

Silk's secrets

Edward Atkins

Despite centuries of human use of silk fibres from silkworm cocoons, and an emerging industry devoted to making artificial silk, questions remain about how insects produce it. New work *in vitro* tackles the problem.

Once solely the purview of insects and spiders, the production of silk fibres is now a biotechnological reality. Fibrous silk is used widely, in materials from clothing to carpets to parachutes, so there's a great deal of interest in understanding the precise details of how it forms from silk proteins — whether *in vivo* or in artificial circumstances. Hence the importance of the paper on page 1057 of this issue, where Jin and Kaplan¹ describe several early steps in fibre production.

The traditional method of obtaining silk involves meticulously unravelling the fibres from silkworm cocoons (Fig. 1) and weaving them into fabrics. But other sources of silk fibres are now available. For example, Nexia Biotechnologies, based in Montreal, has developed 'transgenic' goats that express spiders' silk proteins in their milk². These proteins have been processed into fibres with the registered trade name BioSteel.

The production, or spinning, of silk fibres by silkworms and spiders incorporates many facets of polymer physics, as well as chemical and biochemical control³. Properties such as strength, toughness and (in certain spider silk fibres, for instance) elasticity are now being understood at a fundamental level and can be manipulated. For example, the dragline silk of the spider *Nephila clavipes* — hailed as a 'super-fibre'²⁻⁵ — is much stronger and more extensible than traditional silk from the silkworm *Bombyx mori*. Indeed, dragline spider silk has been reported to have a strength only 15% lower than that of high-tensile engineering steel, and, because of the much lower relative density of silk (17% of that of steel), it is a far stronger material³.

In terms of manipulation, Shao and Vollrath⁶ have shown that, by changing the reeling conditions, silkworm silks can be made stronger, stiffer and more extensible, approaching the properties of spider dragline silk. And the opportunity exists for modified silk proteins — designed to give even better silk fibres — to be genetically engineered and produced in large quantities, thereafter being mechanically spun using controlled water content and elongational stress. This would form the basis for a renaissance in silk materials. Given these many possibilities, it is important that any remaining puzzles about the mechanism of silk spinning should be solved.

Silk proteins — known as silk fibroins — are stored in the glands of insects and spiders as an aqueous solution. During the spinning process, by which fibres are produced from this silk 'dope', the concentration of silk in the solution is gradually increased, and finally elongational stress is applied to produce a partly crystalline, insoluble fibrous thread in which the bulk of the polymer chains in the crystalline regions are oriented parallel to the fibre axis.

It is known that silk fibroin consists of both hydrophilic and hydrophobic regions — it is a block-like polymeric system. But what scientists are still not sure about is how this complex silk protein can be maintained in a concentrated silk dope without fear of irreversible precipitation or crystallization, potentially blocking the whole spinning device. It is understood that the water is acting as a plasticizing agent, keeping the protein malleable, but the nature of the silk itself in this environment remains largely

unknown. Nor is it known how the protein changes in structure, texture or morphology with increasing concentration, finally emerging, after the final stages of elongational stress, as an insoluble fibre.

Enter Jin and Kaplan¹, who, in their elegant experiments, have followed the behaviour of silk solutions as a function of a controlled decrease in the water content. Starting with cocoons of *B. mori*, the authors first 'degummed' them — removing the sericin proteins, which glue the fibroins together in the cocoon — and then redissolved the silk fibroin. Next they created an osmotic stress by adding gradually increasing amounts of the high-molecular-mass compound polyethylene glycol (either mixed in with the fibroin dope or segregated by dialysis membranes), which preferentially competes with the silk fibroin for the water molecules in which the protein is dissolved.

The results show the development of phase separation and the appearance of nanoscale colloidal-like particles (micelles) as water levels are reduced. These micelles are believed to form by the folding of silk chains through their hydrophilic blocks, thereby allowing the hydrophobic blocks to be in close proximity; the folded entities then associate with each other to generate spherical micelles with diameters in the range 100–200 nm. The micelles themselves aggregate as the water content is decreased still further, forming micrometre-scale globules and gel-like states.

The appearance of similar globular structures in the fracture surfaces of native silk fibres supports the contention that these laboratory experiments are mimicking the natural process. The authors suggest that an explanation of this phase behaviour lies in the hydrophobic/hydrophilic partitioning and folding of the silk fibroin — both of which are processes regulated by the water content. Jin and Kaplan show further that adding directional stress causes deformation of the globules, which then line up in the same orientation.

Quite how the deformed globules then form fibres is a question for the future. But Jin and Kaplan's findings should already prove useful, providing a basis for researchers to investigate how far it is possible to manipulate silk spinning, and how to engineer new silk proteins that can still form fibres. ■

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Figure 1 Silk maker: *Bombyx mori*.

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