Direct Observation of the Crystallization Process of Cocoa Butter Using a Transmission Electron Microscope (TEM)

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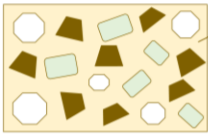
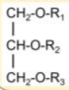
1. Introduction

<Chocolate>

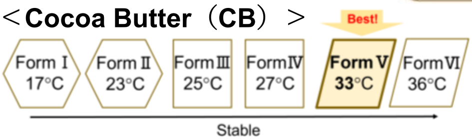


Cocoa butter determines the physical properties of chocolate, such as snap and mouthfeel.



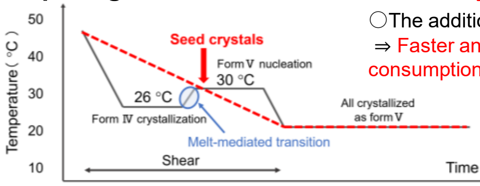
Triacylglycerol ⇒POP, POS, and SOS account for about 80%.

<Cocoa Butter (CB)>



⇒It is important to control the polymorph to **Form Ⅴ** of CB.

<Tempering and The addition of seed crystals>



○The addition of seed crystals ⇒ Faster and lower energy consumption than tempering.

< Objectives of this Study >

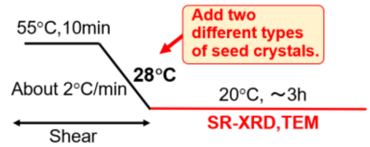
To clarify the crystallization process of CB by adding seed crystals by means of TEM and synchrotron radiation X-ray diffraction (SR-XRD) measurements.

2. Method

<Sample>

- Cocoa butter
- Seed crystals
  - ① Crystallization accelerator 1wt% (**Form Ⅵ**)
  - ② Chocolate particles 2wt% (**Form Ⅴ**)

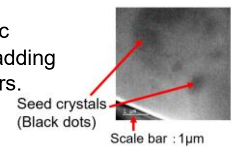
<Temperature conditions>

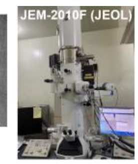


<TEM>

Using a solution cell, the polymorphic transition of CB was observed after adding seed crystals at 20 °C for 2 to 3 hours.

Kimura Laboratory: ILTS, Hokkaido Univ.

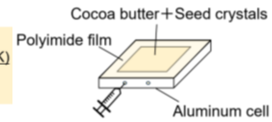


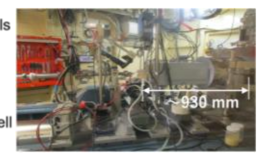


<SR-XRD>

- Observation of the crystallization process from seed crystals at 20 °C for one hour.

High Energy Accelerator Research Organization (KEK)
Photon Factory BL-6A
Wavelength : 1.50Å





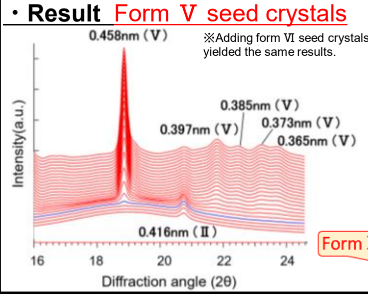
- Analysis of Surface Roughness

Camera distance : Just under 1 meter・・・A somewhat short distance for SAXS measurements.

3. Results and discussions

<SR-XRD (WAXS)>

・Result Form Ⅴ seed crystals

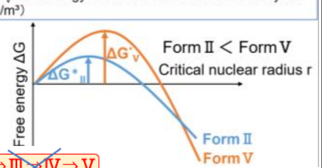


・Discussion

$$\Delta G^* = \frac{16\pi\gamma^3}{3\Delta G_v^2}$$

The influence of γ is dominant. Interfacial : Form Ⅱ < Form Ⅴ

γ: Interfacial energy between crystals and melt (J/m²)
ΔG_v: Free enagy difference between melt and crystal (J/m³)



Form Ⅱ ⇒ ~~Ⅲ ⇒ Ⅳ~~ ⇒ Ⅴ

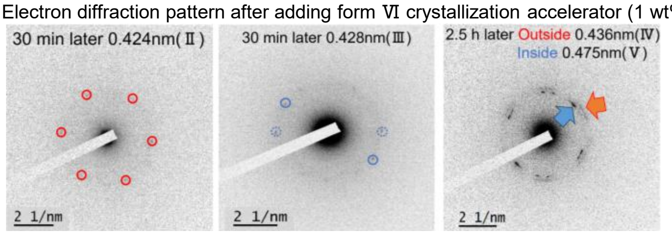
The Ostwald's step rule is limited!

<TEM>

※ Photographing at different locations

・Result ① Form Ⅵ seed crystals

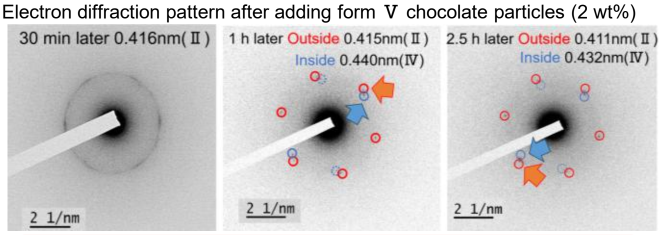
Electron diffraction pattern after adding form Ⅵ crystallization accelerator (1 wt%)



Form Ⅱ was transformed to Form Ⅴ via Form Ⅲ and Ⅳ
⇒ Establishment of Ostwald's step rule

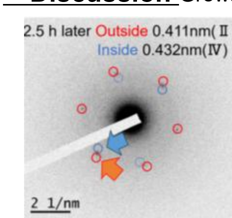
・Result ② Form Ⅴ seed crystals

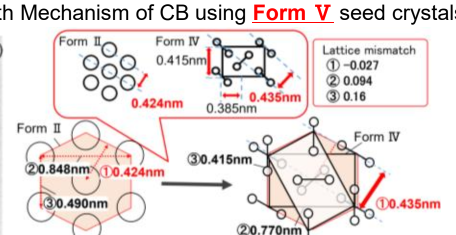
Electron diffraction pattern after adding form Ⅴ chocolate particles (2 wt%)



Form Ⅱ and Form Ⅳ spots were observed in close locations

・Discussion Growth Mechanism of CB using **Form Ⅴ** seed crystals

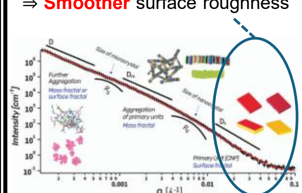




Form Ⅳ was grown on Form Ⅱ with aligned directions

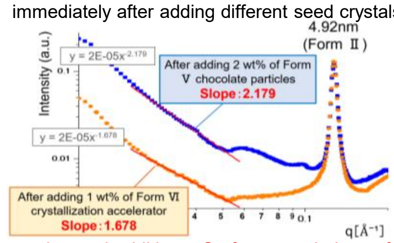
<SR-XRD (Analysis of Surface Roughness)>

Larger slope value
⇒ **Smoother** surface roughness



Alejandro G. Marangoni.et.al :*Soft Matter*, 2020, 16, 289-306

○Form Ⅱ particle surface morphology immediately after adding different seed crystals



Form Ⅴ exhibits greater slope after seed crystal addition = Surface morphology of Form Ⅱ is smoother. ⇒ The surface structure of Form Ⅱ varies depending on the seed crystals form, and the smoother one is more likely to become a Form Ⅳ substrate. Form Ⅱ is smooth after introducing Form Ⅴ seed crystals.

4. Conclusion

Polymorphic transition to stable polymorphs according to Ostwald's step rule.

Form Ⅵ seed crystals: Form Ⅲ, Ⅳ, and Ⅴ crystals formed without using form Ⅱ as a substrate.

Form Ⅴ seed crystals: Form Ⅳ crystal grew on top of Form Ⅱ crystal with aligned orientations.

⇒ Differences in seed crystals structure influenced the surface roughness of Form Ⅱ, resulting in distinct growth patterns.