	Experiment title: High resolution fiber diffraction study of α-chitin and high-temperature structure of cellulose	**Experiment number**: SC2028
Beamline:	**Date of experiment**: from: 06/10/06 to: 08/10/06	**Date of report**:
Shifts:	**Local contact(s)**: Philip Pattison	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Yoshiharu NISHIYAMA
CERMAV/CNRS

Report:

The aim of the study was to elucidate, by fiber diffraction studies, the structures of crystalline polysaccarides that are of biological and industrial importance. This was the first attempt fo fiber diffraction at this beamline and several data collection strategies were tested with CCD and imaging plate detector.

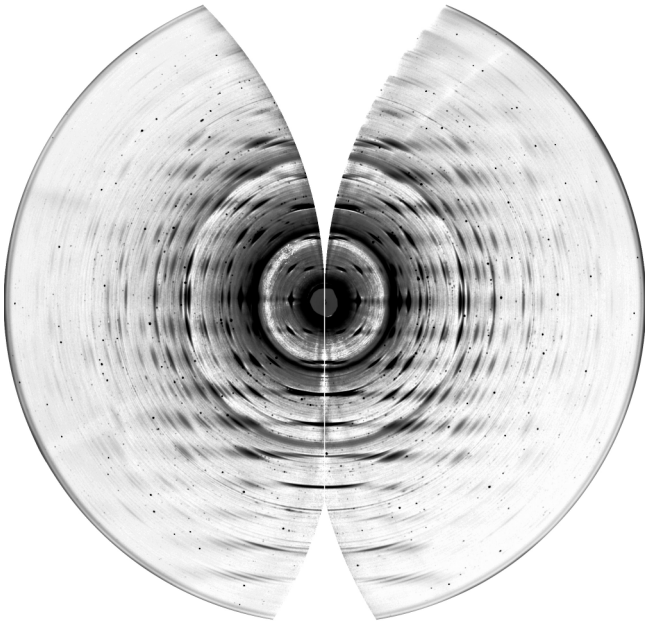

figure 1. Fiber diffraction diagram of α-chitin with the unique axe vertical.

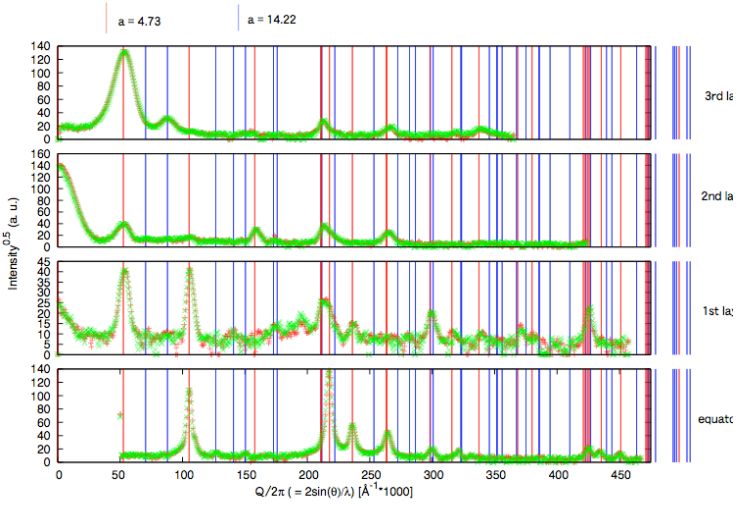

figure 2. Intensity profiles of equator and layerlines with expected reflection positions calculted from unit cell parameters *a* = 4.72 (red lines) and a = 14.22 (blue lines), *b* = 18.86 , *c* = 10.32 Å, a = b = g = 90°

Whisker like crystals of 20 – 50 nm in lateral dimension and micrometers long were embedded in aquaous PVA gel matrix, stretched and dried to make an uniaxially oriented fiber. X-ray diffraction patterns at 1Å resolution were collected at different temperatures, controlled with a cryo-stream or a heating device, in the range between 100K and 500 K. Wavelength of 0.7840 Å was used

alpha chitin

The amount α chitin embedded in the matrix was very small, so a long exposure time was needed to enhance the noise to signal ratio at high angles. A series of diffraction patterns were recorded using 0.5 mm beam and 150 μm resolution detection, as well as 0.2 mm beam with 100 μm resolution. Detector was placed at 165 mm from the sample for most of the experiments and 350 mm detector distance was used to observe the diffraction broadening of the peaks due to the crystal sizes.

Figure 1 shows the fiber diffraction diagram of a chitin at 1Å resolution remapped to cylindrical reciprocal coordinates with the unique axe vertial. Images with different fiber tilts were combined to cover the region close to the meridian. Background was subtracted by Sonneveld algorithm. Clearly resolved peaks could be observed up to 1Å resolution. All the diffraction position could be indexed with a unit cell of a = 14.22 b = 18.86 c = 10.32 Å a = b = g = 90°, which is 3 times larger in the direction of a axe as was proposed by Minke and Blackwell. The existence of 0 0 1 indicates a deviation from $P2_1$ symmetry.

The unit cell determined from the diffraction could accommodate 6 parallel chitin chains without any steric conflicts. This gives an alternative to the proposed anti-parallel chain model of Minke and Blackwell accepted today. Structural refinement is underway to elucidate the polarity of chains which is essential for the understading of biosynthesis of chitin and related polysaccharides.

Cellulose at high temperature

Good signal to noise ratio could be achieved even at 1Å resolution with 2 minutes exposure because the crystal content in the sample was high (~20%). Highly resolved diffraction could be observed upto 320°C, and suddenly lost crystallinity due to thermal degradation. Anisotropic thermal expansion could be measured in the range of 100K to 580K. Contrary to our expetation, no phase transition could be observed at 270°C for cellulose I_α and 220°C for cellulose I_β, probably due to the complete absence of water in the system. In fact, samples that were composite of cellulose and PVA deformed when heated directly from ambient condition, and well oriented diffraction could be only measured when completely dried under hot nigtrogen flow. Sealing the sample in a quatz capilary seems to be a solution to observe high tempearture phase. On the other hand, change in intensity ratio could be observed at low temperature. Structure refinement will be carried out to clarify whether it is related to the hydrogen-bonding disorder observed at room temperature.

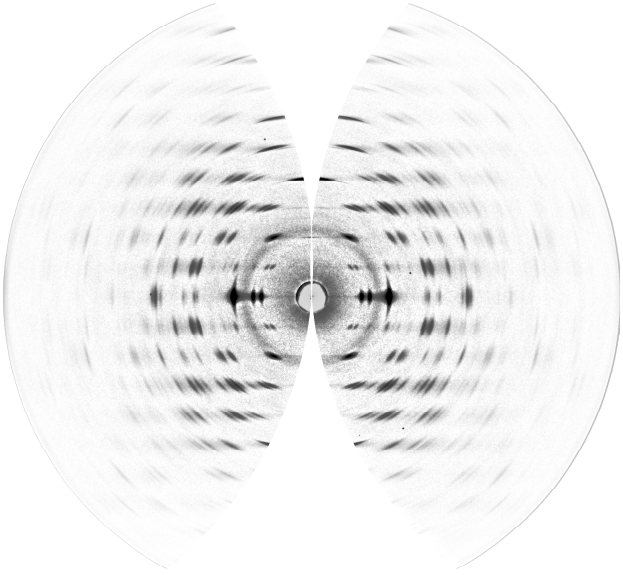

figure 2. Fiber diffraction of cellulose I_α at 230°C

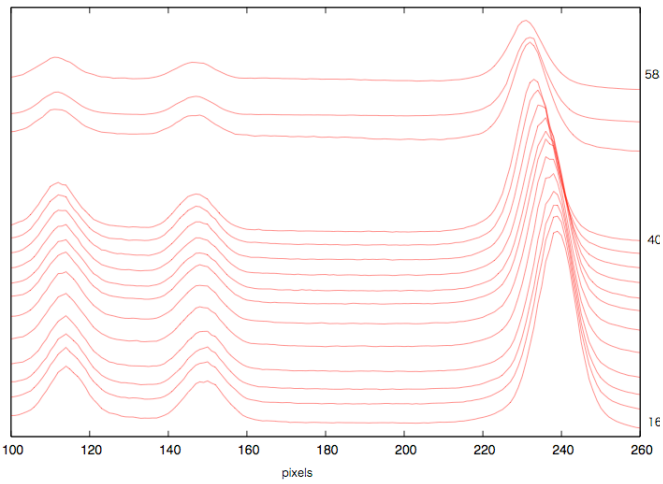

Figure 3. Evolution of equatorial intensity profile of cellulose I_α from 160K to 580K/