Experimental report

29/03/2017

Proposal: TEST-2747 **Council:** 10/2016

Title: SANS characterization of Northern European woods

Research area:

This proposal is a new proposal

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Samples: Pieces of wood (mainly cellulose, hemicelluloses and lignin) in D2O

Instrument	Requested days	Allocated days	From	To
D11	1	1	23/01/2017	24/01/2017

Abstract:

1. Background

Wood is an abundant and renewable material with various applications, which would benefit from a better understanding of its nanoscale structure. Small-angle neutron and x-ray scattering (SANS and SAXS) are excellent tools for studying the nanoscale structure of wood and plant cell walls, but currently the interpretation of the scattering data is not clear. In this experiment, we collected SANS data from samples of Northern European woods on a wide q-range and in both wet and dry states. The results of these experiments will pave the way for small-angle scattering studies on plant cell wall based materials and they can be used to improve various chemical, physical, and enzymatic treatments of cellulosic materials.

2. Experimental

Pieces from native woods, including birch (*Betula pubescens*), Scots pine (*Pinus sylvestris*) and Norway Spruce (*Picea abies*), were collected from Eastern Finland in August 2016 and stored refrigerated in 30% ethanol solution. Radial-longitudinal (RL) and tangential-longitudinal (TL) sections of 1-2 mm thickness were cut with a knife and immersed in H_2O for two times one day to wash out the ethanol. After altogether two days in H_2O, samples were immersed in 100% D_2O and stored for one day at 6°C. Then the D_2O was replaced with fresh one and the samples were let to equilibrate for 3 days at room temperature. For the SANS measurements, the wood sections together with excess D_2O were placed in quartz cells with a light path of 2 mm and loaded in a sample changer adjusted to a temperature of 25°C. SANS patterns with a neutron wavelength of 6 Å were collected at detector distances 1.5 m, 8 m and 34 m and with 13 Å at 34 m. The total q-range covered by this setup was from 0.0009 to 0.35 $Å^{-1}$.

After the first SANS measurements, the wood samples were removed from the quartz cells and allowed to dry for 6 days in room air. SANS patterns from the dried samples were measured inside of dry quartz cells using the same setup as before, except that the pattern at 34 m detector distance and 13 Å wavelength was collected only for some of the samples.

3. Results

All of the wood samples produced the typical, highly anisotropic SANS pattern with strong equatorial streaks. The two-dimensional patterns were corrected and normalized to the absolute scale using the LAMP software. Subsequently, azimuthal integration on sectors 25° in width, centered on the equatorial streak and perpendicular to it, was carried out and the data from different instrument setups (Figure 1) was merged to a single data set. The equatorial peak around 0.15 $Å^{-1}$ (~4 nm) in the wet samples was enhanced by subtracting the isotropic scattering intensity, represented by the meridional sector, from the equatorial sector (Figure 2). Similar treatment for the dried samples (Figure 3) yielded a considerably weaker peak that was shifted to around the q-value 0.2 $Å^{-1}$ (~3 nm). If the location of the peak is interpreted to correspond to the average distance between neighboring cellulose microfibrils, this result is an indication of their tighter packing in the dry state.

Preliminary fits to the equatorial SANS intensities from samples in 100% D_2O was done using a model based on partially-aligned cylinders packed according to the hard-sphere model, which is an approximation of the cellulose microfibril bundles present in the secondary cell wall of woods. In addition, a power law with exponent close to –4 was included in the fits to account for the scattering from pore surfaces. Fitting with the SASfit software (Figure 4) yielded a cylinder diameter of 1.9 to 2.0 nm, length of 14 to 18 nm, hard-sphere diameter of 3.0 to 3.4 nm and volume fraction of 0.11 to 0.21 for all samples. Assuming a less-ordered and D_2O-containing surface layer with 0.5 nm thickness surrounding the cellulose microfibrils, these results are in good agreement with values around 3 nm typically determined for the width of cellulose crystallites in dry samples of wood. Fitting of the same

model to the dry samples did not yield reliable results, because the contrast between microfibrils and their matrix was too low in the absence of water.

Further fitting to the SANS data is currently being pursued and is accompanied by the development of new data analysis tools. The current SANS data will be complemented by SAXS measurements of the same samples at the ESRF, which will show the form factor of the cellulose microfibrils with better *q*-resolution and facilitate the construction of the model. In addition, new SANS measurements during controlled drying will be necessary for observing the scattering at intermediate stages of drying and following the changes in the packing of microfibrils. SANS experiments using water-soluble molecules of different sizes to modify the contrast from differently sized pores are also planned to understand the accessibility of the pores and the origins of the power-law scattering on small *q*-values.

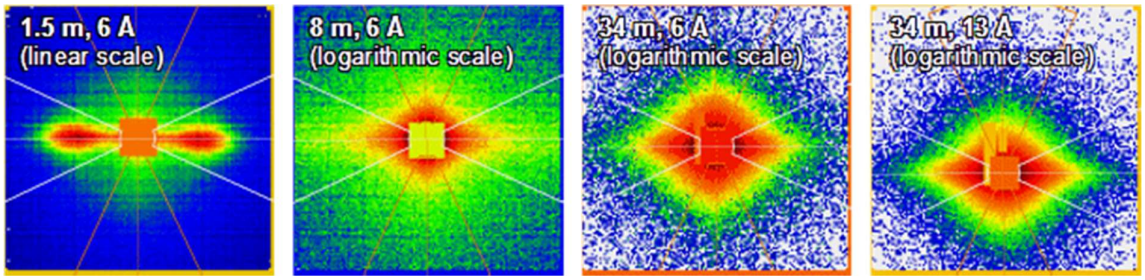

Figure 1. Two-dimensional SANS patterns of a pine sample (RL section) in 100% D_2O, showing the 25° wide sectors used for integration.

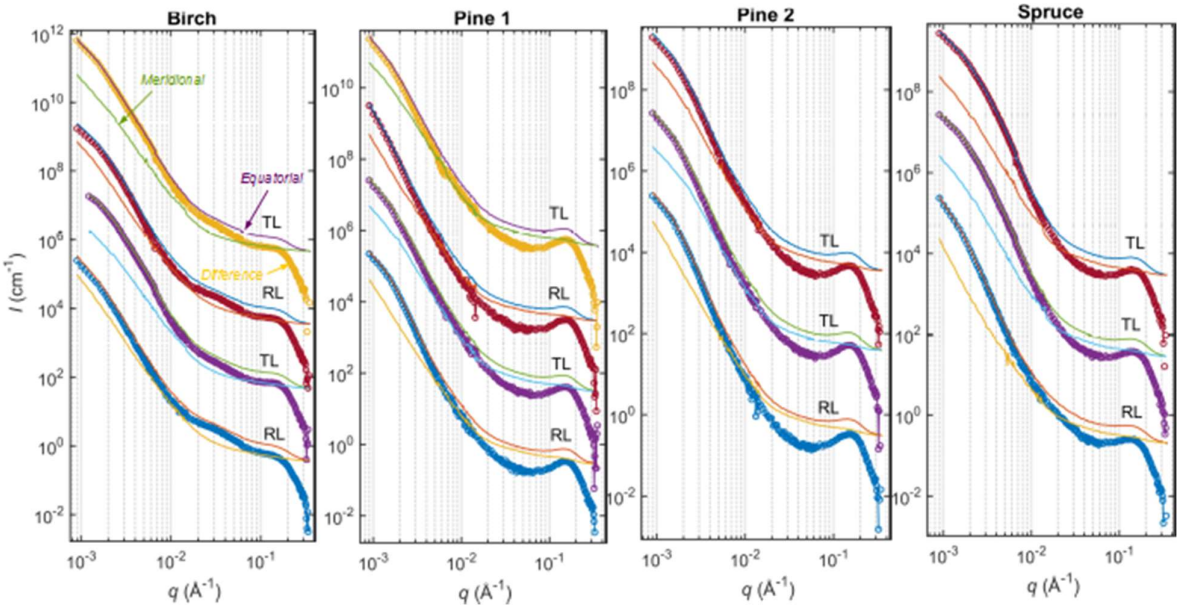

Figure 2. SANS intensities integrated on equatorial and meridional sectors (*thin lines*) and their difference (*circles*) for samples measured in 100% D_2O (vertically shifted for clarity).

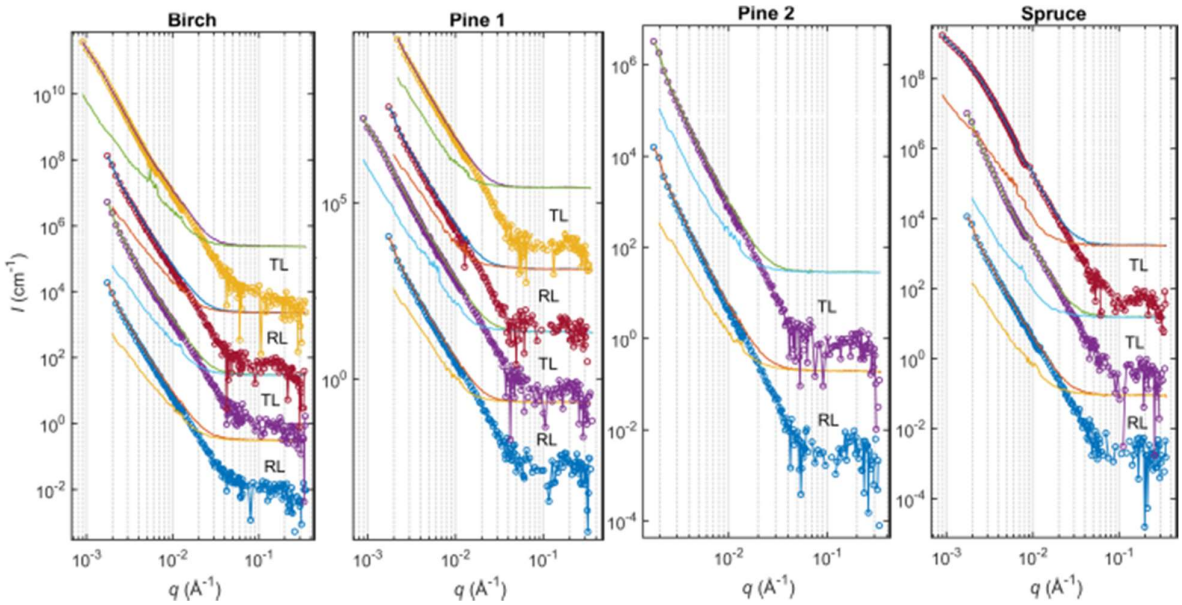

Figure 3. SANS intensities integrated on equatorial and meridional sectors (*thin lines*) and their difference (*circles*) for samples measured after drying in air (vertically shifted for clarity).

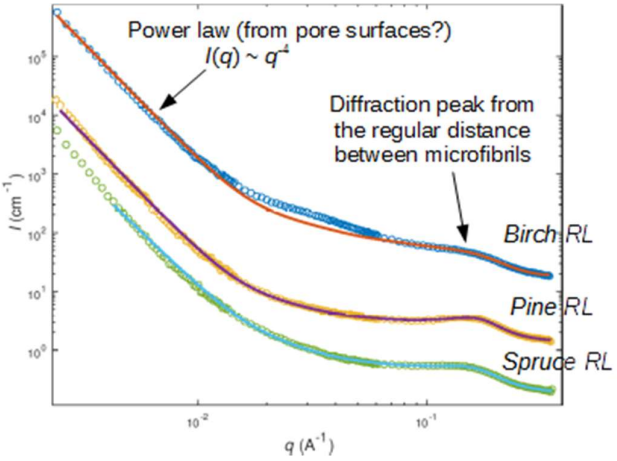

Figure 4. Preliminary fits (*solid line*) of a power law and partially-aligned, closely-packed cylinders to the equatorial SANS intensities of samples in 100% D_2O (vertically shifted for clarity).