

Physical Analyses of Gel-like Behavior of Binary Mixtures of High- and Low-Melting Fats

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ABSTRACT: Gel-like fat mixtures of high-melting (HM) and low-melting (LM) fats were formed by means of rapid cooling and subsequent heating. No “non-fat” ingredients such as emulsifiers, water, or waxes were added to the mixtures. The gel-like fats having solid fat content (SFC) values below 2.0 wt% formed crystal networks of HM-fats that entrapped the liquid oil fraction of LM-fats. In a search for optimal fat combinations exhibiting gel-like behavior, fully hydrogenated rapeseed oil with a high amount of behenic acid (FHR-B), fully hydrogenated rapeseed oil with a high amount of stearic acid (FHR-S), tristearoyl-glycerol (SSS), triarachidonoyl-glycerol (AAA), and tribehenoyl-glycerol (BBB) were examined as the HM-fats. For LM-fats, sal fat olein (SFO), cocoa butter (CB), palm super olein (PSO), and olive oil were examined. The following results were obtained: (i) the gel-like behavior was observed in mixtures of FHR-B/SFO and FHR-B/CB with initial concentrations of FHR-B of 1.5–4.0 wt%. (ii) Rapid cooling to T_c (crystallization temperature) from 70°C and subsequent heating to T_f (final temperature) were necessary to reveal the gel-like behavior, whereas simple cooling without a cooling/heating procedure did not form the gel-like fat mixture. (iii) Optimal values of T_c and T_f were related to the m.p. of the LM-fat and HM-fat, respectively. (iv) Temperature variations of SFC as well as X-ray diffraction spectra showed that the melt-mediated transformation from α to β of the HM-fat crystals was a prerequisite to reveal the gel-like behavior. Consequently, the fat mixture revealing the gel-like behavior might be called β -fat gel.

Paper no. J10361 in *JAOCs* 80, 263–270 (March 2003).

KEY WORDS: Cocoa butter, fully hydrogenated rapeseed oil, gel-like fat, polymorphism, sal fat olein.

Fats and oils are, in general, employed in industrial applications in solid (crystalline), semisolid, emulsion (oil-in-water and water-in-oil), gel, and liquid states. A gel state is defined as a two-phase colloidal system consisting of a solid and a liquid in a more solid form than sol, although there are various definitions representing the complicated nature of gel states (1). Because of their smooth texture, viscoelasticity, appearance, easy handling, and comfortable mouthfeel, gel materials have attracted much attention in food, cosmetic, and pharmaceutical sciences and technology (2–5). Therefore, a wide variety of research into gel phases made of polysaccha-

rides, proteins, and other biopolymer materials has been performed (6,7).

In a gel phase made of lipid emulsifiers and water, a lamellar-type lyotropic liquid crystal (LC) phase is formed at elevated temperatures. In the LC phase, a water phase is swelled into a continuous lamellar LC phase. When this LC phase is cooled to undergo the transformation from the LC phase to a crystallization phase, the lamellar structure involving the swollen water phase is maintained, forming a highly viscous phase called an α -gel phase (8–10). Further cooling forms a rheologically hard phase called a coagel. These gel phases are employed as low-fat table spreads (11,12).

A gel phase containing oils and fats without lipid emulsifiers and water was formed by hydroxystearic acid, the hydrogen bonding of which played the role of solidus network to entrap the liquid oil phase (13,14). These gel fat materials have been applied to nonedible uses. As for edible fats, certain types of shortening containing high-melting (HM) fats and liquidus oil exhibit gel-like behavior in the presence of emulsifiers (15). It is known that peanut butter is formed by gel-like fats made of HM-fat fractions. However, the formation mechanisms and physical properties of edible gel fats have not been clarified in detail.

The aim of this work was to identify optimal combinations of HM-fat and low-melting (LM) fat mixtures that exhibit gel-like behavior and to clarify the formation mechanism of the gel-like fat. No other ingredients such as emulsifiers, water, or waxes were included in the mixtures. Throughout this study, we set the highest concentration of HM-fat as 4.0 wt%. The reason is that the presence of large amounts of HM-fats often results in a discontinuous texture of the fat blend mixture, which causes granular crystal formation and a sandy mouthfeel. These properties are not favored for food uses such as confections and creams.

In the present work, five kinds of HM-fats and four kinds of LM-fats were examined, and various HM-fat and LM-fat mixtures were subjected to different modes of cooling and heating treatment (tempering). Unique combinations of the HM- and LM-fats were found to form gel-like fats when the liquid mixture was rapidly cooled from a high temperature and a subsequent heating procedure was applied. Solid fat content (SFC) and X-ray diffraction (XRD) analyses showed that the transformation from the α to the β form of the HM-fat fraction was a prerequisite for the formation of gel-like fat mixtures.

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MATERIALS AND METHODS

TAG components, FA components, and melting points (T_m) of fully hydrogenated rapeseed oil with a high amount of behenic acid (FHR-B), fully hydrogenated rapeseed oil with a high amount of stearic acid (FHR-S), sal fat olein (SFO), palm super olein (PSO), olive oil, and cocoa butter (CB) are shown in Table 1. Multiple DSC melting peaks were observed for LM-fats since various TAG with high and low T_m are contained. The T_m shown in Table 1 correspond to those of the major fat components with highest DSC melting peaks. Minor HM-components are also present in the LM-fats. For example, SFO contains a few percent of the HM-fraction that makes a contribution to the SFC values of the mixtures. Tri-stearoyl-glycerol (SSS) ($T_m = 73.1^\circ\text{C}$), triarachidonoyl-glycerol (AAA) ($T_m = 78.0^\circ\text{C}$), and tribehenoyl-glycerol (BBB) ($T_m = 82.5^\circ\text{C}$), each having a purity of >99%, were purchased from Tokyo Kasei Co., Tokyo, Japan.

After weighing the component fats, the HM- and LM-fats were mixed at 70°C and then subjected to a tempering process. Three factors of the tempering process were varied to search for the optimal thermal treatments producing the gel-like behavior: (i) Cooling rate (V_c) is the rate of cooling from 70°C to crystallization temperature (T_c); 10 and $1.5^\circ\text{C}/\text{min}$ were examined as typical V_c values. (ii) T_c determines the polymorphic forms of the first crystallized structure of the HM-fats. The T_c values examined were 20, 25, 30, 35, and 38°C . The crystallized samples were held at T_c for 10 min and then subjected to heating at a rate of $2^\circ\text{C}/\text{min}$. (iii) Heating to T_f (final temperature) and isother-

mal treatment at T_f caused melting of the crystal form that was crystallized at T_c and transformation to more stable forms. The T_f values examined were 30, 35, 38, 41, 43, and 45°C .

Gel-like behavior was observed visually by putting the fat mixtures in test tubes and tilting them 45° from vertical. Gel-like behavior was identified when no deformation occurred and liquid and solid phases did not separate.

A rotator-anode (RA) XRD spectrometer using a RINT-TTR (Rigaku, Tokyo) (8.4 kW; 42 kV; 200 mA) was employed to determine the polymorphic forms of the crystallized HM-fats, with a vertical goniometer and an RA of Cu-K α (wavelength, 0.154 nm) radiation with Ni filter. The molten sample (*ca.* 0.5 g) was mounted on the XRD aluminum plate in a horizontal arrangement, and the sample temperature was decreased in a temperature-controlled sample holder.

SFC values were measured by pulsed NMR (PC120; Bruker, Karlsruhe, Germany). Sample (1.5 g) was placed in a glass cell (diameter: 7 mm), in which a tempering process was performed by using the temperature-control system of the NMR equipment.

RESULTS

Visual observation. This section describes the results of visual evaluation of fluidity of various fat mixtures that were subjected to the tempering procedures with different values of V_c , T_c , and T_f .

In Figure 1 one can see the gel-like behavior of the FHR-B (2.0 wt%)/SFO fat mixture that was subjected to three ther-

TABLE 1
Melting Points, FA Compositions, and Carbon Number of TAG in High-Melting Fats and Low-Melting Fats^a

Melting point ($^\circ\text{C}$)	High-melting fats		Low-melting fats			
	FHR-B	FHR-S	SFO	PSO	Olive oil	CB
	65.8	68	12	7.0	5.0	34
FA composition						
12:0	—	—	—	0.3	13.1	—
14:0	0.1	—	0.1	1.0	0.5	—
16:0	3.2	4.9	8.5	32.0	—	24.4
16:1	—	—	—	0.4	—	—
18:0	37.3	91.3	24.2	3.0	2.1	35.4
18:1	0.2	—	56.0	49.0	79.3	38.1
18:2	—	—	3.9	13.5	4.7	2.1
18:3	—	—	0.7	0.8	0.2	—
20:0	9.8	2.5	4.9	—	0.1	—
22:0	47.8	1.3	0.4	—	—	—
24:0	1.6	—	—	—	—	—
Carbon number						
48	—	—	0.2	2.1	—	1.2
50	0.7	4.2	3.4	24.0	4.8	17.0
52	3.5	17.5	14.0	58.5	29.8	44.0
54	8.3	67.5	51.8	14.9	65.4	34.8
56	9.4	4.7	10.0	0.5	—	—
58	15.4	—	—	—	—	—
60	19.4	—	—	—	—	—
62	39.6	—	—	—	—	—

^aFHR-B, fully hydrogenated rapeseed oil with a high amount of behenic acid; FHR-S, fully hydrogenated rapeseed oil with a high amount of stearic acid; SFO, sal fat olein; PSO, palm super olein; CB, cocoa butter.

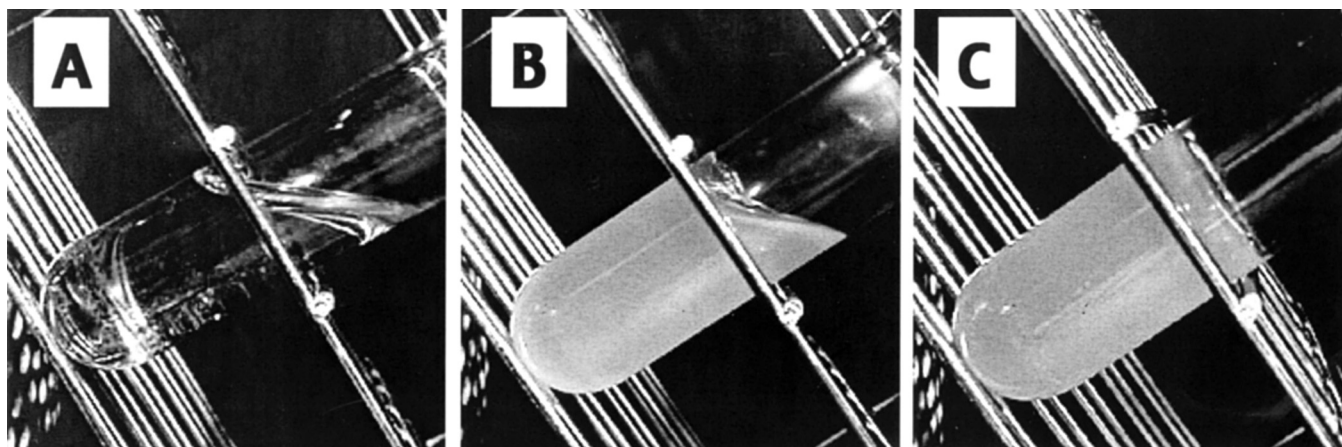


FIG. 1. Optical photographs showing sol-like and gel-like behavior of a fat mixture of FHR-B (2.0 wt%)/SFO. $T_c = 20^\circ\text{C}$, $T_f = 38^\circ\text{C}$. A ($70^\circ\text{C} \rightarrow T_f$); B ($70^\circ\text{C} \rightarrow T_c \rightarrow T_f$, $V_c = 1.5^\circ\text{C}/\text{min}$); C ($70^\circ\text{C} \rightarrow T_c \rightarrow T_f$, $V_c = 10^\circ\text{C}/\text{min}$). FHR-B, fully hydrogenated rapeseed oil with a high amount of behenic acid; SFO, sal fat olein; T_c , crystallization temperature; T_f , final temperature.

mal treatments with $T_c = 20^\circ\text{C}$ and $T_f = 38^\circ\text{C}$. When the mixture was directly cooled from 70 to 38°C (no tempering), a sol-like fat mixture was formed (Fig. 1A). The tempered fats that were cooled to $T_c = 20^\circ\text{C}$ with $V_c = 1.5^\circ\text{C}/\text{min}$ and heated to $T_f = 38^\circ\text{C}$ also showed sol-like behavior (Fig. 1B). In contrast, gel-like behavior was exhibited when the fat mixture was tempered a $V_c = 10^\circ\text{C}/\text{min}$ as shown in Figure 1C under the same conditions as in Figure 2B. The same results were

observed for the other fat mixtures that exhibited gel-like behavior (see below). Therefore, the V_c value was maintained at $10^\circ\text{C}/\text{min}$ during all the experiments that followed.

Table 2 shows the results of visual evaluation of the fat mixtures of FHR-B/SFO at different concentrations of FHR-B when T_c was varied from 20 to 38°C , and the tempered fats were kept at $T_f = 38^\circ\text{C}$ for 60 min. At all T_c values examined, sol-like mixtures were formed when concentrations of FHR-B did not exceed 1.5 wt%. At the 1.5 wt% concentration of FHR-B, gel-like behavior was observed at $T_c = 20^\circ\text{C}$, whereas the mixture became sol-like when T_c increased above 20°C . At FHR-B concentrations of 2.0 and 4.0 wt%, the mixtures became gel-like below $T_c = 25^\circ\text{C}$ (FHR-B: 2.0 wt%) and below $T_c = 30^\circ\text{C}$ (FHR-B: 4.0 wt%). This result shows the importance of the crystallization of the α form of FHR-B in the FHR-B/SFO liquid mixture at $T_c = 20\text{--}25^\circ\text{C}$ by chilling from 70°C at a rate of $10^\circ\text{C}/\text{min}$ at the concentrations of FHR-B above 2.0 wt%. The α crystals of FHR-B thus formed are converted to β crystals through α -melt mediation after subsequent rapid heating, as shown below.

Table 3 shows the results of visual evaluation of fluidity behavior of the fat mixtures of FHR-B/SFO kept at different

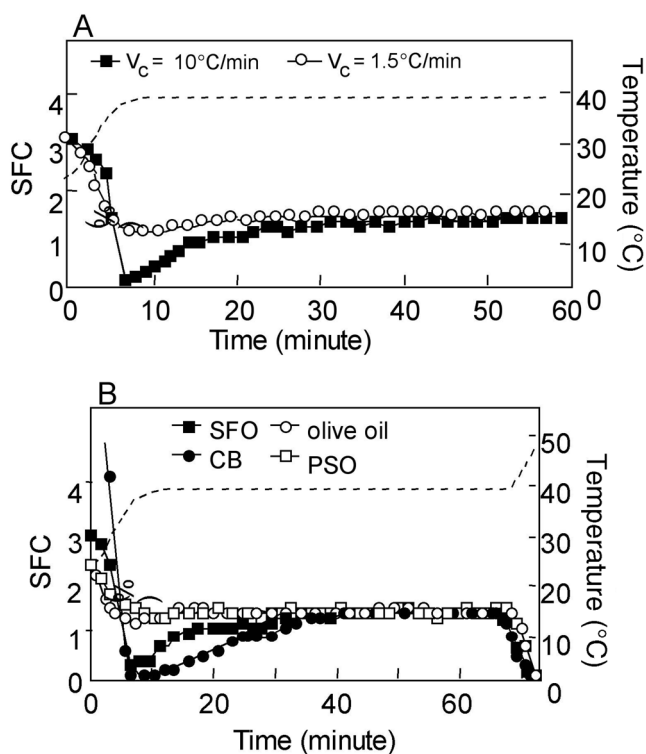


FIG. 2. (A) Difference in solid fat content (SFC) values of FHR-B (2.0 wt%)/SFO mixture. $T_c = 20^\circ\text{C}$, $T_f = 38^\circ\text{C}$ for 60 min. (B) SFC values of the different low-melting fats with FHR-B (2.0 wt%) during the tempering process. $20^\circ\text{C} \rightarrow 38^\circ\text{C}$ (60 min) $\rightarrow 60^\circ\text{C}$, $V_c = 10^\circ\text{C}/\text{min}$. For abbreviations see Figure 1.

TABLE 2
Effects of T_c on Gel-like Behavior of FHR-B/SFO Mixtures at $V_c = 10^\circ\text{C}/\text{min}$ and $T_f = 38^\circ\text{C}$ (for 60 min)

Concentration of FHR-B (wt%)	Concentration of SFO (wt%)	T_c ($^\circ\text{C}$) ^a				
		20	25	30	35	38
0	100	—	—	—	—	—
0.5	99.5	—	—	—	—	—
1.0	99.0	—	—	—	—	—
1.5	98.5	△	—	—	—	—
2.0	98.0	○	○	—	—	—
3.0	97.0	○	○	△	—	—
4.0	96.0	○	○	○	—	—

^a○: gel-like, △: somewhat gel-like, —: liquidus. T_c : crystallization temperature; T_f : final temperature; V_c : cooling rate; for other abbreviations see Table 1.

TABLE 3
Effects of T_f on Gel-like Behavior of FHR-B/SFO Mixtures at $V_c = 10^\circ\text{C}/\text{min}$ and $T_c = 20^\circ\text{C}$

Concentration of FHR-B (wt%)	Concentration of SFO (wt%)	T_f ($^\circ\text{C}$) ^a					
		30	35	38	41	43	45
0	100	—	—	—	—	—	—
0.5	99.5	—	—	—	—	—	—
1.0	99.0	—	—	—	—	—	—
1.5	98.5	○	○	△	—	—	—
2.0	98.0	○	○	○	—	—	—
3.0	97.0	○	○	○	○	○	—
4.0	96.0	○	○	○	○	○	○

^aThe mixtures were held at each T_f for 60 min. For abbreviations see Tables 1 and 2; for symbols see Table 2.

T_f values for 60 min, after crystallization at $T_c = 20^\circ\text{C}$ with $V_c = 10^\circ\text{C}/\text{min}$. Gel-like behavior was noted with increasing amounts of FHR-B at all T_f values, whereas the sol mixture was formed at T_f above 41°C at FHR-B concentrations of 1.5 and 2.0 wt%. As for FHR-B concentrations of 3.0 and 4.0 wt%, gel-like behavior was revealed by the fluidity evaluation. However, the formation behavior was quite different between the T_f values below and above 38°C , as shown by the SFC measurement (see next section).

Table 4 summarizes the occurrence of the gel-like behavior of various combinations of the HM- and LM-fats at concentrations of 2.0 and 98.0 wt%, respectively. The tempering conditions were as follows: $V_c = 10^\circ\text{C}/\text{min}$, $T_c = 20^\circ\text{C}$, and $T_f = 38^\circ\text{C}$ (60 min). The two LM-fats, PSO, and olive oil did not show gel-like behavior with the five HM-fats, probably because α crystals were not formed in the mixtures using PSO and olive oil.

Similarly, FHR-S, SSS, AAA, and BBB did not demonstrate gel-like behavior with the four LM-fats. As for the mixtures of AAA/SFO, AAA/CB, BBB/SFO, and BBB/CB, solidus mixtures were formed at 38°C , yet slight separation of fats and liquids occurred after 60 min, meaning that those mixtures did not form gel-like fats.

Isothermal treatment at $T = T_f$. The visual observations described in the previous section reflected the fact that the tempering process, with rapid cooling of the liquid mixture and subsequent heating, was necessary to reveal the gel-like behavior. To analyze these properties *in situ*, SFC values were

TABLE 4
Evaluation of Occurrence of Gel-like Behavior^a of the Fat Mixtures of Different Combinations of High-Melting Fats (2.0 wt%) and Low-Melting Fats (98.0 wt%)

High-melting fat	Low-melting fat			
	SFO	PSO	Olive oil	CB
FHR-B	○	—	—	○
FHR-S	—	—	—	—
SSS	—	—	—	—
AAA	—	—	—	—
BBB	—	—	—	—

^aSSS: tristearoyl-glycerol; AAA: triarachidonoyl-glycerol; BBB: tribehenoyl-glycerol; for other abbreviations see Table 1. For symbols see Table 2.

measured during the isothermal treatment of the fat mixture of FHR-B (2.0 wt%)/SFO at $T_f = 38^\circ\text{C}$ after cooling to $T_c = 20^\circ\text{C}$ at $V_c = 10^\circ\text{C}/\text{min}$ and $V_c = 1.5^\circ\text{C}/\text{min}$. In addition, visual observation was also made during the isothermal treatment.

Figure 2A shows the SFC values of a FHR-B (2.0 wt%)/SFO mixture at V_c of 10 and $1.5^\circ\text{C}/\text{min}$ during isothermal treatment at $T_f = 38^\circ\text{C}$ for 60 min. The SFC value was about 3.0% before the temperature changed from 20°C . This value increased to more than the initial concentration of the HM-fat in the mixture owing to crystallization of the HM-fraction in SFO at 20°C . At about 6 min after the isothermal treatment started, the SFC value fell to 1.2% and did not change within 60 min. By contrast, the SFC value of the fat mixture that was cooled at $V_c = 10^\circ\text{C}/\text{min}$ to 20°C decreased to 0% at 8 min after the isothermal treatment started. The SFC value then gradually increased to 1.4% at around 30 min. This result showed that the crystals, which were formed by rapid cooling to 20°C in the FHR-B/SFO mixture, completely melted at $T_f = 38^\circ\text{C}$, and recrystallization occurred during the isothermal treatment. Therefore, melt-mediated transformations occurred during the heating from 20 to 38°C and isothermal treatment at 38°C .

Figure 2B shows the time variation of the SFC values of the four fat mixtures, in which the HM-fat was FHR-B (2.0 wt%) and the LM-fats (98.0 wt%) were SFO, PSO, olive oil, and CB. These fat mixtures were subjected to a tempering process of $V_c = 10^\circ\text{C}/\text{min}$, $T_c = 20^\circ\text{C}$, and $T_f = 38^\circ\text{C}$. During heating from 20 to 38°C , the SFC values of the mixtures of FHR-B/SFO and FHR-B/CB decreased to 0% and thereafter increased to 1.4%, whereas the other two mixtures did not show this conversion. Figure 2B also shows that the four fat mixtures melted when the temperature was raised above 38°C , indicating that the HM-fraction crystals melted and the gel-like property disappeared.

Figure 3 shows the effects of the duration of isothermal treatment at $T_f = 38^\circ\text{C}$ on the conversion from sol-like to gel-like behavior of FHR-B (2.0 wt%)/SFO that was tempered with $V_c = 10^\circ\text{C}/\text{min}$ and $T_c = 20^\circ\text{C}$. Ten minutes after T_f was reached (Fig. 3A), the fat mixture was sol-like. However, the gel-like property was observed as the duration of the isothermal treatment was extended, and a completely gel-like fat was formed at 40 min (Fig. 3D). This result showed good agreement with those shown in Figures 2A and 2B.

Figure 4 shows *in situ* RA-XRD experiments in which a fat mixture of FHR-B (4.0 wt%)/SFO was subjected to the tempering procedures of $T_c = 20^\circ\text{C}$, $T_f = 38^\circ\text{C}$ at (A) $V_c = 10$ and (B) $1.5^\circ\text{C}/\text{min}$. The peaks in the XRD spectra were broad since the concentration of the fat crystal was low and liquid content was high. However, it was confirmed that the α form was crystallized at 20°C when the mixture was cooled at $V_c = 10^\circ\text{C}/\text{min}$, as revealed in a long-spacing spectrum of 1.96 nm (003 reflection) and a short-spacing spectrum of 0.41 nm (16) as shown by arrows in Figure 4A. After heating to 38°C , the XRD peaks of the α form disappeared and those of the β form, having a long-spacing spectrum of 1.73 nm (003 reflection) and a short-spacing spectrum of 0.46 nm, appeared (16).

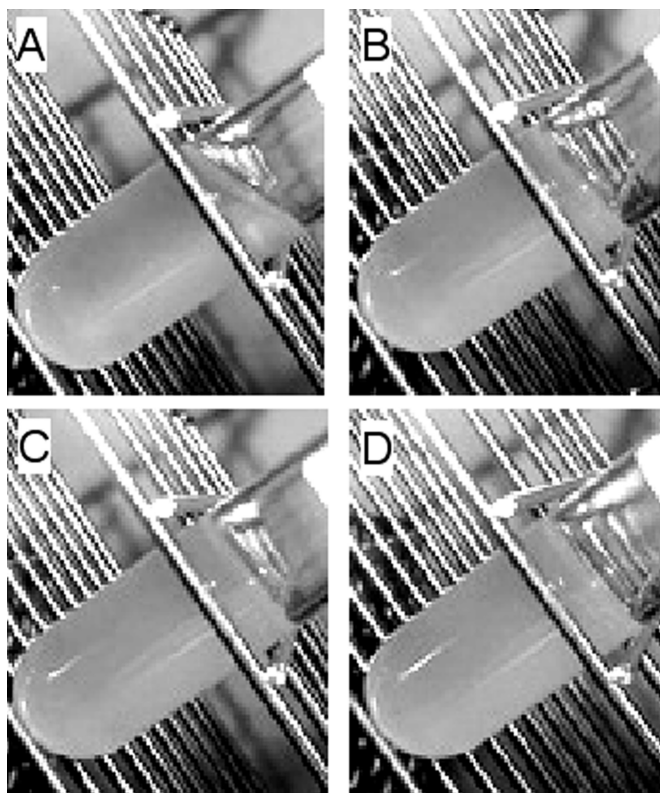


FIG. 3. Time variation of the liquidus to gel-like fat mixtures of FHR-B (2.0 wt%)/SFO during isothermal treatment at $T_f = 38^\circ\text{C}$, after tempering with $V_c = 10^\circ\text{C}/\text{min}$, $T_c = 20^\circ\text{C}$. (A) 10 min, (B) 20 min, (C) 30 min, and (D) 40 min. For abbreviations see Figure 1.

By contrast, the β' and β forms were formed at 20°C when the liquid fat mixture was cooled to 20°C at $V_c = 1.5^\circ\text{C}/\text{min}$ (Fig. 4B), and the β' form transformed to the β form during the process of heating to 38°C .

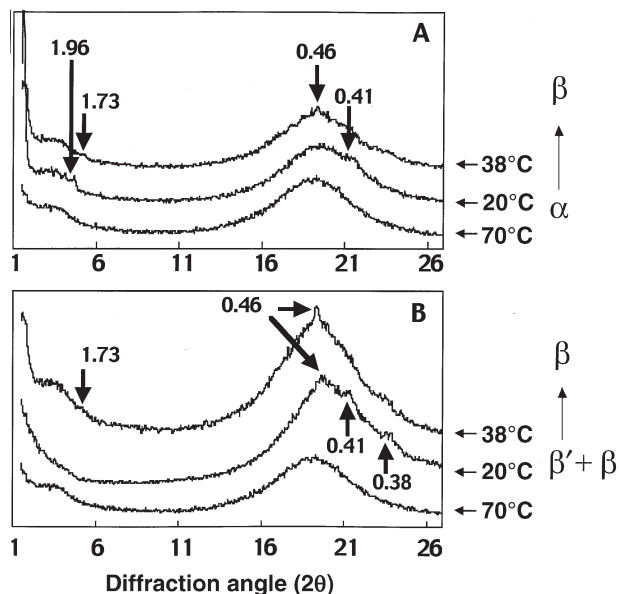


FIG. 4. X-ray diffraction spectra of fat mixture of SFO/FHR-B (4.0 wt%) during tempering. (A) $V_c = 10^\circ\text{C}/\text{min}$; (B) $V_c = 1.5^\circ\text{C}/\text{min}$. Units: nm. For abbreviations see Figure 1.

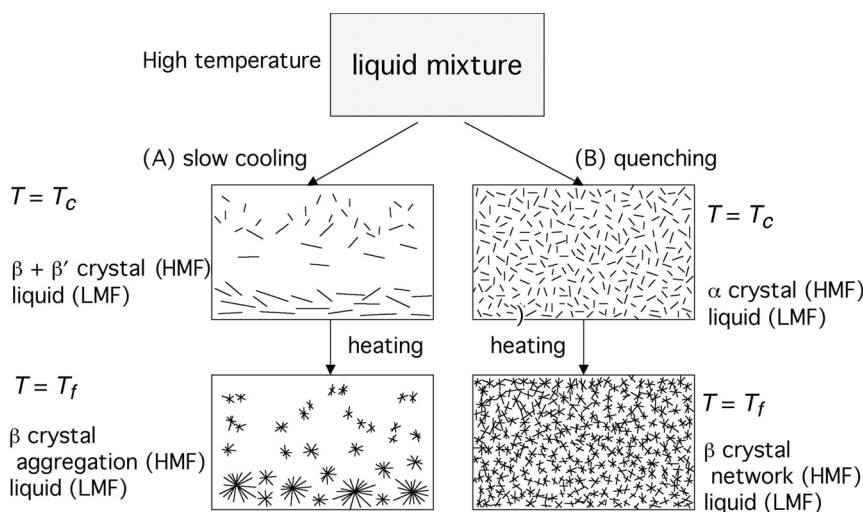
From these results, it can be concluded that the melt-mediated transformation of the fat mixture of FHR-B/SFO during isothermal treatment after tempering of $V_c = 10^\circ\text{C}/\text{min}$ and $T_c = 20^\circ\text{C}$ was due to the melt-mediated transformation from the α form to the β form of FHR-B crystal fractions in the mixtures.

DISCUSSION

The visual evaluation, SFC, and X-ray diffraction analyses of various binary mixtures of HM- and LM-fats can be summarized as follows: (i) Two combinations of FHR-B/SFO and FHR-B/CB exhibited gel-like behavior in a temperature range above the T_m of the LM-fat and below the T_m of the HM-fat fraction in the mixture phase. The other combinations did not show the gel-like behavior. (ii) Simple cooling of these two mixtures, from high-temperature liquidus mixture to T_f , did not result in formation of the gel-like fat. Instead, a proper tempering process was a prerequisite. This tempering process involved rapid cooling to T_c , to induce the crystallization of the HM-fat, and subsequent heating to T_f , to induce the melting of the first-crystallized form and crystallization of the more stable form. (iii) The process of heating from T_c to T_f caused melt-mediated transformations in which the α form, which was crystallized by rapid cooling to T_c , completely melted and the most stable β form was crystallized. As the isothermal crystallization of the β form proceeded at T_f , the gel-like behavior was intensified and was completed after 40 min. (iv) Consequently, the fat mixture exhibiting the gel-like behavior might be called β -fat gel, in a comparative manner to the previously reported α -gel (8–10).

To understand these results, we propose a mechanistic model for the formation of the β -fat gel mixture containing the HM (1.5–4.0 wt%)- and LM (96–98.5 wt%)-fats, as shown in Scheme 1. Two key mechanisms are prerequisites in this model (where HMF = high-melting fat and LMF = low-melting fat): (i) The α -form crystals of the HM-fat formed in the cooling process at T_c are randomly distributed in a liquid phase of the LM-fat; (ii) the α -melt-mediated transformation provides heterogeneous nucleation sites for the β crystals, which form a network of randomly distributed crystals through the melt-mediated transformation from the α crystals. In the present heating treatment from T_c to T_f , it is reasonable to assume that solid-state transformation from α to β was not a dominating process, as judged from the variation of the SFC values with time–temperature (Fig. 2). The proposed model may explain our experimental results as follows.

The fact that V_c must be large, e.g., $10^\circ\text{C}/\text{min}$, is related to the formation of the α crystals, which are prerequisites for gel formation. In general, β form crystals are usually crystallized from solution; α and β' forms are rarely crystallized from solution (17). To interpret this observation, it is assumed that high diffusion rates of molecules in solution may cause the crystallization of the β form, which has the most densely packed subcell structure; the less stable α or β' forms, with less densely packed subcell structures, are not formed from solution phase (18). If a highly supercooled condition occurs



SCHEME 1

during the crystallization from solution phase, the α or β' forms may be crystallized. In this regard, the α form was recently reported to crystallize from mixtures of fats and oils, as the viscosity of the oil phase is increased and the rate of crystallization is increased (19). This phenomenon may have occurred in the present case, although further examination is needed to confirm this consideration. The facts that slow cooling to T_c did not lead to the formation of the α form (Scheme 1) and that subsequent heating did not reveal gel-like behavior may be explained by this mechanism. It is assumed that the LM-fats of SFO and CB may satisfy the condition to crystallize the α form, whereas the other LM-fats may be too fluid (i.e., unviscous) (or too low-melting) to permit crystallization of the α form of the HM-fat fraction even at a high V_c value.

The products of the melt-mediated $\alpha \rightarrow \beta$ transformation of the HM-fat at T_f form the sites of further rapid growth of the β crystals. It has been reported that the α -melt mediation induces the crystallization of the more stable β' and β forms much faster than the simple cooling from liquid, as quantitatively measured for PPP (tripalmitoyl-glycerol) (19), SOS (1,3-stearoyl-2-oleoyl glycerol) (21–23), POP (1,3-palmitoyl-2-oleoyl glycerol) (20), and POS (24). In particular, *in situ* synchrotron radiation XRD analysis of the α -melt-mediated transformations of SOS showed that highly accelerated nucleation was induced by α -melt mediation (22).

The β crystals of the HM-fats might be nucleated at the very sites of the α crystals that melted during heating from T_c to T_f . Since the nucleation rates of the β form are so high by the α -melt mediation that the number of the β crystals is large compared with that formed by simple cooling. In addition, the α crystals are distributed randomly in the liquid phase of the LM-fat, and thereby the heterogeneous nucleation sites of β crystals are also randomly distributed. Thus, the sizes of the β crystals are so small and the nucleation sites of the β crystals are so randomly distributed that randomly distributed tiny β crystals may form a crystal network that incorporates the

liquid phase of the LM-fat as depicted in Scheme 1. By contrast, the β crystals formed by simple cooling to T_f or by tempering with $V_c < 1.5^\circ\text{C}/\text{min}$ are too small in number and too large in size to form the gel-like fat mixture. These β crystals might be precipitated and aggregated so that liquid and solid fractions are separated to form the sol phase as shown in Scheme 1.

To verify this, optical images of the β crystals of FHR-B (2 wt%) in the FHR-B/SFO (98 wt%) mixtures formed at $T_f = 38^\circ\text{C}$ are shown in Figure 5. Figures 5A and 5B show β crystals with tempering at $V_c = 1.5$ and $10^\circ\text{C}/\text{min}$, respectively. The former crystals are large in size and nonuniformly distributed, but small crystals are uniformly distributed in the latter case.

In this regard, the morphology of the β form may also be important. The fact that FHR-B exhibited gel-like behavior, whereas the other HM-fats did not, must mean that the T_m is not the major cause for the formation of gel-like fat mixture. The T_m of the β forms of the HM-fats examined in this work are 65.8°C (FHR-B), 68.0°C (FHR-S), 73.5°C (SSS), 78.1°C (AAA), and 82.5°C (BBB); FHR-B, with the lowest T_m , exhibited gel-like behavior. Alternatively, morphology and network formation of the β form of the high-melting fat must be highly influential. It is known that needle-like morphology is typical for the β form (25). This morphology is evident in the β forms of the five HM-fats examined. However, it is also possible to infer that specific needle morphology, such as thinness and sharpness, and network formation of β crystals of FHR-B might be most suitable to incorporate the liquid fraction of the LM oils, compared to those of FHR-S, SSS, AAA, and BBB.

Although not shown here, the five HM-fats exhibited the α -melt-mediated transformation into the β form in SFO during the temperature processes. This means that randomness in the β crystal distribution may also be significant, probably as it relates to fractal analyses (26–28) in addition to morphological influence.

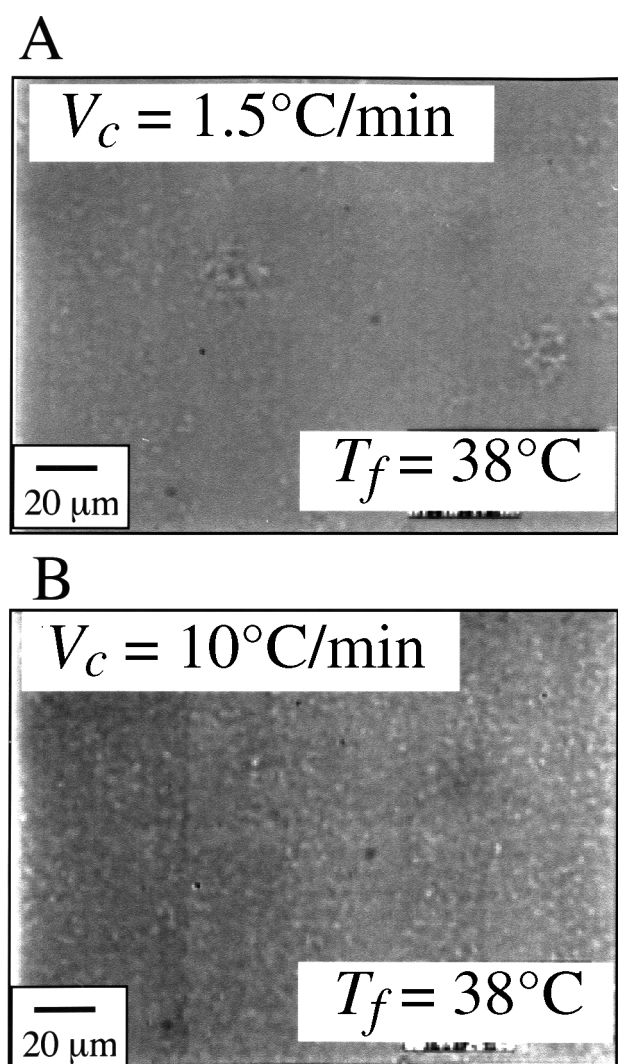


FIG. 5. Optical micrographs of fat mixtures of SFO (98.0 wt%)/FHR-B (2.0 wt%) crystallized with two V_c values. For abbreviations see Figure 1.

ACKNOWLEDGMENTS

The authors are deeply indebted to Dr. Satoru Ueno and Morio Takeuchi, Graduate School of Biosphere Science, Hiroshima University, for their kind assistance in RA-XRD measurements and valuable discussion.

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[Received June 21, 2002; accepted November 25, 2002]