reheating), and heat of crystallization ( $\Delta H_c$ , J g<sup>−1</sup>).

In the present study, the proportion of crystalline fat in the ice cream emulsions and non-isothermal kinetic of emulsified fat at different concentrations of GMS was analyzed from DSC data.

## 2.6. Confocal laser scanning microscopy

Micrographs of the microstructure of the freshly prepared ice cream emulsions and whipped-frozen emulsions were recorded with a confocal laser scanning microscope (CLSM) (Leica TCS SP2, Leica Microsystems, Mannheim, Germany). FITC and Nile red were used to stain proteins and fat, respectively. In this study, 1 mL of FITC (1% in dimethyl sulfoxide) and 2 mL of Nile red (0.1% in dimethyl sulfoxide) were added to 900 g of ice cream emulsions just before whipping and freezing. After whipping and freezing the stained ice cream samples were immediately visualized. The samples were observed by using a 63 × oil immersion objective. Excitation of FITC and Nile red were performed at Argon 488 nm and Helium Neon 633 nm lasers, respectively, and their emission was recorded at 500–588 nm and 640–755 nm, respectively.

## 2.7. Viscoelastic properties

The rheology properties of aged ice cream emulsions were determined using a Malvern Kinexus rheometer (Malvern Instrument company Ltd., Malvern, UK). Frequency sweep experiments were done using a 40 mm parallel-plate geometry with a gap of 1 mm and samples were subjected to 0.05–5 Hz at a constant strain of 0.5% (within the linear viscoelastic range). Each sample was measured in triplicate at a temperature of 4 °C. The viscoelastic properties of storage modulus ( $G'$ ), loss modulus ( $G''$ ) and  $\tan \delta$  ( $G''/G'$ ) for the samples were recorded.

## 2.8. Statistical analysis

Statistical analysis was performed using SPSS 16.0 (SPSS Inc., Chicago, IL). Data were analyzed by analysis of variance (ANOVA) and the differences between means were compared using Duncan multiple comparison test. The results were considered significant at  $p \leq 0.05$ . Spearman was used to evaluate whether the correlation was significant between variables.

# 3. Results and discussion

## 3.1. Emulsion droplet size

In emulsions systems, depletion flocculation can be induced by the excess casein micelles or sub-micelles in the aqueous continuous phase (Dickinson & Golding, 1997). In order to avoid the flocculation resulted from protein-bound cluster and provide a deeper insight into the emulsions size distribution in the presence of GMS, the  $D_{4,3}$  values in freshly prepared emulsions dispersed in SDS solution (2%) were analyzed. Fig. 1 shows the droplet size distribution of ice cream emulsions stabilized by milk proteins with a concentration of 4% (w/w) and GMS with varying concentrations (0–0.4%, w/w). It was found that all emulsions exhibited a unimodal size distribution regardless of fat type and GMS concentration. Pertaining to AMF emulsions, no significant

effect of GMS concentration on the average droplet size ( $D_{4,3}$ ) was observed ( $p > 0.05$ ), with an average  $D_{4,3}$  and span value around 0.61  $\mu\text{m}$  and 1.68  $\mu\text{m}$ , respectively. For CO emulsions, the droplet size distributions were also independent of GMS concentration, with a mean size value around 0.54  $\mu\text{m}$ . Moreover, narrower particle size distributions compared to AMF emulsions were observed, with a span value around 0.88. Lower viscosity of CO at 45 °C (data not shown) ensuring easier droplet disruption during homogenization was expected to contribute to the formation of smaller droplets (Jafari, Assadpoor, He, & Bhandari, 2008). Similarly, some studies previously mentioned the influence of fat composition on the characteristics of emulsion droplets. An increase of the replacement ratio of soybean oil by palm kernel olein resulted in a significant increase in droplet size in emulsions based on soybean oil/palm kernel olein blends (Nor, Che, Tan, & Nor, 2007). Partial substitution of anhydrous milk fat (AMF) by olein (O) fraction was accompanied by a decrease in droplet size in AMF/O emulsions (Bazmi et al., 2007).

In this present study, the protein concentration was approximately 4% which is more than required to stabilize fat droplets (10% fat). The flocculation degree increased as the GMS concentration increased for both two fat emulsion systems (data not shown). This result was ascribed to the increased micellar or sub-micellar milk proteins in the continuous phase due to the competitive adsorption between milk proteins and small molecule surfactant GMS. However, the competitive adsorption did not affect the droplet sizes in the SDS solutions. Similar phenomenon was also observed in emulsions stabilized by a mixture of lactoferrin and  $\beta$ -lg at higher protein concentrations (> 0.1%) where competitive adsorption occurred (Ye & Singh, 2006).

## 3.2. Protein coverage of the fat globule surface

The property of the interface layer around the fat globules is of great importance with respect to the stability of emulsions and ice cream quality. In order to provide a deeper insight of the protein adsorption behavior, the effect of GMS concentration on protein surface coverage was determined (Supplementary material Fig. S1). As shown in Fig. S1, a significant effect of GMS concentration was observed in the two emulsion systems based on different fats. In the case of AMF ice cream emulsions, coated fat globules exhibited a protein surface coverage of 9.8 mg/m<sup>2</sup> in the absence of GMS, which is similar to previously reported ice cream emulsions (Segall & Goff, 1999). The protein surface coverage gradually decreased with increasing GMS concentration for emulsions with two types of fat. The decrease in protein load could be a consequence of competitive adsorption of milk proteins and small molecule emulsifier GMS, since emulsifier has more distinct hydrophobic and hydrophilic regions (Matsumiya, Takahashi, Nakanishi, Dotsu, & Matsumura, 2014). In the case of CO emulsions, the protein load was higher than that of AMF emulsion with the exception of emulsion at 0.3% (w/w) GMS. This result was probably due to the higher match (15%) in composition of fatty acids between AMF and GMS than that of match levels between CO and GMS (5%). This favored specific interactions between the fatty acids of the AMF and that of the GMS thus, leading to the formation of highly interacting droplets and decreased protein adsorption (Granger, Leger, Barey, Langendorff, & Cansell, 2005). A thick protein layer provides significant steric stabilization which prevents the close contact between globules necessary for partial coalescence under shear conditions.

## 3.3. DSC analysis of emulsions and bulk fat

### 3.3.1. Crystallization and melting behavior of fat in the bulk and emulsified state

Partial coalescence of fat globules in ice cream emulsions requires that the fats are partially crystallized. Since the emulsifier potentially could modify the crystallization behavior of fat, the effect of GMS on the crystallization and melting behaviors of both bulk and emulsified

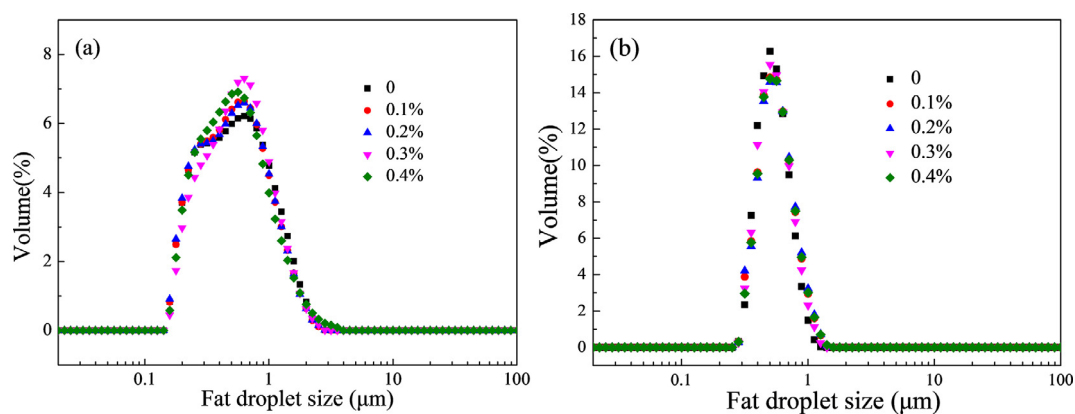


Fig. 1. Effect of GMS concentration on the fat particle size distribution in ice cream emulsions based on anhydrous milk fat (a) and coconut oil (b).

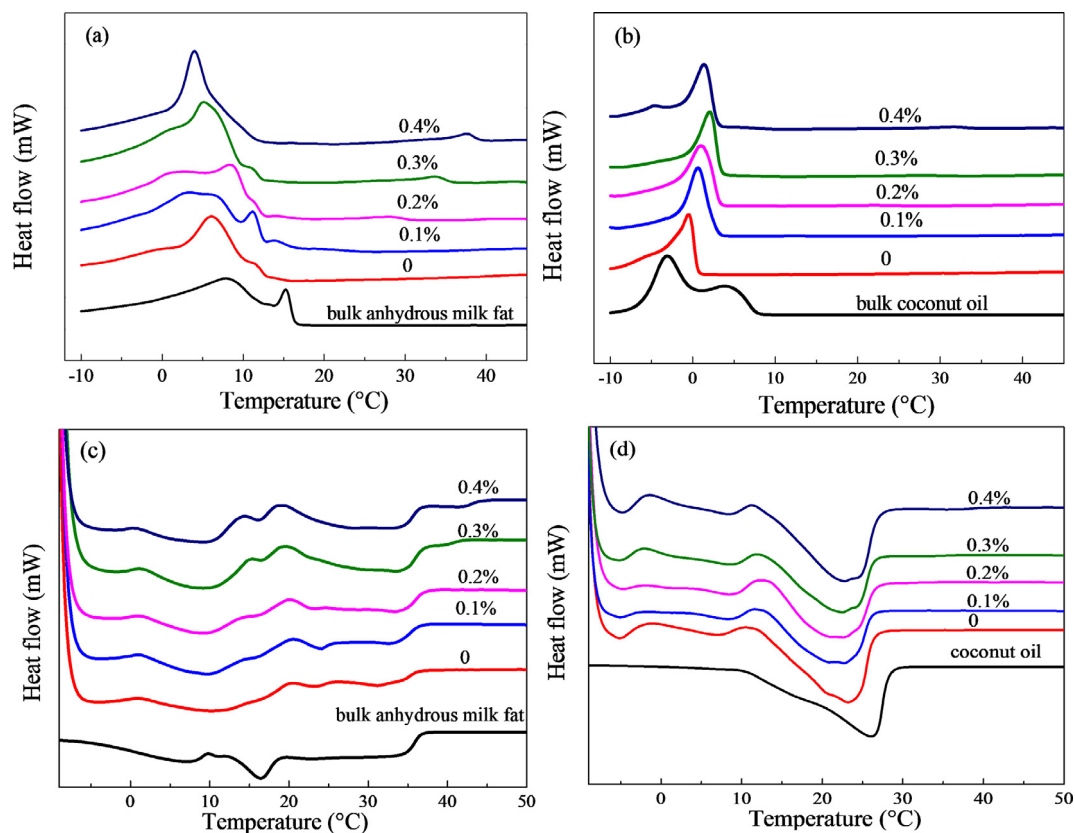


Fig. 2. DSC cooling (a, b) and melting (c, d) curves of ice cream emulsions based on anhydrous milk fat (a, c) and coconut oil (b, d) and different GMS concentrations.

Table 1

Calorimetric parameters of crystalline fat behavior in bulk fat and emulsions containing different concentration of GMS.

|          | $T_{c-onset}$ (°C)        |                          | $\Delta T$ (°C)           |                            | $\Delta H_c$ (J/g)         |                           |
|----------|---------------------------|--------------------------|---------------------------|----------------------------|----------------------------|---------------------------|
|          | Anhydrous milk fat        | Coconut oil              | Anhydrous milk fat        | Coconut oil                | Anhydrous milk fat         | Coconut oil               |
| Bulk fat | 16.37 ± 0.11              | 7.27 ± 0.86              | 19.96 ± 0.26              | 21.21 ± 1.4                | 72.01 ± 0.76               | 102.73 ± 2.0              |
| 0        | 12.90 ± 0.03 <sup>a</sup> | 0.69 ± 0.13 <sup>b</sup> | 23.38 ± 0.49 <sup>c</sup> | 24.97 ± 0.19 <sup>a</sup>  | 39.27 ± 0.30 <sup>b</sup>  | 54.20 ± 0.41 <sup>a</sup> |
| 0.1%     | 12.43 ± 0.14 <sup>b</sup> | 3.46 ± 0.06 <sup>a</sup> | 24.31 ± 0.31 <sup>b</sup> | 22.44 ± 0.21 <sup>c</sup>  | 34.58 ± 1.67 <sup>c</sup>  | 51.63 ± 0.16 <sup>b</sup> |
| 0.2%     | 12.04 ± 0.06 <sup>c</sup> | 3.63 ± 0.06 <sup>a</sup> | 24.85 ± 0.14 <sup>b</sup> | 22.81 ± 0.08 <sup>ab</sup> | 39.72 ± 0.56 <sup>ab</sup> | 50.64 ± 1.82 <sup>b</sup> |
| 0.3%     | 11.91 ± 0.13 <sup>c</sup> | 3.64 ± 0.27 <sup>a</sup> | 24.87 ± 0.01 <sup>b</sup> | 22.62 ± 0.24 <sup>ab</sup> | 41.87 ± 0.07 <sup>a</sup>  | 47.65 ± 0.23 <sup>c</sup> |
| 0.4%     | 10.82 ± 0.15 <sup>d</sup> | 3.58 ± 0.12 <sup>a</sup> | 25.75 ± 0.32 <sup>a</sup> | 22.95 ± 0.14 <sup>b</sup>  | 41.20 ± 1.07 <sup>ab</sup> | 44.01 ± 0.80 <sup>d</sup> |

Data of mean ± SD of three replicate or more.

Mean with different superscripts letters within a column are significantly different ( $p \leq 0.05$ ).

fat were studied by DSC (Fig. 2). Regarding the bulk AMF, two main exothermic peaks were found (Fig. 2a). In the cooling experiment, the high-freezing point fractions crystallized first followed by the low-freezing point fractions. Crystallization of the high-freezing point fractions began at 16.37 °C and the first crystallization peak was within 16.37–13.83 °C at 5 °C min<sup>-1</sup> cooling rate. The second peak extended from 13.83 °C to about -10 °C. The cooling curves obtained from emulsion samples indicated different exothermic peaks and markedly delayed crystallization compared to bulk AMF. The shift to lower crystallization temperatures by emulsified fat compared to their non-emulsified state is well known and has been described for many other emulsions (Relkin & Sourd, 2005; Truong, Bansal, Sharma, Palmer, & Bhandari, 2014). The  $T_{c-onset}$  values in emulsions were observed to decrease with the increase in GMS concentration (Fig. 2a, Table 1). Moreover, as the concentration of GMS increased to 0.2% (w/w), an exothermic peak occurred at temperatures over 25 °C. The new exothermic peak could be a very logical consequence of the crystallization of GMS. The difference in crystallization temperatures of GMS in emulsions ranging from 0.2% to 0.4% would be caused by the different packing behaviors of GMS molecules at the oil-water interface at different concentrations (Mao, Calligaris, Barba, & Miao, 2014). Despite the apparent complexity of adsorption, it can be stated that GMS retarded the nucleation of AMF in emulsions. The mechanism of inhibition of nucleation which occurred in the emulsified AMF may be due to the incorporation into or adsorption of the GMS molecules to the oil-water interface. This may be capable of inhibiting the further incorporation of triacylglycerol (TAGs) molecules in AMF thereby retarding nucleation (McClements, 2012). GMS in this present study contained 2.24 g/100 g C14:0, 96.37 g/100 g C18:0 and 0.75 g/100 g C20:0. The 100% saturation degree and the high amount of long-chain fatty acid determined the easier crystallization in the cooling process. However, AMF contained 35.67% unsaturated fatty acid which crystallized at higher supercooling. Once nucleation of TAGs molecules develop, they grow into crystals. The area of exothermic peak for high-freezing point fractions was found to increase with the increase in GMS concentration (Fig. 2a). This outcome was due to their somewhat similar chemical structure (stearic fatty acid molecules). Re-heating of AMF at 5 °C min<sup>-1</sup> showed three endothermic peaks (Fig. 2c). The first melting peak occurred at -5–10 °C. The second and the third peak were observed at 10–18 °C and 18–37 °C, respectively. In emulsified samples, the area under the second and third endothermic peaks (high-melting point fractions) broadened with increase in GMS concentration. This trend was consistent with the results of crystallization in Fig. 2a which implied that GMS could modify the lipid crystallization behavior and subsequent crystal growth behavior.

For the bulk CO, two main exothermic peaks were caused by crystallization (Fig. 2b). A minor peak occurred within 8.00–1.08 °C and a major peak occurred within 1.08 to -7.08 °C. The  $T_{c-onset}$  values of bulk CO were significantly lower than AMF (Fig. 2a, Table 1). The phenomenon was due to a high ratio of medium-chain fatty acid in CO (43.9%), while AMF contained mainly long-chain fatty acid (94.7%). The emulsified CO samples showed a single exothermic peak and delayed crystallization. However, GMS increased the  $T_{c-onset}$  values of the emulsified samples. This promoting effect was due to surface-active GMS being a high melting point substance, thus, formation of GMS crystals early in the cooling experiment could have promoted the nucleation of CO. However, no significant difference in  $T_{c-onset}$  values was observed in emulsified samples with GMS ranging from 0.1% to 0.4% (Table 1). In the heating process, only one broad endothermic peak ranging from 10 to 30 °C was observed in the bulk CO (Fig. 2d). In the emulsified samples, the final melting temperature ( $T_{m-endset}$ ) was lower than bulk CO.

$\Delta T$  value a reflection of high supercooling effect before fat crystallization was calculated from  $T_{m-endset}$  and  $T_{c-onset}$ .  $\Delta T$  values for emulsified fat were higher than bulk fat. In addition, the  $\Delta T$  values increased and decreased with the increase in GMS concentration for emulsified

AMF and CO, respectively. The different physicochemical mechanisms induced by GMS in the two emulsion systems can be related to different fatty acid compositions of fat and subsequent interactions between fat and GMS. The higher similarity in fatty acid between AMF and GMS favored adsorption of GMS to the AMF-water interface, but depressed the crystallization of low-freezing point fractions. Enthalpy of crystallization ( $\Delta H_c$ ) values which was a reflection of solid fat content during crystallization were significantly lower for emulsified fat than bulk fat which suggests that some fat remained liquid in emulsions. The  $\Delta H_c$  values increased with the increase in GMS concentration for emulsified AMF. This result may imply that GMS facilitated the crystals growth process of AMF and increased the solid fat content, although its nucleation was retarded. The result was opposite in the case of emulsified CO. Considering the results for  $T_{c-onset}$ ,  $\Delta T$  and  $\Delta H_c$  in both fat emulsion systems upon GMS addition, it is presumed that different fat crystals growth mechanisms occurred in ice cream emulsions based on AMF and CO. Thus, the crystallization kinetics with respect to nucleation and growth dimensions was analyzed next.

### 3.3.2. Crystallization kinetic of fat

The Avrami model which involves nucleation and growth concepts was commonly used to analyze the isothermal crystallization kinetics (Li, Dou, Bai, & Lu, 2015). This model described the change in the fraction of crystallized fat over time:

$$X(t) = 1 - \exp(-kt^n) \quad (3)$$

where  $X(t)$  is the relative crystallinity at time  $t$ ,  $k$  is the crystallization rate constant and  $n$  is the Avrami exponent which is related to the crystal growth geometry. In the non-isothermal crystallization process,  $k$  was modified with the cooling rate by Jeziorny (Ozawa, 1971):

$$\lg k_z = \lg k / \phi \quad (4)$$

The crystallization temperature during cooling can be converted to crystallization time:

$$t = (T_0 - T) / \phi \quad (5)$$

where  $T$  is the temperature at time  $t$  and  $T_0$  is the initial temperature. The parameters  $k$  and  $n$  were obtained by a double logarithmic transformation of Eq. (3) as expressed in Eq. (6) (Chiavaro, Cerretani, Paciulli, & Vecchio, 2012):

$$\lg(-\ln(1 - X(t))) = \lg k_z + n \lg t \quad (6)$$

when  $\lg(-\ln(1 - X(t)))$  is plotted versus  $\lg t$ , the slope is  $n$  and intercept is  $\lg k_z$ .

In all cases, goodness of fit of liner regression was observed ( $r^2 > 0.92$ ), indicating that modified Avrami approach well described the non-isothermal crystallization of emulsified fat. Parameters obtained from the modified Avrami fitting are shown in Table 2. The derivation of the Avrami equation is based on solid physical principles and requires  $n$  to be an integer, but fractional values (as found here) are

**Table 2**

Non-isothermal crystallization parameters ( $n$ ,  $k_z$ ) of anhydrous milk fat and coconut oil in emulsions containing different concentrations of GMS.

| GMS  | n                        |                          | $k_z$                    |                          |
|------|--------------------------|--------------------------|--------------------------|--------------------------|
|      | Anhydrous milk fat       | Coconut oil              | Anhydrous milk fat       | Coconut oil              |
| 0    | 1.97 ± 0.03 <sup>b</sup> | 2.01 ± 0.04 <sup>a</sup> | 0.72 ± 0.00 <sup>a</sup> | 0.98 ± 0.02 <sup>a</sup> |
| 0.1% | 1.85 ± 0.04 <sup>b</sup> | 2.05 ± 0.04 <sup>a</sup> | 0.74 ± 0.02 <sup>a</sup> | 0.94 ± 0.01 <sup>a</sup> |
| 0.2% | 1.93 ± 0.02 <sup>b</sup> | 1.92 ± 0.00 <sup>b</sup> | 0.74 ± 0.01 <sup>a</sup> | 0.93 ± 0.00 <sup>a</sup> |
| 0.3% | 2.20 ± 0.00 <sup>a</sup> | 1.90 ± 0.01 <sup>b</sup> | 0.72 ± 0.01 <sup>a</sup> | 0.94 ± 0.03 <sup>a</sup> |
| 0.4% | 2.21 ± 0.02 <sup>a</sup> | 1.89 ± 0.02 <sup>b</sup> | 0.73 ± 0.01 <sup>a</sup> | 0.95 ± 0.01 <sup>a</sup> |

Data of mean ± SD of three replicate or more.

Mean with different superscripts letters within a column are significantly different ( $p \leq 0.05$ ).

usually obtained. According to Foubert, Dewettinck, and Vanrolleghem (2003), these values are found in situations of simultaneous development of two or more types of crystals, or similar crystals built up from different nuclei, in sporadic or instantaneous way. In the case of ice cream emulsions with AMF, the values of  $n$  ranged from 1.85 to 2.21 and gradually increased with an increase addition of GMS. This suggests that the crystal growth had a trend from two-dimensional disclike growth to three-dimensional spherulitic growth. With regard to ice cream emulsions prepared with CO, an opposite trend was observed, indicating that GMS restricted crystallization to one-dimensional rod-like growth. However, no significant difference in  $k_z$  values was observed regardless of GMS concentration for both types of ice cream emulsions. At the same crystallization rate, the increase and decrease in  $n$  value with increasing concentration of GMS implied that the increase and decrease in number of contact points in AMF and CO emulsions during whipping and freezing, respectively. In addition, the values of  $k_z$  for CO emulsions were much higher than AMF emulsions. This result suggests that emulsified CO had less time to undergo crystal growth in the whole crystallization process. This is evident by the lower  $T_{c-onset}$  values of emulsified CO compared with emulsified AMF (Fig. 2a–b and Table 1). Considering the values of  $\Delta H_c$  (Table 1),  $n$  and  $k_z$  comprehensively, it could reasonably be inferred that smaller crystal sizes occurred in emulsified CO in the presence of GMS. The smaller crystal size would affect the rupture of the interfacial film by a protruding fat crystal under shear.

Proportion of crystalline fat (PCF) in the ice cream emulsions as a function of the crystallization temperature is presented in supplementary material Fig. S2. Pertaining to the most significant effect at 0.4% GMS concentration, the PCF values of the control emulsion (without GMS) and emulsions containing 0.4% GMS were compared. At the draw temperature ( $-5^\circ\text{C}$ ) of ice cream from the freezer, the PCF value was found to increase significantly in the AMF emulsions in the presence of GMS, while a negative effect of GMS was observed in the case of CO emulsions.

### 3.4. Viscoelastic properties

The formation of fat crystals largely influences rheological properties and stability of semi-crystalline emulsions. To gain insight on the effect of GMS concentration and fat type on the network structure of aged ice cream emulsions, oscillatory rheology measurements were performed. The storage modules ( $G'$ ), loss modules ( $G''$ ) and loss factor  $\tan \delta$  ( $G''/G'$ ) would provide information on the elastic and viscous response of the viscoelastic system.  $G'$  is an indication of the amount of stored energy in the systems, which refers to the solid elastic behavior of the network.  $G''$  refers to the liquid viscous behavior. The value of  $\tan \delta$  is used to evaluate whether an emulsion system shows more liquid-like behavior or solid-like behavior.

Fig. 3a and b shows  $G'$  and  $G''$  as a function of the frequency for the aged ice cream emulsions stabilized by milk proteins and different concentrations of GMS. Regarding all the emulsions containing AMF or CO,  $G'$  was always higher than  $G''$  and both properties ran parallel to one another over the studied frequency range which implies that all the emulsions exhibited a solid-like behavior. For the ice cream emulsions based on AMF (Fig. 3a), the  $G'$  and  $G''$  increased with an increase in GMS concentration from 0 to 0.4%, indicating the formation of stronger gel-like structures. This phenomenon was related to the increased displaced protein in the continuous phase, the adsorption of crystalline GMS at the oil-water interface and the increased degree of crystallization of fat. However, in the case of aged emulsions based on CO (Fig. 3b), the  $G'$  and  $G''$  increased slightly when GMS concentration was higher than 0.2%.

The variation of  $\tan \delta$  as a function of frequency for aged ice cream emulsions with different fats and GMS concentrations is shown in Fig. 3c and d. For all the emulsions, the values of  $\tan \delta$  showed a strong dependence on the frequency and GMS concentration. For AMF ice

cream emulsions, the inclusion of 0.4% GMS had the most effect in enhancing the solid-like property of emulsions (Fig. 3c).  $\tan \delta$  decreased with increasing frequency up to 1 Hz depending on the GMS concentration. This behavior suggests that the crystalline fat could act as hard particles and therefore contributed to the elastic nature of the network at small frequencies. At higher frequencies ( $> 1$  Hz),  $\tan \delta$  of all the structures remained at a lower region than at low frequencies but showed an upward shift as frequencies increased to 5 Hz. This response may be attributed to the deformability of the liquid part of the fat globules. The turning-point phenomenon exhibited by the AMF ice cream emulsion curves could be related to partial coalescence of fat globules. With respect to the effect of GMS, it was found that  $\tan \delta$  decreased with increasing GMS concentrations in the studied frequency. In addition, the positions of the turning point of  $\tan \delta$ -frequency curve were markedly delayed with increasing GMS concentrations. As a result of the above analysis, it is speculated that the enhanced solid-like property of AMF emulsion systems was attributed to the increased proportion of crystalline fat content after GMS addition. This was in line with the results of crystalline fat content in DSC analysis (Fig. S2). The CO emulsions (Fig. 3d), showed an opposite  $\tan \delta$  response to that of the AMF ice cream emulsions. The addition of GMS was detrimental to the solid-like performance of CO emulsion (increasing  $\tan \delta$ ) at small frequencies in the range of 0.05–1 Hz. This response suggests that GMS weakened the structural networking within the CO emulsions. In addition, this finding coincides with the DSC results which revealed that GMS decreased the proportion of crystalline fat content (Fig. S2). However, at high frequencies in the range of 1–5 Hz,  $\tan \delta$  decreased upon GMS addition. Moreover, the turning point of  $\tan \delta$ -frequency curve existed only for emulsions with no more than 0.1% (w/w) GMS. These results implied that GMS decreased the deformability of fat globules in CO emulsion.

For all aged ice cream emulsions,  $G'$  showed a progressive increase with increasing frequency (Fig. 3a and b). It has been reported that the frequency dependence of  $G'$  possesses a strong power law relation as  $G' \sim \omega^n$  (Zou, Baalen, Yang, & Scholten, 2018). The exponent  $n$  can be determined from a log-log plot of  $G'$  versus the frequency ( $\omega$ ) and provides information about the network structure of emulsions. Fig. 3e shows that the values of  $n$  obtained from all emulsions are larger than 0 which shows all emulsions can be classified as physical gels. It can be noted that the values of  $n$  decreased with an increase in the GMS concentration for AMF emulsions, indicating that a stronger network was formed. On the contrary, the network strength became weak with increasing GMS concentration for CO emulsions. Previous work has shown that an effective incorporation of colloidal particle in the continuous phase can increase the emulsion network strength regardless of the sunflower oil volume (Zou, Yang, & Scholten, 2018). Thus, in the present study, the increased micellar or sub-micellar milk proteins in the continuous phase should increase the network strength of emulsions due to the competitive adsorption between milk proteins and small molecule surfactant GMS with the increase in GMS concentration. However, that was not the case for CO emulsions with increasing GMS concentration. Thus, it can be inferred that the formation of a stronger, more elastic fat globule network rather than the colloid network in the continuous phase contribute to the stronger gel network for AMF emulsion, while more viscous globule network led to the decreased gel network for CO emulsion upon addition of GMS.

### 3.5. The stability of whipped-frozen emulsions

In order to investigate the effect of GMS on the stability of whipped-frozen emulsions, the average particle diameter ( $D_{4,3}$ ) in water and SDS solutions and fat destabilization index (FD and PCD) were measured after whipping and freezing. In the case of whipped-frozen emulsions based on AMF (Fig. 4a), the  $D_{4,3}$  values in water ( $1.23\text{--}7\ \mu\text{m}$ ) were found to increase with increasing addition of GMS. Measuring with SDS, both the weakly and strongly flocculated globules were disrupted.

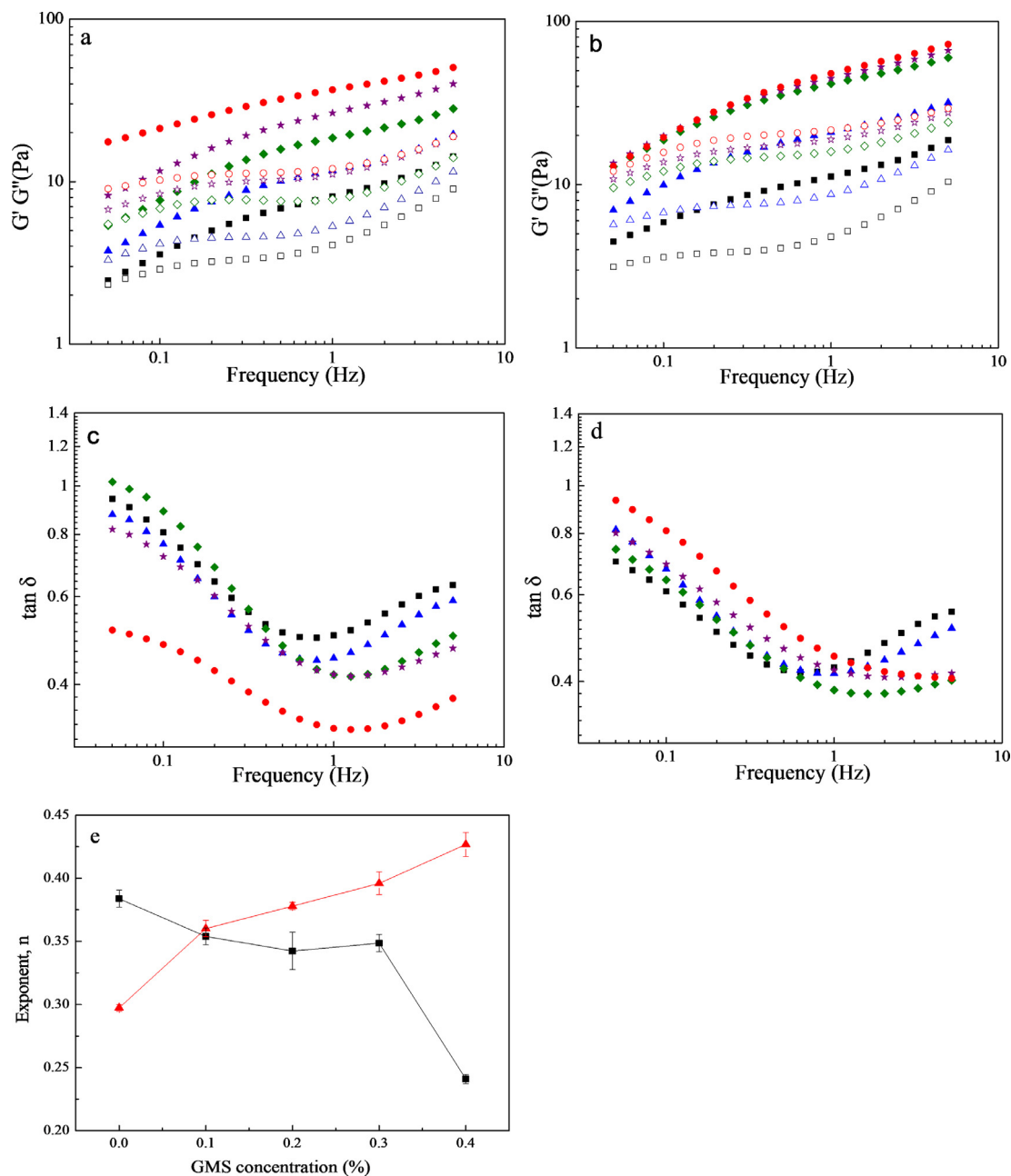


**Fig. 3.** (a, b) Storage modulus ( $G'$ , solid symbol), loss modulus ( $G''$ , open symbol) and (c, d)  $\tan \delta$  as a function of frequency for ice cream emulsions stabilized by milk protein and different concentrations of GMS (0–0.40%) based on anhydrous milk fat (a, c) and coconut oil (b, d). The symbols refer to emulsions with different concentration of GMS: ■, 0% GMS; ▲, 0.1% GMS; ◆, 0.2% GMS; ★, 0.3% GMS; ●, 0.4% GMS. (e) The exponent  $n$  ( $G' \sim \omega^n$ ) as a function of GMS concentration in emulsions based on anhydrous milk fat (■) and coconut oil (▲).

Hence, the  $D_{4,3}$  values in SDS solution (0.79–1.39  $\mu\text{m}$ ) were significantly lower than those in water. As a result of the dissociation of the fat flocculates under the effect of SDS solution, FD values (31.25–403.52%) were also found to increase with the increase in GMS concentration which can be attributed to the increased protein-bound clusters during whipping and freezing. Although, lower size values after dispersion in SDS solution were observed, some large aggregates were still detected after whipping and freezing when comparison was made with fat droplets size values of the freshly prepared emulsions with SDS treatment (0.61  $\mu\text{m}$ ). The increase was attributed to partial coalescence of the fat globules during whipping and freezing. The definition of partial coalescence is given as “an irreversible agglomeration/clustering of fat globules, held together by a combination of fat crystals and liquid fat, and a retention of identity of individual globules as long as

the crystal structure is maintained” (Goff, 2000). The PCD values (9.77–123.99%) calculated from Eq. (2) were found to increase gradually with increasing addition of GMS. The decrease in the protein load (Fig. S1) at lipid globule interfaces due to the competitive adsorption of milk proteins and GMS, decreased the strength of the interfaces and consequently increased partial coalescence. Moreover, the increased number of contact points reflected by increased crystal growth dimension (Table 2) and stronger structural networking within the AMF emulsions (Fig. 3) with increasing GMS concentration favored the crystallization-induced destabilization of the emulsion. A significantly positive correlation between PCD values and crystal growth dimension ( $r = 0.876$ ,  $p = 0.042$ ) was observed. The correlation between PCD values and proportion of crystalline fat content was not significant ( $r = 0.804$ ,  $p = 0.101$ ).

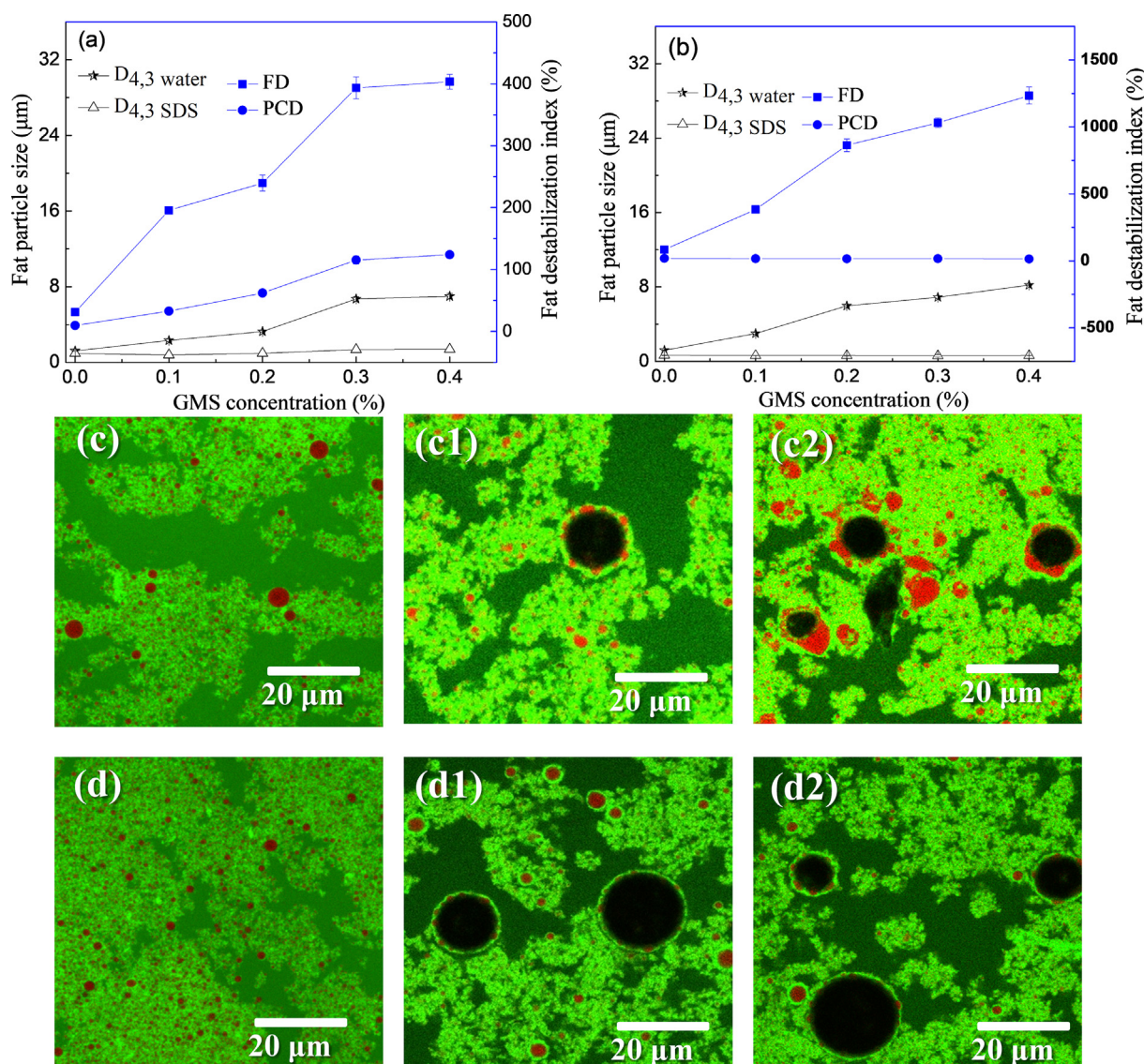


**Fig. 4.** Effect of GMS concentration on the fat particle sizes and fat destabilization index in whipped-frozen emulsions based on anhydrous milk fat (a) and coconut oil (b); Confocal micrographs of freshly prepared ice cream emulsion (c, d) and whipped-frozen emulsions based on anhydrous milk fat (c1, c2) and coconut oil (d1, d2) in the absence (c1, d1) and presence (c2, d2) of 0.4% GMS. In red the fat phase and in green the protein-rich serum phase.

In the case of whipped-frozen emulsions based on CO (Fig. 4b), the  $D_{4,3}$  values in SDS solution were slightly higher (approximately 0.62  $\mu\text{m}$ ) compared to freshly prepared emulsions (around 0.54  $\mu\text{m}$ ). Moreover, no significant effect of GMS was found on the  $D_{4,3}$  SDS values. Thus, the PCD values (14.37–19.3%) were much lower than that of emulsions based on AMF. Nevertheless, a significant effect of GMS concentration on  $D_{4,3}$  and FD values in water was found. The results suggest that GMS favored the flocculation of fat globules. The formation of large fat clusters may be attributed to the increased protein-protein interactions in the continuous phase due to the displacement of milk proteins by GMS. On the contrary, the limited partial coalescence may be due to the decreased proportion of crystalline fat (Fig. S2), weakened network structure and small crystal size (Section 3.3.2), thus, leading to the decline in interfacial protrusion length with increasing GMS concentration. This reduced the possibility of protruding crystals to pierce the thin film between the two globules and the adsorbed layer of the second globule. On the other hand, partial coalescence can be partially inhibited in the presence of crystalline GMS with long saturated chain at oil-water interface. The GMS molecules crystallized at oil-water interface in CO emulsions forming a crystalline shell that would favor Pickering stabilization for emulsion due to the weak interaction

between CO and GMS, and initiating crystallization of the TAGs towards the interior of the fat globules. In the previous study, the effect of surfactant crystallization on partial coalescence in O/W emulsions was investigated. The authors reported a decrease in partial coalescence when crystalline surfactants were added (Goibier et al., 2017).

Given the highest fat destabilization index was induced by 0.4% GMS concentration, the microstructure of freshly prepared ice cream emulsions and whipped-frozen emulsions in the absence and presence of 0.4% GMS were recorded and compared (Fig. 4). Fig. 4c and d shows that there were a large amount of large droplets in the freshly prepared emulsions based on AMF compared to emulsion based on CO. The phenomenon was in line with the results of droplet size determination that AMF emulsions had larger droplet size ( $D_{4,3}$ ) and span values than CO emulsions (Fig. 1). Under the whipping and freezing conditions (Fig. 4c1 and d1), only fewer discrete and intact fat globules could be seen at the air bubble surfaces in the absence of GMS for both two fat whipped systems, which was observed in the micrographs as red regions. Most of the air bubble interfaces were covered with milk proteins (green regions). In the whipped-frozen emulsions based on AMF in the presence of 0.4% GMS (Fig. 4c2), air bubbles were wrapped by connected crystalline fat globules which favored the formation of well

aerated texture. Large clumps of fat globules were also present at the serum phase. This occurrence may be explained in terms of connected crystalline fat globules via liquid oil or in terms of a spreading behavior of liquid oil out of emulsion globules and their adsorption on the air bubble surfaces (Bazmi et al., 2007; Fredrick et al., 2013). In the case of whipped-frozen emulsions based on CO with 0.4% GMS (Fig. 4d2), only some individual fat globules were observed at the air bubble surfaces and even in the serum phase. The observation was consistent with the very low degree of partial coalescence in CO whipped-frozen emulsion.

#### 4. Conclusions

This present study demonstrated that the interfacial layer and fat crystallization behavior was affected by GMS-fat interactions and interfacial competitive adsorption, which subsequently changed the stability of whipped-frozen emulsions. The protein surface load in aged ice cream emulsions based on CO was higher than AMF emulsion. Crystallization behavior and crystallization kinetics analysis elicited that GMS facilitated the crystals growth of AMF, although its nucleation was retarded, while an opposite outcome was found in CO emulsions. Oscillatory rheology results revealed that increasing GMS concentration increased and decreased the deformability of fat globules in AMF emulsions and CO emulsions, respectively. The deformability of fat globules and network structure of emulsions was related to partial coalescence of fat globules. In summary, the increased partial coalescence with increasing GMS concentration in AMF emulsions was attributed to the decrease in protein load, increase in crystal growth dimension and stronger structural networking. However, in the case of CO emulsions, the inhibition of partial coalescence was mainly due to the negative effect of GMS on fat crystallization behavior. The findings presented in this study can be used to better control and improve the stability of whipped-frozen emulsions and to obtain better texture of aerated fat-based emulsion foods.

#### CRedit authorship contribution statement

**Jinju Cheng:** Conceptualization, Methodology, Software, Writing - original draft. **Olayemi Eyituyo Dudu:** Visualization, Investigation, Writing - review & editing. **Dong Wang:** Software, Validation. **Xiaodong Li:** Writing - review & editing, Project administration. **Tingsheng Yan:** Supervision, Writing - review & editing, Project administration, Funding acquisition.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.foodchem.2019.125949>.

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