Transactions of the Materials Research Society of Japan 33[3] 641-644 (2008)

New Polymorphisms in the Surface Region of Cocoa Butter Studied by X-ray Diffraction

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Natural cocoa butter is known to exhibit five structural phase transitions. In situ observation on these phase transitions in surface region has been performed by a combination of grazing incidence X-ray diffraction and X-ray Reflectivity (XR) to compare the phase transitions in bulk. A surface-induced preferred orientation of constituent oil molecules is found, of which origin is the same as the diffuse scattering observed in bulk samples. A novel double-layer to single-layer phase transition is found by XR of Si-supported ultrathin films with thickness of several nm, indicating the anisotropic nature of inter molecular interactions.

Key words: cocoa butter, polymorphism, surface, ultra thin film

1. Introduction

Cocoa butter, as a main constituent of chocolate is widely used in the manufacture of confectionery, cosmetics, as well as drags. Not a few people who are engaged in these industries know that cocoa butter possesses at least six forms[1], and the most stable form is known to be the highest temperature phase called type VI (Table I). Although the other forms tend to transform to type VI in time, type VI is not favourable for consumers of chocolate due to some difficulty of dissolving in mouth. Natural cocoa butter is composed of several similar oils: POP (sn-1,3-dipalmitoyl-2-oleoylglycerol), SOS (sn-1,3-dipalmitoyl-2-stearoyl-glycerol), POS (1,3-rac-palmitoyl-stearoyl-2-oleoylglycerol), etc. Figure 1 shows an illustration of stable molecular stacking of POP and SOS molecules[2]. It is called a triple-chain stacking which can be seen in type V and VI crystallites. In the triple-chain stacking, there are two characteristic lengths: *a* axis length is ~0.5 nm and *c* axis length is ~6 nm, respectively.

Form	typeI	type II	typeIII	typeIV	typeV	typeVI
Melting point [°C]	**17.3**	**23.3**	**25.5**	**27.5**	**33.8**	**36.3**
a [nm]	**0.42**	**0.42**	**0.43**	**0.44**	**0.46**	**0.46**
c [nm]	**5.45**	**4.90**	**4.91**	**4.50**	**6.41**	**6.38**

Table I, Melting points of polymorphic forms. [1, 3]

There are a lot of studies on phase transitions of bulk cocoa butter [4-8], but little has been reported on them in a surface region. In this paper, we perform comparison between phase transitions in bulk and those in the surface region by a combination of conventional grazing incidence X-ray diffraction (GIXD) and X-ray Reflectivity (XR). A surface-induced preferred orientation in type V and diffuse scattering from the molten bulk are found, both of which tells us the anisotropic feature of inter molecular interactions. We also successfully form ultrathin films with several nm thick served to reveal a novel phase transformation in quasi-2D system.

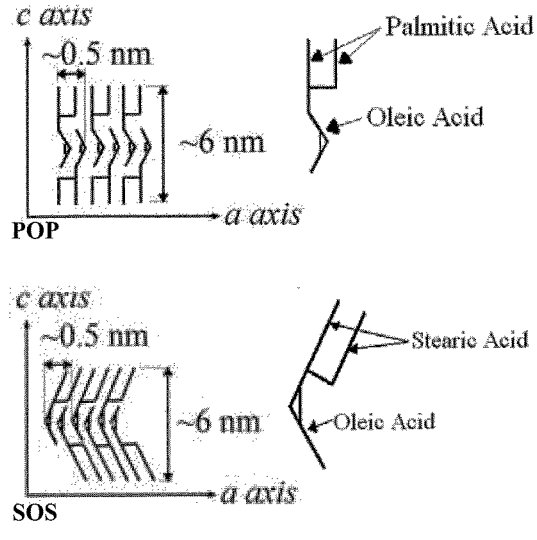


Fig.1 Illustrations of triple-chain molecular stacking of POP and SOS (Left). Schematic representation of POP and SOS are also shown (Right).[2]

2. Experimental

As for the X-ray diffraction for investigating the surface region, we exploited XR and GIXD. Each technique uses total reflection of X-rays, but they give us different information. XR affords precise values of thickness, electron density, and parameters describing surface morphology, e.g., roughness of surface and interface. GIXD is quite sensitive to the crystal structure, crystallinity, and preferred orientation in the surface region.

Natural cocoa butter (Fuji Oil Co., Ltd.) was stuffed into a sample holder with dimensions of 10 mm X 10 mm X 2 mm, and the surface (10 mm X 10 mm in area) was smoothed by a butter knife. Ultrathin films were formed on Si (100) wafers by spin coating method with rotation speed of 3000 rpm. Acetone was used as a

solvent and concentration of cocoa butter was 10 mg/5ml. Sample temperature was monitored by a thermocouple adjacent to the sample holder glued on a home-made heater. The heater was attached on an X-ray diffractometer (CuKα1 radiation, 40 kV X 120 mA, RUH-450, Rigaku Co. Ltd.).

3. Results and Discussion

Figure 2 shows diffraction profiles of cocoa butter measured by GIXD. The profiles indicate that the sample is a mixture of type V and VI. Here, Bragg reflections can be classified by two groups: a bunch of Bragg reflections with $2\theta < 10$ degrees (low-angle Bragg reflections) and those with $2\theta > 10$ degrees (high-angle Bragg reflections). The low-angle ones contain information on molecular stacking along the *c* axis direction, whereas the high-angles Bragg reflections mainly reflect the stacking along the *a* axis direction. Intensity ratio of low-angle Bragg reflection at $2\theta = 6.6$ degrees which corresponds to (005) reflection of type V and high-angle Bragg reflections would tell us a preferred orientation in the surface region where *c* axis of many crystallites are aligned along surface normal direction, e.g. the ratio of (005) reflection and reflection at $2\theta = 19.0$ degrees (it should be one of the (10*l*) reflections) of surface region is about 1.5 (upper graph of Fig.2), whereas that of bulk is about unity (lower graph). Diffraction arcs of low-angle Bragg reflections indexed as (00*l*) shown in Fig. 3 also support the surface-induced preferred orientation.

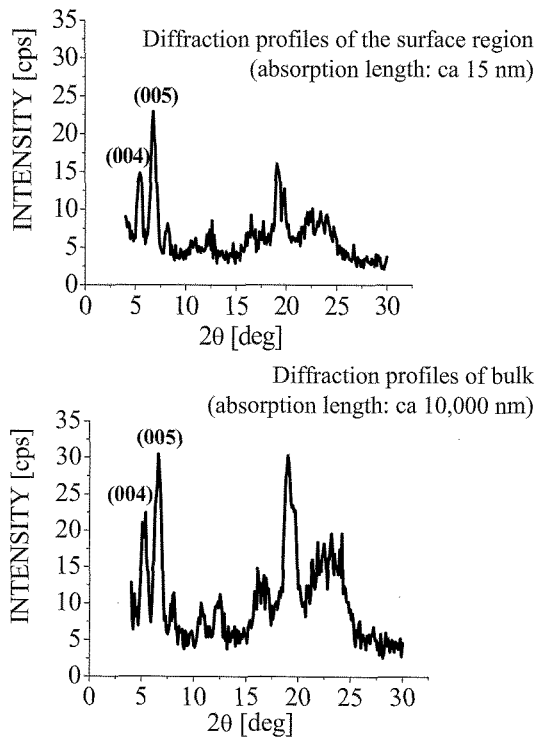


Fig.2 Diffraction profiles at room temperature. In the upper graph, angle of incidence of GIXD was chosen to be 0.05 degrees where diffraction occurs in the surface region to a depth of 15 nm. On the other hand, the lower graph represents bulk crystallinity since the incident angle was set to be 0.2 degrees which is greater than the critical angle for total reflection.

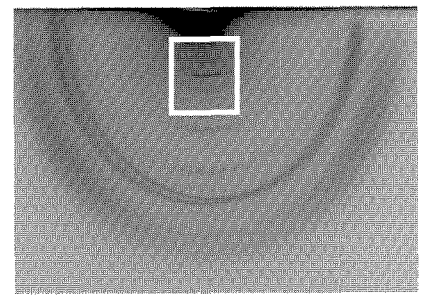


Fig.3 X-ray photograph by GIXD setting with absorption length of 15 nm. In the rectangle, there are arc-shaped (00*l*) reflections, having a contrast with high-angle reflections which indicate a much more isotropic distribution.

Figure 4 shows temperature dependence of GIXD with incident angle of 0.2 degrees. Integrated intensity of (005) and that at $2\theta = 19.0$ degrees are plotted in Figs. 5 and 6. Figure 5 shows that crystallinity along *c* axis direction monotonously decreases with increasing temperature, indicating the so-called long-range order in molecular stacking along this direction is partially destroyed and vanishes in type V[9]. However, Bragg reflection which represents the long-range order in molecular stacking (Fig.6) along *a* axis direction shows maximum in type V, and still remains in type VI. Therefore we can conclude that the molecular stacking along *a* axis direction is more robust than that along the *c* axis.Thermal behavior of diffuse scattering around $2\theta = 19.0$ degrees, i.e. sudden increase at 33 °C and trace in the diffraction profile at 40 °C, also suggests the strong intermolecular interaction along *a* axis direction. Namely, the short-range order of molecular stacking along the *a* axis direction still remains at high temperatures.

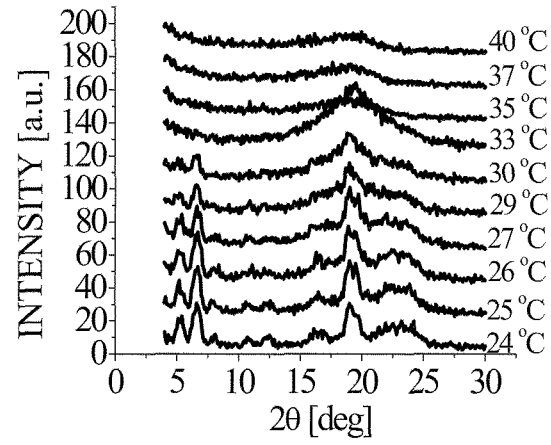


Fig.4 Temperature dependence of GIXD profiles. Angle of incidence was set to be 0.2 degrees. GIXD profiles with angle of incidence of 0.05 degrees were also measured, yielding the same temperature dependence (not shown). Temperature was raised from room temperature.

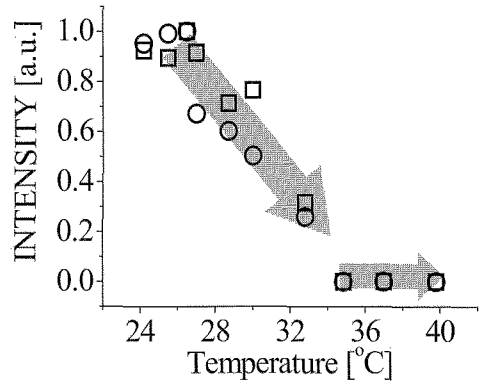


Fig.5 Integrated intensity of (005) reflection. Open circles represent the intensity obtained with incident angle = 0.2 deg., whereas squares are the intensity with incident angle = 0.05 deg. Thick arrows are guide to eyes.

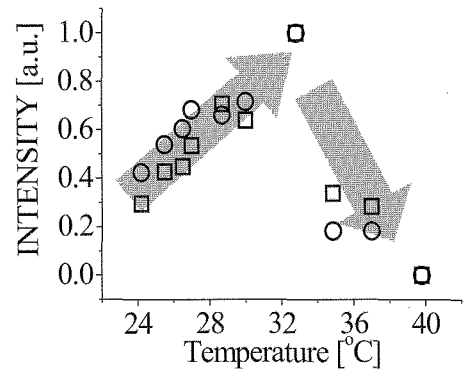


Fig.6 Integrated intensity of Bragg reflection situated at 2θ = 19.0 degrees. Open circles represent the intensity obtained with incident angle = 0.2 deg., whereas squares are the intensity with incident angle = 0.05 deg. Thick arrows are guide to eyes.

Figure 7 shows XRs at various temperatures. Electron density (Fig.8) and thickness (Fig.9) of the film were obtained by least squares fittings. Figure 8 indicates that there is a continuous increase in electron density of the thin film between 26 °C to 39 °C. Since electron density of bulk cocoa butter is about 0.25 electrons/A^3, it is quite likely that cocoa butter forms a partly covered layer on Si wafer. As shown in Fig. 10 (a), after an evaporation of the solvent, cocoa butter forms a dewetted thin layer which consists of a lot of islands with uniform thickness and islands with different size. The former (denoted as "coherent") scatters X-ray coherently to produce the Kiessig fringe pattern in XR, although the latter (denoted as "incoherent") would not contribute to the constructive interference in XR due to the irregularities of size. Average electron density obtained by analysis of XR thus reflects the coverage of the "coherent" islands[10,11,12]. With elevating temperature, thermally-activated islands coalesce into larger "coherent" islands to increase the coverage, as illustrated in Figs. 10 (b) and (c). Coverage of cocoa butter is found to attain 70 % at 39 °C (Fig. 8).

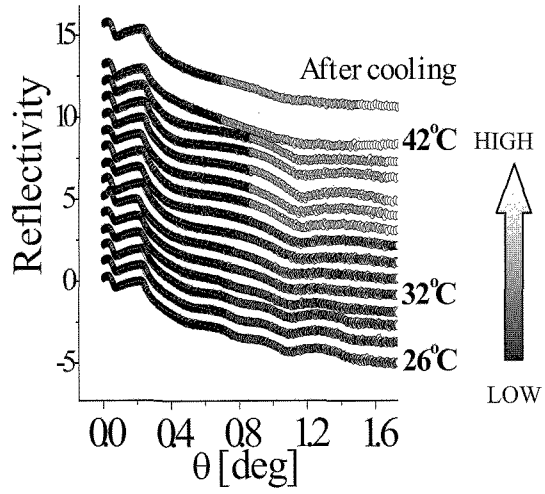


Fig.7 X-ray reflectivity at various temperatures. For Clarity, each XR is shifted vertically. XR was measured during the heating. XR shown in the top is collected at 24 °C after cooling from 42 °C.

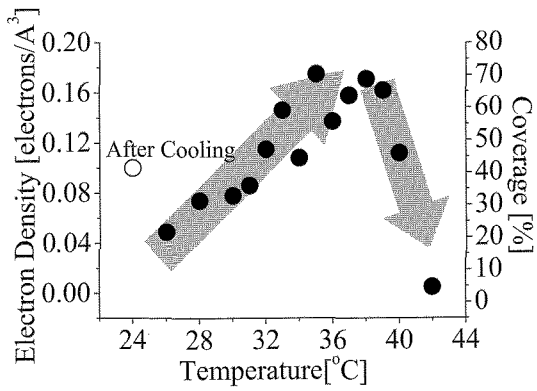


Fig.8 Electron density of ultra thin film. Thick arrows are guide to eyes.

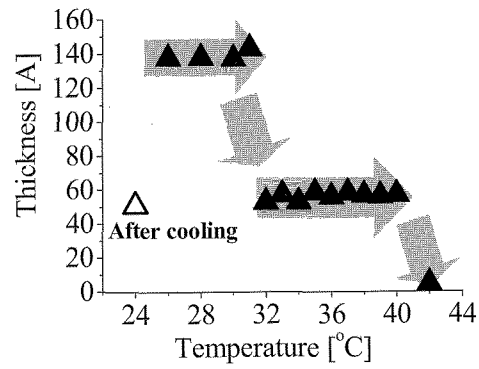
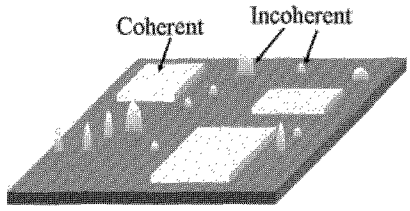
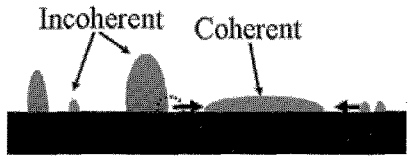


Fig.9 Thickness of ultra thin film. Thick arrows are guide to eyes.

(a) Coverage is about 20 % at 26 °C



(b) Coverage increases between 26 – 39 °C



(c) Coverage is about 70 % at 39 °C

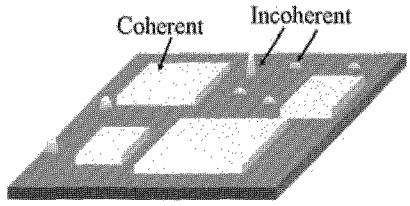


Fig.10 Illustrations of cocoa butter ultrathin film on Si(100) speculated by temperature dependence of electron density. In (b), a side view is shown. The increase in electron density at higher temperatures can be explained by formation of the uniform layer with constant thickness throughout thermally-induced coalition of cocoa butter droplets with different sizes which scatter the X-ray incoherently into backgrounds.

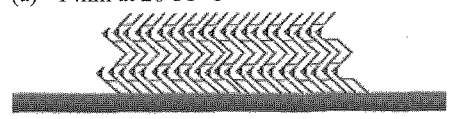
Obtained thickness vs. temperature (Fig. 9) indicates that there is a drastic change in thickness at 32 °C and 42 °C. Since thickness between 24 °C and 32 °C almost corresponds to the double of the *c* axis length, it is quite likely that the "coherent" films with uniform thickness are a double-layer structure of triple-chain stacking with the *c* axis aligned in surface normal direction as schematically shown in Fig. 11 (a). Furthermore, the film between 32 °C and 40 °C would consist of a single layer triple-chain stacking (Fig.11 (b)), accompanying a double- to single-layer transition at 32 °C. It is remarkable that the single-layer structure remains above the melting point of type VI, presumably indicating the strong interaction along the *a* axis direction suggested by the diffuse scattering around 2θ =19 degrees above 33 °C. From the drop in electron density and thickness at 42 °C, we consider that cocoa butter cannot sustain the uniform layer above this temperature (Fig. 11 (c)).

4. Conclusions

GIXD and XR of natural cocoa butter reveal the surface-induced preferred orientation and the double-layer to single-layer transition. Strong diffuse scattering from the bulk and anomalous stability of the single-layer structure are confirmed at high temperatures. All the results strongly claim the fact that the inter molecular interaction in triple-chain stacking of POP and SOS molecules along the *a* axis direction is much stronger than that along the *c* axis direction. We consider that the double-layer structure and single-layer structure observed in ultrathin films would be new polymorphisms peculiar to the quasi-2D system.

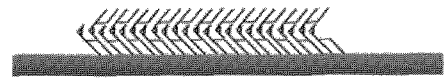
Part of this study was financially supported by The Promotion and Mutual Aid Corporation for Private Schools of Japan (The Science Research Promotion Fund in 2006 and 2007).

(a) ~14nm at 26-31 °C



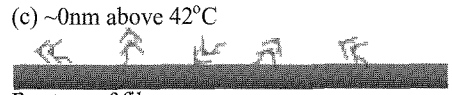
Double layer

(b) ~6nm at 32 °C-40°C



Single layer, stable above melting

(c) ~0nm above 42°C



Rupture of film

Fig.11 A model of ultrathin film

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(Recieved December 10, 2007 ; Accepted February 23, 2008)