European Synchrotron Radiation Facility

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Application for beam time at ESRF – Experimental Method

This document should consist of a maximum of two A4 pages

Aims of the experiment and scientific background

Polymorphism of cocoa butter has a large impact on the product quality of chocolate and confectioneries. Depending on the triglyceride composition of a fat, a different number of polymorphic phases are known. For cocoa butter six forms are generally recognised: γ, α, β_{III}, β_{IV}, β_{V} and β_{VI}. Form β_{V} is desired in the final chocolate product and can only be established by applying a pecrystallisation step. Recently, a new precrystallisation process was developed at our institute, based on seeding with cocoa butter crystals. The suspension used for seeding is obtained by applying high shear to liquid cocoa butter at low temperatures. Using DSC, NMR, XRPD and rheologic analysis methods it has been shown that under shear the α-polymorph is generated first and then transformed directly into a mixture of β_{V} and β_{VI} polymorphs [1, 2]. However, under static conditions α is converted over form β_{III} and β_{IV} into β_{V} [3]. Static time resolved XRPD measurements have been performed within our laboratory but for the fast transformations under shear, synchrotron radiation is highly needed.

In literature only few experiments exist where cocoa butter has been measured under shear using synchrotron X-ray diffraction. Mazzanti *et al.* [4, 5] did investigations at two different shear rates. MacMillan *et al.* [6] investigated the transformation from β_{III} into β_{V} of cocoa butter using a cone and plate geometry at low shear rates. Phase formation and transformation is highly depending on cooling rate, final temperature and applied shear rate. However, systematic investigations of the influence of temperature and shear rate using synchrotron X-ray diffraction are still missing.

Our aim is to understand the kinetics of polymorphic transformation of cocoa butter under shear at different temperatures and different shear rates which cover a much wider range than published so far. As explained above, under shear form β_{V} is meant to develop directly from form α or even directly from the melt, depending on the temperature set. Using only SAXS the diffraction pattern (peaks at $q = 0.97$ and $q = 1.95\ \mathrm{nm}^{-1}$) does not show significant difference between form β_{V} and form β_{VI}. To be sure, whether form β_{V} or even form β_{VI} is developing it is essential to use SAXS and WAXS (peaks between $q = 22$ and $q = 38\ \mathrm{nm}^{-1}$).

Preliminary test at ESRF were run at beamline ID2 in July 2005. Liquid cocoa butter has been measured under shear in a rheometer (Haake RheoStress 300) using a couette cell of polycarbonate with a shear rate of $1000\ \mathrm{s}^{-1}$ and a waterbath temperature of 13 °C. In the SAXS region the fast transition of form α into form β_{V} is clearly visible in figure 1. The data can also be related to the rheological measurement given in figure 2. The first plateau and the subsequent steep increase of viscosity represent the formation of α crystals.

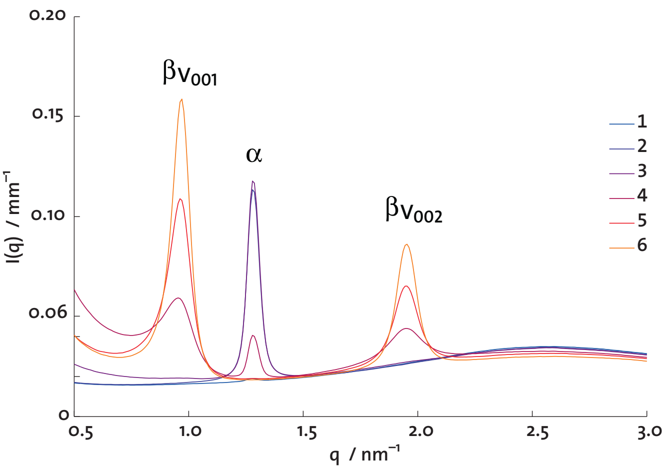

Fig. 1: Time-resolved synchrotron radiation X-ray diffraction patterns. Development of form α (2) and transformation into form β_{V} (6).

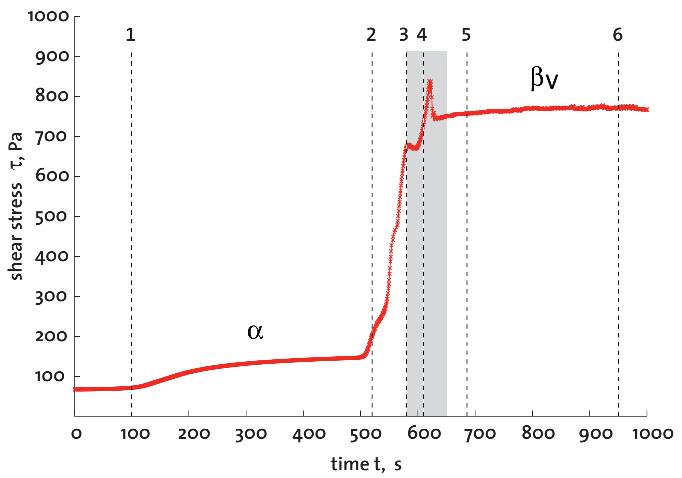

Fig. 2: Development of the shear stress during crystallisation and polymorph transformation at a constant shear rate of $1000\ \mathrm{s}^{-1}$. The dotted lines refer to the diffraction patterns from figure 1. The grey area marks the time frame where α and β_{V} are coexisting.

The transformation α to β_V seems to be stress driven, as it occures at 700 Pas. Further tests with lower shear rates (10 and 100 s^{-1}) and different temperatures have been done. They showed a clear dependence on shear rate and temperature. Additional peaks were observed, which are not explained yet in literature. Moreover, a slight shift of the spacings during crystal growth could be observed which most probably is caused by triglyceride purification in the crystal structure [7]. These preliminary tests proofed our previous assumptions and encourage to do systematic measurements to investigate the dependence of cocoa butter transformation in more detail by varying shear rate and temperature. Also, the unexpected peaks are of high interest in respect of the conditions of occurence.

As mentioned above, temperature control is of utmost importance. An *improved shear cell* will be constructed and provided by our institute. The outer cylinder is constructed with a double wall of stainless steel allowing efficient heat removal from the shearing zone while crystallising. In the two regions where the beam passes through, polycarbonate inlays will be mounted. Fast cooling is obtained with an inlet valve and heating rates can be achieved by remote control of the thermostat. The rotor available at beamline ID2 can be used without modifications.

Experimental method

As *sample preparation* cocoa butter is melted at 50 °C. The liquid cocoa butter is poured into the measuring cell and subsequently the measurement has to be started. Shear rates of 10, 100 and 1000 s^{-1} will be applied (as has been proven to be possible in previous tests). The measureing cell has to be tempered by a thermostat and will be run at 15, 18 and 20 °C (knowing that transformation should vary significantly with these conditions by our preliminary tests at ESRF and with the different analysis methods used described above). Depending on the processing conditions crystal formation can be detected after 50 to 300 s. A single run lasts 2 – 4 hours.

Results expected

As seen in preliminary tests, transformation from α-form into β_V under shear was depending on the shear rate. Roughly half of the time was needed to initiate transformation when the shear rate was increased from 10 to 1000 s^{-1}. Above approximately 23 °C cocoa butter will crystallise from the melt directly into form β_V. In the initial stage of crystal formation a shoulder could be observed at $q = 1.7\ nm^{-1}$. This shoulder was at a similar position as phase X only described by Mazzanti *et al.* [5].

Applying shear rates of 10, 100 and 1000 s^{-1} in combination with different temperatures should provide a detailed picture about the impact on crystallisation kinetics of cocoa butter. Moreover, it should be possible to relate the development of additional peaks in the diffraction patterns to the processing conditions.

Concluding remarks

Triglycerides are complex biomolecules which can crystallise in six known crystal forms. The processing conditions have a big impact on the crystallisation behaviour. Due to the complex nature of the system and the fast transformation under shear conventional XRD measurements are not applicable. For identifying small changes in the diffraction patterns in combination with a sufficient time resolution a high brilliant, collimated X-ray beam is indispensable for these experiments. Preliminary tests at ESRF were run to check feasability and showed encouraging results.

References

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