ESRF	**Experiment title:** In-situ observation of the self-assembly of nanocellulose during freeze-casting	**Experiment number**: 52432
Beamline: BM26	**Date of experiment**: from: 2016-11-14 to: 2016-11-17	**Date of report**: 2018-05-02
Shifts: 9	**Local contact(s)**: Daniel Hermida-Merino	*Received at ESRF:*

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Report:

The aim of this experiment was to *in-situ* characterize cellulose nanofibers (CNF) and cellulose nanocrystals (CNC) and more importantly to monitor ice crystal growth during freeze-casting process. A customized setup for *in-situ* freeze-casting was used for WAXS and SAXS experiments. This study is a part of a larger project, in the area of fibrous biopolymers, where the goal is to study the formation of ordered CNF/CNC structures. Freeze-casting method offers a versatile approach to producing highly anisotropic porous materials, in which ice crystals grow with the temperature gradient and eventually produce a frozen material consisting of anisotropic ice crystals surrounded by the walls formed by the dispersed particles [1]. Freeze-casting has been used to prepare porous scaffolds and our recent work also describes efforts to produce thermally insulating materials based on CNF [2]. Both freeze-casting/thawing are advantageous over evaporation drying due to a more uniform drying, with the possibility to adjust/control the freezing/drying rate, and to set final concentration where the drying stops. For this purpose *in-situ* WAXS and SAXS were used to observe the *in-situ* freeze-casting of cellulose nanofibers. CNF suspensions were poured in 4.0 mm-diameter glass capillaries with a wall width of 10 μm, and each capillary was cooled down and heated up. Then SAXS and WAXS were recorded simultaneously.

Our *in-situ* setup was tested/used during the time-resolved experiments, and we have obtained new insight regarding the alignment of CNF and the reproduction of freeze-casting of CNF/CNC. For instance, Figure 1 and 2 below show WAXS and SAXS results of cellulose nanofibers (650 μeq/g surface charge). Figure 2, clearly shows the change in the ordering of CNF during the freezing process is detectable. By using time-resolved SAXS, we were able to capture the transition between the liquid state and the frozen state within 50 images (corresponding to a time period of about ~ 30 min). As a result of the freezing process, see Figure 2, the intensity of a structural peak (at about 40 nm) is decreased dramatically, indicating better alignment of the CNF in the frozen state. The treatment of the data collected for CNF and CNC samples is ongoing.

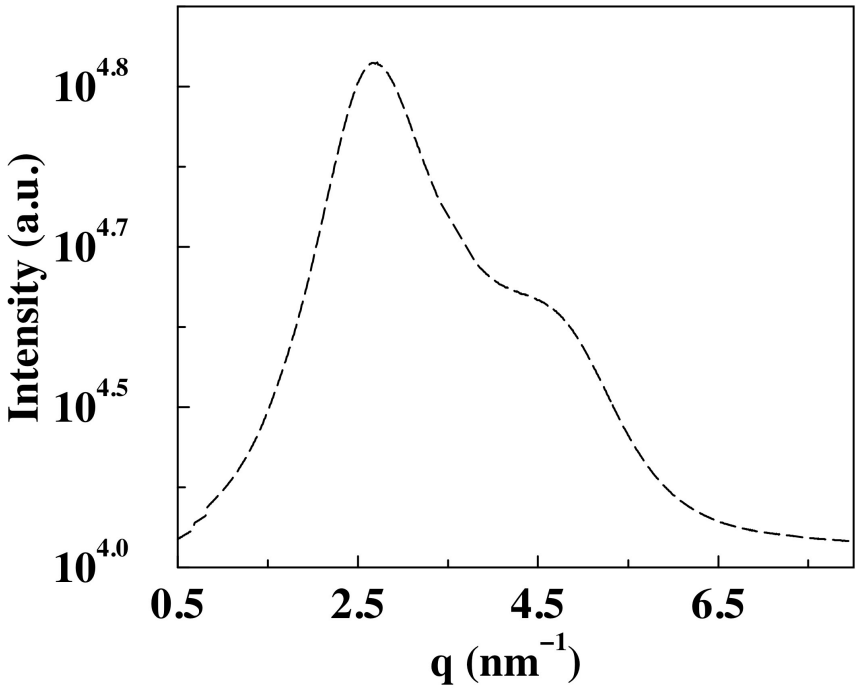

Figure 1: Scattering functions from WAXS of CNF 650 µeq/g sample.

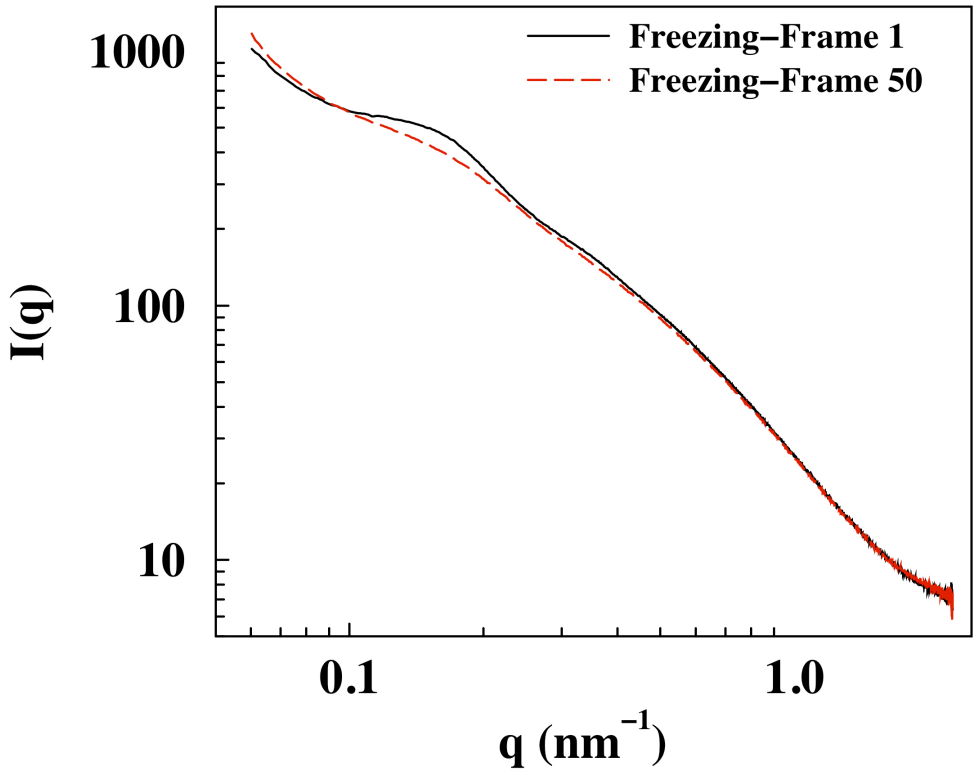

Figure 2: Scattering functions from *in-situ* SAXS of CNF 650 µeq/g sample during the freezing-process.

References

[1] F. Bouville, E. Maire, S. Deville, *Langmuir* **2014**, *30*, 8656.

[2] B. Wicklein, A. Kocjan, G. Salazar-Alvarez, F. Carosio, G. Camino, M. Antonietti, L. Bergström, *Nat. Nanotechnol.* **2014**, *10*, 277.