Experimental report

15/01/2021

Proposal: **DIR-175** **Council:** 4/2019

Title: Trapped water in the nanopores of dried and rewetted wood

Research area: Materials

This proposal is a new proposal

Main proposer: **Paavo PENTTILA**

Experimental team: Paavo PENTTILA
Aleksi ZITTING

Local contacts: Ralf SCHWEINS

Samples: Pine wood

Instrument	Requested days	Allocated days	From	To
D11	2	2	13/01/2020	15/12/2020
D22	2	0		
D33	2	0		

Abstract:

We will use SANS to understand the interactions between water and the nanoscale structure of wood. We are particularly interested in the irreversible aggregation of cellulose microfibrils (CMFs) during drying of wood and the exchange of water in the differently sized pores of the wood cell wall. We will use contrast variation with D2O/H2O to observe the water trapped between CMFs by drying and time-resolved SANS measurements to monitor how water is exchanged inside and between aggregates of CMFs after solvent exchange. The use of SANS is necessary, because it is sensitive to D2O/H2O and it provides information on the location of water in the hierarchical wood structure. The experiment will give direct evidence for the speculated location of water inside and between CMF aggregates in wood, and the results will have a significant impact on the many applications of wood.

DIR-175: Trapped water in the nanopores of dried and rewetted wood

Paavo Penttilä, Ralf Schweins, Aleksi Zitting

1. Background

Wood is a widely-available and renewable material that is utilized for various purposes, from the traditional uses as building material to more recent nanomaterials applications. A key characteristic of wood materials is their sensitivity to moisture, which includes aggregation of wood's basic building blocks, the 2-3 nm thick cellulose microfibrils (CMF), during drying. This aggregation behaviour and the nanoscale wood-water interactions in general are not well understood, despite that they play crucial roles in many applications of wood by affecting its mechanical properties as well as susceptibility to chemical treatments.

The irreversibility of CMF aggregation during drying of wood is still an ongoing discussion [1,2,3], where most results are based on techniques insensitive to the nanoscale morphology of wood. The purpose of this small-angle neutron scattering (SANS) experiment was to elucidate the relationship between water and the CMFs by observing any drying-induced, irreversible aggregation of the CMFs or trapping of deuterium or water in the structure during drying. In addition, *in situ* SANS experiments after solvent exchange were used to monitor the dynamic water exchange in the hierarchical structure of the wood cell wall. The results were expected to demonstrate the location of "readily accessible" water on the surfaces of CMF bundles and the "slowly accessible water" between the CMFs, which have been proposed to exist at least in processed celluloses [4].

2. Experimental

The interactions of water with the wood cell wall nanostructure were studied through SANS measurements of wood samples subjected to different drying and rewetting procedures and contrast variation as illustrated in Fig. 1. Spruce wood (*Picea abies*) sections with dimensions 0.8×10×13 mm^3, cut with a sliding microtome, were prepared in advance by sequential solvent exchange and drying procedures. The drying was done under N_2 flow at room temperature. For the SANS experiments, the samples were placed in quartz glass cells with an optical path of 1 mm.

SANS experiments at D11 were carried out on the full q-range (sample-to-detector distances 1.5 m, 8 m, 34 m; wavelength 6 Å) for all the 7 types of samples shown in Fig. 1 (with multiple parallels). After this, the solvent in the never-dried and dried/rewetted samples with 65% H_2O/35% D_2O (contrast match with the CMFs) was replaced by 100% D_2O, and SANS patterns at the shortest detector distance (high q) were collected with 0.5-5 min intervals.

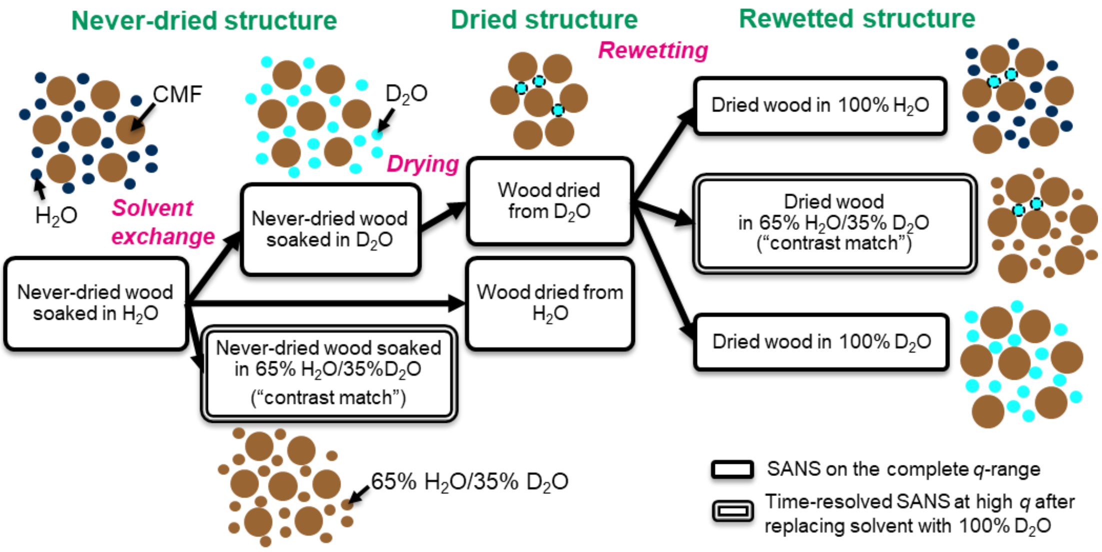

Figure 1. Schematic presentation of the sample series characterized with SANS.

3. Results

The SANS measurements from samples before and after drying/rewetting were carried out to detect any traces of irreversible aggregation of the CMFs. No major differences were observed between never-dried and dried/rewetted samples in D_2O or H_2O (Fig. 2), which indicates that with sufficient time, the wood cell wall nanostructure was able to mostly recover after drying and reimmersing in water at room temperature. The equatorial, anisotropic SANS intensities were fitted with the WoodSAS model [5], which yielded similar values as reported previously for wet and dry softwoods [2,5,6]: CMF diameter 2.1 nm, CMF centre-to-centre distance 3.9 nm (wet) or 2.4 nm (dry), and CMF bundle diameter 17 nm (wet) or 11 nm (dry). The SANS data from wood samples dried from D_2O did not show any clear contribution from residual deuterium, even though the presence of OD groups in the dried samples was confirmed by FT-IR spectroscopy after the SANS experiments.

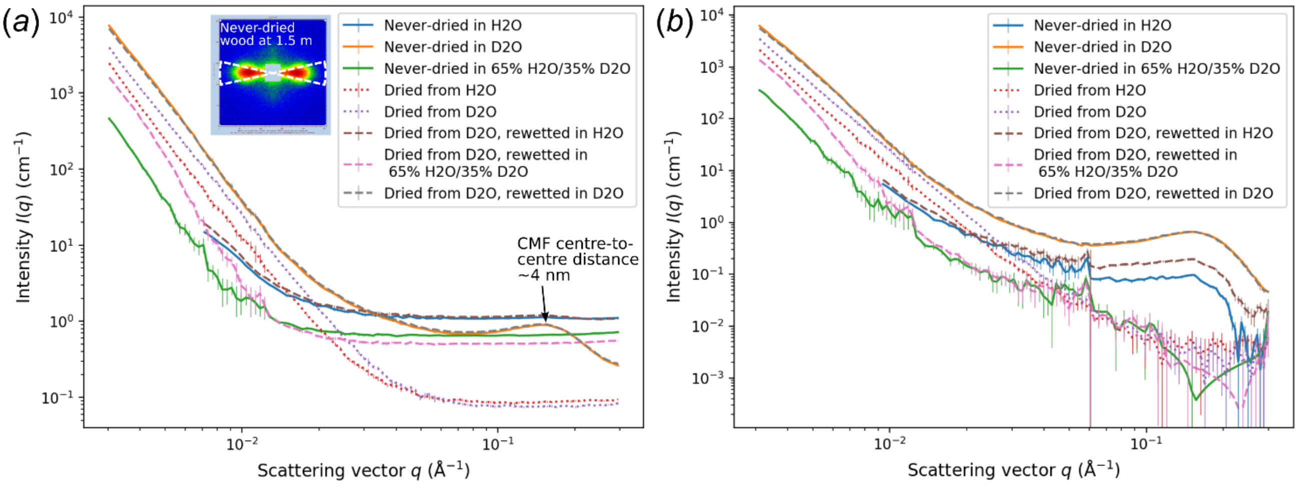

Figure 2. SANS intensities integrated on 25-degree equatorial sectors: before (*a*) and after (*b*) subtracting the isotropic scattering contribution.

In situ experiments after solvent exchange were carried out to follow the diffusion of water to different levels of the hierarchical structure. The results showed that water in the interfibrillar spaces would exchange within tens of minutes. The scattering length density contrast increased at a similar or slightly faster rate at the level of CMF aggregates (q = 0.06-0.1 Å^{-1}) than the level of individual CMFs (q = 0.1-0.3 Å^{-1}) (Fig. 3). No major changes in the structural parameters as described by the WoodSAS model [5] were observed (Fig. 4). The behaviour of never-dried and dried/rewetted wood samples was similar in the solvent exchange experiments.

The SANS data will be analysed further, and the solvent exchange data will be interpreted with the aid of kinetic models. The results will be combined with FT-IR data describing the time-dependent accessibility of OH/OD groups in wood to liquid water. The results will be published in a scientific journal.

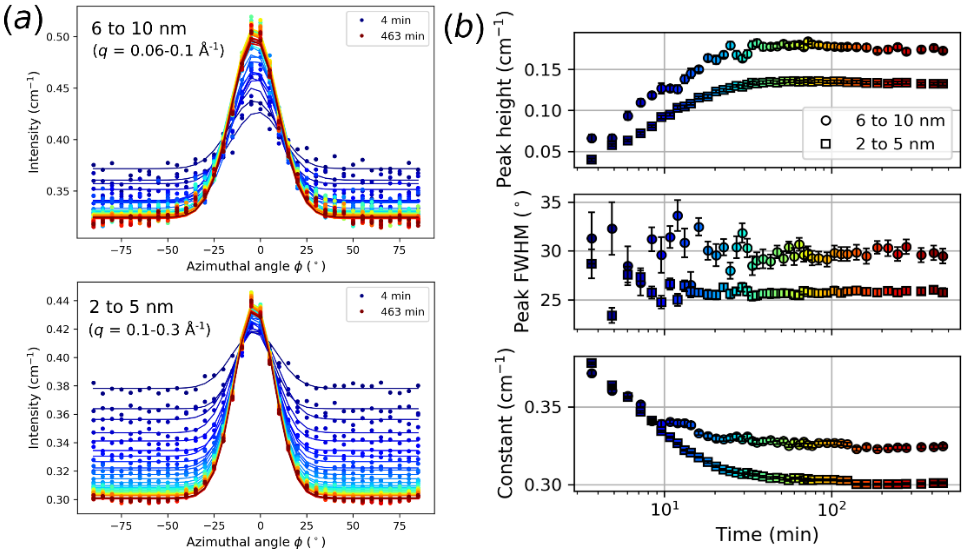

Figure 3. (*a*) Fits of a Gaussian peak to azimuthal SANS intensity profiles from never-dried wood at different times after transferring from 65% H_2O/35% D_2O to 100% D_2O, integrated over two different ranges of *q*. (*b*) Fitting parameters as a function of time.

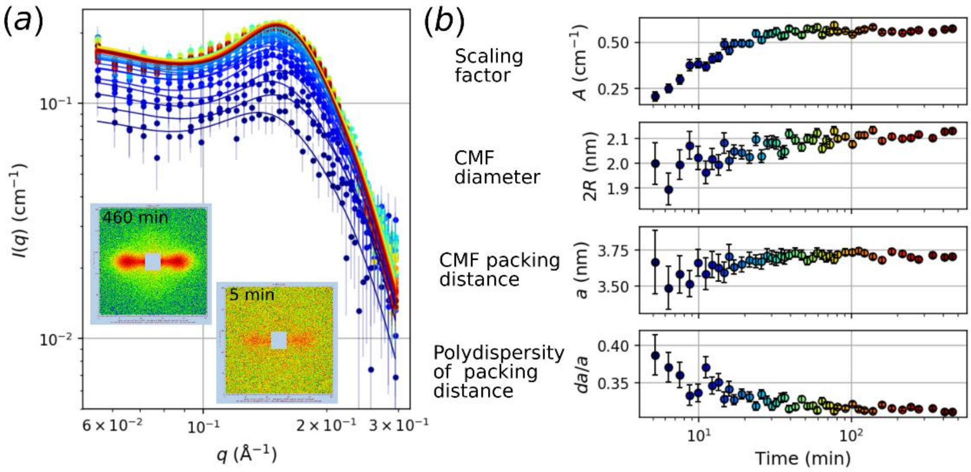

Figure 4. (*a*) Anisotropic, equatorial SANS intensities from never-dried wood at different times after transferring from 65% H_2O/35% D_2O to 100% D_2O, together with the fits of the WoodSAS model [5]. (*b*) Structural parameters as a function of time as determined by the model fitting.

References

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