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14. ABSTRACT We gained significant new insights into the role of hydration for silks with our data allowing us to model in considerable detail the interaction between silk molecules and water. Our fibre and feedstock experiments demonstrated that the hierarchical morphology in the patterning and mesophase assembly is spatially optimised. Our multiscale model, based on experimental data collected iteratively - and focussing on the control of energy storage (strength) and dissipation (toughness) at the molecular level and the distribution and exchange of energy at the nanoscale - allows us to predict the full stress-strain profile to failure of any silk or silk-like material. In our investigations of silk composites we gained novel insights into the structure and functionality of natural silk composites as well as the integration of native silks with synthetic resins. In summary of the composite work packages I conclude that the Bombyx cocoon as given some interesting insights but that the Gonometa cocoon (and others like it) seems poised to provide some truly novel insights. Moreover, the comparison of these cocoons with spider cocoons and webs will lead to a much better understanding not only of natural composites but also about the evolution and constraints on the silk materials themselves.					
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a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (include area code) +44 1865 271216



UNIVERSITY OF OXFORD
DEPARTMENT OF ZOOLOGY
SOUTH PARKS ROAD OXFORD OX1 3PS

Direct line: (01865) 271216
Facsimile: (01865) 310447
E-mail: fritz.vollrath@zoo.ox.ac.uk

From: Prof. **Fritz Vollrath**

19/02/2009

4015 Wilson Boulevard
Room 713
Arlington VA 22203
U.S.A.

Enclosed please find my

Final Report to the AFOSR on:

**SPIDER SILK SPUN AND INTEGRATED INTO COMPOSITES.
2006-2008**

Fritz Vollrath, Oxford University, England

Subject FA9550-06-1-0311

A handwritten signature in black ink, appearing to read 'F. Vollrath'.

Prof. Fritz Vollrath

COVER SHEET

Final (3rd Year) Report to the AFOSR on:

SPIDER SILK SPUN AND INTEGRATED INTO COMPOSITES.

Fritz Vollrath, Oxford University, England

Subject FA9550-06-1-0311

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SPIDER SILK SPUN AND INTEGRATED INTO COMPOSITES.

Fritz Vollrath, 3rd Year Report (starting date of project : Spring 2007)

SUMMARY AND OVERALL OBJECTIVES OF THE PROJECT:

The extreme toughness of some dragline silks does not depend solely on the folding of the major component protein but also on the hierarchical structure of the multi-protein thread. For folding and hierarchy the spider's complex spinning process plays a major role; a process that is largely devoted to the controlled extraction of water. This project offers two approaches to discover the underlying principles and design characteristics responsible for toughness in silks. Firstly, we study the behaviour of silks *in vitro* and compare it to natural *in vivo* spider and insect silk extrusion systems. Secondly, we analyze the results of these measurements and integrate the data into a formal model for silk properties. Thus the first and second goals of our work programmes will lead to a better understanding of not only the material properties of silk fibres (including the comparison with man-made filaments) but also a solid understanding of the extrusion process that leads to fibre formation. The third goal of our work programmes is a better understanding of the use of silks (specifically spider silks) in composites; to this effect we are expanding our studies of silk integration into composites containing a range of matrix materials.

Status of effort: The funds for the three (3) year project were granted in the fall 2005 and the project started as planned at the beginning of 2006.

Accomplishments/New Findings during 2006-2008:

SUMMARY We gained significant new insights into the role of hydration for silks with our data allowing us to model in considerable detail the interaction between silk molecules and water. Our fibre and feedstock experiments demonstrated that the hierarchical morphology in the patterning and mesophase assembly is spatially optimised. Our multiscale model, based on experimental data collected iteratively - and focussing on the control of energy storage (strength) and dissipation (toughness) at the molecular level and the distribution and exchange of energy at the nanoscale - allows us to predict the full stress-strain profile to failure of any silk or silk-like material. In our investigations of silk composites we gained novel insights into the structure and functionality of natural silk composites as well as the integration of native silks with synthetic resins. In summary of the composite work packages I conclude that the Bombyx cocoon as given some interesting insights but that the Gonometa cocoon (and others like it) seems poised to provide some truly novel insights. Moreover, the comparison of these cocoons with spider cocoons and webs will lead to a much better understanding not only of natural composites but also about the evolution and constraints on the silk materials themselves.

INTRODUCTION: Silks are most remarkable biological products. Commercially a champion for over 6000 years, the silk of the *Bombyx* moth larva is well known for its textile qualities, which still ensure an annual market on par with top quality synthetic fibres. Spider silks have no commercial market as yet but have led to revolutionary new insights into silk properties because - unlike insect silks - they have evolved to perform best under tension and are thus uniform in material qualities along the length of the fibre. Moreover spider silks can be drawn from the animal 'on demand' and under highly controlled conditions. Hence much of what we now know about the molecular structure-function relations in the biological elastomer 'silk' derives from recent studies of spider silks. Much of the effort of the Oxford Silk Research Group in the last year was devoted to transferring knowledge gained from studying spider silks to deriving new insights in insect silks.

Silk, unlike other important biological materials, is the result of continuous extrusion and not of cellular growth processes. Polymer extrusion is an industrial reality, while industrially growing controlled structures is as yet a dream. This makes silk the prime contender to provide the template we need in order to design and industrially produce a functional imitation-biomaterial. However, apart from this, silk provides us with many interesting insights into the basics of protein form and functionality, with important implications not only for materials research but also for the interface between the life and the physical sciences.

As we have shown in this reporting period, silk is indeed an ideal natural material to use as a model for a wide range of other biological elastomers, most of which must perform in the hydrated state. Silk can function in a wide range of states of hydration; from dry webs and cocoons through to air-sacs for underwater spiders, and with the subtle control of tightening sagging webs by supercontraction with dew condensation. Understanding the interaction of biological elastomers with water is a key requirement if we are to produce synthetic biomimetic analogues. Biological functionality, after all, relies on wet engineering.

OUTLOOK: There are many other natural hybrid nano-composites. In bone, for example, the hydroxapatite mineral with a thickness of about 2 nm is embedded in a 5 nm thick layer of hydrated tropocollagen, which is tuned precisely to operate in its most efficient energy dissipation state around its glass transition point. At the nanoscale, bone can be seen as a direct analogue of silk, with ordered domains related by mineral and disordered domains by hydrated tropocollagen. Bone is perhaps a more flexible scaffold for mechanical energy distribution over a wider range of dimensional scales, but silk is ideal for direct energy transfer and manipulation at the nanoscale. Combining the two might lead to very interesting novel nanocomposites.

RESULTS AND DISCUSSION: A key factor in the silk's remarkable structure properties relationship is the scaling of its semi crystalline morphology. Silk consists of typically two proteins, one very large and one much smaller, which combine to form a nanoscale morphology of domains that comprise at the simplest level ordered

(crystalline) and disordered (amorphous) polymer. The ordered domains can be attributed quite specifically to oriented beta-sheet crystals with strong amide-amide hydrogen bonding while the disordered domains can assume a wide range of structures with varying degrees of hydrogen bonding. Throughout this heterogeneous complex it is the fact that the dimensions of the various domains are kept at nanoscale, which allows for a highly efficient (i.e. rapid and comprehensive) transfer of energy throughout the material. This, of course prevents the local stress concentrations that would lead to premature failure. Perhaps counter-intuitively, silk has a relatively low stiffness (5 - 15 GPa) for a high strength fibre, and its high degree of orientation is actually fragmented into nanoscale 'beads' of hairpin folds along its length. Quantitatively, our data, analysis and model allows us to estimate that the maximum strength of a spider silk of about 1.4 GPa requires domains of the order 2-4 nm in size, comparable in 'grain dimensions to the units to convey strength in super-hard metals and ceramics.

The inherent simplicity but detailed complexity of the nano-scale interactions give the silks its desirable and highly tuneable properties. It relies on the processing procedure where the protein molecules fold into a complex that contains both the proper intra-molecular self-organisation as well as the required inter-molecular self-assembly. The guidance in these two processes, which occur together and are closely linked, lies in the genetic control of the exact positioning of the amino acids that make up the side chains of the silk-polymer macromolecules. Whether the block co-polymer molecules of the individual silk proteins form true liquid crystals or semi crystalline complexes (that behave like a LCs) is still open to debate. However, a precursor morphology appears already to be generated in the synthesis of the primary structure of the protein. This viscous precursor is converted to a solid nanostructured fibre as minute changes in pH in combination with mechanical forces of the extrusion rheology destabilise the aqueous spinning dope. In this denaturing sol-gel process the solvent water is spontaneously ejected from the fibre as it is drawn.

A fundamental analysis of the role of interactions between water and amide groups in a protein chain suggests how combinations of biological stresses such as temperature, mechanical load, and chemistry can destabilise a protein and destroy its biological function. Our cross-disciplinary models (based largely on polymer theory but applied to protein chemistry and evolutionary biology) use detailed quantum mechanics simulations examine in detail the physics and chemistry of hydrogen bonding between water and amide groups in a protein macromolecule. This allows us to predict an energy condition for the instability, which could then be translated into real biological stress conditions of temperature, mechanical load, and chemistry. An important outcome of the model is the ability it provides to calculate the dynamics of the instability transition over a very wide range of time scales (from seconds to a hundred years). This in turn will provide new insights into the long-term thermo-mechanical stability of silks.

Our analysis allows us to calculate in detail the role of water i.e. the silks hydration properties. For our calculations, we focussed on the state of order (crystal, amorphous, or liquid), which we were able to quantify from energy terms derived from the quantum simulations. Surprisingly, the same quantum simulations allowed us to predict both the

crystal melting point of water/ice and the more esoteric glass transition temperature of disordered water molecules at about 150K. The model was developed largely based on data collected from silk fibres and silk spinning feedstock's, although it was later taken by Dr Porter further deep into the wider field of polymer structure properties relationships.

In our project 2006-2008 we set out, firstly, to study the importance of the experimental and natural spinning (extrusion) processes for fibre formation and its mechanical properties. These studies of *in vitro* and *in vivo* silk formation are a crucial step for any deeper understanding of the material itself. In addition, secondly, we set out to explore the use of silks in composites, both natural and man-made.

Spider silks combine basic amino acids into strong and versatile fibres where the quality of the elastomer is attributed to the interaction of highly adapted protein motifs with a complex spinning process. Studying of a range of spider silks allows us to measure structural disorder and correlate this with amino acid content. A first analysis of the glycine residue content gave interesting and, we think, important insights into the evolution of the elastic properties of silks. A novel concept, the protein folding index γ , helps us to quantify disorder in the spider's silk precursor proteins. Circular dichroism (CD) spectroscopy allowed us to determine the characteristics of the silk proteins folding and thermal stability. The temperature-induced structural transition of freshly-extracted silk protein feedstock and determined their folding index, γ . This folding index γ is defined as the ratio of the two minima in the spectrum and is indicative of the degree of unfolded structure present in solution at the temperature of the silk dope. A low γ corresponds to predominantly unfolded structures and a high γ indicates mostly folded structures. Thus the folding index γ represents a normalized measure of disorder. Using the 7 different silks of *Nephila edulis* as a benchmark system we demonstrate that γ is highly correlated with ratio of glycine present. This correlation was tested against all other amino acids in these silks, as well as silks from other spiders. From these data we derive to a general model about the role of glycine residues in the structure-property relationship of silk proteins. Interestingly, biophysical and evolutionary considerations suggest that silk elastomericity evolved in tandem with specialisations in the process of silk spinning.

Previous experimental and modelling work in our group suggested not only that glycing is a key determinant but also that the amino acid proline plays a special role for silk properties. In order to study this hypothesis, we collected major ampullate (MAA) silks from a variety of spider species by artificial silking tuned (in silk speed) to produce samples with similar breaking strains. Such silks can be 'made' to be nearly identical in post-yield mechanical properties. However, the super-contraction behaviour and their initial moduli of such silks will vary over a wide large range with both parameters correlating with the content of proline in the silk. These relationships, in combination with protein sequence data, support the hypothesis that the proline-related motif i.e. GPGXX plays a key role for the structure-function relationship in spider silk. This conclusion would explain the large interspecific variability of spider dragline silks observed by us and other groups. Moreover, MAA silks from three representative species studied in some more detail were prepared in a range of processing conditions and their

mechanical properties were compared. Here our observations give some indications on how the chemical composition of silk interacts with the processing conditions and how together the two shape the mechanical properties of a silk.

Native silk dope taken straight from the gland can easily and without chemical assistance be drawn into strong fibres. Artificial silk fibres, on the other hand, rely on spinning dopes typically 'reconstituted' from natural silk fibres by strong chaotropic agents. Such fibres do not form readily, and often require chemical post-spin treatment for stabilisation. In addition these fibres tend to be brittle, and so far have been unable to match native fibres. We were able to collect novel rheometric data, which show that native and reconstituted silkworm silk dope differ in kind, not just in degree. While native silks behave like typical molten polymers, reconstituted silks do not. We conclude that rheometry provides a powerful tool in the quest to learn from the Nature's polymer fibre technology. The origin for the vast difference in the observed rheologies of native and reconstituted silks is in all probability due to the severe degradation of the silk proteins during the reconstitution process, which appears to reduce molecular size as well as affect its conformation. Such changes would directly determine the impact of shear energy and could explain the reduced viscosities and modulus values we observed in our measurements. Determining, in future work, the individual contributions of, amongst others, size, shape, stability and integrity of reconstituted silk molecules to their 'spinnability' will allow us to devise sensitive protocols aimed to minimise both physical and chemical damage to the silk proteins. This, in turn, will not only increase our understanding of the requirements for silk to be spinnable, but also affect our understanding of the natural spinning processes. Thus, hopefully, comparative studies of the rheological behaviour of native and reconstituted silk dopes in vitro will lead to a better understanding of the in vivo behaviour of the many thousand silks evolved in Nature. And further, such understanding will provide the insights required if we wish to 'design' synthetic silks that can be spun a fully functional biomimetic extruder.

Most importantly, the massive gap in spinning behaviour existing between the native and the regenerated dopes may explain why it has not been possible to create a reconstituted 'silk' fibre with neither the mechanical properties nor the structural complexity of a natural silk, let alone process it in the same way. Clearly these two materials are already different before they are even spun, and it is questionable whether the first can even be called a silk. For biomimetic spinning, i.e. the important step towards the economic and ecological production of artificial silks, it will be necessary, so we believe, to first match the rheologies of reconstituted and native dopes.

In this, the ultimate goal of our studies, to design and produce a silk feedstock that can be spun bio-mimetically we must fully understand the structure-properties-function relationships between the different silk components. Most importantly, we must understand the role in water, silk-dope stability and the processes of silk-protein denaturation because, after all, spinning is controlled denaturation of the silk feedstock.

Key for this goal is an understanding of the stability of the silk proteins in its hydrated states. Thermal, mechanical or chemical stresses can quickly lead to loss of stability.

Key events for many of these denaturation processes are the disassociation of hydrogen-bonded water molecules from the amide groups of the chain backbone and their replacement by stronger inter- or intra-molecular amide-amide bonding. We were able to show quantitatively how thermal, mechanical, and chemical conditions can affect the kinetics of the instability, not only of silk but of any protein, through the probability of release of core water molecules over a very wide range of time scales. For this study we applied an elastic instability criterion to localised quantum mechanics simulations of water-amide bond energy. The kinetics of bond instability were quantified by an expression for a second order phase change using parameters derived directly from the quantum simulations. Thus, our model tells us why and how water stability can control structure and thereby function of, specifically, silk but also, more generally any fibrous protein. This study shows why silk is a perfect model that straddles polymer science and biology, and thus can provide important novel insights for both disciplines.

And, if we ever want to use spider silks in composites we need to better understand their performance in the context of fibre-matrix integration; hence a major goal of our studies is the focus on both the physical properties of silk fibres and the best use of these fibres in composite materials. And how better to study this question as to first analyse the natural composite, the cocoon, in which and for which commercial silk has evolved. Hence we have started, with the employment of Fujia Chen (M.Sc.) , on a systematic analysis of all aspects of this natural composite. with the following first conclusions: (a) silkworm cocoon is an in-plane isotropic composite; (b) the tensile breaking mechanism of silkworm cocoon is shear splitting and multiple delamination; (c) the inner cocoon layers have more damage than the outer layers of cocoon; (d) the delamination starts from two ends of specimen on the inner layer, leading to more delamination among layers; (e) fibre breakage results in the final damage, both breaking strength and elongation of sericin is lower than those of fibroin and, finally, (f) local shear damage is dominant in damaged sericin between fibres, while the sericin at fibre-joint often shows microflow. These analytical studies are presently being expanded to include synthetic composites made of both, native cocoon composite and of single native fibres with a range of 'resins', both natural and synthetic.

In order to develop a quantitative model for silk, we took the radical step of looking at silk from the perspective of a user. Silk fibres are produced by the spider to manage mechanical energy for different tasks without breaking. In particular the silk must store elastic energy in order to support the spider's own weight and in the structural framework of a web it must be able to absorb kinetic energy to capture flying insects. We set out to identify the mechanisms at a molecular level that dictate energy storage and dissipation in a polymer and derive straightforward analytical relations for the full range of mechanical properties that are possible in silk. These relations are expressed in terms of a small number of energy-based parameters with a direct fundamental link to chemical composition and morphological order. In this way, we hope to elucidate some of the key design principles in natural polymers. Moreover, this approach can be applied also to much simpler man-made polymers, thereby offering the potential for the design of improved synthetic polymers. So far our studies so far have shown that the full range of thermo-mechanical properties of silk fibres can be predicted from mean field theory for

polymers in terms of chemical composition and the degree of order in the polymer structure. Thus, we can demonstrate an inherent simplicity at a macromolecular level in the design principles of natural materials. This surprising observation allows in depth comparison of natural with man-made materials.

In the last year of the grant we continued our studies of fibre properties but focused on feedstock properties. Two sets of experiments were particularly interesting. Experiments on the importance of molecular weight on flow properties showed that only silk molecules above 50K Da contributed to the rheological properties and that below 2.5% DW gelation of the material occurs that endows it with rheological properties of a reconstituted silk 100x more concentrated. This has important implications for the area of respinning of silks. Reconstitution somehow damages (e.g. breaks-up or reconfigures) the silk molecules with measurable effects on their rheological properties. Such 'damages' may well be the reason as to why reconstituted fibres and materials are so far from living up to their natural potential. We further continued to work on the rheological characterisation of silk dissolved in an ionic liquids by examining the flow properties of silk dissolved in EMIM Cl. A direct comparison was made to silk dissolved in BMIM, within our "spinnability" analytical framework. These experiments have shown that this is a stable and rapid platform for the rheological comparison of potentially interesting artificial silk feedstocks. The culmination of the technical and theoretical achievements in the silk rheology aspect of the project was seen in work on the rheological instability criteria of the natural silk dope. We have developed a platform to combine temperature and stress energy into a single, quantitative, phase transition diagram. In addition this has begun to provide validation for our theoretical models regarding the stress induced phase transition of silk.

In summary of the fibre and feedstock work packages I conclude that evolution, more than 400 million years of it in the case of spider silk molecules, has seen to it that the hierarchical morphology in the patterning and mesophase assembly is spatially optimised for each of the many specific functions required for survival of the spider and silkworm. In our research this year we have used this natural optimisation of energy resources by evolution, and the wealth of data provided through this process, as the basis and framework for further tuning our a multiscale model that is based upon the control of energy storage (strength) and dissipation (toughness) at the molecular level and the distribution and exchange of energy at the nanoscale in order to predict the full stress-strain profile of silks to failure; right from the strongest dragline threads to the most compliant capture threads in the web. Thus, as this year's data and analysis has demonstrated further, silk is indeed an ideal natural material to use as a model for a wide range of other biological elastomers, most of which must perform in the hydrated state. Silk can function in a wide range of states of hydration; from dry webs and cocoons through to air-sacs for underwater spiders, and with the subtle control of tightening sagging webs by supercontraction with dew condensation. Understanding the interaction of biological elastomers with water is a key requirement if we are to produce synthetic biomimetic analogues. Biological functionality, after all, relies on wet engineering.

In addition to our work on silk feedstock and fibre properties we also studied the integration of native silks into composites, specifically natural composites. A typical natural silk composite is either a web or a spider or silkworm cocoon. Webs are lightweight structures with special design criteria; and we had studied them in detail some years ago. This year we focused on natural silkworm cocoons. These are natural polymer composite shells constructed from a single continuous silk strand that is infused and conglutinated with sericin. Such a cocoon consists of three main parts: an outermost loose mesh structure, the middle shell layers and the innermost tetelette; all of which have different microstructures and functions. The main objective of our investigations this year was to gain a thorough understanding of the cocoon structure and the mechanical behaviour of its components.

To this effect we focused on the cocoon first of *Bombyx mori* where we mechanically tested single fibres, sericin resin and entire cocoon layers. Cocoon material, has strength of 31MPa and an average modulus of 330MPa and is an isotropic material with zero Poisson's ratio. Tensile testing of cocoons shows that the failure mechanism of cocoons is shear breaking and multiple delamination instead of fibre breaking. Samples with different widths have a range of moduli from 250 MPa to 350MPa

Tensile tests on silk fibres from the *Bombyx mori* cocoons revealed that breakage of sericin (1 to 2_μm long) on the fibre could be seen at a tensile strain of 6%. Because of the difference of moduli between sericin and fibroin, the sericin attached on the fibroin broke down into discrete lengths when stretched. This leads to breakage of the sericin between the fibroin. A study of the sericin resin coating was carried out by comparing the strength of natural and degummed silk fibre and calculating the strength of sericin using a *Law of Mixtures*, which says that the strength of the composite (fibre) is given by the volume fraction adjusted sum of the strength of the constituents. We found that the strength of sericin can vary from 15 to 30MPa.

As a *Bombyx mori* cocoon is a 3D structure fibre network, it is rather difficult to define a "layer" in the cocoon. Basically, literature suggests that it consists of three main parts: the outermost cocoon coating, the middle shell layers and the innermost tetelette, which have different microstructures and functions. The innermost layer tetelette has a completely different morphology from other layers. The sericin coats the individual fibres and connects them into a net structure. In the other cocoon layers, the double brin filaments in the fibre bave are not always parallel and can separate from each other when crossing with other fibres. The tetelette layer has the highest tensile strength (50MPa) but the lowest breaking elongation (25%) compared with cocoon shell layers (30MPa and 45%), while the cocoon coating layer has 25MPa breaking strength. Also, the strength of fibre from the cocoon coating (outermost layer) is only one third (100MPa) of that of fibre from the cocoon shell (320MPa), and the strength of sericin in the coating layer (4.5MPa) is less than that in cocoon shell (15-30MPa).

Peel tests of layers of *Bombyx mori* cocoons provide a simple independent test to validate the properties that have been used to interpret the mechanical properties of a

cocoon from the component material properties. The test results show that the peel load decreases with decreasing sample width, probably due to the decreasing number of bonds between layers. Simple models were formulated to help understanding the mechanisms operating in cocoons that determine their mechanical properties. The tensile strength of cocoons largely depends on the number of inter-fibre bonds in the sample, while the modulus of cocoons depends upon its density, and the peel testing provides a simple independent test to validate the above properties using consistent material parameters.

In addition to our intensive examination of the commercial silkworm *Bombyx* cocoons we also started a, still more extensive, analysis of another, independently evolved and very interesting silk composite: the cocoon of the African *Gonometa postica*. These cocoons have a very different morphology. The innermost layer consists of fibres (with a diameter about 20 μm) connected by sericin, and microfibrils with a diameter about 1 μm . Fibres in this layer are similar to those in the tetelette (innermost layer) of mori cocoon. The layers in the cocoon shell are similar to *Bombyx mori* cocoon. There are two brins in one bave, although they are not as closely aligned to one another with the bave fibres being aligned (rather than criss-crossing one another). The outermost layer lacks a clear fibre network structure and instead contain's crystals of 10 to 20 μm length.

Gonometa postica cocoon is more like an orthotropic material. It has higher strength in the 90° direction (37MPa), and the yielding point of cocoon in the 90° direction occurs at higher strain (13%). The tensile energy of *Gonometa postica* cocoon is about twice of that of *Bombyx mori* cocoon, as its yield zone of former is longer than that of *Bombyx mori* cocoon, but their strengths are similar. The inner layers have higher strength (20 to 35MPa) than the outer layers (8 to 15MPa). There is a large variation in the mechanical properties even in the same cocoon. The fibres in the wet cocoon entangle with each other. The wet cocoon has lower strength (25MPa) and modulus (25MPa), but higher tensile energy.

In summary of the composite work packages I conclude that the Bombyx cocoon as given some interesting insights but that the Gonometa cocoon (and others like it) seems poised to provide some truly novel insights. Moreover, the comparison of these cocoons with spider cocoons and webs will lead to a much better understanding not only of natural composites but also about the evolution and constraints on the silk materials themselves.

Personnel: Mr Chris Holland submitted his PhD thesis in spring 2008 and was successfully examined in Sept. Ms Chunli Mo (a PhD student of Prof. Shao's at the Department of Macromolecular Chemistry at Fudan University) left my laboratory in Jan 2008 to return to Shanghai to finish her PhD. Ms Fujia Chen, fully funded by the AFOSR grant, worked throughout the year, after joining us in October '07 from Imperial College, London, and has been admitted to Oxford University as a prospective PhD student. Dr. David Porter continued throughout the period 2006-08 (funded by the AFOSR) to analyse our data and use his modelling work to provide hypotheses for further hypothesis testing. Dr Cedric Dicko continued throughout the period 2006-08 to work within the group now (personally now funded by an EPSRC fellowship but involved in

using the project funded equipment and working on its goals) while Dr Ann Terry also continued to collaborate. New group members in 2008 were Mr Tom Gheysens and Ms Imke Diddens, both PhD students, working on silk post-processing and Neutron diffraction, respectively.

Publications:

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2006 Emile, O. Floch, A.L. Vollrath, F. The self shape-memory effect in spider draglines. *Nature* 440, 621

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2006 Vollrath F, Porter, D. Spider silk as a model biomaterial. *Applied Physics A: Materials Science & Processing* 82, 205-212.

Interactions:

Talks/Lectures : In spring 2007 Fritz Vollrath attended the AFOSR meeting in Hawks Cay in order to present and discuss the progress of our research with the ASFOR. David Porter visited the Polymer Group at Fudan University in order to conduct experiments and participate in teaching. Fritz Vollrath, David Porter and Chris Holland gave a number of invited talks and lectures at national as well as international polymer and biology conferences and meetings. Chris Holland conducted a number of 'webinars' on rheometry posted on the www of Malvern Instruments. Fritz Vollrath visited Princeton University to continue discussions of possible collaborations. In spring 2008 Chris Holland attended the AFOSR meeting in Hawks Cay in order to present and discuss the progress of our research with the ASFOR. David Porter visited the Polymer Group at Fudan University in order to conduct experiments and participate in teaching. Fritz Vollrath, David Porter, Cedric Dicko and Chris Holland gave a number of invited talks and lectures at national as well as international polymer and biology conferences and meetings. Fritz Vollrath visited Princeton University to continue discussions of possible collaborations.

AFOSR 'internal' collaborations : In October 2007 Fritz Vollrath visited Dr Kathy Wahl (Naval Research Laboratory Tribology Section, Code 6176) in order to discuss her findings and discuss how the Oxford lab could help with some problems. Dr Lawrence Drummy of the Air Force Research Laboratories (AFRL/MLBP, Materials and Manufacturing Directorate) visited Oxford for joint research and throughout 2008 this collaboration continued while discussions and material exchange continued with Dr K Wahl.

New Discoveries, Inventions, or Patent Disclosures : We continue to believe that our insights, derived from the silk modelling work, into protein denaturation and folding will have been a major contribution to a better understanding of protein form and function. Patents-none.

Honours/Awards: 2007: Best undergraduate lecture in the Sciences Division of Oxford University given by Chris Holland; Wellcome VIP award to Chris Holland, EPSRC Fellowship to Cedric Dicko (3 yrs), 2008: Chris Holland was awarded a Junior Research Fellowship at Magdalen College Oxford. David Porter was awarded a Visiting Professorship at Sheffield University. Fritz Vollrath received one of the prestigious Advanced Award from the European Research Council

Markings: n/a

Fritz Vollrath, Oxford, Feb 19th, 2009