ESRF	**Experiment title:** Microstructural characterization of spider silk (MAS, miS and Flag) and bionspired fibers	**Experiment number**: SC3072
Beamline: ID13	**Date of experiment**: from: 10.9.10 to: 12.9.10	**Date of report**: 7.2.11
Shifts: 9	**Local contact(s)**: C. Riekel, M. Burghammer	*Received at ESRF:*

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Report:

Four sets of materials were studied: two sets of natural fibers (spider silk MAS either natural or after ultraviolet irradiation), one set of regenerated fibers produced through a wet spinning technique, and a set of collagen-rich membranes.

(1) Evolution of the microstructure of natural spider silk (MAS) fibers under tensile loading.

Spiders have the ability to modify the properties of spider silk to adapt it to their immediate requirements. This property had been assessed in our group through tensile tests, and the results obtained during this experiment have allowed obtaining, for the first time, detailed information on the microstructural changes associated with the changes in the mechanical behaviour (Figure 1).

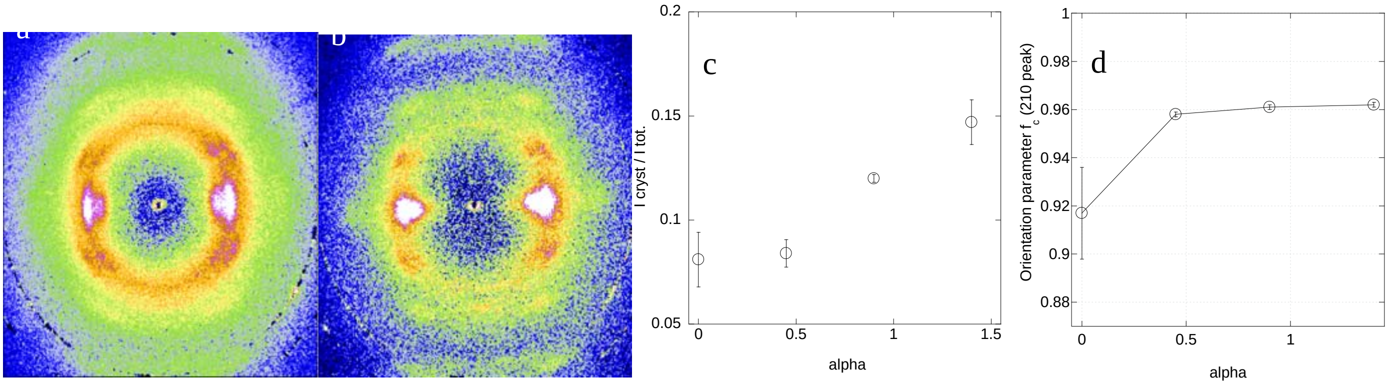

Figure 1. (a) XRD diffraction pattern of a minimum aligned sample (alignment parameter, α=0.0), (b) XRD diffraction pattern of a maximum aligned sample (alignment parameter, α=1.4), (c) evolution of the crystalline fraction with the alignment parameter, α, (d) evolution of the orientation of the nanocrystals with the alignment parameter, α.

The results show intriguing microstructural changes as the alignment parameter, α, is increased through tensile loading in water. It is found that the orientation of the nanocrystals increases at low values of the alignment parameter, and it finally reaches a plateau at high values of α. In contrast, the nanocrystalline volume fraction remains constant at low values of the alignment parameter, and increases monotonically at high values of the α. (Figure 1, (c) and (d)).

(2) Evolution of the microstructure of spider silk (MAS) irradiated samples.

Previous results obtained in our group had shown that UV irradiation exerts a significant influence in the tensile properties of silk fibers. The results obtained during this experiment have allowed studying the microstructural changes associated with irradiation and its evolution with irradiation time.

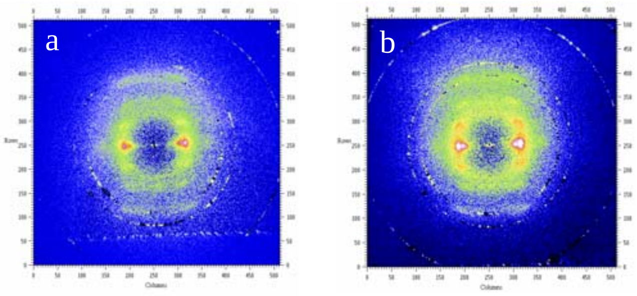

Figure 2. (a) XRD diffraction pattern of a spider silk (MAS) fiber prior to irradiation (control sample), (b) XRD diffraction pattern of the same fiber after 14 h UV irradiation.

(3) Microstructure of silkworm silk regenerated fibers. The microstructure of regenerated silkworm silk fibers (i.e. spun from a dope of previously dissolved silkworm silk proteins) have been analyzed. It was found that regenerated fibers, under the spinning conditions used for their production, do not show any crystalline fraction in their microstructure (Figure 3a).

(4) Microstructure of collagen rich membranes. Collagen rich membranes have a number of applications as biomaterials, such as replacements for heart valves, due to their high biocompatibility. The properties exhibited by these materials depend critically on the orientation of the collagen fibrils at a micrometer scale. The preliminary work has shown that XRD diffraction patterns that allow determining the preferential orientation of the fibers can be obtained at ID13 (Figures 3b-3d).

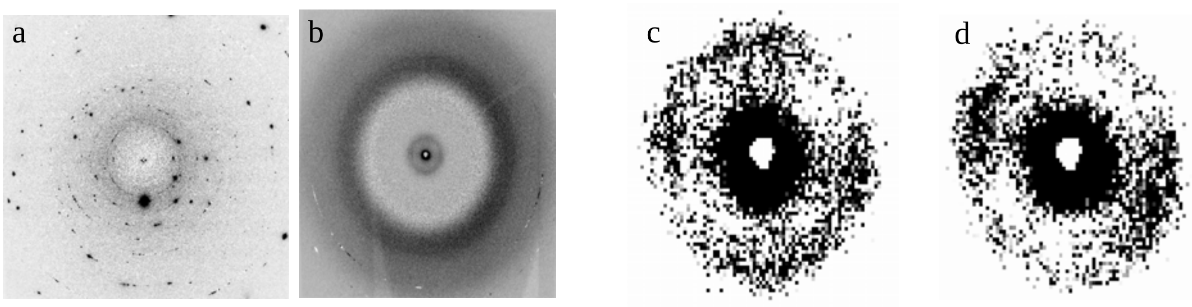

Figure 3. (a) XRD diffraction pattern of a regenerated fiber. No spots of fibroin nanocrystallites were found. (b) Typical diffraction pattern of a collagen rich membrane. Observation area is 1 μm^2. (c) and (d) Average patterns of a collagen rich membrane at different observation areas. The preferential orientation is apparent from the variation in intensity between both observation areas.