ESRF	**Experiment title:** Comprehensive SAXS/WAXS characterization of the wood cell wall nanostructure	**Experiment number**: 02-01-885
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Shifts: 9	**Local contact(s)**: Dr. Isabelle Morfin	*Received at ESRF:*

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Report:

Objectives of the experiment

The purpose of the experiment was to characterize the nanostructure of wood and observe how it reacts to changes of humidity. Small and wide-angle x-ray scattering (SAXS and WAXS) patterns from samples of two wood species, one softwood and one hardwood, were collected at different relative humidities (RH) as well as in never-dried state and after drying and rewetting in liquid water. The humidity was controlled by a custom-made humidity cell kindly designed and provided by the Partnership for Soft Condensed Matter (PSCM)/ESRF.

Experiment description

Never-dried blocks of mature wood from European beech (*Fagus sylvatica*) and European silver fir (*Abies alba*) were cut to approximately 1×1×15 mm pieces and either conditioned at RH 95 % in a desiccator with saturated KNO_3 solution for 9-10 days prior to the measurements ("preconditioned samples"), dried first in room air for 2 days, then in a desiccator for 3 days, and finally rewetted in liquid water for 5 days ("dried and rewetted samples"), or stored as such in liquid water at 7°C ("never-dried samples"). For the x-ray measurements, the preconditioned samples were placed in a custom-made humidity chamber adjusted to RH 90% and allowed to equilibrate for 4-5 h. After measuring the SAXS and WAXS patterns, the RH was changed to 45%, 15%, 45% and again to 90%, collecting SAXS and WAXS patterns at each RH point after an equilibration time of 1.5-8 h. The never-dried and rewetted samples were measured in the same humidity chamber but without humidity control and in the presence of excess water. During the time required for the equilibration of the samples, the beamtime was utilized by measuring complementary samples.

SAXS and WAXS were measured at the BM02/D2am beamline using an x-ray beam energy of 16 keV and two setups for the XPAD hybrid-pixel detectors. In the first setup, a D5 detector was placed at a distance 216 cm from the sample to cover the low-q SAXS region (0.006-0.13 $Å^{-1}$) and a WOS detector at distance 13 cm to measure WAXS (0.61-4.0 $Å^{-1}$). In the second setup, the D5 detector was placed at 58 cm from the

sample in order to cover the high-q SAXS region (0.02-0.49 Å^{-1}). In each measurement, the wood samples were scanned horizontally with 7 points within a 1 mm range, with an exposure time of 40 s per point. The samples were always positioned with the longitudinal axis of wood fibers in approximately vertical orientation, perpendicuar to the x-ray beam.

Preliminary results of the experiment

All samples showed highly oriented SAXS and WAXS patterns, which were integrated on an azimuthal sector of 25° comprising the equatorial streak arising from the lateral structure of cellulose fibrils (Figure 1). An example of corrected and rebinned equatorial SAXS data of an early-wood sample from European silver fir is presented in Figure 2. Based on a preliminary analysis of the data (Figure 2 inset), the humidity changes affected the SAXS intensity mostly at q-values above 0.08 Å^{-1} (below 8 nm in real space), which is the q-region where scattering from cellulose microfibrils is observed. The decrease and shift of the peak/shoulder-feature to higher q-values indicates tighter packing of the cellulose microfibrils at low RHs, which was only partly recovered by increasing the RH back to 90%. Reimmersing a once-dried sample in water, however, seemed to revert the packing of the microfibrils close to the original, never-dried state.

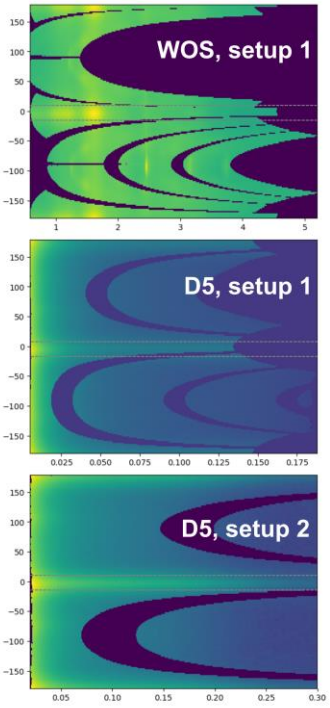

Figure 1. 2D scattering data of European silver fir early wood at RH 90%, with scattering vector q (in Å^{-1}) on x-axis and azimuthal angle (in °) on y-axis.

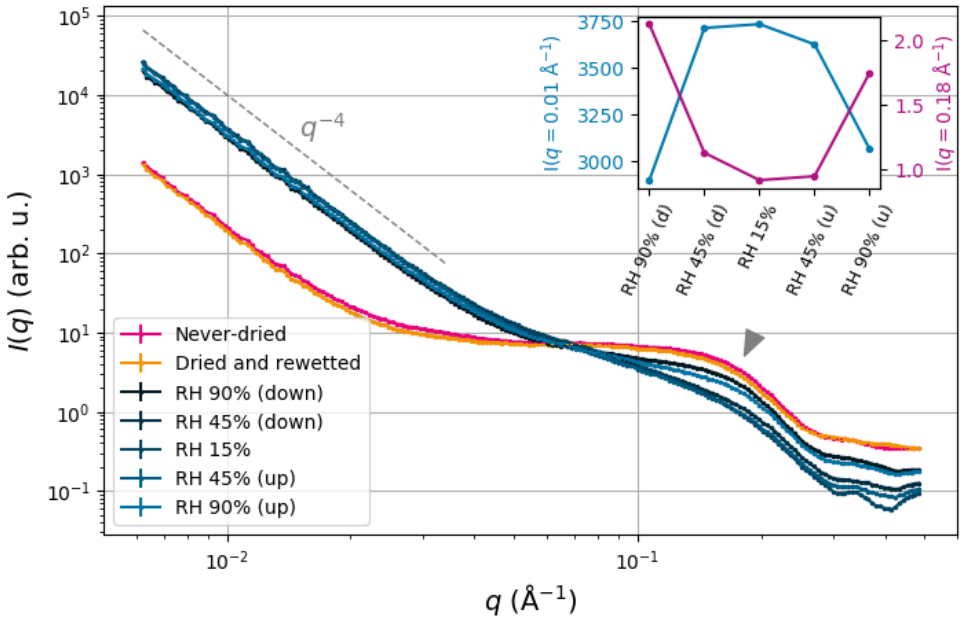

Figure 2. Equatorial SAXS data of an early-wood sample from European silver fir. The low q-values are dominated by a power law with exponent –4, originating from the surfaces of large pores, and the peak/shoulder-feature around 0.1-0.2 Å^{-1} (marked by an arrowhead) corresponds to the cellulose microfibrils and their mutual arrangement. Variation of the intensity at q-values 0.01 Å^{-1} and 0.18 Å^{-1} is shown in the inset.

Plans for further exploitation of the results

The analysis of the SAXS data will be continued by performing fits with a model of hexagonally packed cylinders [1]. We expect the fitting to yield numerical values for the cross-sectional diameter of cellulose microfibrils and their packing distance as a function of the humidity conditions. The variations of the diffraction peak locations in the WAXS data will be used to describe the effects of moisture changes on the cellulose crystals. The x-ray scattering results will later be complemented by dynamic vapor sorption (DVS) measurements to determine the moisture content at each RH point and by small-angle neutron scattering (SANS) measurements conducted at the neutron instrument D11 of the Institut Laue-Langevin (ILL). A publication based on the results of the experiment will be submitted by the end of the year 2018.

References

[1] Penttilä PA, Rautkari L, Österberg MK, Schweins R (2018), Small-angle scattering methods for efficient characterization of wood nanostructure and moisture behavior. *Abstracts of the 255th American Chemical Society National Meeting & Exposition*, New Orleans, USA.