

## PhD defence by Irina Iachina

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# Spider silk and artificial spider silk

Spider silk is one of nature's super materials due to its superior mechanical properties such as extraordinary elasticity and strength. With these properties spider silk would be of use in industries such as transportation and textiles, thus motivating the research into the properties of natural silk and the production of artificial silk.

The aim of this project is to characterise the micro- and nanoscopic structure of Major Ampullate silk (MAS) and Minor Ampullate silk (MiS) spider silk fibres from the orb web weaving spider *Nephila madagascariensis* in both natural and super contracted state. A review of the current state-of-the-art of spinning artificial silk is also presented.

Using Confocal Raman mapping, Coherent anti-Stokes Raman scattering (CARS) microscopy and confocal microscopy it was found that spider silk fibres consist of an outer hydrophobic lipid containing layer >500 nm thick. The core of the fibres was found to be two separate protein layers where in MAS fibres the inner component showed an increased amount of proline, tyrosine, leucine, alanine and disordered structures, which confirmed the presence of MaSp2 in the core. It was also found that the outer protein core had a higher content of tryptophan, where the hydrophilic dye Rhodamine B, in both MAS and MiS fibres, showed a higher affinity towards these inner proteins and FITC showed a higher affinity towards the outer protein layer.

Using scanning Helium ion microscopy and ultra-resolution confocal scattering fluorescence depletion (CSFD) microscopy it was found for the first time in a pristine spider silk fibre that the protein core consists of fibrils with a diameter between 89 and 228 nm arranged parallel to each other and to the length of the fibre.

During super contraction it was found that length of both MAS and MiS fibres decreases, and with CARS and confocal microscopy it was found that the diameter of MAS fibres increases by around 2  $\mu\text{m}$ , while the diameter did not increase in MiS fibres. Confocal microscopy showed that super contraction causes a change in the material properties of the fibre as affinity of the dyes used changed compared to non-super contracted fibres.

With CSFD microscopy it was found that super contraction in MAS fibres causes an increase in diameter of the fibrils and an increased distance between the fibrils.

Through a literature study it was found that the current systems for making artificial spider silk proteins are not able to produce large enough proteins except for one case in *E. coli*. The mechanical properties of the produced artificial spider silk fibres were found to be very dependent on the size of the spider silk proteins as the highest quality silk is made from the largest proteins. But the mechanical properties of artificial silk are still inferior to natural spider silk.

It was found that the spinning techniques wet spinning, electrospinning, and microfluidics in their current state are not able to produce high quality silk with proper mechanical properties. This is thought to be due to the lack of biomimicking in these experiments i.e., that the production methods do not include the same process as found in the spider.

In this work wet spinning of artificial spider silk was done but the resulting fibres were of poor quality. Preliminary results from different 3D focusing microfluidic chips are presented. However, more research is needed to successfully create artificial spider silk using these chips.

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