ESRF	**Experiment title:** Nanostructure of silk fibres - as a function of tensile stress and humidity	**Experiment number**: SC-2845
Beamline: ID13	**Date of experiment**: from: 25. 01.2010 to: 30.01.2010	**Date of report**:
Shifts: 12	**Local contact(s)**: Sebastian Schoeder	*Received at ESRF:*

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Report:

As stated in the proposal, natural silks exhibit extraordinary mechanical properties, because they combine high tensile strength with a high elongation at failure. Although desired by many fields of industry for a long time, none of the efforts to synthesize the nanocomposite material silk so far have led to fibres with comparable mechanical properties as the bio-spun fibres. This is mainly due to the still unknown structure on a nanometre sized length scale. In fact, only little is known about the very shape of the crystallites. Particularly in doubt is the structure of the interfacial region between the crystallites and the amorphous matrix and its modification due to presence of free water in the amorphous phase.

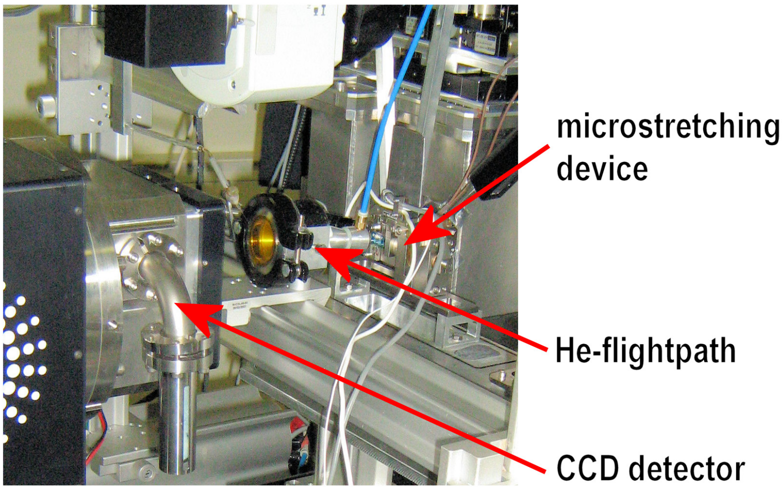

Fig . 1 Photograph of the experimental setup (as used in the SAXS part).

An attempt to fill in this gap was a combined SAXS/WAXS experiment performed on single fibres of silkworm silk (*Bombyx mori*) at the microfocus beamline ID13 (EH2) in January 2010. The single fibre samples (fibre diameter typically 10-15µm) were prepared before the experiment and were fixed to plastic carriers, in this way to be inserted into the homebuilt, piezo-driven microstretching device. A more detailed description of the microstretching device design is given in [1]. Measurements in SAXS and WAXS geometry were performed with in situ stretching of the irradiated fibre. Both the applied force on the fibre as well as the resulting strain were measured in real time by means of the force and displacement sensors included in the microstretching device. A video image of the sample was used as an aid for the alignment of the sample into the beam after sample exchange as well as a visual check for fibre failure. In SAXS geometry the sample to detector distance was ~17 cm while in the WAXS part of the experiment the distance was reduced to ~10 cm, in both configurations the photon energy was set to 12.5

keV and a CCD detector (Frelon 4M) was used. The X-ray spot size at the sample position was 5 × 2.5 µm² (horizontal × vertical) focused by means of a KB mirror optics. Due to the weak scattering power of single silk fibres at small angles, the parasitic air scattering soon turned out to be a major contribution to the recorded SAXS patterns. This is why it had to be significantly reduced by a short, improvisational helium filled flight-path of 10cm length, covering the space between the sample and the beamstop. A photograph of the experimental setup is shown in figure 1. Still, to retain a decent signal after subtraction of the background scattering the data were recorded with a 4x4 binning of the CCD detector and the exposure time was chosen to be 3 seconds, this being the limit at which radiation induced degradation of the scattering pattern (i.e. radiation damage) proved to be just acceptable. The main intention of the experiment was to record SAXS images from single silk fibers for the first time. All of the SAXS data on silk fibres previously recorded by us (DELTA in Dortmund and HASYLAB in Hamburg) suffered from a distinct orientational "smearing" caused by the necessity to use bunches of fibres rather than single fibres, which in turn was required to obtain a sufficient SAXS data at these synchrotron sources.

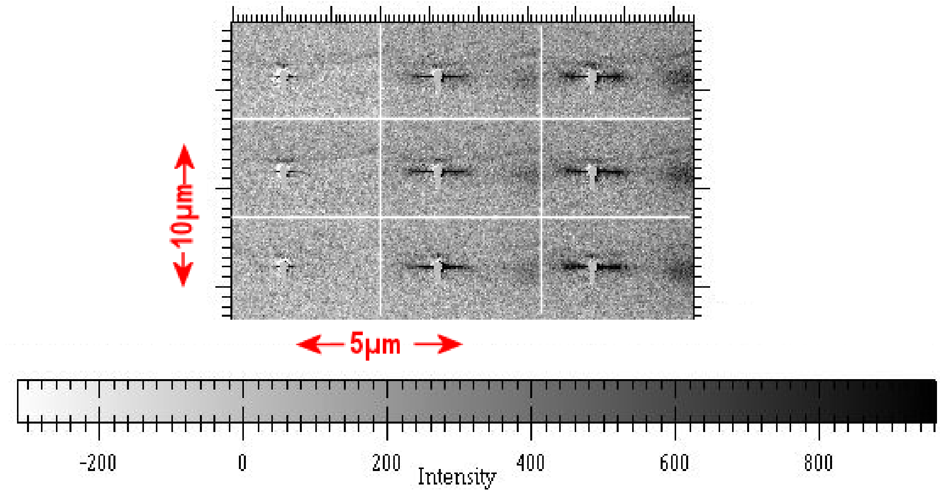

Fig. 2 Excerpt of a 2d-mesh-scan performed on a single silk fiber with a step width of 5µm (horizontally) and 10µm (vertically). Each of the 9 separate images show only the (slightly offset) region of interest close to the beamstop. The fiber is aligned vertically (diameter 12µm) and the increase of scattering signal, resulting from the beam gradually passing over the fiber's edge (from left to right) is clearly visible.

As shown exemplarily in the excerpt of a mesh-scan in figure 2, the recorded SAXS patterns expose no significant lateral or axial position dependency as only an intensity scaling effect is apparent, caused by the gradual illumination of the fibre by the beam during the scan. Nevertheless, SAXS images from all of the investigated samples (9 samples, each with a single fiber) contained an equatorially oriented signal at low angles and a well-defined intensity maximum at an equatorial q-value of about 6.5 nm^{-1}. This peak, whose major origin assumably is the 010 reflection of the nanocrystallites, was not observed before in our SAXS measurements. A further analysis of this peak needs therefore to be performed, particularly to verify that it does not originate from small amounts of the silk-wax sericin that – depending on the degumming method employed – occasionally remains on the surface of the fibres.

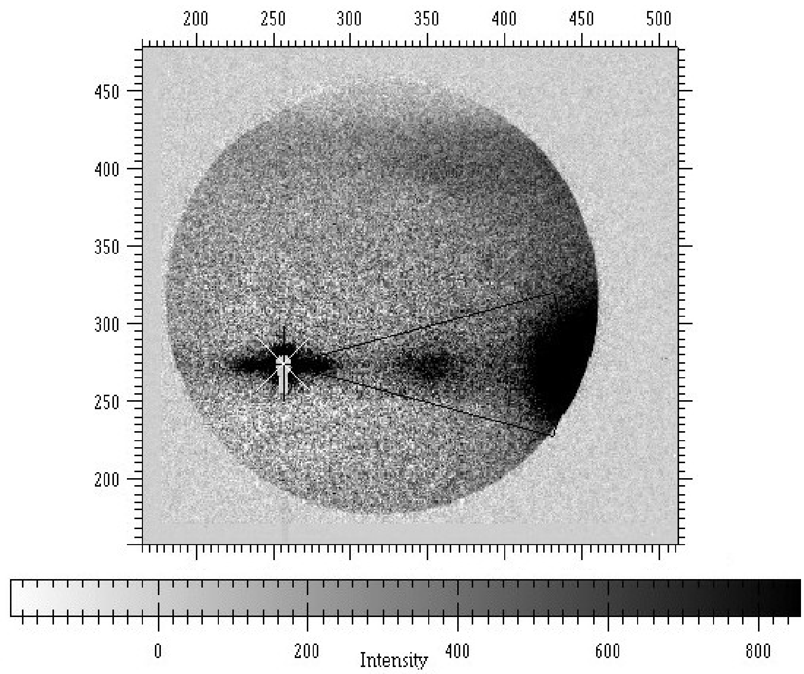

Fig. 3 Full size SAXS image recorded on a single silk fiber at 2% strain. At the left side the beamstop is visible and the 020 reflection clearly visible on the right side, although cropped by the flightpaths circular aperture. The peak in the middle (q ~ 6.5 nm^{-1}) was observed for the first time in X-ray diffraction measurements on silk. The lines indicate a radial section used for the subsequent integration.

The influence of the fibre strain on both, the equatorially at small angles oriented signal as well as the "new" peak needs to be examined thoroughly. For this purpose we have recorded images at different fibre strain values, ranging from 0% (i.e. tight but not elongated fibre) to 2%.

Although we were able to measure a higher maximum strain of up to 6% in preceding measurements on bundles of fibres at HASYLAB, the fibres in the experiment reported here generally failed at slightly over 2% strain at the latest. This is obviously a consequence of the required, long exposure of the fibres by the high flux, microfocused x-ray beam.

Contrary to the proposal we have not varied the humidity within the measurements because our latest SAXS data taken at HASYLAB on (thin) silk bunches exposed no significant effect of humidity.

However, in addition to the SAXS measurements we have recorded WAXS data. For this reason the sample to detector distance was reduced and the flight path removed. In this geometry unrestrained images were recorded at different fibre tensions at single fibres. These data will be used not only as a reference for the SAXS measurements but also will be very helpful to verify previously recorded WAXS data, taken at both single fibres as well as fibre bundles.

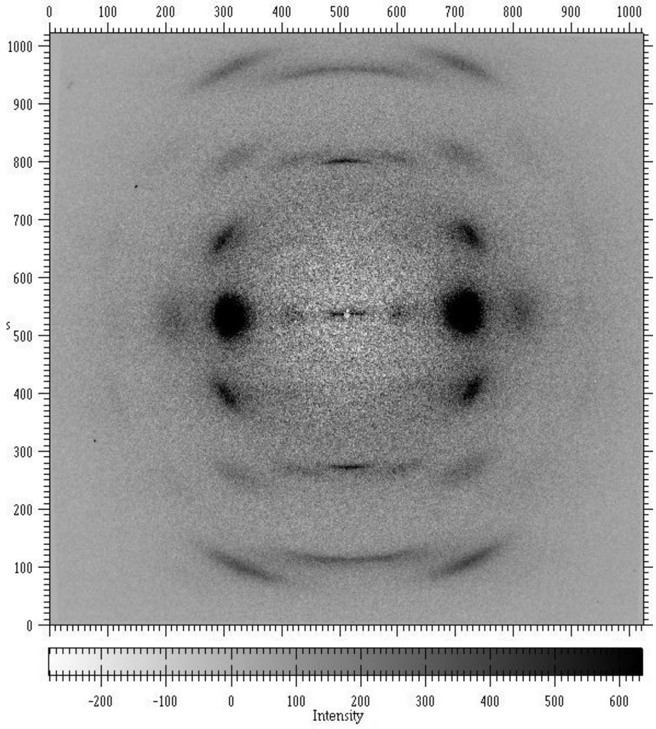

Fig. 4 Full size WAXS image recorded on a single silk fiber at 0% strain.

References

[1] Krasnov et al. *Phys. Rev. Lett.* **100**, 048104 (2008)