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Fat Crystal Migration and Aggregation and Polymorphism Evolution during the Formation of Granular Crystals in Beef Tallow and Palm Oil

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ABSTRACT: Six rectangular block all beef tallow (BT)-based and all palm oil (PO)-based model shortenings prepared on a laboratory scale, denoted BTMS and POMS, respectively, were stored under two storage conditions, (1) constant temperatures (5 and 20 °C, respectively and (2) temperature fluctuations (5 °C for 12 h and 20 °C for 12 h for a cycle), to induce granular crystals. The fat crystal migration and aggregation, sensory evaluations, and polymorphism evolutions during the formation of granular crystals in the above samples were investigated systematically. In comparison to the constant temperature storage, the crystal growth and hierarchical aggregation process were more quick and the conversion rate of the β-form crystal was also faster in both BTMS and POMS under temperature cycling storage and, concomitantly, easier to induce the formation of granular crystals. From the comprehensive analysis of crystal sizes and the sensory evaluation results, it can be concluded that the detection threshold for graininess ranged from 40 to 90 μm, with the smaller size being perceived only at higher crystal concentrations. The possible formation mechanism and the realistic control approaches for granular crystals in plastic fats also are clarified in the present study.

KEYWORDS: *beef tallow, palm oil, granular crystals, crystallization behavior, polymorphism, formation mechanism*

INTRODUCTION

Beef tallow (BT) is an important animal fat, which is widely used in baking plastic fat manufacturing ascribable to its beneficial properties, e.g., (i) high heat and oxidative stability and (ii) typical desirable aroma after baking. Palm oil (PO) has also been a prominent oil and fat resource for the vegetable-oil-based fat products, because of its plasticity, trans-free characteristic, thermal stability, and price competitiveness. However, when the BT or PO is used as solid fats in plastic fats, the products easily encountered serious structural defects, such as growth of granular crystals with diameters of 0.1−3 mm or above, impairing the plasticity and consistency of BT-/PO-based plastic fats, e.g., shortenings and margarines. This phenomenon is particularly serious in spring and autumn when the temperature fluctuates over a large range during the plastic fat handling, storage, and transportation, and granular crystals can be detected by consumers by rubbing between their fingers or when melting in their mouths.[1−3] Thus, the understanding and control of granular crystal formation in high-fat formulations have been a major focus in the specialty fat industry. The studies of the granular crystals in BT-based shortening[1,2] and BT and PO[3] by our team suggested agglomerates of high-melting triacylglycerols (TAGs) with simultaneous transformation to the more complicated crystal structures, in which the β- and β'-form crystals of triple and double chain length structures simultaneously coexist; concomitantly, a slower crystallization rate with an increase in crystal growth led to the formation of large crystals and further aggregated to larger granular crystals in plastic fat products. However, TAGs are nanosized components, the intrinsic link of which has macroscopic dimension granular crystals, and the rules of the fat crystal migration and aggregation and polymorphism evolutions during the formation of granular crystals are still unclear.

Until now, oil migrations and polymorph transitions also remain the key issues that cause chocolate product quality defects. Ghosh et al.[4] and Lonchampt et al.[5] reviewed more than 100 papers that discussed the relationships between oil migrations. Polymorph transitions in chocolate with fat bloom indicate which are the important reasons for the chocolate bloom. In particular, when different types of fats closely contacted the system (e.g., filling type chocolate), the concentration gradient of TAGs raised fat migration.[6] However, Guiheneuf et al.[7] studied fat migrations in chocolate using magnetic resonance imaging and realized that the concentration gradient of TAGs is not the sole driving force for the chocolate bloom. The lack of a deep understanding of food microstructures and fat-migration-related mechanisms limited the use of some models to a quantitative or semi-quantitative study of the fat migrations in the chocolate foods.[8] Therefore, only extensive literature through microscopic imaging techniques, such as atomic force microscopy,[9−11] magnetic resonance imaging,[12−14] scanning electron microscopy,[15] optical microscopy,[16] descriptively evaluate fat migrations in the process of the chocolate bloom. The microscopic methods stated above have strong advantages for chocolate fats, which can maintain the fixed shape and have a hard surface, particularly, the tapping mode atomic force microscopy widely used; however, soft

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plastic fats cannot be imaged when used, resulting in oil migrations in plastic fats rarely reported.

For polymorphs, the three fundamental polymorphs for TAGs and their mixtures are called α, β', and β, among which, generally, β is the most stable, β' is less stable, and α is the least stable. Owing to their monotropic nature, the polymorphic transformation occurs irreversibly from the least stable α form to the most stable β form, the rate of which is both time- and temperature-dependent. There are two modes of polymorphic transformation processes, namely, solid−solid and melt-mediated transformations. The former occurs below the melting points of all of the polymorphs involved; in contrast, the latter occurs when the temperature is above the melting points of the less stable forms.[17] Szydlowska-Czerniak et al.[18] analyzed the polymorph of five kinds of fat mixtures using differential scanning calorimetry (DSC) and X-ray diffraction (XRD). Fatty acid composition was found to be the key factor affecting the stability of fat polymorphs. Slightly higher contents of palmitic acids had little effect for the polymorph transition rate of β' to β crystal, while trans fatty acids and stearic acids increased β' crystal stability. During the research of polymorph transformation in hydrogenated cottonseed oil, Rousseau et al.[19] found that the β'-type crystal would be formed from the molten state to a 25 °C crystallization; however, from the melted state to 5 °C crystallization, because of the sufficient cooling, for the formation of the β-type crystal, when it was static or stirred, crystallization, polymorphism, and crystal morphology were not significantly changed. The above studies indicated that changes in polymorphism were closely related to compositions and processing methods of the specific fats. Besides, some emulsifiers can be used as "crystal structure modifiers" and "polymorphic retardant agents" in plastic fats, which can crystallize together with TAGs and therefore retard or even prevent the polymorphic transformations.[20] From the aforementioned analysis, it can be seen that there are few reports on the law of fat crystal migration and aggregation and polymorphism evolution in plastic fats.

In the present study, the granular crystals in beef tallow model shortening (BTMS) were induced under two storage conditions, (1) constant temperatures (5 and 20 °C, respectively) and (2) temperature fluctuations (5 °C for 12 h and 20 °C for 12 h for a cycle), while the palm oil model shortening (POMS) was used as the control. The fat crystal migration and aggregation, sensory evaluations, and polymorphism evolutions during the formation of granular crystals were investigated and comparatively analyzed systematically. Therefore, the present study may be able to give an in-depth understanding of the law of oil and fat migration and polymorph transition during the formation of granular crystals in plastic fats, which is helpful to understand fat crystal structure changes in the dynamic formation process of granular crystals, and it also has great significance to clarify the mechanism causing the formation of granular crystals further. According to the results of the present study, the realistic control approaches for preventing the formation of granular crystals in plastic fats may be developed.

MATERIALS AND METHODS

Materials. Refined, bleached, and deodorized (RBD) BT [iodine value (IV) of 45.15 g of I_2/100 g and slip melting point (SMP) of 44.5 °C] and PO (IV of 52.87 g of I_2/100 g and SMP of 34.6 °C) were produced and generously provided by Kerry Specialty Fats, Ltd. (Shanghai, China). The composition information of these two fats can be referenced to the previous paper by our teams.[3] In China, these two kinds of fats were widely used as one of the ingredients in animal-fat- and vegetable-oil-based plastic fat products, respectively. All other solvents and reagents were of chromatographic or analytical grade, purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), to meet the test requirements.

SMP. The SMP was determined according to American Oil Chemists' Society (AOCS) standards, method Cc 3-25.[21] Briefly, fat filled up to 1 cm in open capillary tubes was pre-solidified by touching over a piece of ice and then chilled at 10 ± 1 °C for 16 h. Three capillaries were attached gently to a thermometer using a rubber band before being immersed in a beaker of cold distilled water. The water was stirred and heated, and the temperature was recorded when the fat column begins to rise in the tubes. Triplicate measurements were made, and the average value is reported above.

Preparation of Model Shortenings. The model "shortenings" were prepared according to the modified method by Braipson-Danthine and Deroanne.[22,23] About 1400 g of the melted fats (BT and PO, respectively) contained in the 2000 mL beaker were kept in an oven at 80 °C for 30 min to erase the crystal memory. Divided into six copies, each sample of 200 g was placed in six small rectangular block plastic vessels (8 × 7 × 5 cm) and kept in liquid form at 45 °C with gentle stirring for 30 min. They were then put in a freezer at −20 °C for another 1 h to simulate a laboratory scale of an industrial scraped surface heat exchanger. The fat samples were subsequently stored in room temperature (25 ± 1 °C) for 48 h. Then, six model shortenings of BT and PO were obtained, respectively, and denoted BTMS and POMS.

Induction of Granular Crystals in Model Shortenings. Just after the shortenings were produced, one model sample above was subjected to 5 and 20 °C constant temperature storage and one model sample was subjected to temperature cycling storage in a KBF115 programmable oven (Binder, Tuttlingen, Germany), in which the temperature was held at 5 °C for 12 h and 20 °C for another 12 h. These induction procedures were performed in duplicate.[24,25] At the beginning of the storage and storage after each week cycle, the model shortenings were evaluated for crystal morphology by polarized light microscopy (PLM), sensory evaluation, and crystal polymorphism by XRD continuously.

Crystal Morphology by PLM. The morphology of crystallized samples was observed using PLM (DMRX, Leica, Germany) with a Canon A640 digital camera attached (Canon, Tokyo, Japan). The desired amount of crystallized sample (~50 mg) was placed on a carrier glass slide, which has been precooled or preheated to needed temperatures (5 and 20 °C, respectively). A coverslip was then placed parallel to the plane of the carrier slide and centered on the drop of the sample to ensure uniformity and desirability of sample thickness, avoiding the introduction of air bubbles into the sample. The photomicrograph of the crystal was taken at 100× magnification. A number of images were acquired, each representing a typical field. All operations were performed triplicate.

Sensory Analysis. A total of 10 assessors were selected for the panel. The assessors were trained during five sessions on profiling shortenings, including two commercial shortenings and two of our produced shortenings, prior to the evaluation of the samples. Sensory analysis was carried out in a standard sensory room using the quantitative descriptive analysis (QDA). The graininess attribute, the amount of grain sensed between the fingers and tongue, was evaluated as follows: very little or no graininess development, hardly perceivable graininess development, acceptable graininess development, high graininess development, and very high graininess development. A scale from 1 to 5 was employed to correspond to the above five different levels, where 1 indicates no intensity with no graininess and 5 indicates the highest intensity with very high graininess development. Triplicate analyses were performed for each sensory analysis. Analysis of variance (ANOVA) with Duncan's multiple-range test was carried out by the Statistical Analysis System software (SAS, Cary, NC). Differences were considered significant at $p < 0.05$, and values of the means of triplicates ± standard deviations are presented.

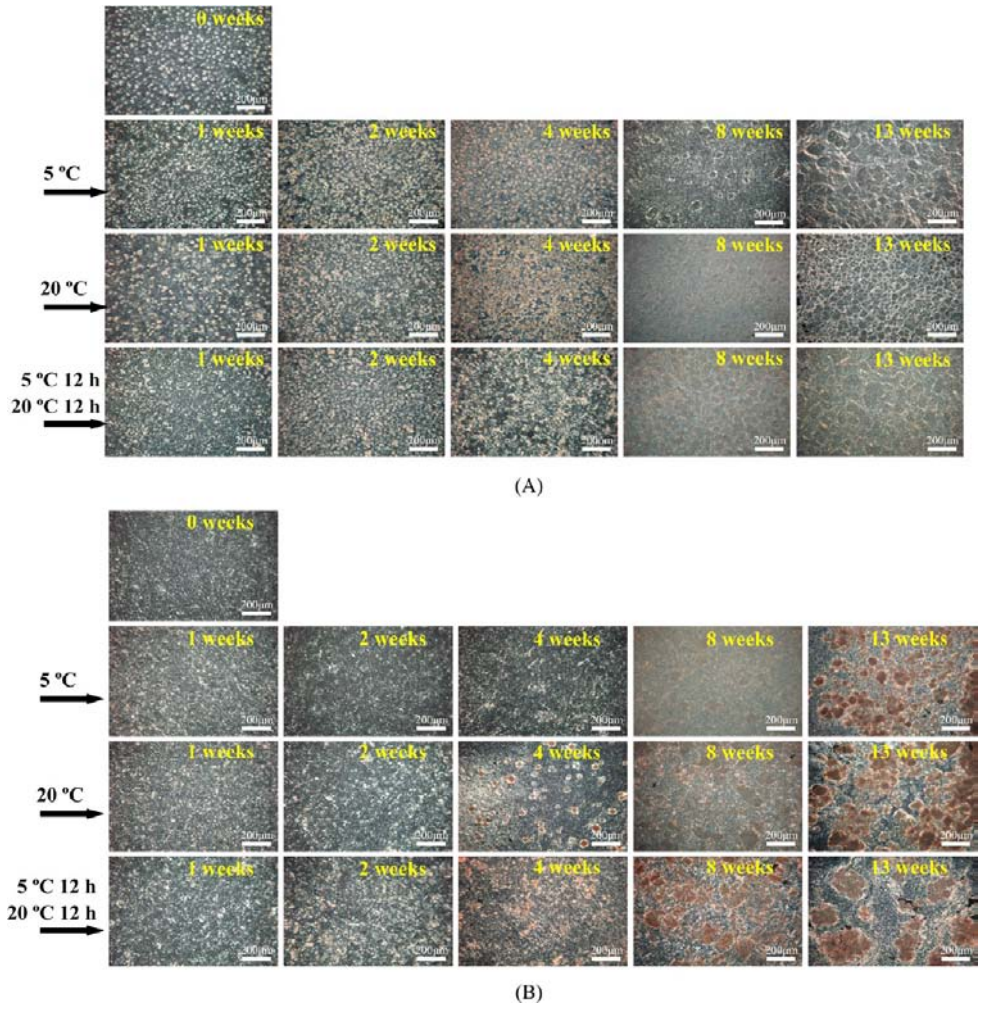

Figure 1. Polarized light micrographs of (A) BTMS and (B) POMS stored at a constant temperature (5 and 20 °C) and temperature cycling (5 °C for 12 h and 20 °C for 12 h) for 0, 1, 2, 4, 8, and 13 weeks.

Crystal Polymorphism by XRD. The polymorphic forms of fat crystals in the blends were determined by D8 Advance XRD (Bruker, Karlsrube, Germany), using Cu Kα radiation with a Ni filter (k = 1.540 56 Å, voltage of 40 kV, current of 40 mA, and fixed 1.0, 1.0, and 0.1 mm divergence, antiscatter, and receiving slits, respectively). Samples were scanned from 10° to 30° (2θ scale), and the scan rate was set at 2°/min. The analyses were performed at ambient temperature, and triplicate analyses were carried out. The short spacing of the α form appears near 4.15 Å; the spacing of the β' form appears at 4.2 and 3.8 Å; and the spacing of the β form appears at 4.6 Å (single strong spacing).

RESULTS AND DISCUSSION

Crystal Morphology Analysis. Crystal sizes and morphology are essential for the consistency and acceptability of final plastic fat products with intensive crystal aggregates, with smaller crystals leading to firmer products, whereas larger size crystals make the product deteriorate, resulting in sandy mouth feel. Miura et al.[25] reported that, when the fat crystal size ranged between 100 and 300 μm, which could be observed by the naked eye, the granular crystals could be perceived in the mouth. For further discussion of the aggregation behavior of fat crystals during the formation of granular crystals, the structures of the fat crystal network under the two kinds of storage conditions, in terms of crystal network density, crystal morphology, crystal sizes, etc., were continuously observed by PLM. The initial crystal morphology of BTMS and polarized light micrographs after storing for 1, 2, 4, 8, and 13 weeks at constant temperatures (5 and 20 °C) and temperature cycling (5 °C for 12 h and 20 °C for 12 h) are shown in Figure 1A. The POMS as the control stored under the same conditions above were also each visualized by PLM, and its crystal morphology is shown in Figure 1B. The initial crystal morphology of BTMS showed well-organized spherulites with needle-shaped crystals oriented radially from the center, sparser distribution of crystal morphology, and small crystals (no more than 20 μm) (Figure 1A). After 1 week of storage under the above-mentioned conditions, of which the crystal distribution was significantly more dense in 5 °C and temperature fluctuations (5 °C for 12 h and 20 °C for 12 h), because of the melting of partial lower melting components under 20 °C storage, the crystals showed lesser intensity distribution than the former. Because of the continued crystal growth during the storage, the crystal sizes were slightly larger than the initial state in both conditions, especially for the storage conditions of temperature fluctuations, in which there was a small amount of scattered large crystals (about 20 μm). During the storages for 2−4 weeks, the crystal growth was more obvious. The spherical crystal morphology changed little, but the crystal size increased and a more dense crystal network was presented, wherein the overall sizes of formed crystals under temperature fluctuation

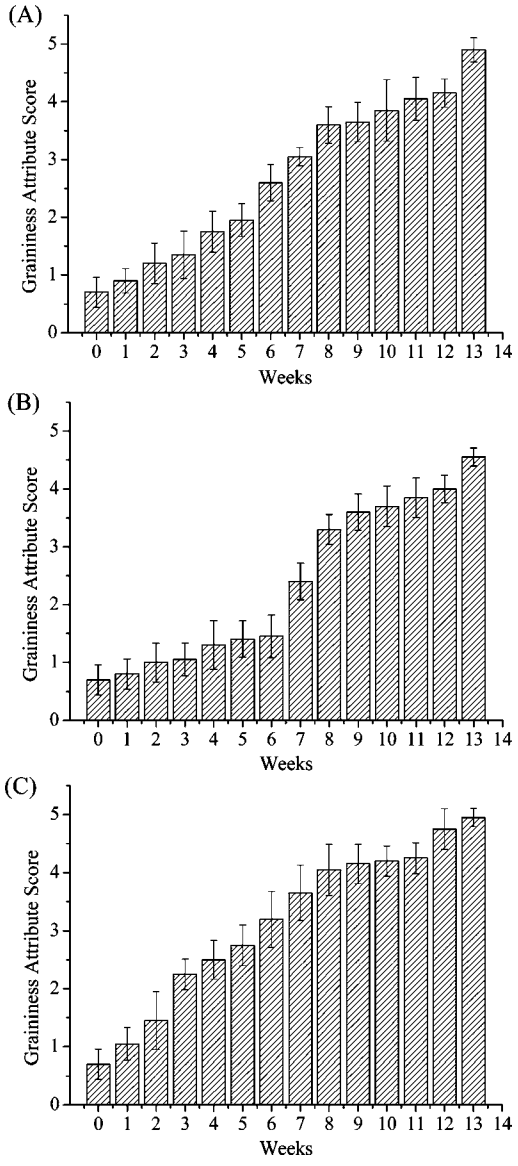

Figure 2. Average graininess attribute scores for QDA of the BTMS stored at a constant temperature (A, 5 °C; B, 20 °C) and temperature cycling (C, 5 °C for 12 h and 20 °C for 12 h) for 0−13 weeks.

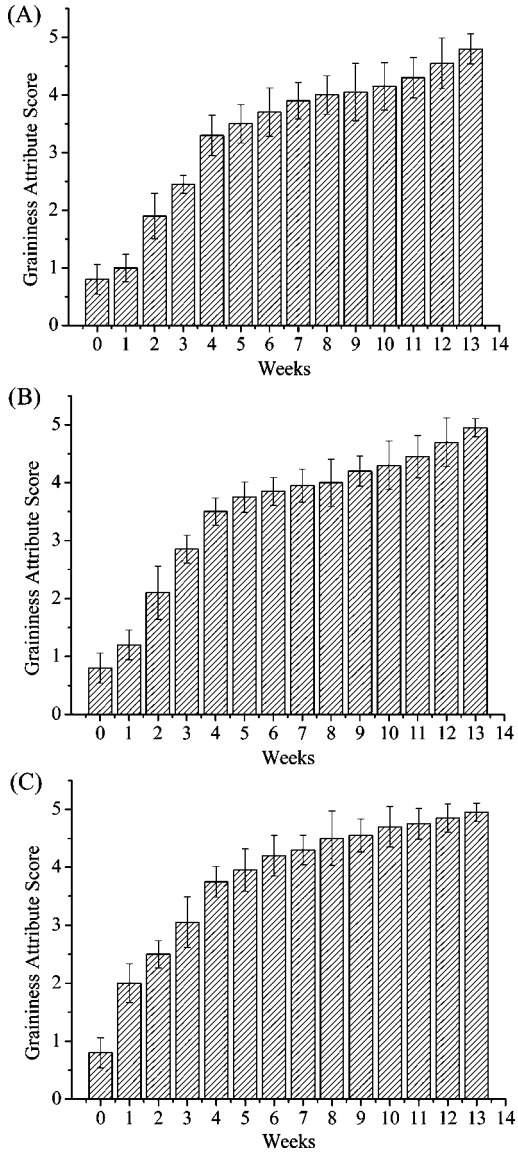

Figure 3. Average graininess attribute scores for QDA of the POMS stored at a constant temperature (A, 5 °C; B, 20 °C) and temperature cycling (C, 5 °C for 12 h and 20 °C for 12 h) for 0−13 weeks.

conditions were larger (about 30 μm). After the continued storage to 8 weeks, these differences became more apparent. At this time, a large number of large lamellae crystal blocks ranging between 90 and 180 μm in size appeared in the samples, which were stored under temperature fluctuation conditions and distributed densely, and under the constant temperatures (5 and 20 °C, respectively), the sample showed only a few small scattered lamellae crystal blocks (30−90 μm), which were caused by the crystal aggregation during storage. When the storage time extended to 13 weeks (about 3 months), granular crystalline blocks in samples were distributed more closely with the size of the largest crystalline aggregates at nearly 200 μm.

Under the same storage conditions, variations of crystal aggregates in POMS, which as the control samples, were substantially the same as BTMS described above. At the beginning of storage, samples showed delicate irregular crystal morphology. When storing during 1−2 weeks, crystals further grow, aggregate, and form more dense, overlapping alternating crystal networks, wherein the aggregation of the crystal is more obvious under temperature fluctuation conditions. During storage for 4−13 weeks, under the conditions of 20 °C and temperature fluctuations (5 °C for 12 h and 20 °C for 12 h), the crystal hierarchical aggregation behavior appeared earlier in POMS than in BTMS and the phenomenon was more evident. This is because the ratio of liquid oil contained in PO was higher than that in BT, when the storage conditions were 20 °C and temperature fluctuations. A large amount of liquid oil flowed more easily, which made the fat classification and crystal suspension migrate together to form the large fat crystal blocks, with the size ranging from about 40 μm in 4 weeks to nearly 300 μm in 13 weeks. In this case, the tiny granular crystals in the samples can be observed through the naked eye.

It can be found from the observation of the procedure of fat aggregation during the formation of granular crystals, whether in BTMS or POMS, that a more rapid crystal growth and hierarchical aggregation process occurred under temperature fluctuation conditions, in which it was easier to induce the

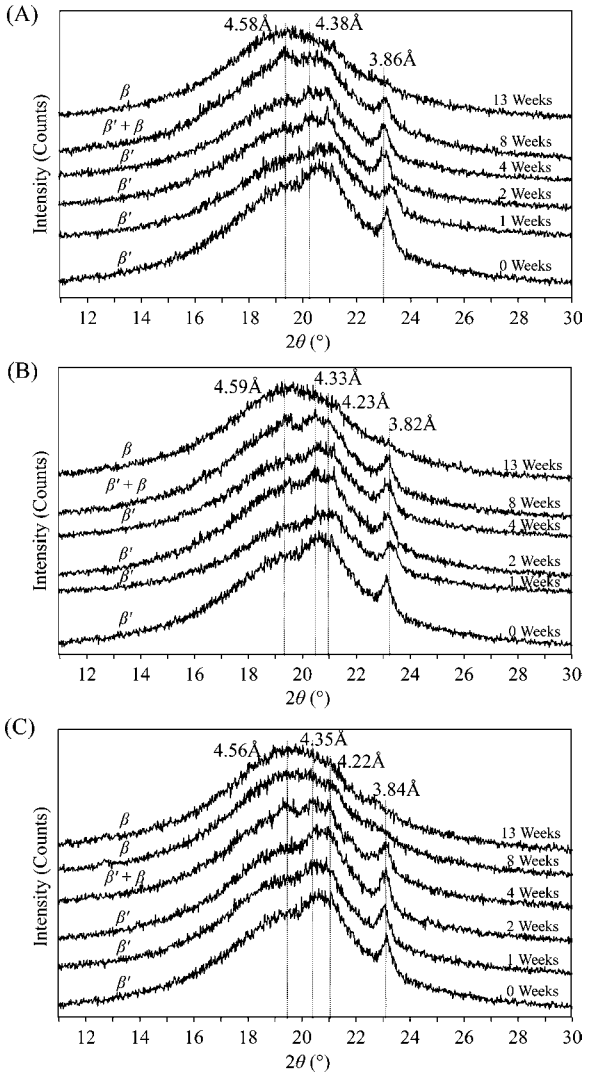

Figure 4. Diffractograms for short spacings of BTMS stored at a constant temperature (A, 5 °C; B, 20 °C), and temperature cycling (C, 5 °C for 12 h and 20 °C for 12 h) for 0, 1, 2, 4, 8, and 13 weeks, determined by XRD.

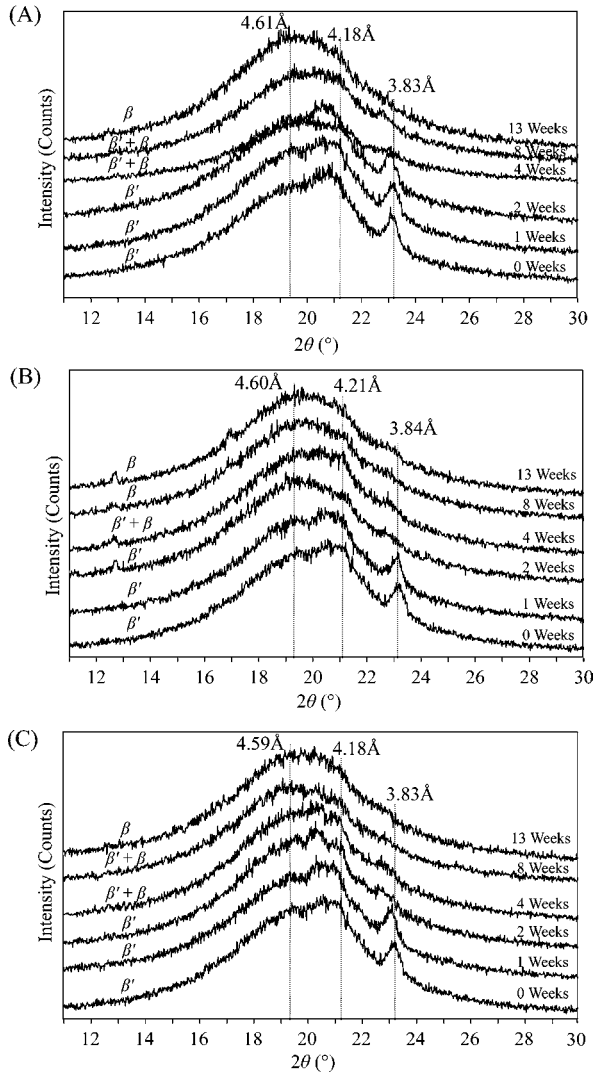

Figure 5. Diffractograms for short spacings of POMS stored at a constant temperature (A, 5 °C; B, 20 °C) and temperature cycling (C, 5 °C for 12 h and 20 °C for 12 h) for 0, 1, 2, 4, 8, and 13 weeks, determined by XRD.

formation of granular crystals compared to constant temperature conditions (5 and 20 °C, respectively).

Sensory Analysis. Graininess is a kind of structural defect for plastic fat products, e.g., shortenings, margarines, and spreads. It can be seen from the analysis above, which can develop if the solid fat crystals aggregate and pack together to form particles sufficient in size and number to be perceptible. QDA was performed to describe the crystal aggregation attributes of BTMS and POMS under two storage conditions by giving them a score, respectively. The average scores given by the 10 assessors, focused on graininess, were used for evaluating the effects of constant temperatures (5 and 20 °C, respectively) and temperature cycling storage time at weeks 0−14 for the BTMS (Figure 2) and POMS (Figure 3), respectively. The graininess of the samples was affected by both the storage time and temperature conditions.

As seen from the Figure 2, the graininess attribute score for BTMS increased fastest under temperature fluctuation conditions. When stored at 5 °C for 5 weeks and at 20 °C for 6 weeks, the granular crystals in the sample were almost not felt; however, under the temperature cycling storage for 6 weeks, there is a small amount of granular crystals that are perceptible. When the storage lasted 8 weeks, under conditions of 5 and 20 °C, only a small amount of granular crystals can be assessed. Until 13 weeks, a large amount of granular crystals can be assessed. There is a high content of granular crystals under the temperature cycling storage of 8 weeks, which was consistent with the crystal aggregation behavior aforementioned observed by PLM in Figure 1A. POMS was found to have a quicker rate for the formation of granular crystals than BTMS under all of the corresponding conditions mentioned above (Figure 3). Acceptable tiny sandy crystals in the sample can be perceived under conditions of 20 °C and temperature cycling storage for 3 weeks. After continued storage to 7 weeks, high graininess development can be perceptible. Overall, the crystal changes measured using PLM were thus reflected in the sensory analysis for BTMS and POMS. When comprehensive analysis on the crystal size and sensory evaluation results above are taken into account, it can be concluded that the detection threshold for graininess ranged from 40 to 90 μm, with the smaller size being perceived only at higher crystal concentrations.

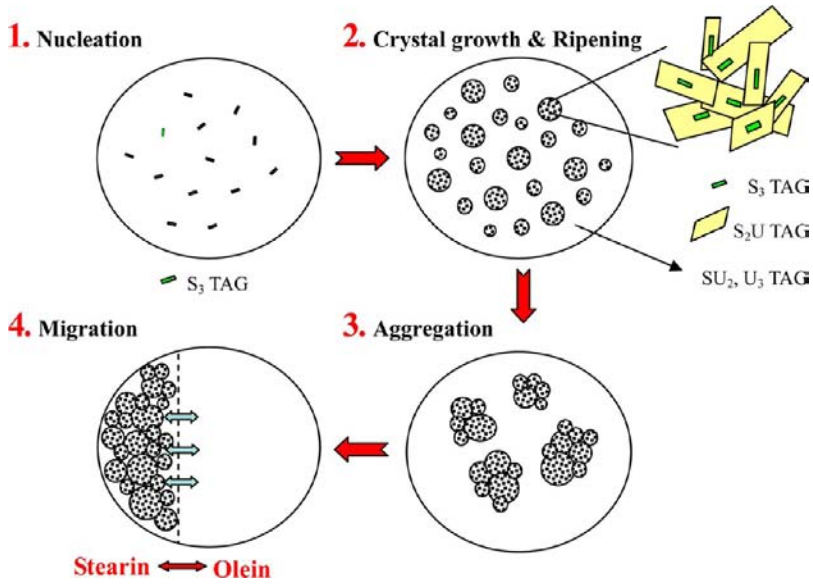

Figure 6. Schematic presentation of the possible formation pathway and structure model of granular crystals in plastic fats.

Polymorphism Evolution Analysis. In addition to changing the crystal morphology and sensory properties of the samples, polymorphism was also heavily influenced by storage conditions of temperature and time. Diffractograms for short spacings of BTMS (Figure 4) and POMS (Figure 5) stored for 1, 2, 4, 8, and 13 weeks at constant temperatures (5 and 20 °C) and temperature cycling (5 °C for 12 h and 20 °C for 12 h) were determined by XRD. Figure 4 reflects all of the β'-type crystals presented in the fresh BTMS at a storage time of 0 weeks, which have a fine crystal structure and were consistent with crystal morphology observed by PLM aforementioned (Figure 1A). When BTMS was stored for 4 weeks under constant temperatures (5 and 20 °C), it still maintained the small β'-type crystals, which had been partially converted into β-type crystals under the temperature cycling storage of 4 weeks; nevertheless, this shift just occurred at 8 weeks for the above samples when storing at the constant temperature. Under temperature cycling storage of 8 weeks, BTMS fully crystallized in β forms, yet until the storage lasted for 13 weeks, samples under the constant temperatures (5 and 20 °C) just fully converted to β-type crystals, which were also consistent with the aforementioned variation of crystal morphology. It can be clearly seen that the temperature fluctuation storage of the sample accelerated the convert rate to β-form crystals.

For the control of POMS, the laws of polymorphism evolution were similar to the aforementioned BTMS samples. After storing for 4 weeks, POMS contained both β'- and β-form crystals at all storage conditions. Under temperature cycling storage of 8 weeks, POMS fully converted to β-form crystals, which corresponded to the graded aggregate of solid fat and liquid oil within the samples to form large crystal blocks discussed in preceding sections; however, samples just fully crystallized in β forms under the constant temperatures (5 and 20 °C) until the storage lasted for 13 weeks.

Formation Mechanism of Granular Crystals in Plastic Fats. BTMS and POMS above were continuously subjected to temperature cycling storage for 6 months until granular crystals (diameter of ~2−3 mm) were observed visually and easily picked out from the inside of each model shortening by tweezers; namely, granular crystals were reproduced in BTMS and POMS. Following the structure hierarchy of fat crystal networks, the lipid composition, thermal properties, polymorphism, and crystallization behaviors of granular crystals and their surrounding materials were carried out in a comparative study systematically in our previous research.[3] When the conclusions of our preceding studies are combined with the laws of fat crystal migration and aggregation, polymorphism evolution during the formation of granular crystals in BTMS and POMS was obtained in the present research, suggesting the possible formation pathway and structure model of granular crystals in plastic fats shown in Figure 6.

The results suggested the mechanism of granular crystal formation in plastic fats. In the initial stages of crystallization, high melting point trisaturated (S_3) TAG as the seed crystal forms double chain length β'-type nuclei and crystallized first in the plastic fat system, such as SSS, PSS, PPS, and PPP in BTMS and PPP in POMS. Disaturated and monounsaturated (S_2U) TAG attached to the nucleus surface, promoting the growth of crystal nuclei in the case of the driving force provided by the temperature fluctuation, such as SOS and POS in BTMS and POP and POS in POMS. After further aging, the number of spherulitic crystals and the size of a single crystal increase, with crystalline network further intensifying, including S_3 and S_2U TAGs becoming crystal backbone components and most monosaturated and diunsaturated (SU_2) and triunsaturated (U_3) TAGs being excluded from the crystal. Concurrently, accompanied by part of the β' crystal of the double chain length structure transforming to the complex crystal, in which the β- and β'-form crystals of triple and double chain length structures of TAG stacking simultaneously coexist, crystals further aggregate, grow, even occur in the migration, and form large crystal clusters. When the microstructure size of these crystal aggregates exceeded the sensory threshold (40−90 μm), the aggregates could be detected upon visual and physical examination (by rubbing between the fingers or melting in the mouth) and, therefore, impaired the sensory and functional properties of the finished products, leading to the formation of large granular crystals in plastic fats.

Therefore, the present study may be able to give a better understanding the mechanism causing the formation of granular crystals in plastic fat products. Accordingly, the results above demonstrated that possible techniques to prevent the formation of the granular crystals may be developed, by paying attention to the high-melting TAGs and the aggregation and polymorphism evolution of crystals. From the current production of the plastic fat products, the realistic approaches of control the formation of granular crystals may be shown as follows: by a suitable method for modifying fats, such as interesterification, fractionation, blending, or a combination of the above methods, making TAG composition of base stocks more reasonable, and additionally, adding emulsifiers as the crystallization controller and polymorphic retardant agents to retard the polymorphic transformation and improve crystal stability. All of the changes combined could assist in eliminating the profound graininess formation phenomena in the plastic fat products.

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Notes

The authors declare no competing financial interest.

ABBREVIATIONS USED

BT, beef tallow; PO, palm oil; BTMS, all beef-tallow-based model shortenings; POMS, all palm-oil-based model shortenings; TAG, triacylglycerol; DSC, differential scanning calorimetry; XRD, X-ray diffraction; RBD, refined, bleached, and deodorized; IV, iodine value; SMP, slip melting point; PLM, polarized light microscopy; QDA, quantitative descriptive analysis; ANOVA, analysis of variance; S_3, trisaturated; S_2U, disaturated and monounsaturated; SU_2, monosaturated and diunsaturated; U_3, triunsaturated

REFERENCES

(1) Jin, Q. Z.; Gao, H. Y.; Shan, L.; Liu, Y. F.; Wang, X. G. Study on grainy crystals in edible beef tallow shortening. *Food Res. Int.* **2007**, *40*, 909−914.

(2) Meng, Z.; Liu, Y. F.; Jin, Q. Z.; Huang, J. H.; Song, Z. H.; Wang, F. Y.; Wang, X. G. Characterization of graininess formed in all beef tallow-based shortening. *J. Agric. Food Chem.* **2010**, *58*, 11463−11470.

(3) Meng, Z.; Liu, Y. F.; Jin, Q. Z.; Huang, J. H.; Song, Z. H.; Wang, F. Y.; Wang, X. G. Comparative analysis of lipid composition and thermal, polymorphic, and crystallization behaviors of granular crystals formed in beef tallow and palm oil. *J. Agric. Food Chem.* **2011**, *59*, 1432−1441.

(4) Ghosh, V.; Ziegler, G. R.; Anantheswaran, R. C. Fat, moisture, and ethanol migration through chocolates and confectionary coatings. *Crit. Rev. Food Sci.* **2002**, *42*, 583−626.

(5) Lonchampt, P.; Hartel, R. W. Fat bloom in chocolate and compound coatings. *Eur. J. Lipid Sci. Technol.* **2004**, *106*, 241−274.

(6) McCarthy, K. L.; McCarthy, M. J. Oil migration in chocolate−peanut butter paste confectionery as a function of chocolate formulation. *J. Food Sci.* **2008**, *73*, E266−E273.

(7) Guiheneuf, T. M.; Couzens, P. J.; Wille, H.-J.; Hall, L. D. Visualisation of liquid triacylglycerol migration in chocolate by magnetic resonance imaging. *J. Sci. Food Agric.* **1997**, *73*, 265−273.

(8) Aguilera, J. M.; Michel, M.; Mayor, G. Fat migration in chocolate: diffusion or capillary flow in a particulate solid?—A hypothesis paper. *J. Food Sci.* **2004**, *69*, 167−174.

(9) Hodge, S.; Rousseau, D. Fat bloom formation and characterization in milk chocolate observed by atomic force microscopy. *J. Am. Oil Chem. Soc.* **2002**, *79*, 1115−1121.

(10) Rousseau, D.; Sonwai, S. Influence of the dispersed particulate in chocolate on cocoa butter microstructure and fat crystal growth during storage. *Food Biophys.* **2008**, *3*, 273−278.

(11) Smith, P.; Dahlman, A. The use of atomic force microscopy to measure the formation and development of chocolate bloom in pralines. *J. Am. Oil Chem. Soc.* **2005**, *82*, 165−168.

(12) Miquel, M. E.; Hall, L. D. A general survey of chocolate confectionery by magnetic resonance imaging. *LWT—Food Sci. Technol.* **1998**, *31*, 93−99.

(13) Miquel, M. E.; Carli, S.; Couzens, P. J.; Wille, H.-J.; Hall, L. D. Kinetics of the migration of lipids in composite chocolate measured by magnetic resonance imaging. *Food Res. Int.* **2001**, *34*, 773−781.

(14) Miquel, M. E.; Hall, L. D. Measurement by MRI of storage changes in commercial chocolate confectionery products. *Food Res. Int.* **2002**, *35*, 993−998.

(15) Kinta, Y.; Hatta, T. Composition, structure, and color of fat bloom due to the partial liquefaction of fat in dark chocolate. *J. Am. Oil Chem. Soc.* **2007**, *84*, 107−115.

(16) Afoakwa, E. O.; Paterson, A.; Fowler, M.; Vieira, J. Effects of tempering and fat crystallization behaviour on microstructure, mechanical properties and appearance in dark chocolate systems. *J. Food Eng.* **2008**, *89*, 128−136.

(17) Sato, K.; Ueno, S. Polymorphism in fats and oils. In *Bailey's Industrial Oil and Fat Products*, 6th ed.; Shahidi, F., Ed.; John Wiley and Sons: Hoboken, NJ, 2005; Vol. *1*, pp 77−120.

(18) Szydłowska-Czerniak, A.; Karlovits, G.; Lach, M.; Szłyk, E. X-ray diffraction and differential scanning calorimetry studies of $\beta' \rightarrow \beta$ transitions in fat mixtures. *Food Chem.* **2005**, *92*, 133−141.

(19) Rousseau, D.; Hodge, S.; Nickerson, M.; Paulson, A. Regulating the $\beta' \rightarrow \beta$ polymorphic transition in food fats. *J. Am. Oil Chem. Soc.* **2005**, *82*, 7−12.

(20) Garbolino, C.; Bartoccini, M.; Flöter, E. The influence of emulsifiers on the crystallisation behaviour of a palm oil-based blend. *Eur. J. Lipid Sci. Technol.* **2005**, *107*, 616−626.

(21) American Oil Chemists' Society (AOCS). *Official Methods and Recommended Practices of the American Oil Chemists' Society*, 5th ed.; AOCS: Champaign, IL, 1998.

(22) Braipson-Danthine, S.; Deroanne, C. Determination of solid fat content (SFC) of binary fat blends and use of these data to predict SFC of selected ternary fat blends containing low-erucic rapeseed oil. *J. Am. Oil Chem. Soc.* **2006**, *83*, 571−581.

(23) Braipson-Danthine, S.; Deroanne, C. Influence of SFC, microstructure and polymorphism on texture (hardness) of binary blends of fats involved in the preparation of industrial shortenings. *Food Res. Int.* **2004**, *37*, 941−948.

(24) Watanabe, A.; Tashima, I.; Matsuzaki, N.; Kurashige, J.; Sato, K. On the formation of granular crystals in fat blends containing palm oil. *J. Am. Oil Chem. Soc.* **1992**, *69*, 1077−1080.

(25) Miura, S.; Konishi, H. Crystallization behavior of 1,3-dipalmitoyl-2-oleoyl-glycerol and 1-palmitoyl-2,3-dioleoyl-glycerol. *Eur. J. Lipid Sci. Technol.* **2001**, *103*, 804−809.