Elucidation of formation mechanism of granular crystal for margarine

Xiaohu Le, Haruhiko Koizumi, Satoru Ueno

Hiroshima University, Hiroshima, Japan

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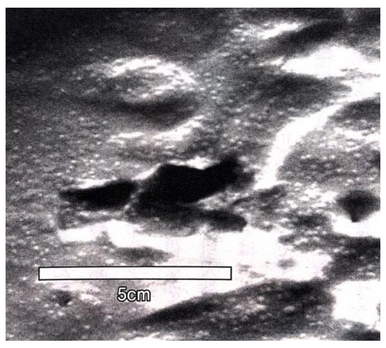
1.Introduction

In the past, hydrogenation was used in the industry to produce margarine, but it resulted in the presence of *trans* fatty acids. Consuming excessive amounts of *trans* fatty acids increases the risk of heart disease, cardiovascular disorders, and obesity. To reduce the content of *trans* fatty acids, palm oil is now being used in the industry to manufacture margarine. However, that leads to granular crystals with diameters ranging from 0.5 to 3 mm may form due to temperature changes. The formation of granular crystals significantly deteriorates the appearance and quality of the product, making it a critical issue in the food industry.



Granular crystal

2.Objective

Previous research on granular crystals has revealed that the main component of granular crystals is POP, and the main polymorph is β-form. However, the samples used in previous research were granular crystals that grew granular after long-term storage, and the growth process of granular crystals was unknown. In recent years, there have been studies on the growth process, but the sample used was shortening, not margarine. Therefore, in this study, we aimed to clarify the growth process of granular crystals and elucidate the growth mechanism by observing granular crystals over time.

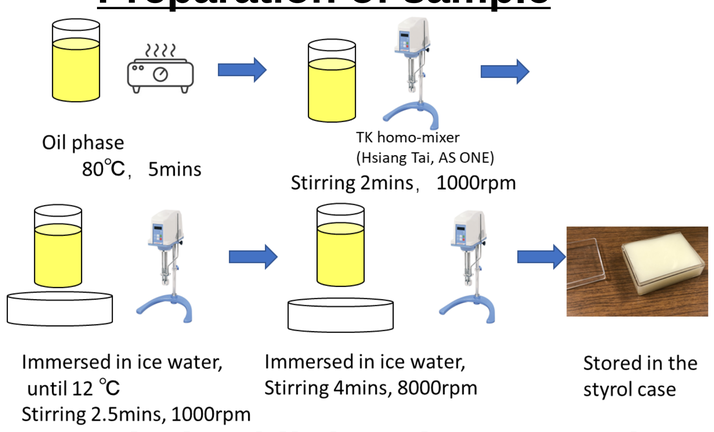
3.Materials and methods

Materials

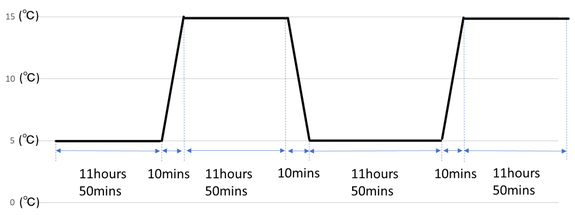
Margarine

・Monoglyceride (1-oleoylglycerol)	0.5%
・Fully hydrogenated Rapeseed Oil	2%
・Palm oil	25%
・Soybean oil	52.5%
・Ultrapure water	20%

Preparation of sample

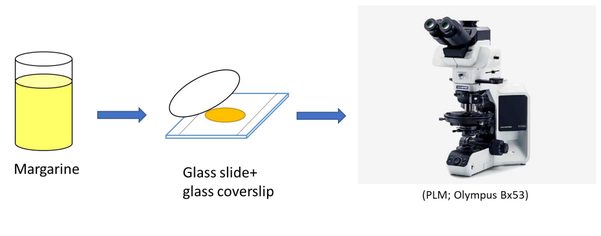


Preservation method



Temperature program for the incubator

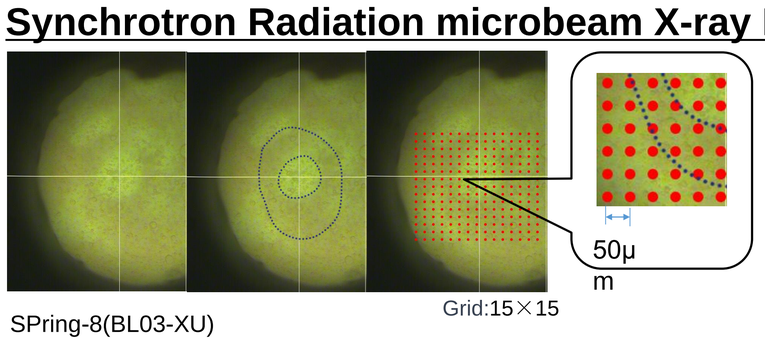
Polarized light microscopy(PLM)



Experimental device

・polarized light microscope(PLM; Olympus Bx53)

Synchrotron Radiation microbeam X-ray Diffraction (SR-XRD)

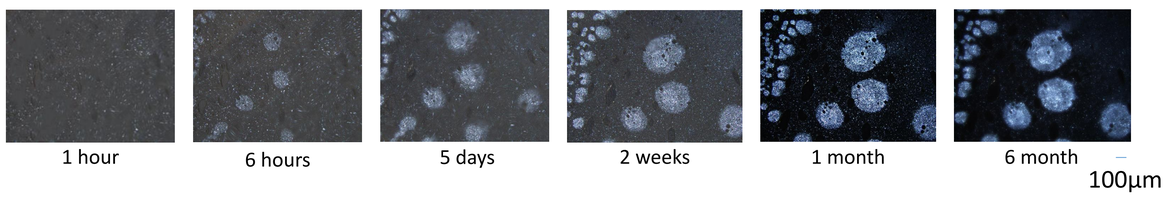


- Wave length： 1Å
- Beam size：7μm
- Exposure time：1s

X-ray diffraction pattern within a localized area (beam size: 7μm, spacing between grid points: 50μm) → Short lattice spacing, Long lattice spacing → Identification of TAGs constituting each component

4.Result and discussion

Polarized microscope observations for 6 months



After 6 hours from the manufacturing of margarine, granular crystals begin to form. 5 days later, a thin layer of crystals appears on the outside of the granular crystals, and the thin crystalline layer expands. No changes occur after two weeks.

Results of SR-μ-XRD

Table 1. Composition and characteristic of each TAG ($T_m \geq 7$ ℃)

TAG	content	β'		β	
	%	T_m (℃)	d_{LS} (Å)	T_m (℃)	d_{LS} (Å)
POP	7.9	33.5	42.4	35.1	61.0
POO	5.9	19.5	64.1		
SOO	2.0	24.5	66.0		
PPO	1.8	35.2	65.0		
PPP	1.8	56.6	42.3	66.4	40.9
Total	19.4				

Among the TAG components present in the sample in amounts of 1% or more, the components with the lowest melting points of stable crystal polymorphs above 7° C are POP (1,3-dipalmitoyl-2-oleoyl-glycerol), POO, PPO, PPP, and SOO. The fractional composition of each TAG molecule, crystal polymorph (β', β), their respective melting points (Tm), and the long spacing (inter-chain distance; dLS) are presented in Table 1).

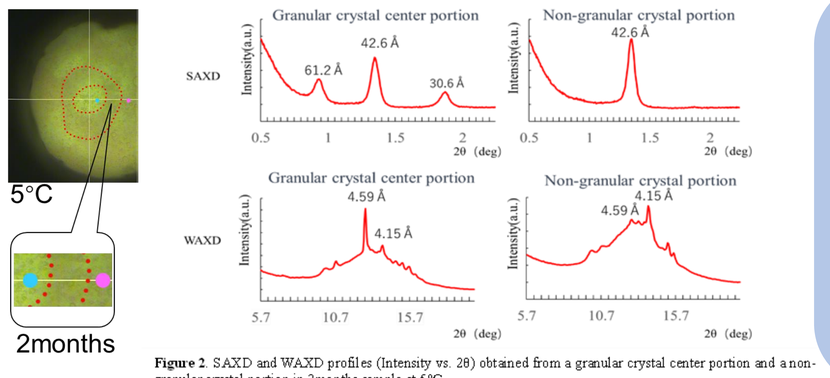


Figure 2. SAXD and WAXD profiles (Intensity vs. 2θ) obtained from a granular crystal center portion and a non-granular crystal portion in 2months sample at 5°C

In the granular crystals, a polymorphic transition occurred. (Within the granular crystals, both β-form and β-form are present, but the β-form has a higher crystalline quantity.)

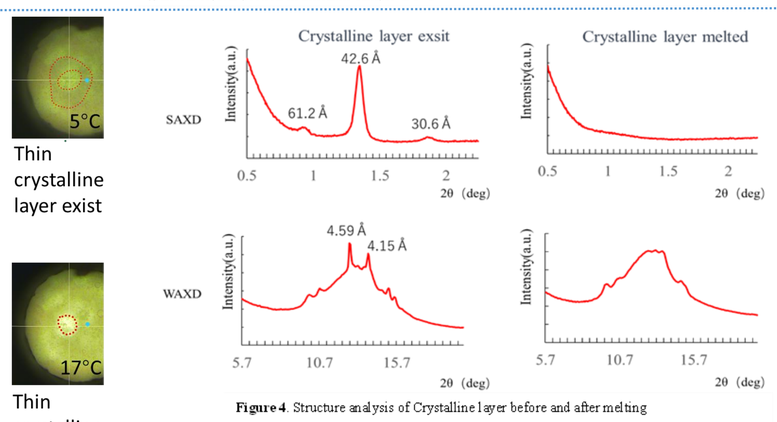
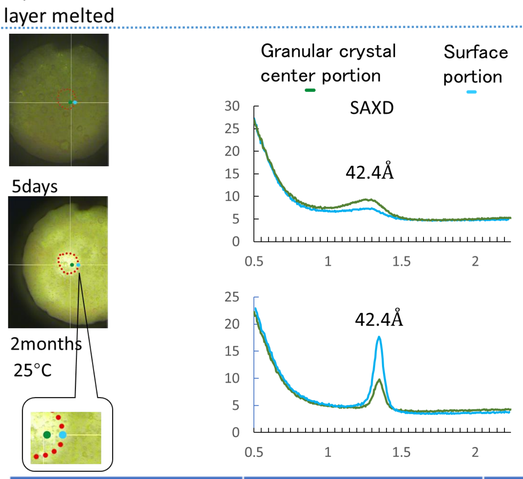


Figure 4. Structure analysis of Crystalline layer before and after melting

The diffraction peaks of both β' and β-forms of POP almost disappeared and melted at 17° C. The growth of granular crystals is thought to occur as the polymorphic transition from β' to β of POP propagates slowly from the central to peripheral regions, and as the transformed β-form microcrystals of POP grow while diffusing within the sample.



5days sample Prevalent in the central region of granular crystals

2months sample Prevalent in the surface of granular crystals

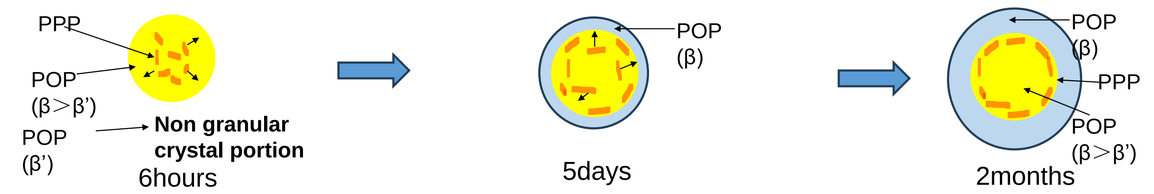
Crystals that were present in the center of the granular crystals have moved outward.

		T_m (℃)	d_{LS} (Å)	Suspected TAGs
Granular crystal center portion	Before 5 days	14	61.5 42.4	POPβ,β' (β > β')+PPPβ'
	After 2 weeks	20	61.2	POPβ,β' (β > β')
Thin crystalline layer		12	61.6	POPβ
Surface		30	42.4	PPPβ'

Melting points, long lattice spacing, and short lattice spacing of each part of granular crystals.

5.Conclusion

Model of growth process of granular crystal:



According to this study, the normal region of palm oil-containing margarine is mainly composed of the metastable β' -form with double-chain-length of POP. The temperature change treatment between 5 ℃ and 15 ℃ promotes the polymorphic transition of the β' -form with double-chain-length of POP crystals changes to β-form with triple-chain-length structure. With increasing storage time, PPP migrate from the interior to the exterior of granular crystals, localize, and form surface regions.

6.Acknowledgement

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