ESRF	**Experiment title:** Structural evolution of woody biomass during annealing	**Experiment number**: 02-01-864
Beamline:	**Date of experiment**: from: 27.08.2015 to: 01.09.2015	**Date of report**: 1.9.2015
Shifts:	**Local contact(s)**:Cyrille Rochas	*Received at ESRF:*

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Report:

1. Background

Woody biomass has a well controlled spacial organisation form maccroscopic scale (mm length scale) to atomistic lengthscale. Such biomass experiences hydro-thermal history during the industrial transformations such as kiln drying, pulping or pre-treatment for biofuel production. The macroscopic morphologies are usually conserved in a simple thermal process, but the material properties can drastically change. We followed the microstructural evolution of wood at elevated temperatures under various water contents to get insight on the imcrostructural modification in such processes.

2. Samples

Block of bamboo, Japanese cedar (*Cryptomeria japonica*), Japanees beech (*Fagus grenata*) were shaped into cyllinder with the long axis along the grain to fit into the 3 mm glass tube. The water content were conditioned by equilibration under different relative humidity for the samples below fiber saturation point (i.e. about 30%-solid base) and by drying upto the target weight in 98% relative humidity condition at room temperature. The glass tube containing the samples were sealed to keep the water content in the system throughout the experiment

3. Experiment

The samples were mounted on a sample exchanger with temperature control. The detector distances were set to about 16 and 160 cm covering a q range of 0.01 to 2 ($Å^{-1}$) using and X-ray energy of 16 keV. The scattering images recorded on the CCD camera was corrected for dark current and spatial distortion using bm2img program. Intensity profiles corresponding to

anisotropic scattering component perpendicular to the fiber and an isotropic scattering component by fitting the azimuthal profile at each radius into a constant and a Gaussian peak.

4. Results

Appearance of a new allomorph by prolonged hydrothermal treatment

Figure 1 shows the wide angle scattering pattern of beech specimen with about 80 % water (dry-base) before and after annealing at 200˚C for two hours. The strongest equatorial diffraction peak corresponding to the distance between pyranose plane in cellulose crystal became sharp and moved outwards, indicating increased apparent crystallite size and compaction of the structure. The corresponding d-spacing was 3.9 Å, identical to the crystal of native cellulose obtained from tunicate but smaller than ordinary wood cellulose which is closer to 4.0Å.

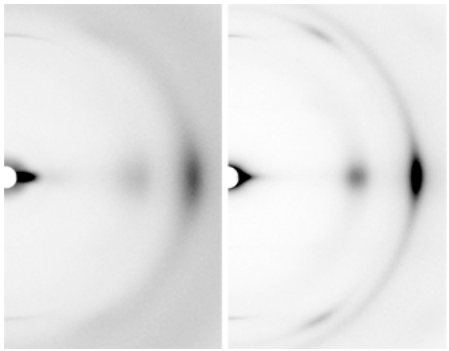

Figure 1. beech sample (80% water) before and after treatment at 200˚C

The equatorial profile of the beech specimen with 130 % water content during the heat treatment was summerised in **figure 2**. During the heating, the 2 0 0 peak shifted towards lower angle due to the thermal expansion, which is a well known phenomenon for cellulose. No significant modification can be seen in the wide anlge region during the holding at 200˚C, but when cooled down after 2 h annealing at 200˚C, the peak drastically moved towards higher angle and sharpened. A similar transformation could be observed for bamboo and beech sample in a range of water content above fiber saturation point (30%), while the Japanese cedar only showed a moderate increase in crystallinity in any condition studied. A relatively long residence time (1h) at 200˚C for this tranformation to occur during which the intensity of small angle scattering continued to grow.

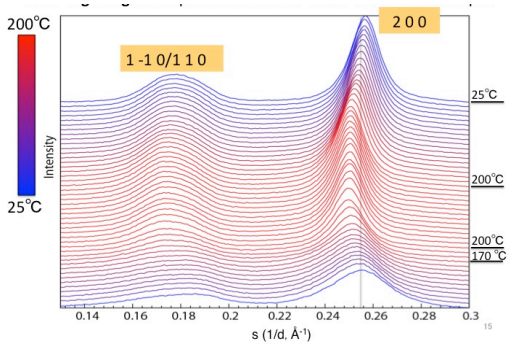

Figure 2 . WAXS equatorial profile of beech with 130% water content during annealing

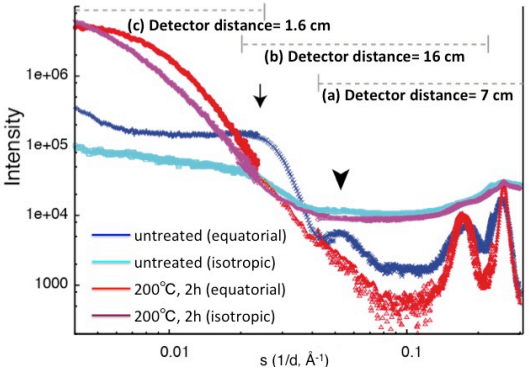

Figure 3. Whole scattering profiles corresponding to Fig. 1.

Existence of 2-nm correlation peak and disappearance during hydrothermal treatment.

We noticed the presence of a well defined peak at q = 0.36 corresponding to about 1.7 nm d-spacing in bamboo and beech in the presence of water (**Fig 3**). This peak has never been reported in the literature. Only a correlation peak at around q = 0.15Å corresponding to 4 nm distance was reported for *Picea abies,* and was interpreted as due to the spatial correlation between microfibrils. The Japanese cedar, another softwood, showed this peak, but not the peak at q= 3.4 nm. The microfibril organization at nanometric length scale seems to be species dependent. We are planning to check this feature more systematiccally including wider range of specie to establish correlation wtih the type of hemicellulose and plant genealogy.