Relationship Between Characteristics of Oil Droplets and Solidification of Thermally Treated Creams

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ABSTRACT: The relationship between the characteristics of oil droplets and the change in appearance of cream was investigated. The model creams (40 wt% oil-in-water emulsion), similar to commercial products, were prepared with vegetable fat, milk protein, and emulsifier. The thermal treatment, in which the cream was exposed to a certain temperature and subsequently recooled, was performed on the assumption that the temperature was temporarily elevated during transportation and storage of commercial products. Solidification of the cream was observed when it was exposed to a temperature where there was a small percentage in solid fat content (SFC) of fat in oil droplets and recooled, whereas the cream remained in the liquid state when it was exposed to the temperature where SFC was zero and recooled. When the SFC of oil droplets was 0% at the treated temperature, greater supercooling prior to fat crystallization occurred and the crystallization rate after the initial formation of crystals was much higher. On the other hand, the polymorphism of fat in the droplets was not directly affected by the thermal treatment. These results indicate that the crystallization in oil droplets at the heating temperature may be closely connected with the destabilization of oil droplets *via* a partial coalescence mechanism, which will cause the solidification of cream.

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KEY WORDS: Cream, fat crystal, oil droplet, polymorphism, SFC, solidification, X-ray.

Whipped cream, which is widely used as a topping on cakes and desserts, is produced by stirring and aerating liquid cream. Resistance to destabilization, caused by factors such as temperature and vibration during storage and distribution, is required along with good whippability. The temperature during transportation and storage is an influential factor in the stability of whipping cream because a temporary elevation of the temperature is known to induce increased viscosity or solidification of cream after recooling (1,2). The increased viscosity or solidification is closely related to the necessity for containing semisolid fats in oil droplets of cream to achieve whippability (3,4). Boode *et al*. (1) and Noda and Yamamoto (2) have already reported that cream solidified when it was exposed to a temperature at which the solid fat content (SFC) of fat was small (a small percentage) and then recooled slowly, whereas the cream remained in the liquid state when it was exposed to the temperature where the fat was completely melted and then recooled (1,2).

The difference in the appearance of cream after recooling between the above two thermal changes implies that the crystallization behavior of fat in oil droplets is closely connected to solidification. It has already been reported that the crystallization of fat in oil droplets is affected by the type of emulsifier, the droplet size distribution, the temperature cycling, and the presence of any impurities (5). Crystallization during recooling from the temperature where the SFC of fat is zero is thought to be different from that where the SFC of fat is a small percentage. Partial coalescence is well known as the mechanism that contributes to instability of an emulsion containing semisolid oil droplets (6,7). Partial coalescence occurs between two droplets that are partly crystalline when a solid fat crystal from one droplet penetrates into the liquid oil portion of another droplet. This phenomenon, as a positive role, was related to the formation of structure in whipped and ice creams (3,8), but coalesced droplets may also possibly exist in solidified creams after recooling at the thermal treatment.

However, the mechanism of the solidification of cream, or the change in crystallization behavior of oil droplets, which leads to solidification during the recooling process, remains unclear because methods to evaluate the state of oil droplets in cream are not sufficiently established. Although ultrasonic measurement and differential scanning calorimetry have been reported as evaluation methods, these were only applied in the case of simple emulsions using a hydrocarbon or a pure triacylglycerol (9,10). No research about the crystallization behavior of oil droplets in whipping cream, which contains natural semisolid fat composed of many kinds of triacylglycerols, has been reported.

The aim of this research is to clarify the change in oil droplets in whipping cream as related to solidification of cream. The model creams, similar to commercial products, were prepared with vegetable fat, milk protein, and emulsifier. Thermal treatment of the model cream consisted of temporary heating, followed by a recooling process. The change in the observed SFC and polymorphism of fat crystal in the

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cream oil droplets was investigated during the thermal treatment.

EXPERIMENTAL PROCEDURES

Cream preparation. The composition of the model cream is shown in Table 1. The oil phase of the cream consisted of vegetable fat, soy lecithin (The Nisshin Oil Mills, Ltd., Tokyo, Japan) and glycerol monostearate (Taiyo Kagaku Co., Ltd., Mie, Japan). In this research, three kinds of vegetable fats were used, and the SFC curves of these are shown in Figure 1. Fat A, whose major fatty acid is oleic acid, was purchased from Ueda Oils and Fats Mfg. Co., Ltd. (Hyogo, Japan). Fats B and C, whose major fatty acids are lauric acids, were purchased from Fuji Oil Co., Ltd. (Osaka, Japan). Fat B was prepared by hydrogenation of fat C to change the melting point. The water phase of the cream was composed of skim milk powder (Snow Brand Milk Products Co., Ltd., Tokyo, Japan), sucrose ester (Daiichi Kogyo Seiyaku Co., Kyoto, Japan), sodium metaphosphate (Taihei Kagaku Sangyo Co., Osaka, Japan), and guar gum (Sigma Chemical Co., St. Louis, MO).

The oil phase, heated to 75°C, and the water phase, heated to 65°C, were mixed together at 60°C by a TK homomixer (Tokusyu Kika Kogyo Co., Ltd., Osaka, Japan) at 10,000 rpm for 5 min. This mixture was then homogenized in a two-stage homogenizer (Sanwa Machine Co., Inc., Numazu, Japan) using operating pressures of 10 MPa in the first stage and 2 MPa in the second stage. The homogenized cream was immediately divided into packs of 250 mL each and then cooled to 5°C in ice water. The cooled pack was stored in a refrigerator at 5°C, and the sample cream was stored at least overnight in the refrigerator prior to thermal treatment. In this paper, creams prepared with fat A, fat B, and fat C were called cream A, cream B, and cream C, respectively.

Thermal treatment of cream. The thermal treatment, temporary heating, and recooling were performed with the following procedure. The pack of cream, stored at refrigerator temperature, was moved to a water bath kept at a certain temperature. This temperature is called the treated temperature in this paper. After holding in the water bath for 1 h, the pack was moved to the refrigerator and recooled. In the refrigerator, the temperature of the cream was decreased to 5°C at about 0.5°C/min without any temperature control. The treated temperature was 25, 30, 35, and 45°C for cream A, 35, 40, 45, and 60°C for cream B, and 25, 27, 30, and 45°C for cream C, respectively. For all the thermal treatments of the creams, three containers were used and supplied for the measurement.

TABLE 1
Composition of the Cream

Oil phase (%)	
Vegetable fat (fat A or B or C)	40.0
Lecithin	0.50
Glycerol monostearate	0.10
Water phase (%)	
Water	55.03
Skim milk powder	4.00
Sucrose ester	0.20
Phosphate	0.10
Guar gum	0.07

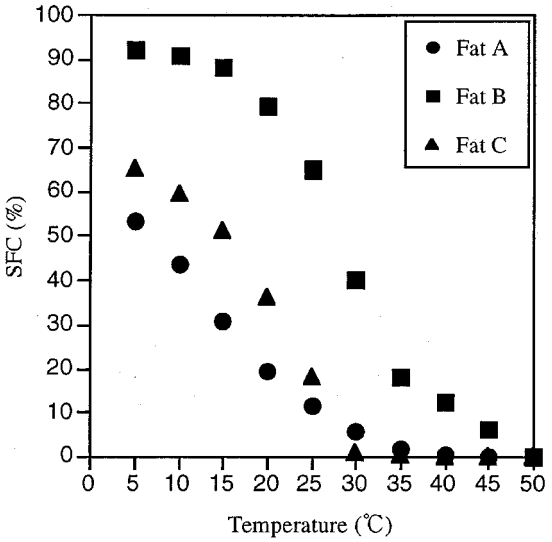

FIG. 1. The solid fat content (SFC) curve of bulk fats A, B, and C.

Evaluation of cream solidification. The state of cream after the thermal treatment was classified into three categories based on visual observation. The first category was liquid state (L), which had the ability to flow. The second category was solid state (S), which lost the ability of flow. The third category was an intermediate state of the above two states (M), which flowed slowly but visible aggregates were observed in the cream.

Measurement of particle size of oil droplets in cream. The particle size of oil droplets in cream was determined by a laser diffraction particle size analyzer (SALD-2000; Shimadzu Corp., Kyoto, Japan). The cream was diluted with deionized water, and the absorbance of the diluted sample was adjusted to the optimized level for this apparatus. The sample solution was then introduced into the measurement cell, and the particle size distribution was measured. From the distribution of volume of the average particle size, the 50% value (median value) of particle size was calculated.

Measurement of extent of destabilization of oil droplets in cream. The extent of destabilization of oil droplets in cream was determined by measuring spectroturbidity. The cream was diluted 3,000-fold with deionized water, and this diluted sample was centrifuged for 5 min at 1,000 rpm. The absorbance of this subnatant was measured at 540 nm on an ultraviolet (UV)-visible spectrophotometer (UV-160; Shimadzu Corp.). The extent of destabilization of oil droplets was calculated as: $[(A_{\text{before thermal treatment}} - A_{\text{after thermal treatment}})/A_{\text{before thermal treatment}}] \times 100$ (%).

Measurement of SFC of fat and oil droplets in cream. The SFC of bulk fat and fat in oil droplets was measured by a pulsed nuclear magnetic resonance (NMR) spectrometer

(Minispec NMS-120; Bruker Japan Co., Ltd., Tsukuba, Japan). One milliliter of fat or cream was poured into a glass cell for measurement, and the measurement was carried out under temperature control by an attached heater. The SFC value was determined by the direct method calculated as: $[fS'/(fS' + L)] \times 100$ (%), where S' and L are the NMR magnetization curve at 8.5 and 67.5 μs, respectively, and f is the extrapolation factor (11,12). In this research, the parameter f was determined by the use of three calibration samples for this instrument, which contained 0, 31.0, and 72.2% solid (Plexiglas in mineral oil), respectively. Calibration was done according to the fully automatic calibration routine of this instrument. The SFC of fat in oil droplets was taken to be 2.5 times the SFC in whole emulsion because the cream contained 40% fat. The measurement for the SFC curve of bulk fat was carried out after keeping fat at each temperature for 30 min. The change in SFC of bulk fat and fat in oil droplets of cream during the thermal treatment was measured by the following procedure. The sample cream or fat in the glass cell was put into a water bath controlled at a certain treated temperature for 30 min and cooled to 5°C at 0.6°C/min. Then, the cell was maintained at 5°C for 90 min. The SFC measurement was performed every 5°C during the recooling process and every 30 min during the stable process at 5°C. The maximal crystallization rate was calculated from the slope of the linear change in the SFC during the recooling process.

Evaluation of polymorphism of fat crystals in the cream oil droplets. The polymorphism of fat crystals in the cream oil droplets was evaluated by an X-ray diffractometer (Rint Ultima; Rigaku Co., Tokyo, Japan). The sample cream was set on a glass dish for measurement, and the measurement was taken between 18 and 25° in diffraction angle at the rate of 2°/min. The power of X-ray was adjusted at 0.8 kW (40 kV, 20 mA). Samples were held in a temperature-controlled chamber during the measurement. The temperature was first increased to a certain treated temperature from 5°C and maintained for 30 min, and then recooled to 5°C at 0.5°C/min. The measurement for X-ray diffraction was performed at 5°C before temporary heating and after the recooling process. The polymorphism of oil droplets was classified into α, β′, and β from the X-ray diffraction pattern according to Larsson (13).

RESULTS AND DISCUSSION

Effect of SFC of fat at the treated temperature on the solidification of cream. The relationship between the treated temperature and the solidification of the cream was investigated with the three kinds of creams. Table 2 shows the state of the cream after recooling in the various thermal treatments. The SFC values of fat at the treated temperatures in each cream are also shown in Table 2. Solidification of the cream was observed when the SFC of fat at the treated temperature was below 11.5% in cream A, below 17.9% in cream B, and below 18.1% in cream C, respectively. On the other hand, all creams remained liquid when the SFC at the treated temperature was 0%. These results showed that the solidification was affected by the SFC of fat at the treated temperature and not necessarily by the treated temperature itself. Boode *et al.* (1) previously reported that the SFC of fat at the treated temperature that brought the solidification of cream was from 1.5 to 8.0%. The range of SFC at treated temperature which induced the solidification in this research is almost similar to this reported range of SFC. However, the range of SFC at the treated temperature which led to the solidification after recooling was found to be wider for creams B and C which were lauric acid-rich fats. Cream A remained in the liquid state, while creams B and C converted into the solid state after recooling when the SFC at the treated temperature was 11–13%.

TABLE 2
Relationship Between the SFC of Fat at the Treated Temperature and the State of the Cream After Recooling in the Thermal Treatment[a]

	Cream A		Cream B		Cream C	
Temperature (°C)[b]	SFC of fat (%)[c]	State[d]	SFC of fat (%)	State	SFC of fat (%)	State
5	53.2	L	92.0	L	65.4	L
25	11.5	L	NT	NT	18.1	L
27	NT	NT	NT	NT	11.0	S
30	5.7	M	NT	NT	0.9	S
35	1.7	S	17.9	L	NT	NT
40	NT	NT	12.1	M	NT	NT
45	0	L	5.9	S	0	L
60	NT	NT	0	L	NT	NT

[a]L, liquid state; S, solid state; M, middle state. NT, not tested; SFC, solid fat content.
[b]Treated temperature in thermal treatment.
[c]SFC of each fat at the treated temperature.
[d]State of cream after recooling in thermal treatment.

The median particle sizes of oil droplets in the creams after recooling in various thermal treatments are shown in Figure 2. The particle size of oil droplets increased when the solidification arose irrespective of kind of cream. The extent of destabilization of oil droplets in the thermal-treated creams is

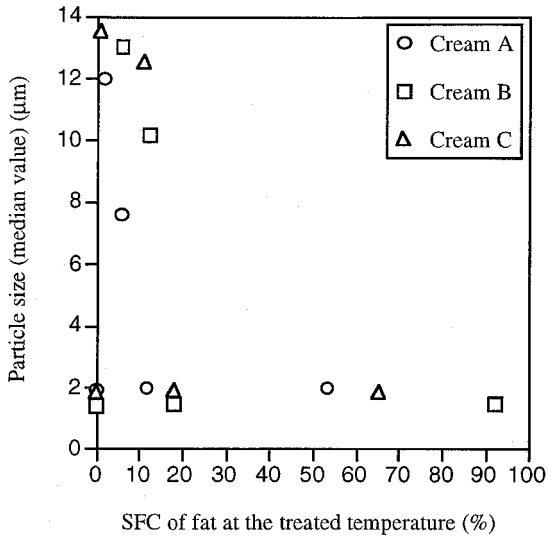

FIG. 2. The median particle size of oil droplets in cream after thermal treatment and cooling to 5°C. See Figure 1 for abbreviation.

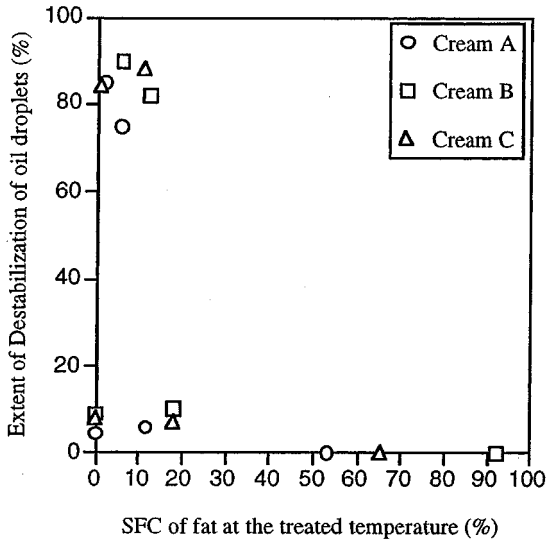

FIG. 3. The extent of the destabilization rate of oil droplets in cream after recooling in the thermal treatment. See Figure 1 for abbreviation.

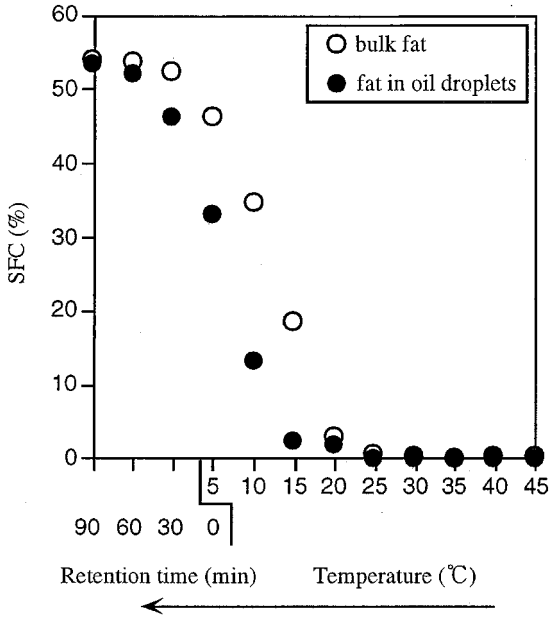

FIG. 4. The change in the SFC of bulk fat A and fat in oil droplets of cream A during recooling in 45°C treatment. An arrow shows the course of time. See Figure 1 for abbreviation.

shown in Figure 3. The extent of destabilization of oil droplets was found to be high at the treated temperature that induced the solidification of cream. The high extent of destabilization may imply the increase in the number of aggregated oil droplets and the leakage of free fat. In our case, the aggregation of oil droplets may bring the solidification of cream. In order to clarify the mechanism of cream solidification, we should focus on the physical change arising within the oil droplets which causes their destabilization during the thermal treatment. As described above, the results of Table 2 indicate the close relationship between the solidification of thermal-treated cream and the SFC of fat at the treated temperature. In the next section, the physical change in oil droplets (the actual change of the SFC of oil droplets in cream during thermal treatment) was investigated in connection with the solidification of cream.

Crystallization behavior of oil droplets during the thermal treatment. Crystallization of oil droplets during thermal treatment was examined by the change of SFC. The changes in the SFC of bulk fat A as well as fat in oil droplets of cream A (including 40% fat A) during the recooling process for 45 and 35°C thermal treatments are shown in Figures 4 and 5, respectively. As mentioned in the former section, the treatment at 35°C induced the solidification of cream, whereas the cream remained in a liquid state with the 45°C treatment. For the cream treated at 45°C, the SFC started to increase rapidly at *ca.* 15°C, whereas the SFC of the bulk fat started to increase rapidly at *ca.* 20°C. Thus, the cream seemed to be supercooled about 5°C further than the bulk fat, although both were supercooled below the final melting point of the fat. That is, greater supercooling prior to fat crystallization occurred in the cream exposed to the 45°C treatment compared to the bulk fat at the same temperature. In the case of the 35°C treatment, however, similar increasing patterns of SFC during the recooling process were obtained whether fat A was emulsified or not. No supercooling was needed in either case during the recooling process. A small percentage of SFC values was already observed at the treated temperature (35°C), and the SFC of fat increased more slowly with the decrease of temperature as compared to the cases of 45°C treatment.

In Figures 4 and 5, the SFC values of fat in oil droplets were calculated by the direct method, which is normally used for the measurement of the SFC of bulk fat. The parameters,

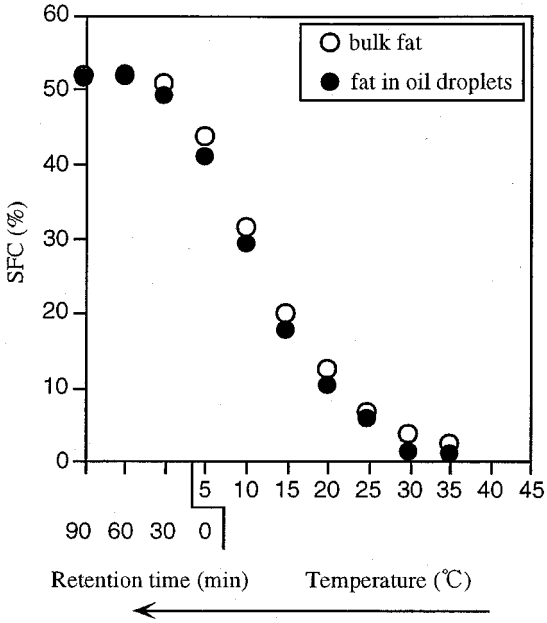

FIG. 5. The change in the SFC of bulk fat A and fat in oil droplets of cream A during recooling in 35°C treatment. An arrow shows the course of time. See Figure 1 for abbreviation.

such as *L* and *f*, to calculate the SFC are thought to be different between the bulk fat and the emulsion system. However, the change in SFC of bulk fat and fat in oil droplets was quite similar at the 35°C treatment. Based on this result, we may judge that these parameters are almost the same for bulk fat and an emulsion, and the SFC of fat in oil droplets measured by the direct method is very close to the actual value of SFC of fat in oil droplets. In the case of Figure 4 therefore it can be said that the difference in the change in SFC of fat between the bulk state and the emulsified state at the 45°C treatment actually shows the difference of the crystallization behavior of fat between both states.

The change in the SFC of fat in cream during the recooling process in the thermal treatment was found to be different between the two treated temperatures at which the SFC of fat was 0 and 2–3% for 45 and 35°C, respectively. When the SFC of fat in oil droplets was 0% at the tempered temperature, the cream must have been supercooled prior to crystallization. The supercooling in the crystallization of hydrocarbon emulsion was reported by McClements *et al.* (10), and they pointed out that homogeneous nucleation of fat was a cause of supercooling. It is thought that homogeneous nucleation of fat also occurs in the triglyceride emulsion. On the other hand, when the SFC of fat was a small percentage, nucleation was not observed since growth of remaining crystals could occur. The SFC of fat in oil droplets followed the equilibrium phase diagram for that bulk fat, so similar SFC patterns were obtained in bulk fat and fat in oil droplets. These phenomena were also observed in creams B and C (data not shown). The maximal rate of crystallization of cream during recooling calculated from the slope of the linear increase in the SFC is shown in Figure 6. For all the creams, the maximal rates of crystallization were greater at treated temperatures where SFC was 0% compared to treated temperatures where SFC of fat was a small percentage. From these results, it is suggested that the crystallization behavior in oil droplets is affected by the SFC at the treated temperature. This indicates, in combination with the results of the previous section, that the fat crystallization behavior is related to the destabilization process of the oil droplets in cream during recooling in the thermal treatment.

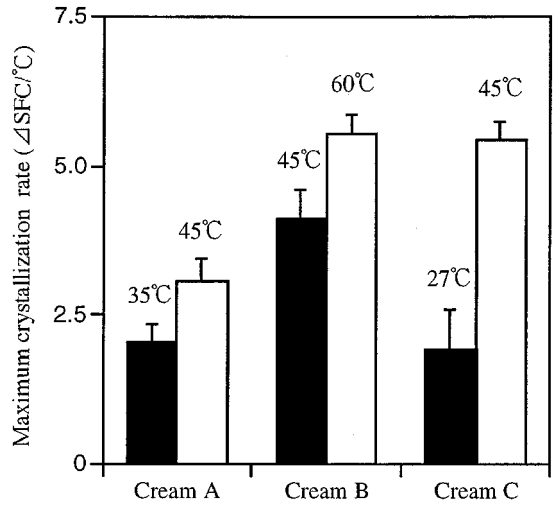

FIG. 6. The maximal crystallization rate of oil droplets during recooling in the thermal treatment. The temperature in the figure shows the treated temperature. Data represent the mean ± SD of three determinations. See Figure 1 for abbreviation.

Effect of polymorphism on the solidification of cream. As a structural characteristic of a fat crystal in oil droplets, the difference in the polymorphic form of fat crystals in oil droplets was investigated between the thermal treatments. Table 3 shows the polymorphism of the oil droplets in three kinds of creams before and after the thermal treatments at which the treated temperature was 0% and a small percentage in SFC of fat. In cream A, the polymorphism of oil droplets tended to move from β′ to β after the thermal treatment regardless of the treated temperature. However, the polymorphism of oil droplets in creams B and C was stable (β′) before and after the above thermal treatments. This means that the polymorphism of oil droplets in solidified cream was dependent on the type of fat and that the polymorphism of oil droplets did not change with the transformation from liquid to solid state of creams, at least in some cases. Therefore, we can say that the polymorphism of oil droplets does not directly affect the solidification of cream.

Potential mechanisms of solidification. Johansson (14) reported that the structural factors of fat crystal which determine the characteristics of foods containing solid fats are crystal size, morphology, and mutual adhesion. In this research, a change in polymorphism was not detected in oil droplets between the thermal treatments which induced the solidification of cream and kept the cream in liquid state. On the other hand, the change in the SFC of fat in oil droplets was found to be different according to the above two thermal treatments. When the SFC of fat is 0% at the treated temperature in the thermal treatment which remains the cream in liquid, a high crystallization rate after homogeneous nucleation due to the supercooling will result in the production of small crystals in oil droplets. When the SFC of fat is a small percentage at treated temperature in thermal treatment, which leads to the solidification of cream, some crystals left at the treated temperature grow larger in oil droplets. Thermodynamically, it is more favorable for the remaining crystals at the treated temperature to be located at the oil–water interface rather than in

TABLE 3
The Polymorphism of Oil Droplets Before and After the Thermal Treatments[a]

	Cream A	Cream B	Cream C
SFC is a small percentage at treated temperature			
Before thermal treatment	β′	β′	β′
After thermal treatment	β	β′	β′
SFC is 0% at treated temperature			
Before thermal treatment	β′	β′	β′
After thermal treatment	β	β′	β′

[a]See Table 2 for abbreviation.

the interior of oil droplets (5). That is, extremely large crystals will exist at the interface of oil droplets after recooling in the case of this thermal treatment. It therefore seems that the large crystals at the interface of the oil droplets are closely related to the solidification of cream. We speculate on two mechanisms whereby the large crystals at an interface lead to the solidification of the cream. One is the partial coalescence between two oil droplets by the large crystals breaking an oil droplet from the inside. These crystals penetrate into the liquid oil portion of another droplet and form a large aggregation of coalesced droplets. Furthermore, a small distance between droplets and a sufficient amount of solid fat were reported as the factors influencing partial coalescence (6). The creams in this research are thought to satisfy these conditions, so partial coalescence possibly occurs in solidified cream. The other mechanism relates to the effects of large crystals on the adsorption behavior of proteins at oil-droplet surfaces. In this experiment, skim milk powder was used for the preparation of the creams as a major emulsifier, indicating that the oil-droplet surface was stabilized by the adsorbed layer of caseins. It remains unclear whether the crystal penetration into the liquid oil portion of another droplet is possible in the presence of such adsorbed layers of proteins, i.e., thick layers consisting of macromolecules. It is likely that the large crystals which have grown at the oil droplet surface may affect the conformation and adsorption behavior of proteins, thereby causing the destabilization of emulsion creams. In addition to the partial coalescence mechanism as described, the second mechanism including the adsorbed proteins may also contribute to the destabilization of the creams in our case. To clarify this point, we carried out research reported in Reference 15.

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