



Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:
<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal (“relevant report”)

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a “*preliminary report*”),
- even for experiments whose scientific area is different from the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as “relevant report(s)” in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



Experiment title: Understanding of the crystallization behaviour and kinetics of cocoa butter and cocoa butter equivalents for rational design of more sustainable chocolate products

Experiment number: SC-5324

| | | |
|--------------------------|---|--------------------------------------|
| Beamline: ID02 | Date of experiment: from: 2/09/2022 to: 5/09/2022 | Date of report: 23/01/2023 |
| Shifts: 9 | Local contact(s): William Chevremont | <i>Received at ESRF:</i> |

Names and affiliations of applicants (* indicates experimentalists):

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Report:

For the experiments we used the rheometer setup available on ID02. We chose the sample holder in polymeric material as it was better for heat transfer. It was clear after a few trials that the cooling capacity of the system was not sufficient. In fact, the Peltier was not able to quickly cool down below 25°C. Since we work with mixtures of edible triglycerides (TAGs) that are industrially crystallized at 15°C, this lower temperature was not sufficient. We then decided to increase the cooling capacity by flowing cold air on the sample holder. The air was coming from the hutch compressed air line and cooling was achieved by flowing it in a heat exchanger where the cold medium was water at 5°C from a chiller. We had to adjust the distance of the tube of flowing air to avoid local cold spots on the sample holder but after a few trials we managed to achieve the correct cooling capacity and reasonable uniformity. As a note for the beamline scientists, it might be useful to have a setup of the rheometer that can cool down fast and at temperature lower than ambient. This might be useful for soft matter people that work with food or pharmaceutical formulations like myself.

A photo of the setup is shown in Figure 1.

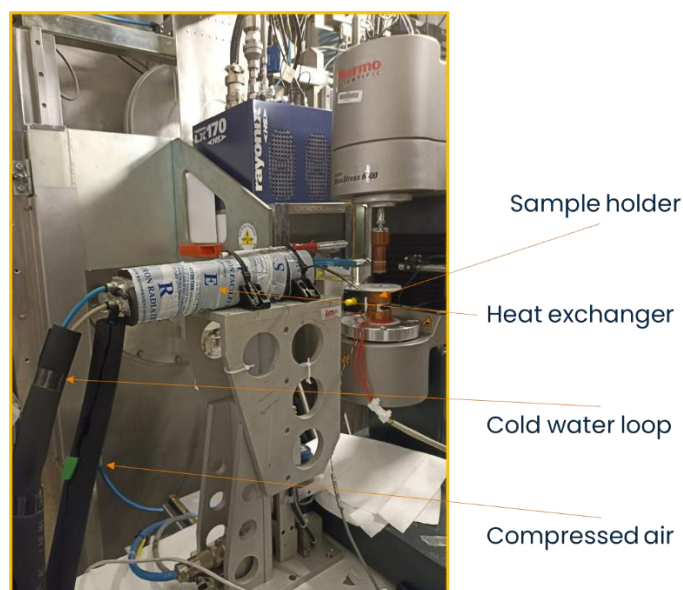


Figure 1: Setup used for the experiments to increase the cooling capacity of the rig.

The different mixtures of TAGs were loaded in the sample holder after melting a 50°C. The temperature was increased to 65°C and then a cooling rate of -2°C/min to 22-23°C was applied. In terms of shear we used 1000 s⁻¹, which was a typical value reported in the literature for these systems. To test the effect of shear we repeated the same experiment with and without shear. It was clear that shearing promoted nucleation and had a dramatic effect on the kinetics of polymorphic transformation, particularly in favour of the most stable polymorph β . Figure 2 shows the crystallization behaviour of cocoa butter (CB) with and without shear. While the nucleation temperature is very similar (around 24°C) the polymorphic behaviour is very different. In the case without shear the first crystal structure to appear is the α form, followed by the β' , which is still present after 1.5 hr of experiment. For this experiment we did not observe the more stable β crystal, consistently with our previous experiments in capillaries (smaller volume but still no shear).

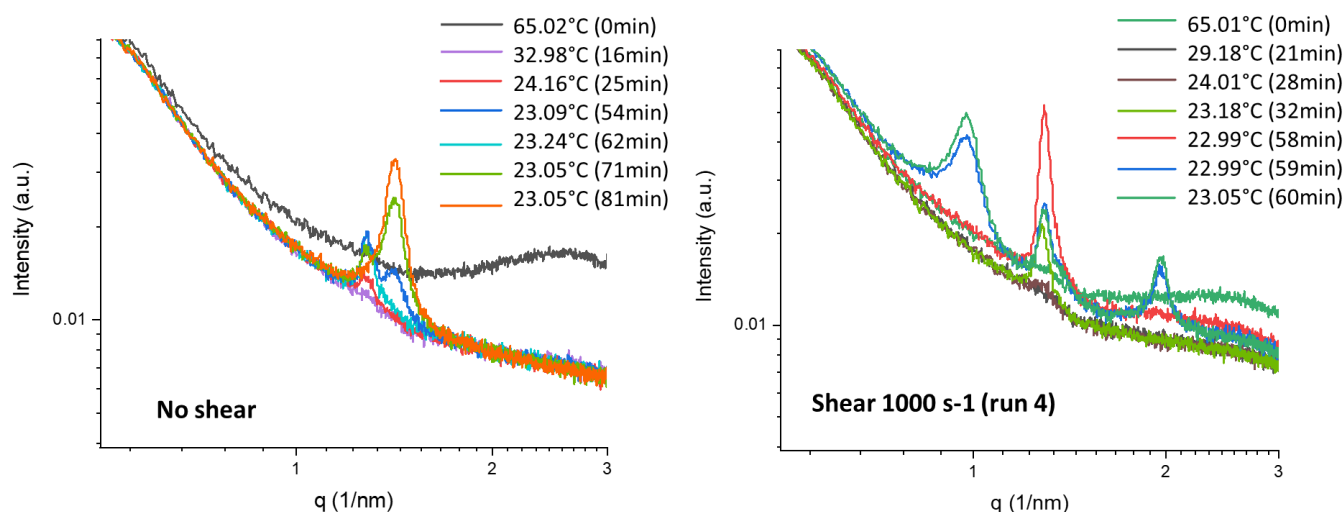


Figure 2: (left) crystallization of cocoa butter without shear and (right) with shear.

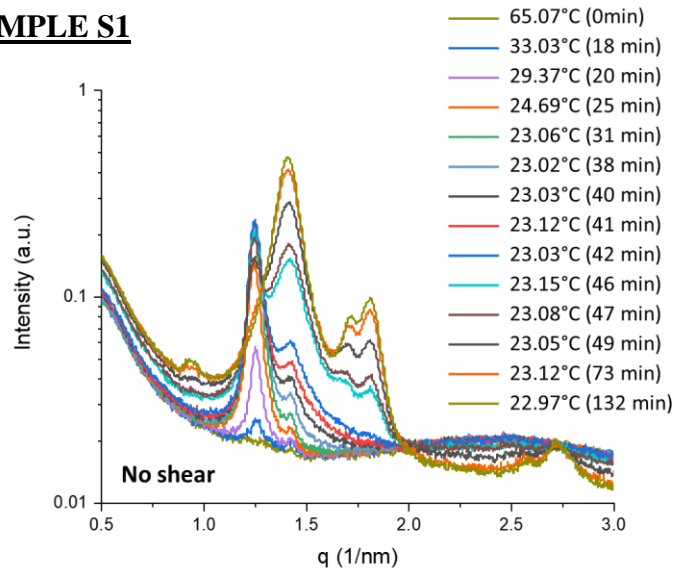
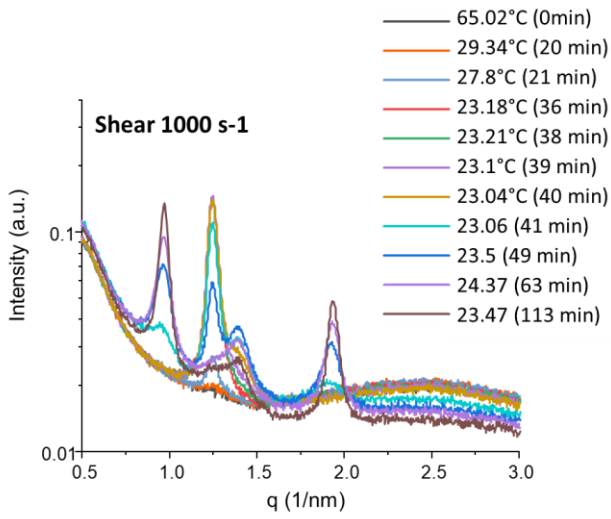
The stable polymorph appears after about an hour of the sheared experiments and grows very quickly at expense of the co-existing α polymorph. Interestingly the β' polymorph is not observed (perhaps it exists only in traces) for this experimental conditions. Slower cooling rates of -1 and -0.5°C/min were tested with the same sample and level of shear and similar behaviour was observed.

In fact, the tendency to transform quickly to the β polymorph, without the nucleation and growth of the β' , in the presence of shear was observed also in the cocoa butter equivalent (CBEs) samples (at different chemical composition compared to CB). This indicates that this is a genuine effect of the shear and does not depend on the CBE composition.

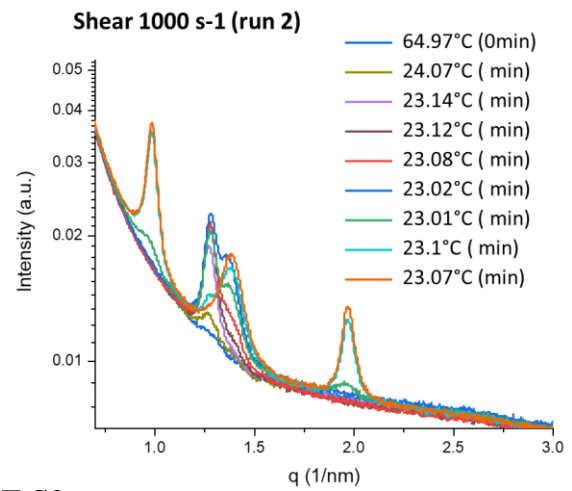
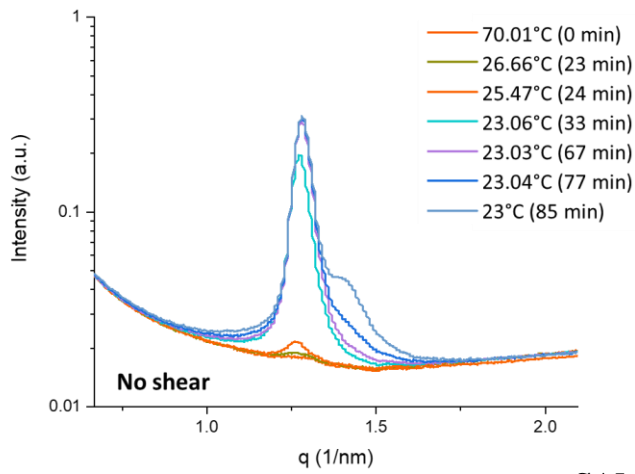
Figure 2 shows the comparison of sheared and not sheared crystallization for three different CBEs. S1 is more rich in TAGs coming from stearic acid, S2 has a higher concentration of palmitic acid while S7 presents a mixture of PPO and SSS together with the characteristic TAGs of CB (POP, SOS and POS). Finally, sample S13 does not contain trisaturated fats but it presents a significant amount (>1% w/w) of PPO, which can form a molecular compound with POP.

In all cases, similarly to CB the shear promotes the formation of the stable β polymorph. For sample S2 the β structure appears after about an hour of experiment and without the nucleation of the β' (only the liquid crystalline phase α is visible). Without shear the stable form is not observed, even after 2 hrs of isothermal conditions. For sample S1, in unsheared conditions several polymorphs are observed (α , γ , $\beta(3L)$, $\beta'(3L)$, $\beta'(2L)$), in agreement with previous data collection. For the sheared experiment only the most unstable γ , and $\beta'(3L)$ structures are not visible and the transformation towards the $\beta(3L)$ is faster. In the case of S7 and S13 the $\beta(3L)$ polymorph appears earlier compared to the unsheared conditions and the absence of the $\beta'(2L)$ is evident, similarly to CB. For these two samples a stable 2L structure (immiscible with the 3L form) is visible and appears earlier in sheared conditions compared to the non-sheared ones. This polymorph has a high melting temperature, even higher than the $\beta(3L)$ structure, indicating that it might be a $\beta(2L)$ polymorph. It is still unclear the nature of this structure, as a 2L arrangement of a β polymorph is relatively uncommon.

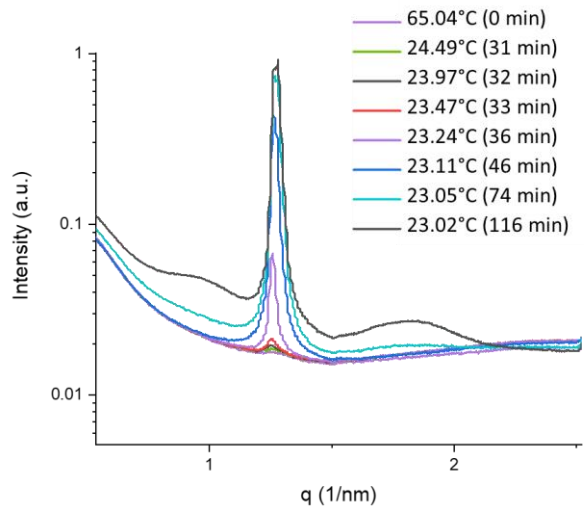
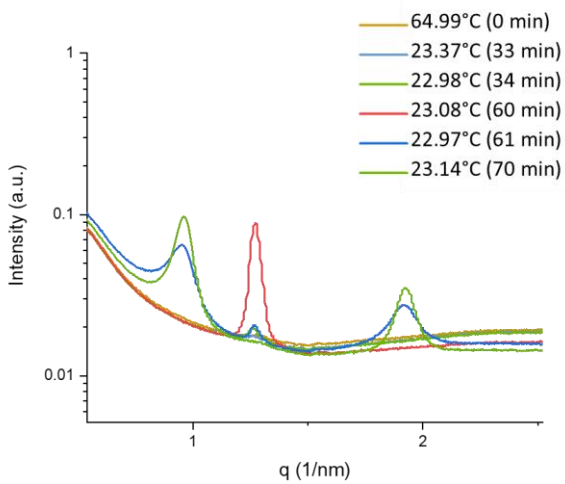
SAMPLE S1



SAMPLE S7



SAMPLE S2



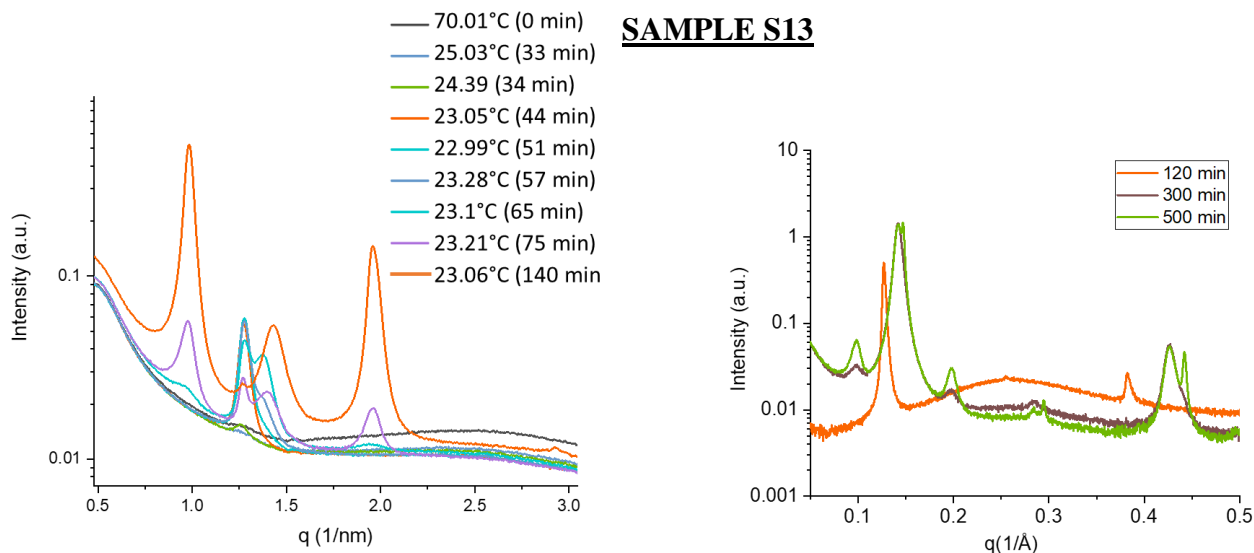


Figure 3: comparison of sheared and non-sheared crystallization

For S7 (and other samples tested such as S8) the presence of trisaturated TAGs (SSS or PPP), which are immiscible with the cocoa butter TAGs might be reason for this extra solid phase. In fact, the high melting point of trisaturated TAGs might be the explanation for the high melting point of this polymorph. However, sample S13 also present a high melting 2L structure but there are no trisaturated TAGs present. In this case, it is possible that this solid phase correspond to a PPO/POP molecular compound (which exist in a 2L arrangement). However, the melting point reported in the literature for this polymorph is around 30°C, much lower than what observed experimentally. Perhaps this structure is a solid solution containing also SOS, which might increase the melting point. A comparison of the d-spacings and the estimation of the electron density profile might help clarifying this problem.

In conclusion, it is very evident that the presence of shear significantly speeds up the transformation towards the more stable β polymorphs (3L and 2L) and inhibits the nucleation of the β' metastable form (2L). This is an interesting observation and more investigation is ongoing.

Finally, the use of the rheometer allowed to monitor the viscosity of the samples during crystallization. Nucleation was detected by a large change in viscosity while polymorphic transformations were not easily detected. Figure 4 shows some viscosity trends, the formation of the liquid crystalline phase α generate a very little change in viscosity while the formation of β structures (2 and 3L) is characterized by a more significant change due to both the higher amount of crystals and the rigidity of this structure compared to the α form.

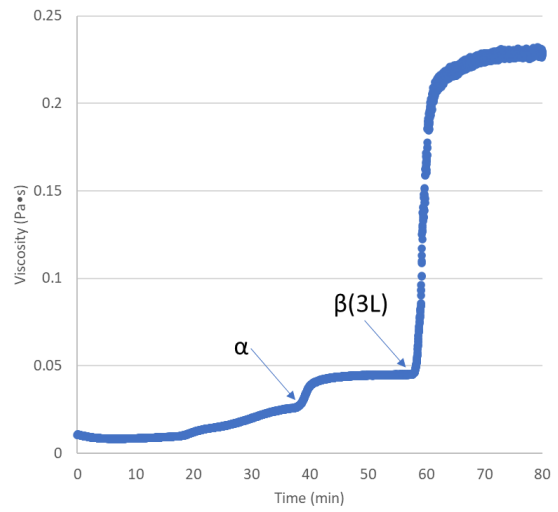
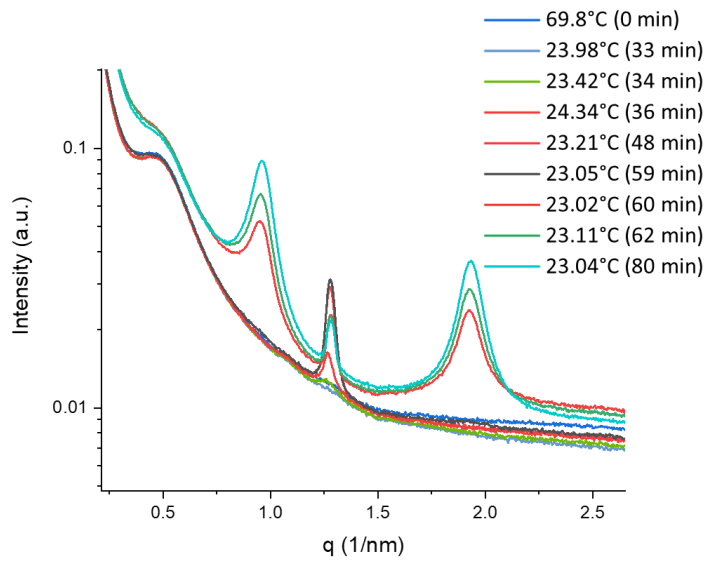
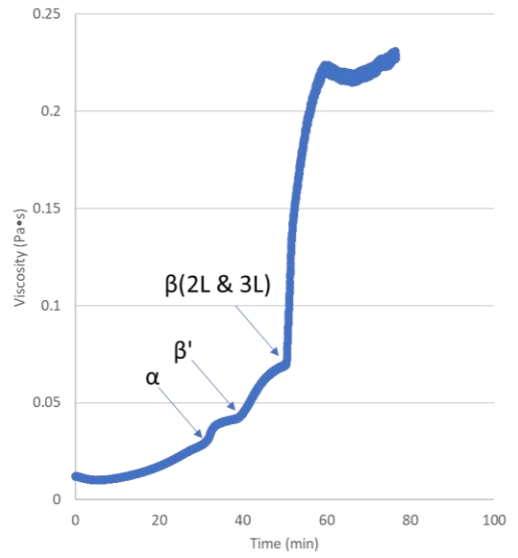
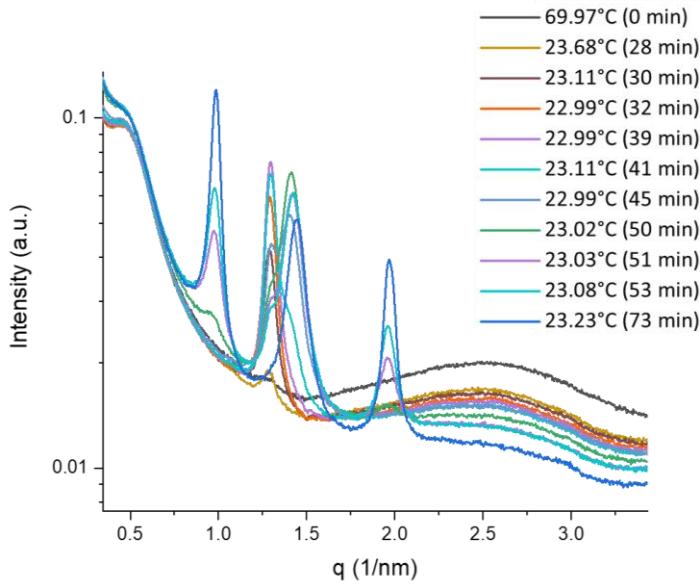


Figure 4: viscosity trends for sample S8 and S9 (two different origin fats). The formation of a β' and a $\beta(2L)$ phases is visible for S8 (top) while only α and $\beta(3L)$ are visible in the sample S9 (bottom)