ESRF	**Experiment title:** Structure of Silkworm Silk Fibroin Crystallites as a Function of Hydrostatic Pressure	**Experiment number**: SC-3062
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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. 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, mainly because the process how the liquid fibroin solution eventually turns into a silk fibre is still poorly understood. In fact, even the knowledge about the structure of the fibre's nanocomposite elements is incomplete, e.g. the very shape of the nanocrystallites as well as their exact inner structure.

An attempt to fill in this gap was a high-pressure WAXS experiment at the microfocus beamline ID13 (EH2) in December 2010 performed on silkworm silk (*Bombyx mori*) and spider silk (*Nephila edulis*). Data was also recorded from other fibrous biological and synthetic samples: different cellulose fibres, wood, hair (without bulb), polyaramide, polyethylene, carbon, polyamide, polypropylene, polytetrafluoroethylene, polyester, polyethylenterephtalate. The photon energy was 23keV and the beam size was ~ 30 × 30 µm². The employed detector was a MAR CCD at a sample-to-detector distance of ~35 cm. In all measurements the self-built high-pressure hydrostatic cell [1] with diamond-windows was used (see Fig. 1). Mounted into a sample holder, each sample was inserted into the pressure cell where it was subsequently surrounded by the pressurizing liquid (water). Data was recorded at selected pressures within the pressure range of 100 to 5500 bar and the acquisition time for each measurement was 10 to 60 seconds, depending on the sample type. The data at 100 bar were considered to be equivalent to atmospheric pressure as at this low pressure no structural changes in the sample were expected. However, at 100 bar we could

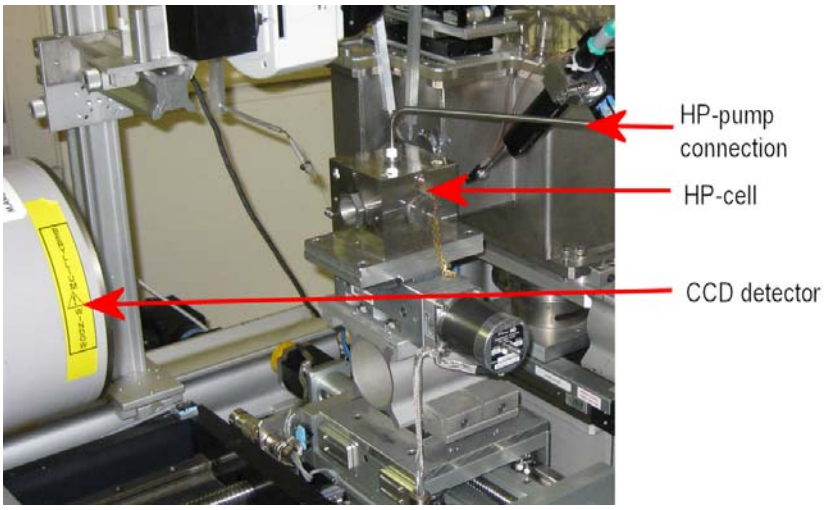

Fig . 1 Photograph of the high pressure (HP) experimental setup.

assume that no gas bubbles remained in the pressurizing liquid. Fig. 2 shows exemplary, background subtracted diffraction images recorded from every of the investigated samples, with the sample being aligned horizontally. After azimuthal integration of selected equatorial and meridional sections of the 2D-data several corrections were applied to the so achieved 1D-data. These corrections were necessary to compensate for the pressure induced changes in scattering contrast, caused by water and the sample having different, non-negligible compressibilities. Also, the pressure dependent weakening of the scattered intensity had to be accounted for, which is due to the density increase of the pressurizing medium (water) through which the scattered signal must pass before it exits the sample cell. For the data already evaluated, a similar pressure dependence is evident. On one hand, all equatorial peaks exhibit a more or less pronounced, reversible shift to higher q-values when pressure increases. On the other hand, the meridional peaks appear to remain constant over the entire pressure range. This finding fits well into the model assumed for the nanostructure of the corresponding biological and synthetic polymers. Within that model the main equatorial peaks are attributed to an intersheet or interchain spacing of the nanocrystallites which in turn are aligned mostly parallel to the fibre axis. Consequently, the equatorial peak shift corresponds to a closing in of the beta sheets or polymeric chains. For silkworm silk the obtained data complement very well our previous WAXS data recorded with tensile strain applied (i.e. stretching the fibre) where there is only an increase of intra-sheet distances, i.e. a shift of the meridional to lower q-values [2]. Having the shifts of each peak the elastic modulus of compression (E modulus) for the corresponding crystal axis can be easily obtained from a compression-pressure plot (plots for some of the already evaluated data are shown in Fig. 3). By this a better understanding is accessible for both, the geometry and properties of the nanocrystallites, which in turn contribute significantly to the mechanical properties of the silks. Further data evaluation is in progress.

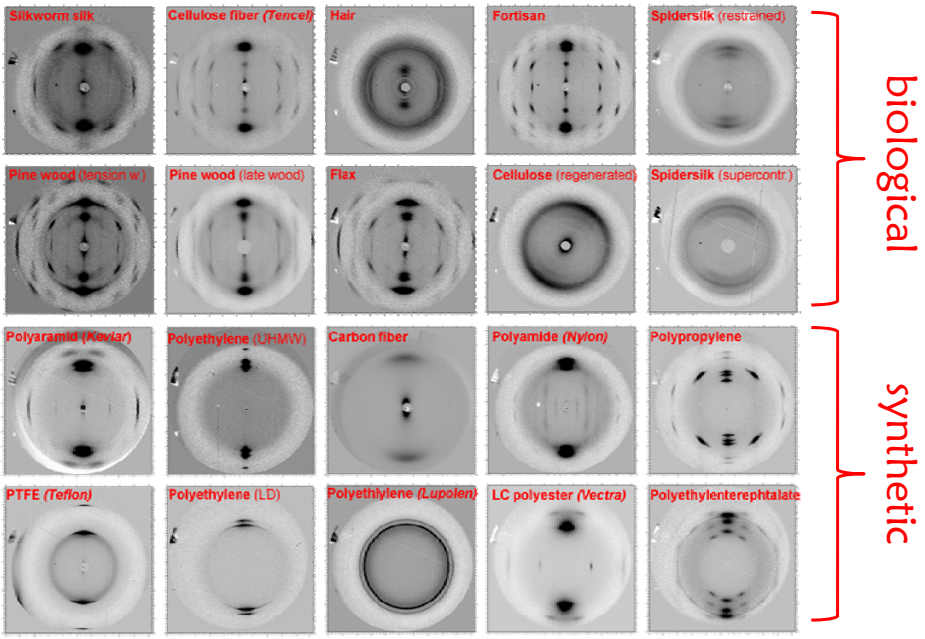

Fig. 2 Background subtracted data for all investigated samples recorded in the high-pressure sample cell at the reference pressure of 100 bar. The fiber axis is horizontal.

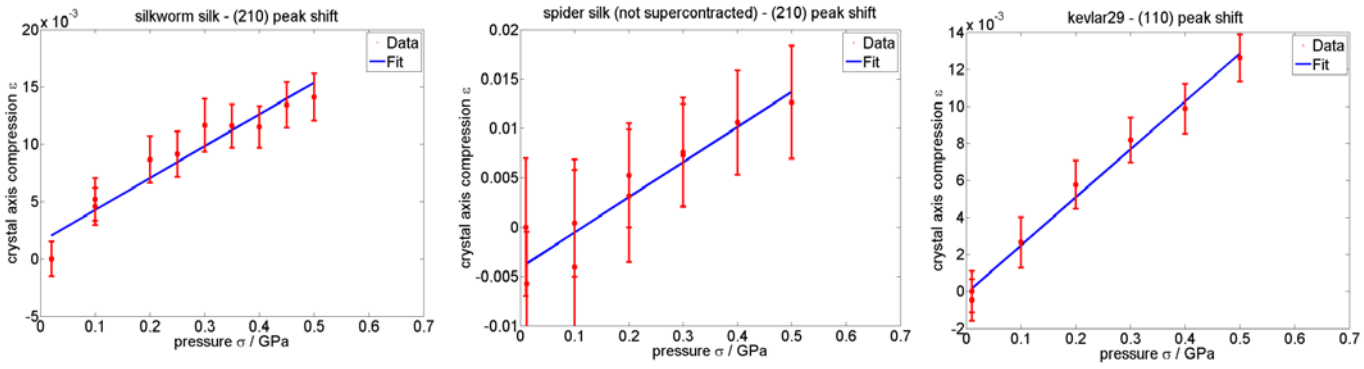

Fig. 3 Compression-pressure plots for selected equatorial peaks of three exemplary samples: *Bombyx Mori* silkworm silk, *Nephila Edulis* spider silk, Kevlar29 polyaramid. From each fit the corresponding compression modulus (E modulus) can be obtained.

References

[1] C. Krywka et al. *Chem. Phys. Chem.* **9**, 2809 (2008)
[2] Krasnov et al. *Phys. Rev. Lett.* **100**, 048104 (2008)