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Communications

Novel Shear-Induced Phases in Cocoa Butter

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Ⓜ This paper contains enhanced objects available on the Internet at <http://pubs.acs.org/crystal>.

ABSTRACT: We report on the discovery of a new solid phase in cocoa butter, the main structural component of chocolate. We also report on novel effects of shear on the phase behavior of this material. These findings are both of fundamental and industrial interest, since the properties of solid fat networks are determined by their microstructure and polymorphic crystalline state.

In this communication, we report on the discovery of a new solid phase in cocoa butter, the main structural component of chocolate. We also report on novel effects of shear on the phase behavior of this material. These findings are both of fundamental and industrial interest, since the properties of solid fat networks are determined by their microstructure and polymorphic crystalline state.^{1,2} The type of microstructure formed strongly depends on the thermal and shear treatment history of the material,³ but the effects of shear on phase transitions are not yet well understood.

Cocoa butter crystallizes in six generally recognized phases, identified by Roman numerals I to VI⁴ in order of melting temperature. Time-resolved synchrotron X-ray diffraction (XRD) studies are ideal for following the evolution of the crystalline phases and understand the genesis of the structures. The additional application of shear makes measurements difficult, so it is not surprising that only two in-situ XRD studies under shear have ever been published.^{5–7}

Although it has been known for a long time that shear induces the acceleration of the formation of the desirable phase V,^{8–10} it has only been recently documented that the application of shear induces cocoa butter to transform directly from phase III to phase V, bypassing phase IV.^{5,6} Shear can also induce significant orientation of the crystallites.⁵ In this communication, we demonstrate that the qualitative phase behavior is far more complex. Using synchrotron XRD and a special temperature-controlled shear cell, we found the presence of the phase IV under

certain shear-temperature conditions, as well as the existence of a new crystalline phase of cocoa butter, which we will refer to as phase X.

Experiments were conducted at ExxonMobil beamline X10A at the National Synchrotron Light Source (Brookhaven, NY), using a concentric cylinder Couette shear cell described elsewhere.⁵ Two different pairs of concentric cylinders were used, one with inner diameter of 39 mm and outer diameter of 41 mm, and one with inner diameter of 15 mm and outer diameter of 17 mm. Diffraction patterns of the low angle peaks (long *d* spacing) were collected continuously using a Bruker 1500 two-dimensional CCD detector, with exposure times of 50 s, located 1132 mm from the sample. Data were collected in the range $0.01 < q < 0.30 \text{ \AA}^{-1}$, where $q = (4\pi/\lambda) \sin \theta$, where 2θ is the diffraction angle and λ is the wavelength (1.097 Å). The *d* spacing can be computed using $d = 2\pi/q$. The beam size was 0.5×0.5 mm giving a resolution of $\sim 0.003 \text{ \AA}^{-1}$.

Two different samples of commercially available cocoa butter were used, one from Cacao de Zaan (Netherlands) and the other from Barry-Callebaut (Belgium). These will be referred to CZ and BC, respectively. The cocoa butter was heated to $\sim 50^\circ\text{C}$, and the shear rate was then continuously applied to the melt. The sample was kept liquid at 50°C for 30 min under shear before the temperature was decreased at a rate of $3^\circ\text{C}/\text{min}$ to the final temperature. Measurements with final temperature of 17.5°C were conducted for 30 min after reaching the crystallization temperature, those with a final temperature at 20°C for 45 to 60 min, and those with a final temperature of 22.5°C for 60 or 90 min.

Figure 1 shows selected X-ray diffraction patterns obtained from radial intensity averaging of the 2D scans captured by the detector. Most of the 2D scans display

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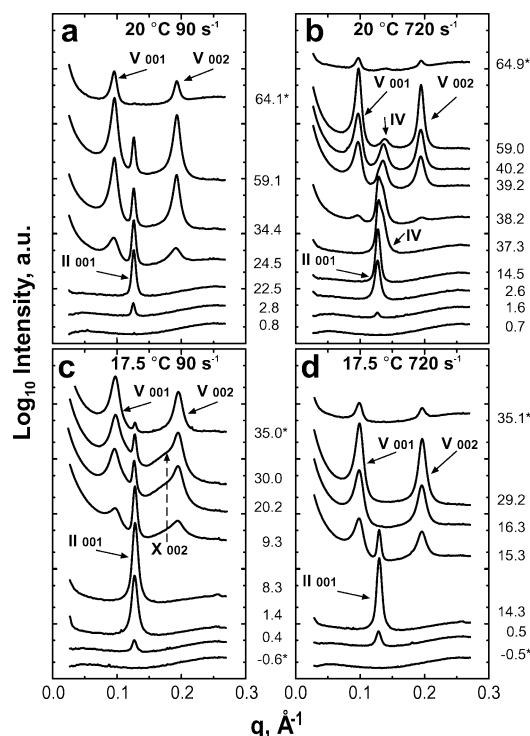


Figure 1. Selected synchrotron X-ray diffraction patterns from radial intensity averaging of two-dimensional scans. The times, measured in minutes from the moment the sample reaches the crystallization temperature, are printed at the right of each curve. The scans were taken at the crystallization temperature, except those indicated by an asterisk, taken at the end of the cooling ramp or during the subsequent heating. (a) Scans taken at a crystallization temperature of 20 °C and a shear rate of 90 s⁻¹. Scan at 64.1 min taken during subsequent heating at ~36 °C. (b) Scans taken at a crystallization temperature of 20 °C and a shear rate of 720 s⁻¹. Scan at 64.9 min taken during subsequent heating ~36 °C. (c) Scans taken at 17.5 °C and 90 s⁻¹. Scan at -0.6 min was taken during cooling at ~20 °C. Scan at 35.0 min was taken during subsequent heating at ~36 °C. (d) Scans taken at 17.5 °C and 720 s⁻¹. Scan at -0.5 min was taken during cooling at ~20 °C. Scan at 35.1 min was taken during subsequent heating at ~36 °C.

Ⓜ A movie in .mpg format of (a) and (b) is available.

Ⓜ A movie in .mpg format of (c) and (d) is available.

crystalline orientation,⁵ but we will focus here only on the phase behavior, which was observed not to be dependent on orientation. The scans progress in time from bottom to top, starting with the liquid fat. The times indicated in minutes are measured from the moment the sample reached the final temperature. The intensities are on a logarithmic scale, and are offset for clarity.

Figure 1a shows scans of cocoa butter cooled to 20 °C under a shear rate of 90 s⁻¹. The first crystalline phase to appear at 2.8 min corresponds to either phase II or phase III, as indicated by the peak at $q = 0.127 \text{ \AA}^{-1}$. In the small angle region, the only reported difference between these two forms is the presence of a weak (002) reflection in phase III that is supposedly absent in phase II.⁴ This (002) reflection was not observed here, but as its intensity is weak, it is difficult to discern the actual phase without access to detailed wide angle scattering information. Preliminary studies of the wide angle scattering data indicate that this peak represents phase II, but the coexistence of phase III cannot be ruled out. We will therefore tentatively refer to this peak as phase II.

This phase II peak grew until 22.5 min, when phase V was first observed at $q_{001} = 0.0974 \text{ \AA}^{-1}$ and $q_{002} = 0.195$

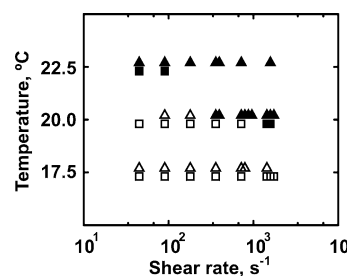


Figure 2. Diagram of the existence of the phase IV depending on shear rate and final temperature. The CZ and BC cocoa butters are represented by triangles and squares, respectively. A filled symbol (▲, ■) indicates that phase IV was present, and a clear symbol (△, □) indicates that it was absent.

\AA^{-1} , consistent with previous reports.^{5,6} The transition coincides with a dramatic increase in SAXS intensity, indicating the formation of numerous small crystallites. The intensity of the phase II reflection was reduced but did not vanish with the formation of phase V, demonstrating the coexistence of both phases. Upon heating, phase II disappeared before phase V, consistent with their melting points.¹¹

Results for cocoa butter cooled to 20 °C under an applied shear rate of 720 s⁻¹ are shown in Figure 1b. As in the low shear case, a phase at $q = 0.127 \text{ \AA}^{-1}$ appeared early on, indicating again the formation of tentative phase II. After 15.5 min, a peak at $q = 0.137 \text{ \AA}^{-1}$ started to grow. The position of this peak is consistent with the characteristic reflection of phase IV,⁴ which had not been previously reported under shear.^{5,6} At 38.2 min, phase V was first evident, together with a very strong increase in small angle scattering. Simultaneously, the phase II and IV peak intensities decreased, with the phase II peak vanishing at time 40.2 min. In contrast, phase IV persisted until the sample was completely melted. Upon heating both forms IV and V melted simultaneously. The melting point of phase IV has been reported¹¹ to be between 26 and 28 °C, while that of phase V is between 31 and 34 °C. However, it is interesting that phase IV did not disappear before phase V, as phase III did in Figure 1a. A possible explanation is the presence of another phase with similar peak position as phase IV. This type of phase has been reported to occur in the tristearin-rich high melting fraction of cocoa butter.¹² Another possible explanation is that phase IV was encapsulated and sterically stabilized by phase V.

A state diagram indicating the conditions for the formation of phase IV is presented in Figure 2 for the two cocoa butters studied. Filled symbols represent the conditions where phase IV was detected. It can be appreciated that high shear rates and high crystallization temperatures favor the formation of phase IV. Phase IV was not found in any of our experiments at 17.5 °C: in those cases, the transition happened directly from the putative phase II to phase V.

The precise temperature-shear boundary for formation of phase IV, in a diagram like Figure 2, depends on the composition of the material used. The somewhat different responses of the two cocoa butter samples in the experiments illustrate this. The BC cocoa butter showed a greater tendency to go into phase V, bypassing phase IV.

Phase II persists after the formation of phase V at the low shear rate of 90 s⁻¹ and final cooling temperature of 20.0 °C (Figure 1a) and 17.5 °C (Figure 1c). This was not observed under a shear rate of 720 s⁻¹ for these two final temperatures (Figures 1b,d).

The new, previously unreported phase in cocoa butter under shear can be seen in Figure 1c (final temperature of

17.5 °C and shear rate of 90 s⁻¹), where phase II emerges initially, and phase V appears at 9.3 min. In addition, a second peak to the left of the phase V (002) reflection can be clearly seen, as indicated by the prominent shoulder on the phase V peak. Least squares curve fitting indicates that the peak position of this new phase is at $q = 0.179 \text{ \AA}^{-1}$ and that a (001) peak can be weakly observed at the left of the phase V (001) reflection. This peak corresponds to a d spacing in the (001) direction of 70.2 Å. We will refer to this phase as phase X. Phase X was observed in both samples of cocoa butter (BC and CZ) and in both the small and the large Couette cells, and was not absent in any experiments conducted under the conditions described above.

Phase X appears simultaneously with phase V at low shear rates and final temperature of 17.5 °C, and was not detected at higher shear rates (Figure 1d) and higher final temperatures. Upon heating, the phase X melts before phase V, as can be seen comparing the scans taken at 30 and 35 min in Figure 1c, indicating that phase X has a lower melting point than phase V.

The d spacing and melting point of phase X were compared with data reported in the literature for cocoa butter fractions and its crystallized components.^{2,11–19} The relatively large d spacing is consistent with the 3L structures formed by triacylglycerides with at least one stearyl group.^{13–16} Pure fractions containing a stearyl group have high melting points,^{12–16} while mixtures exhibit a depression of the melting point.¹⁷ The observed low melting point could then be consistent with phase X being a fractionation induced mixture rich in SOS (1,3-distearoyl-2-oleyl-glycerol) and POS (1-palmitoyl-2-oleyl-3-stearyl-glycerol), which are two of the three main components of cocoa butter.

To conclude, we have reported the existence of a new phase of cocoa butter not previously observed under static conditions, as well as the previously unreported existence of the phase IV structured under shear. Both findings point toward an important effect of shear on the distinct chemical composition and physical characteristics of new phases of cocoa butter, and have potential significant implications for the final structure of cocoa butter and chocolate products that merit considerable further study.

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