Why Silk Rheology is Like Opening a Can of Worms

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Liquids	Fibres	Films	Bulk/Composites
Rheology	Tensile, Compression		

SEM, FTIR, UV-Vis, SAXS, Microscopy

TGA, DSC

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Biodiversity = significance of silk

Variability = challenge of silk

Fibre = processing + feedstock

Photo credit Carnifex82 CC Flikr

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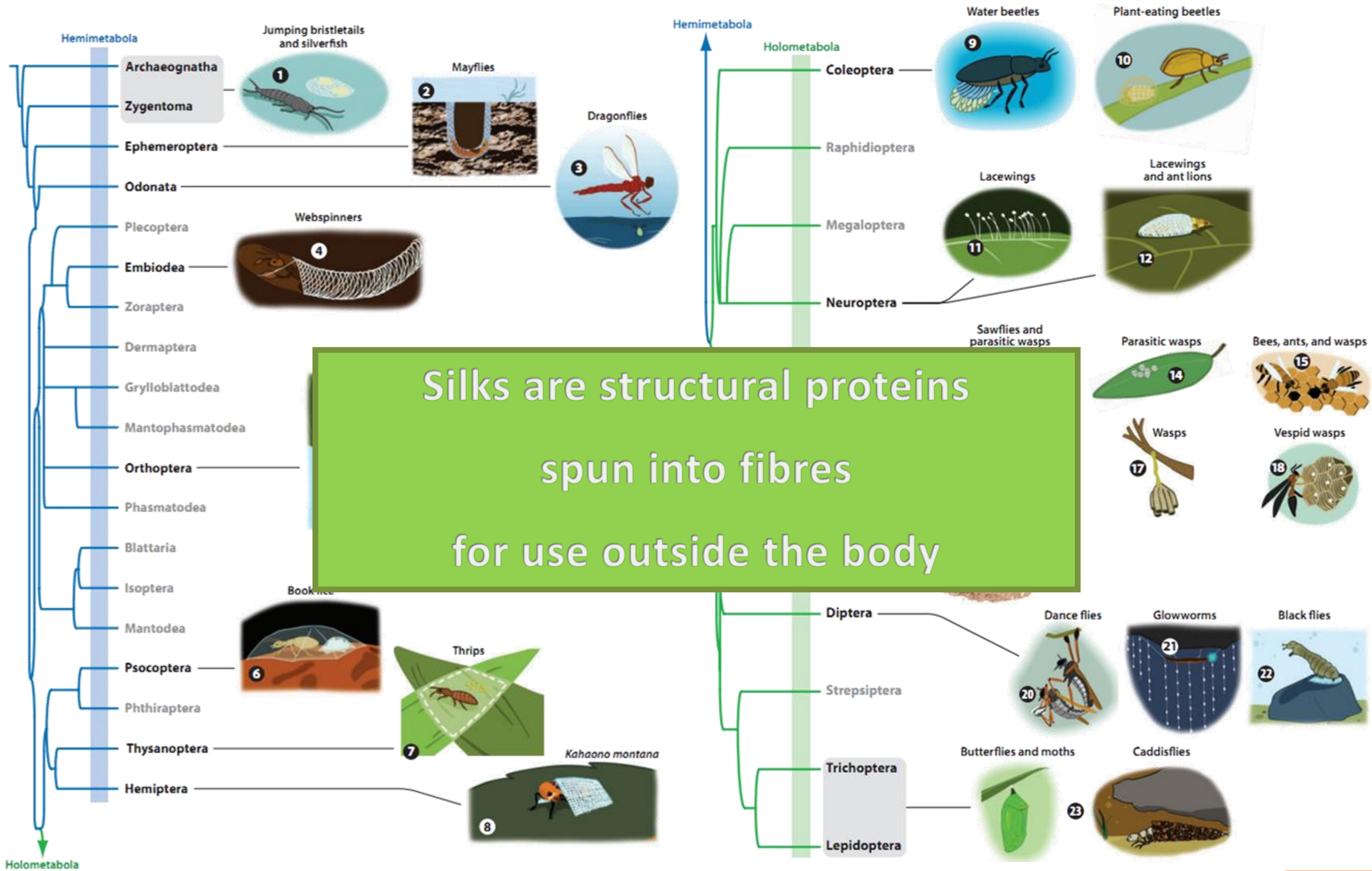
Biology



Silks are structural proteins

spun into fibres

for use outside the body

(Sutherland *et al* (2010) Ann. Rev. Entomol. **55** 171-88)

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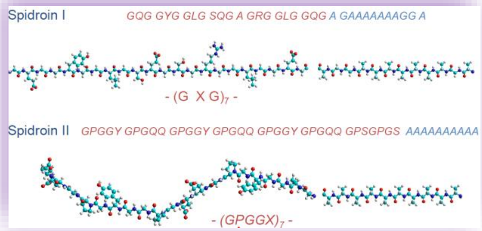
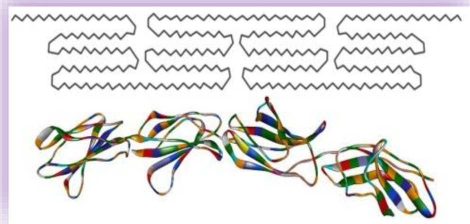
Silk Fibre Structure

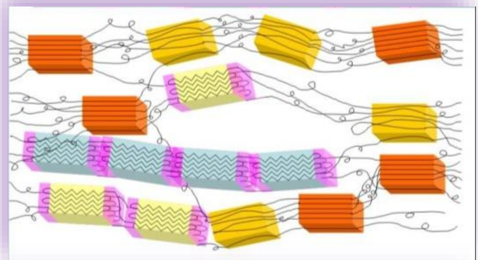
Primary Sequence



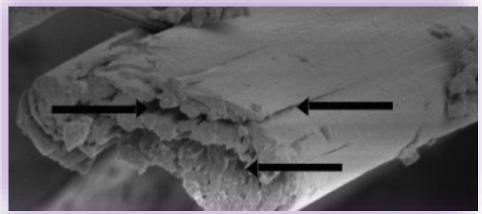
Secondary Structure



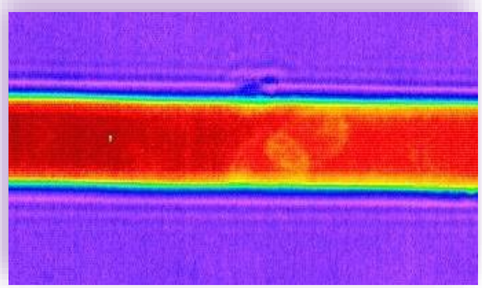
Nanoscale



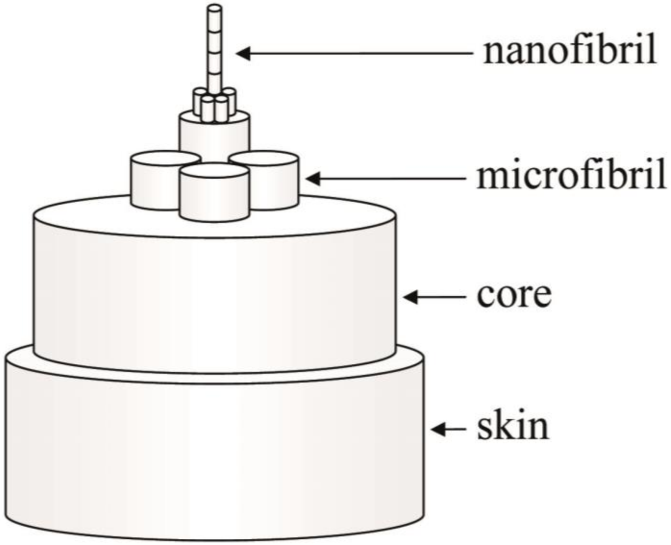
Microscale



Macroscale



Silks are multi-scale hierarchical nano-structured (bio)polymers



Biodiversity = significance of silk

Variability = challenge of silk

Fibre = processing + feedstock

Photo credit Carnifex82 CC Flikr

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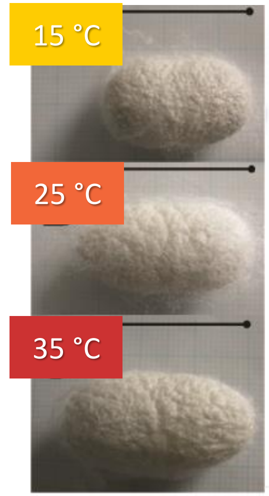
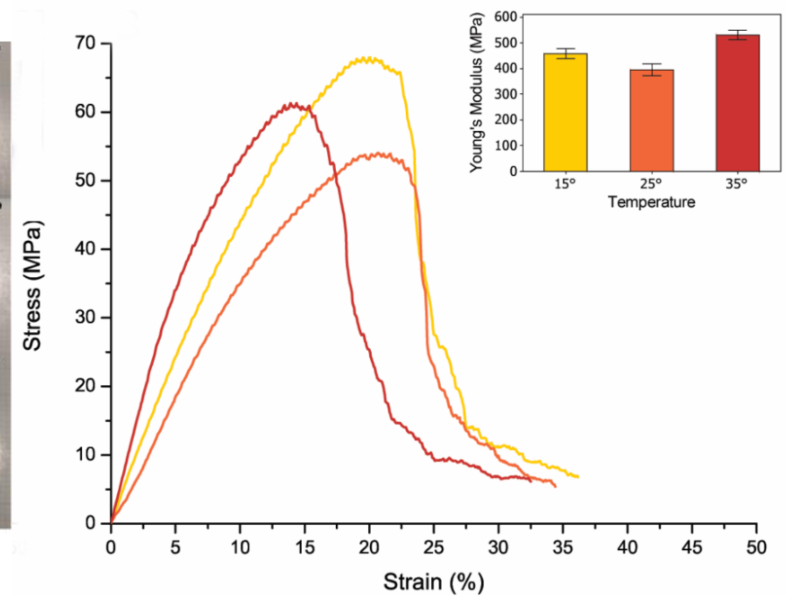
Environmental effects on cocoon properties

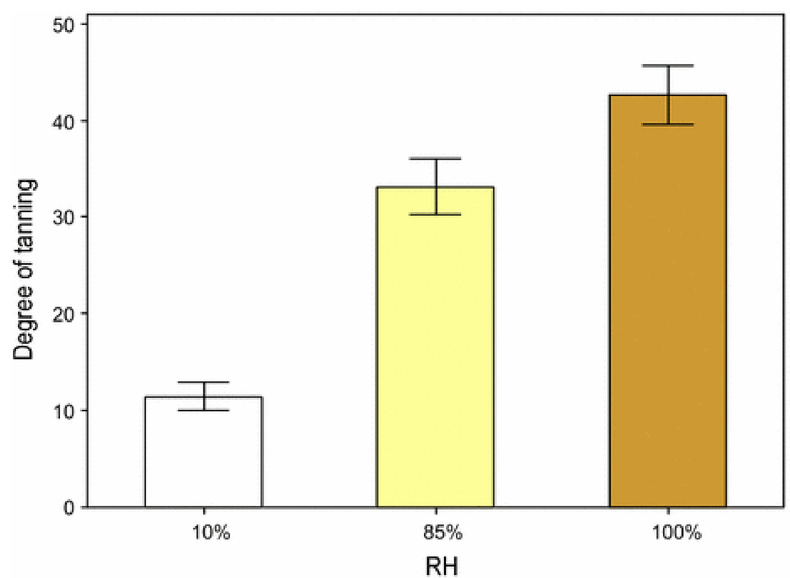
With Catherine Offord, Stanford University, Fritz Vollrath, University of Oxford

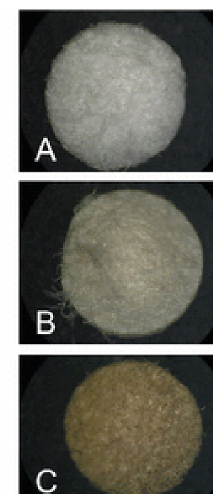




Natural spinning at different temperatures and humidities leads to changes in

- cocoon shape
- mechanical properties
- colour

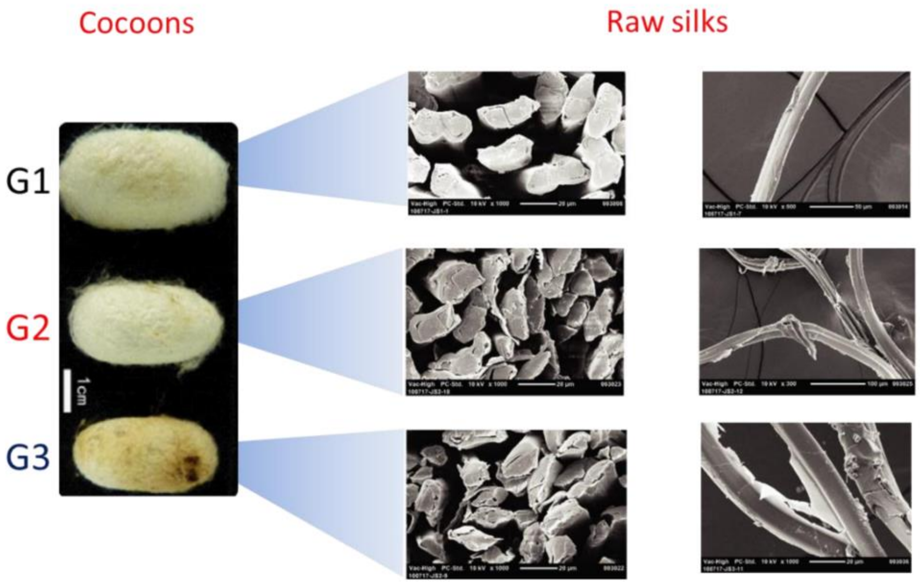


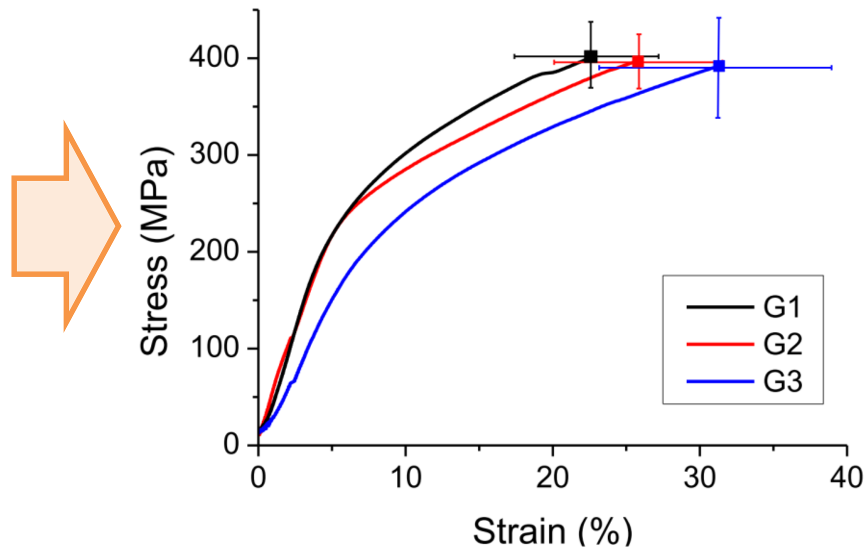


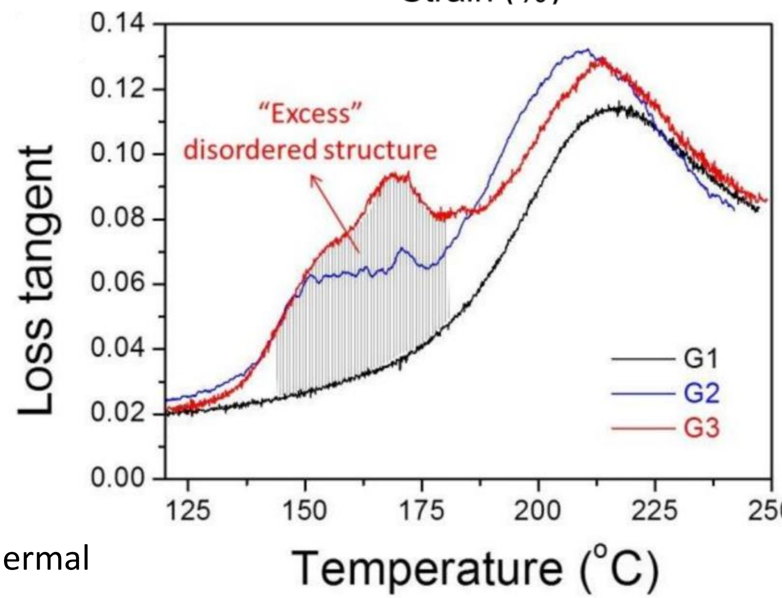
(Offord *et al* (2016) *Journal of Materials Science* doi:10.1007/s10853-016-0298-5)

Relating grade to mechanical properties to structure

Juan Guan, University of Beihang



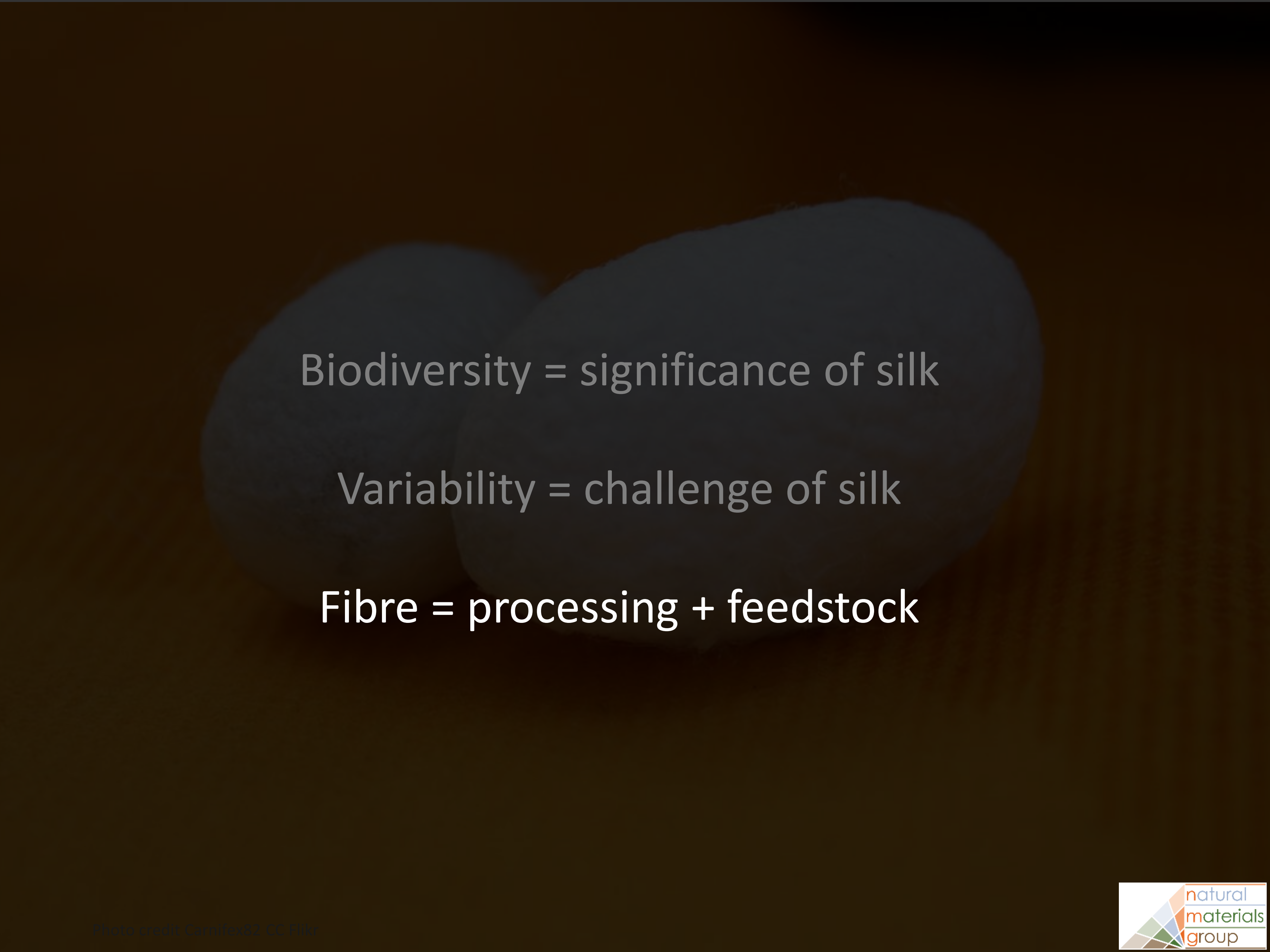




Grades of cocoons have different *single fibre* mechanical properties

Dynamic Mechanical Thermal Analysis (or *mechanical spectroscopy*) links these differences to degree of molecular disorder

(Guan, J. Silk "Quality" Revealed Using Dynamic Mechanical Thermal Analysis (DMTA) (2013) 6 th BACSA International Conference)



Biodiversity = significance of silk

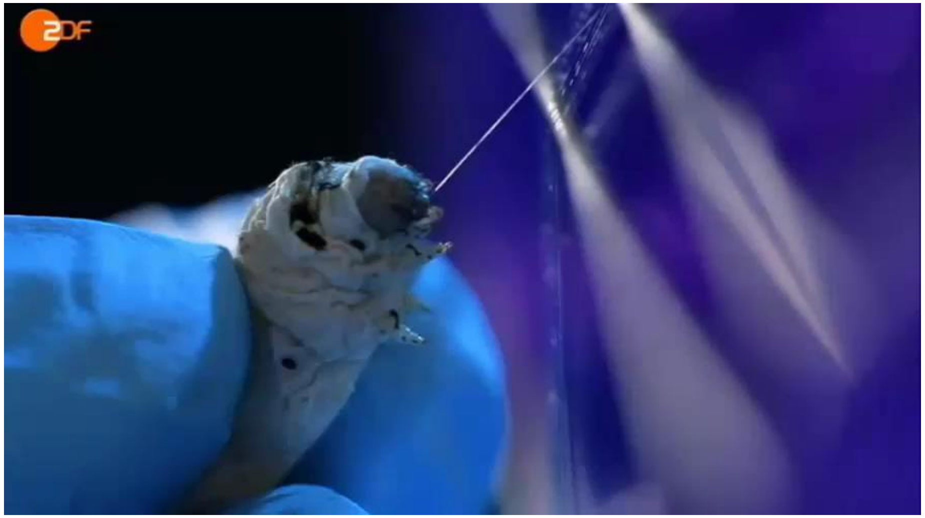
Variability = challenge of silk

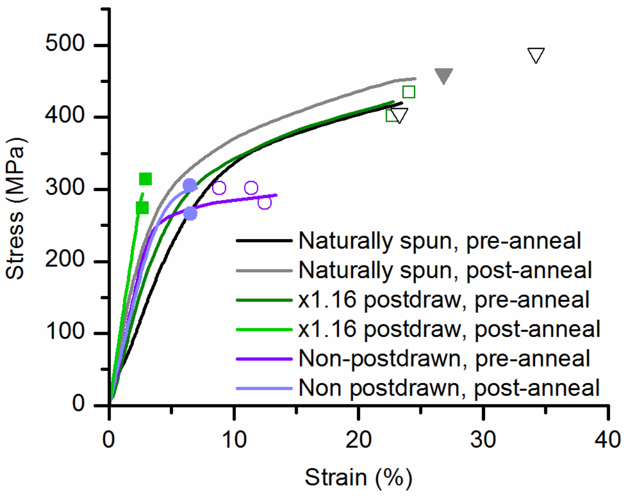
Fibre = processing + feedstock

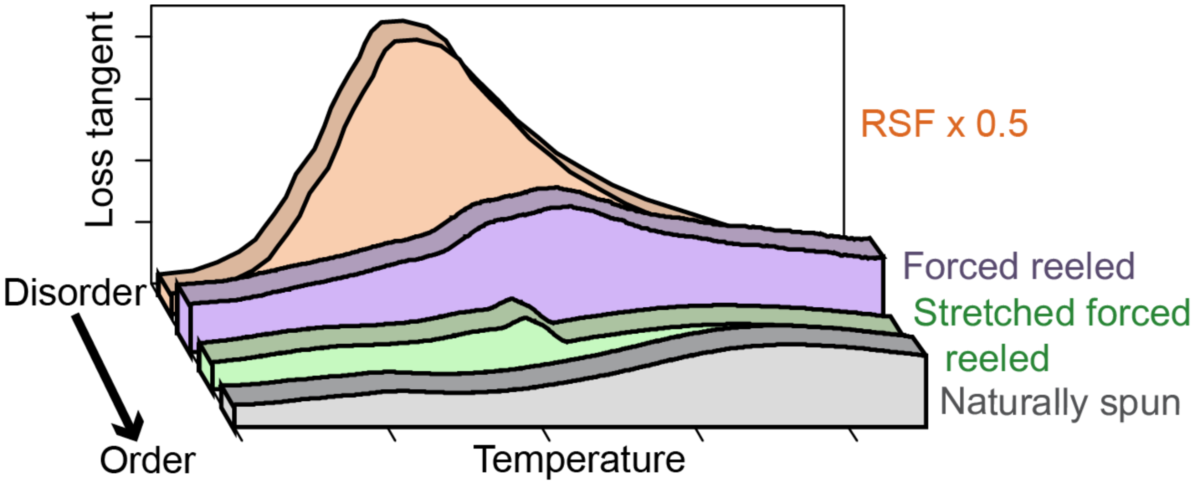
Photo credit Carnifex82 CC Flikr

Linking structure to fibre processing

With Beth Mortimer, University of Oxford, Juan Guan, University of Beihang







Forced reeling / paralysis disrupts natural spinning mechanism

Missing link between artificial and natural fibres?

(Mortimer *et al* (2014) *Acta Biomaterialia* 11: 247-255)

Processing

pH?

Energy

Ions?

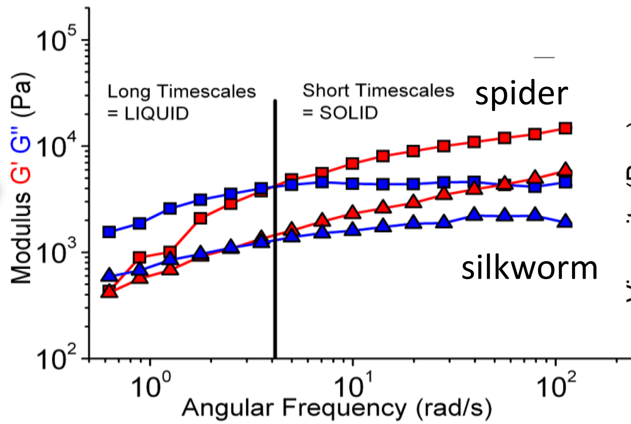
- Apply energy
  - By pulling the dope through the spinning duct
  - Causing it to flow
  - Proteins absorb energy as they are stretched
  - Water is stripped from the protein (water-amide H-bond)
  - Proteins changes conformation
  - Aggregates (amide-amide H-bond)
  - Falls out of solution (dry fibre)

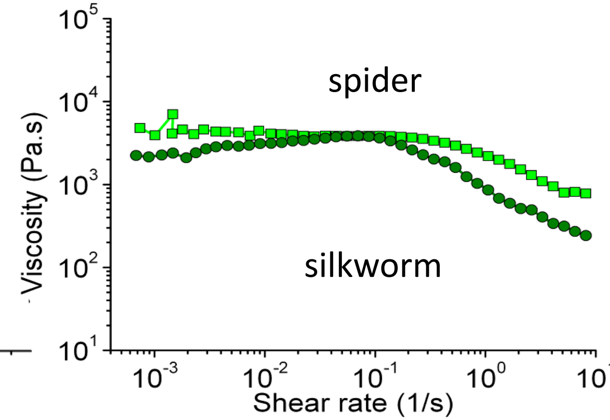
Evolved to be denatured

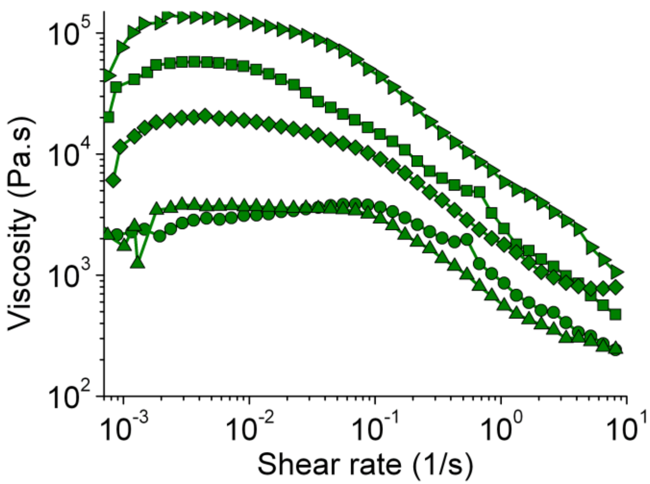
Flow induced crystallisation

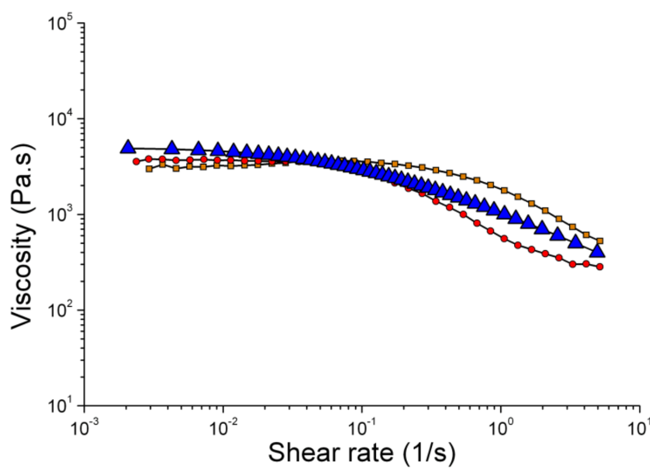
(Knight, D. and Vollrath, F. (1999) Proc. R. Soc. B. 266 519-523, Joanne Flickr)

Silk Rheology









Flow properties are convergent

Shear sensitivity:
Variability?

Akin to polymer melts

(Holland *et al* (2006) *Nature Materials* 5 870-874)

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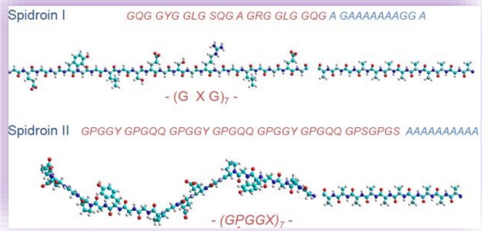
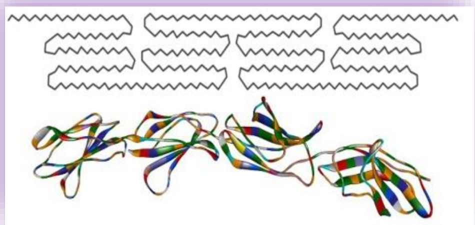
Silk Fibre Structure

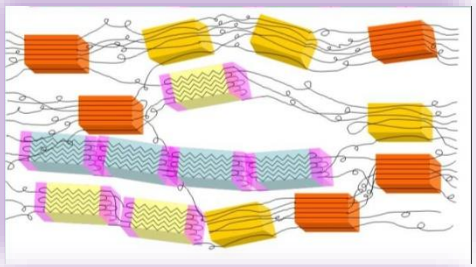
Primary Sequence



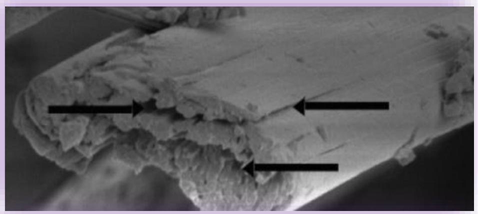
Secondary Structure



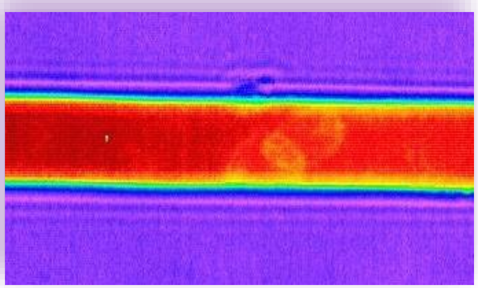
Nanoscale



Microscale



Macroscale



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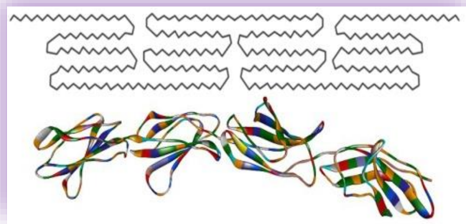
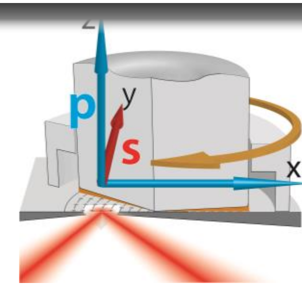
Linking structure to rheological properties

Proteins: Rheo-IR

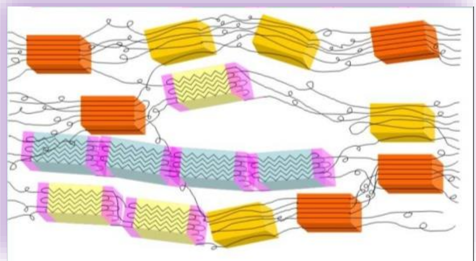
Protein alignment and conformational changes

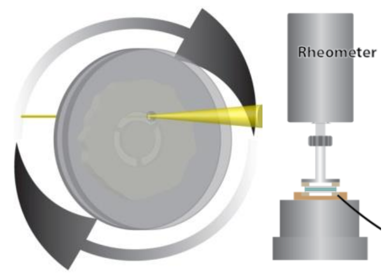




Nanoscale: Rheo-S/WAXS

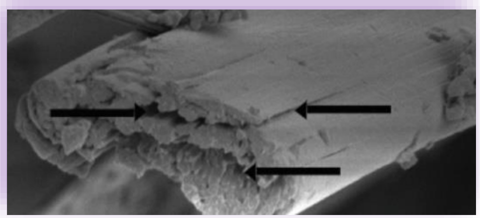
Molecular orientation and aggregation

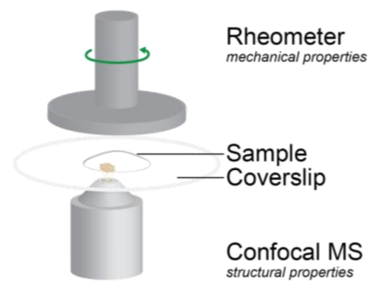




Microscale: Con-Rheo

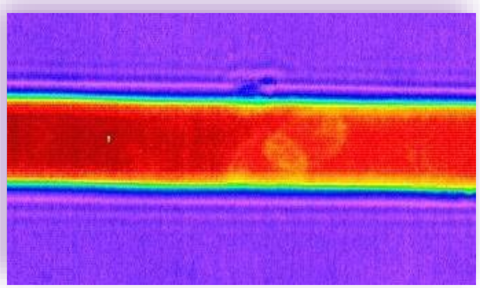
Self assembling complex structures

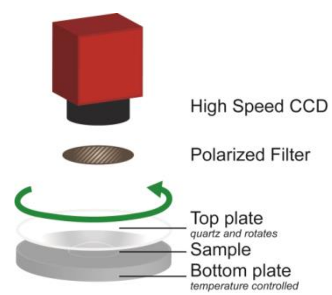


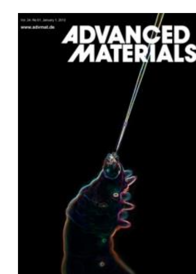


Macroscale: Rheo-SIPLI

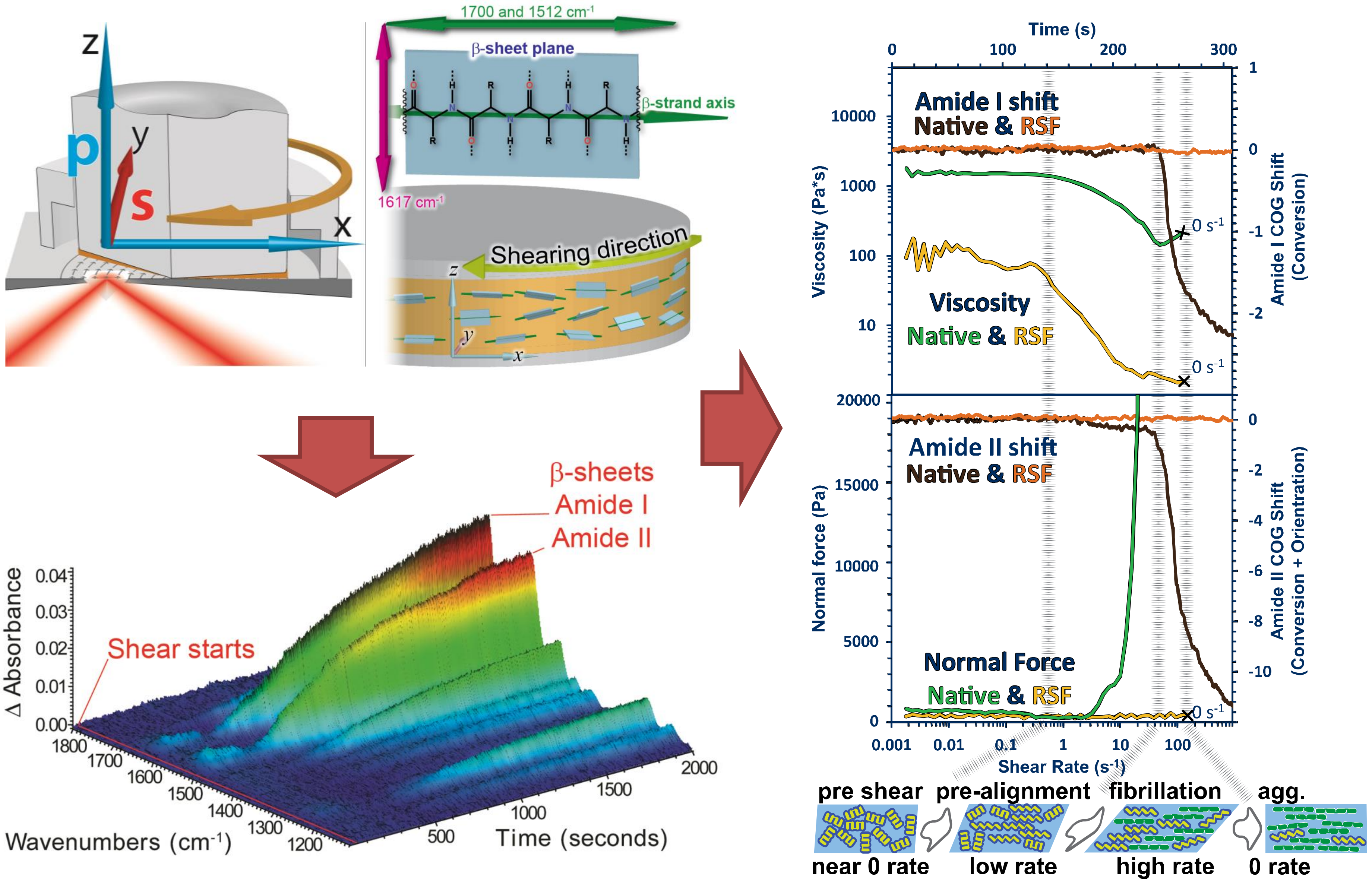
Structural conversion and comparison







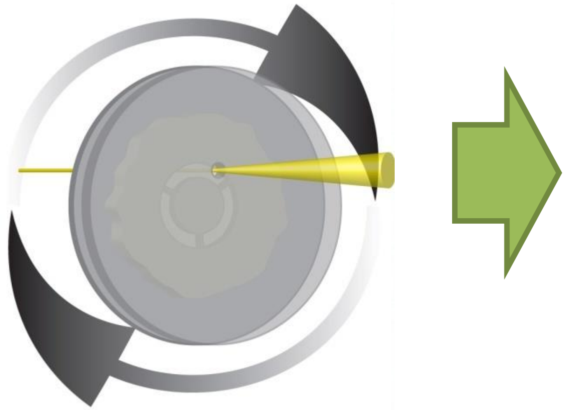
Proteins: Rheo-IR

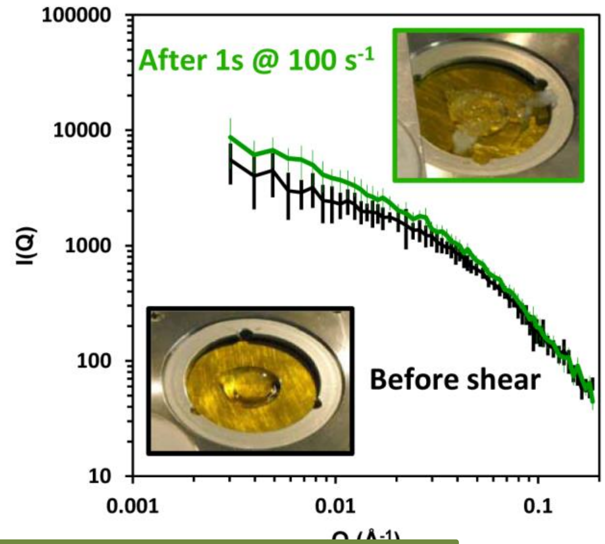


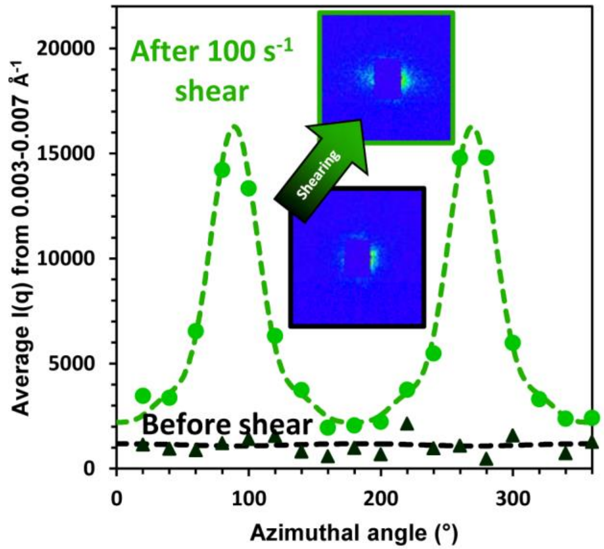
(Boulet-Audet *et al* (2011) *Phys. Chem. Chem. Phys.* 13 3979-84, Boulet-Audet *et al* (2014) *Acta Biomaterialia 10 776-84*)

Nanoscale: Rheo-S/WAXS and SANS

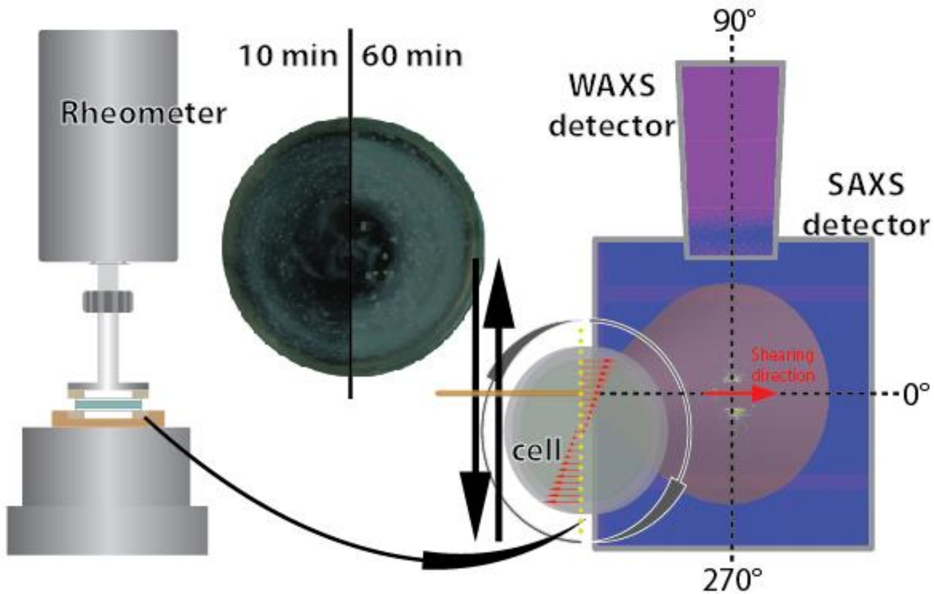
Real-time: S/WAXS







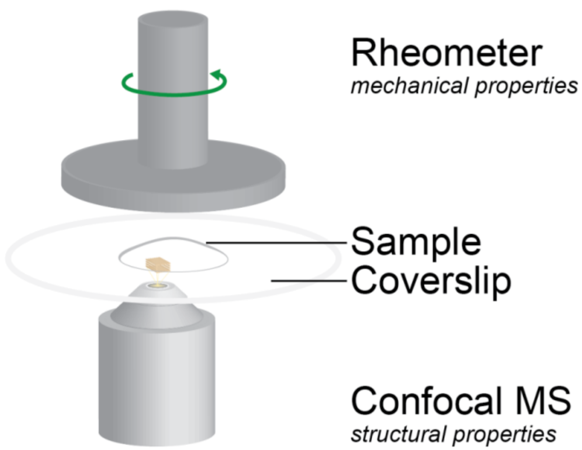
Time/Temperature Aggregation S/WAXS and SANS

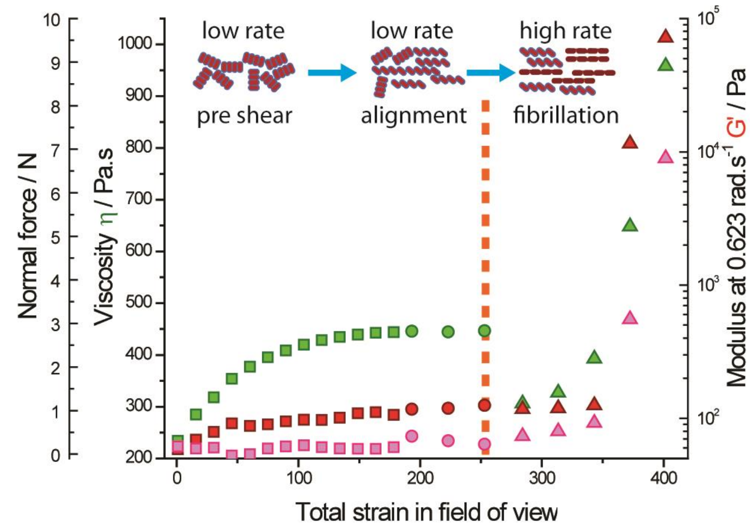


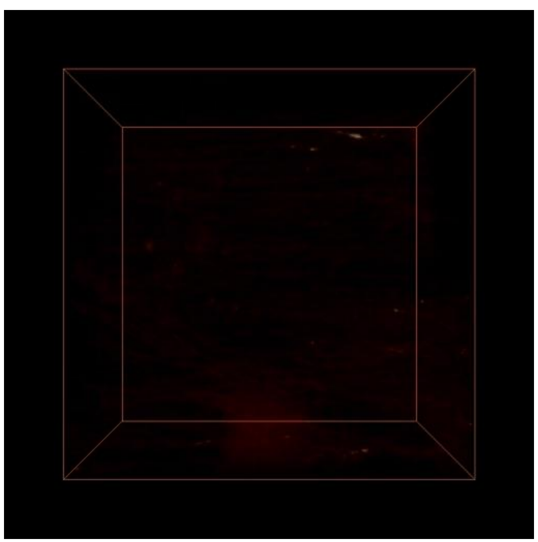
(Boulet-Audet *et al* (2016) *In preparation*)

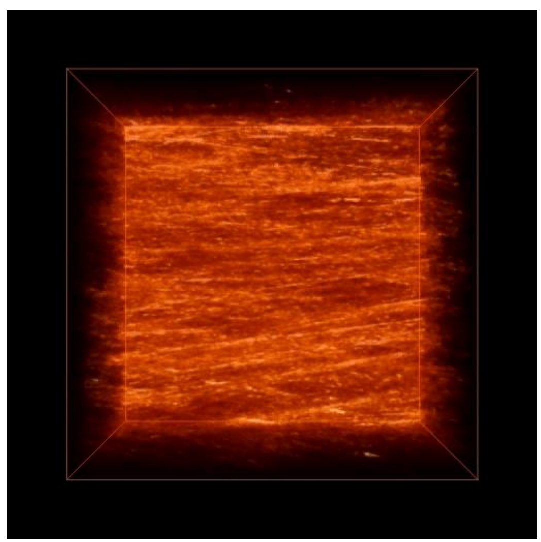
Microscale: Confocal Rheology

With Dan Blair, Jeff Urbach, Georgetown University, DC







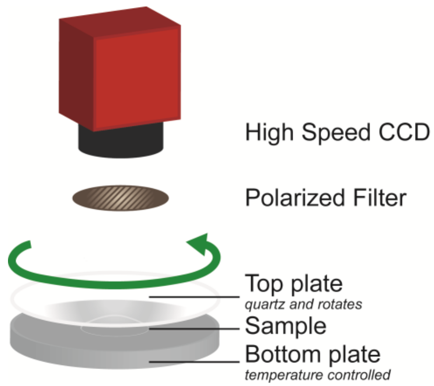


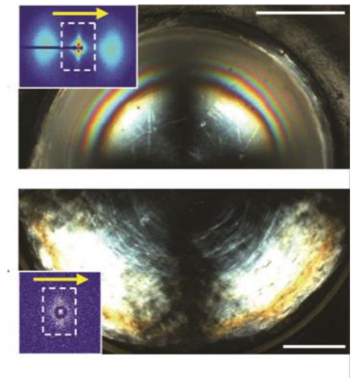
Native silk proteins are able to *spontaneously* self-assemble, fibrillate and develop hierarchical structures upon controlled shearing

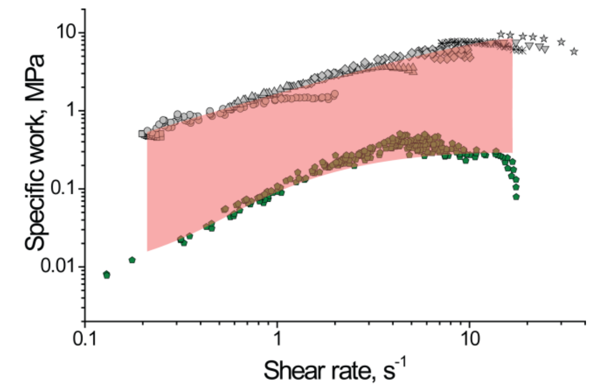
(Holland, Urbach, Blair (2012) *Soft Matter* 8 2590-4)

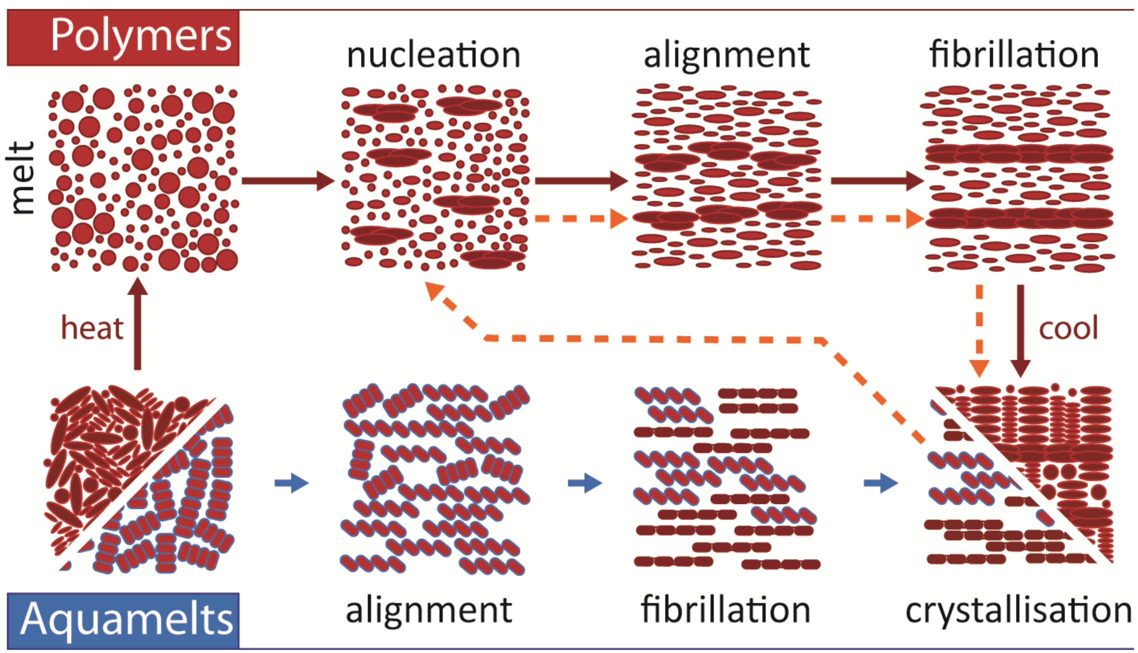
Macroscale: Shear Induced Polarised Light Imagery

With Oleksandr (Sasha) Mykhaylyk, Tony Ryan, Sheffield University







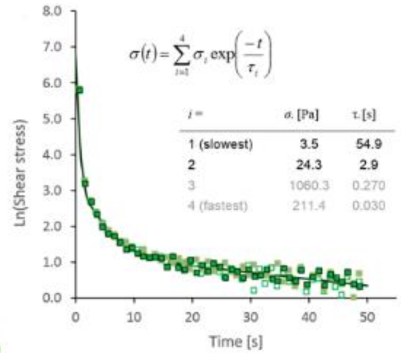


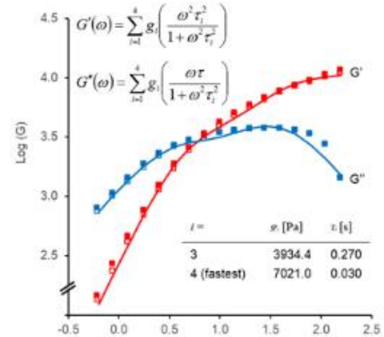
Silks are 1000x more efficient at fibrillation than synthetic polymers

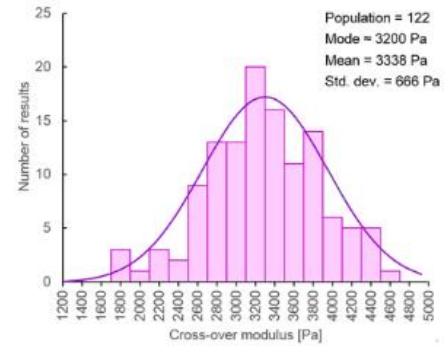
Silk protein hydration is key

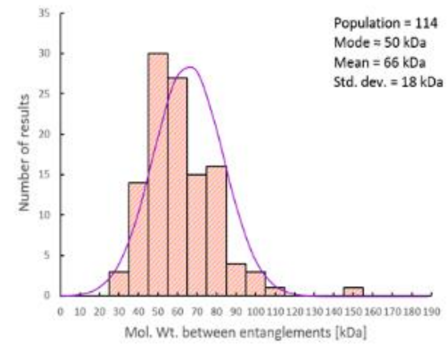
(Holland *et al* (2012) Advanced Materials, 24 (1) 105-109)

Natural variation of silk feedstocks









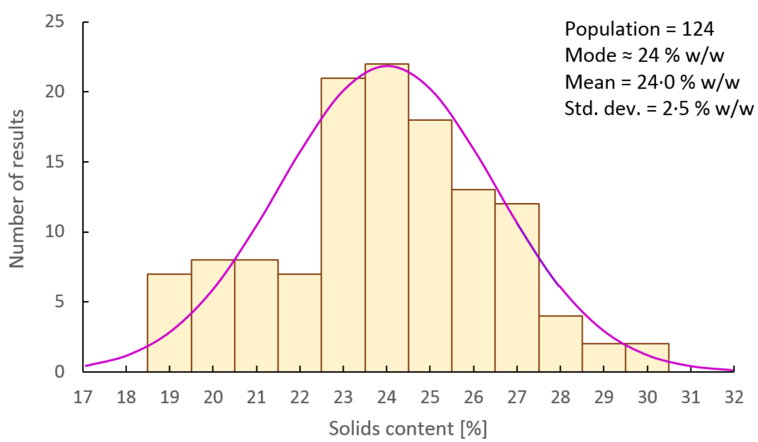
Careful preparation and population distributions (n > 100) and a classical polymer science approach to silk rheology revealed multiple relaxation modes

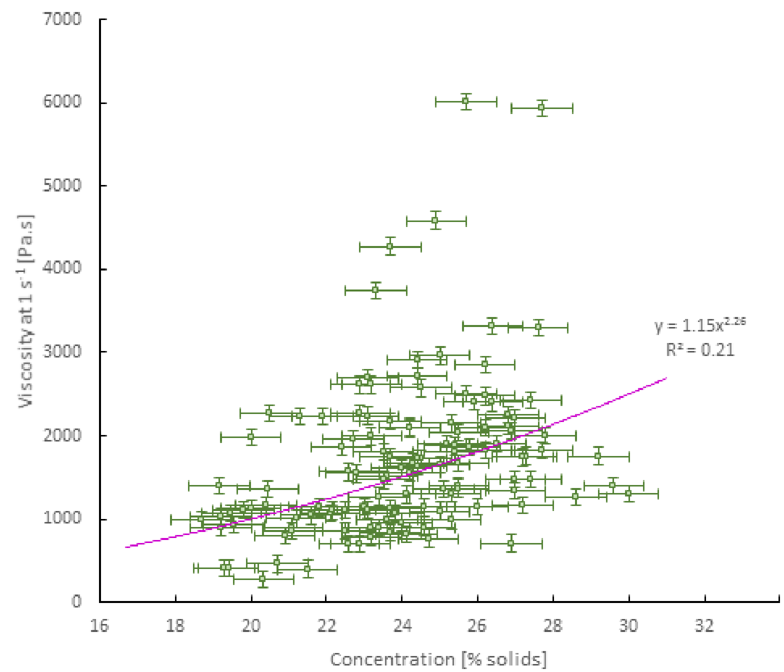
(Laity, P. Gilks, S. Holland, C. (2015) *Polymer,* **67** 28-39)

Natural variation of silk feedstocks

The University Of Sheffield.

Measurement method	Physical property	Mean	Standard deviation (population size)
gravimetry	protein concentration [% w/w]	24·0	2.5 (N = 124)
shear viscosity	viscosity at $\dot{\gamma}$ =1 s^{-1} [Pa.s]	1722	935 (N = 125)
stress relaxation	time constant, τ_1 [s]	66	22 (N = 5)
	modulus contribution, g_1 [Pa]	0·11	0.08 (N = 5)
stress relaxation	time constant, τ_2 [s]	3·4	0.5 (N = 5)
	modulus contribution, g_2 [Pa]	9·3	4·3 (N = 5)
oscillatory sweep	time constant, τ_3 [s]	0·442	0.016 (N = 115)
	modulus contribution, g_3 [Pa]	3701	1744 (N = 115)
oscillatory sweep	time constant, τ_4 [s]	0·055	0.016 (N = 115)
	modulus contribution, g_4 [Pa]	7145	1721 (N = 115)
oscillatory sweep	cross-over modulus [Pa]	3338	666 (N = 122)
	cross-over frequency [rad.s^{-1}]	5·6	2.5 (N = 122)
Mol. wt. between entanglements [kDa] from binary model		66	18 (N = 118)





Natural spinning concentrations appear to have little effect on viscosity

(Laity, P. Gilks, S. Holland, C. (2015) *Polymer,* **67** 28-39)

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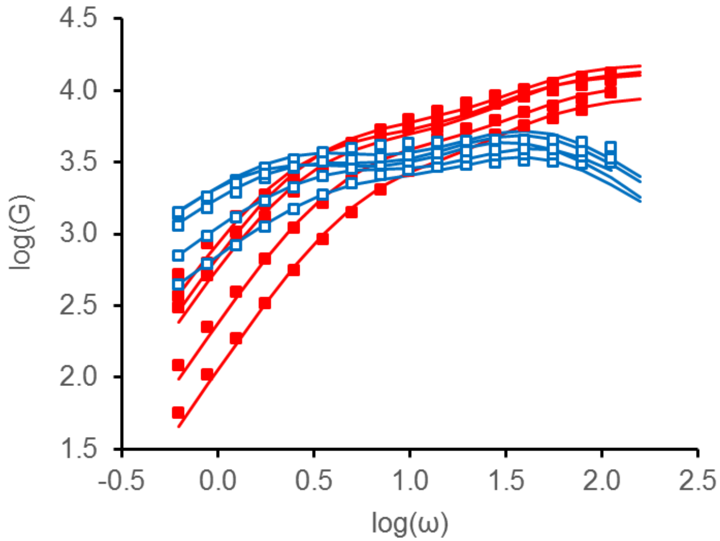
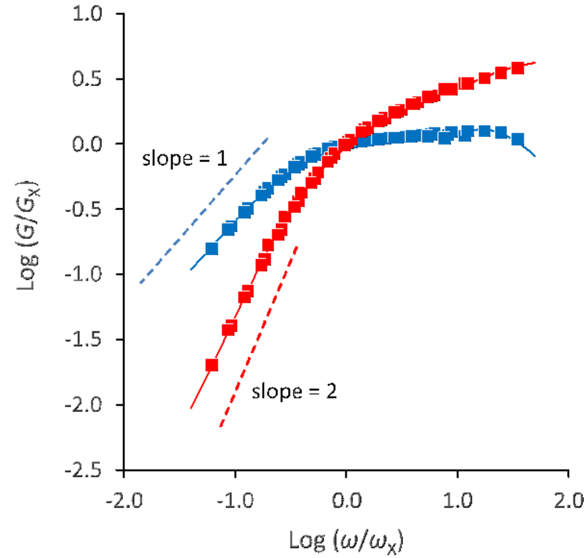
Current Work: Is silk a model polymer?

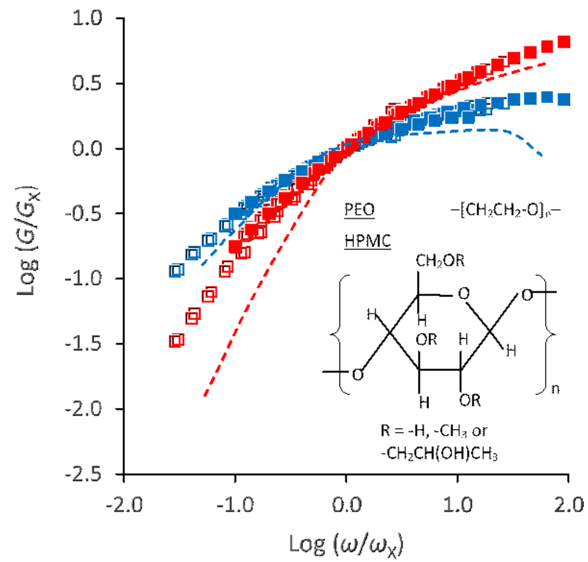




All the variation in samples can be mapped onto a single "master curve"

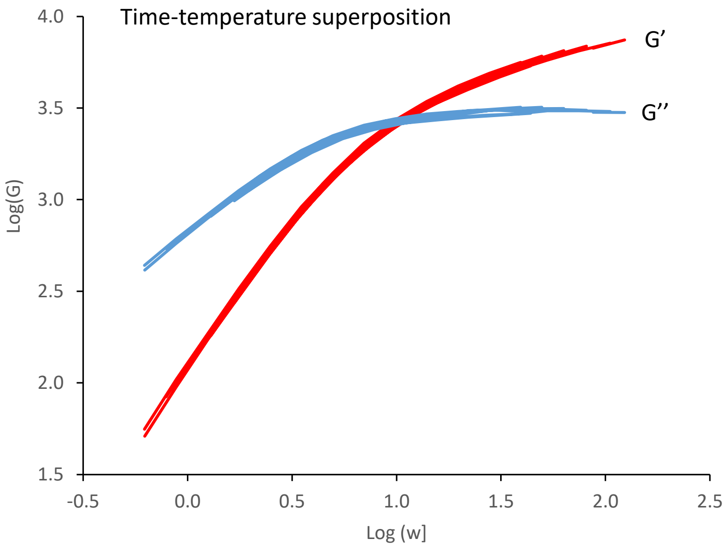
This is not seen in other polymers

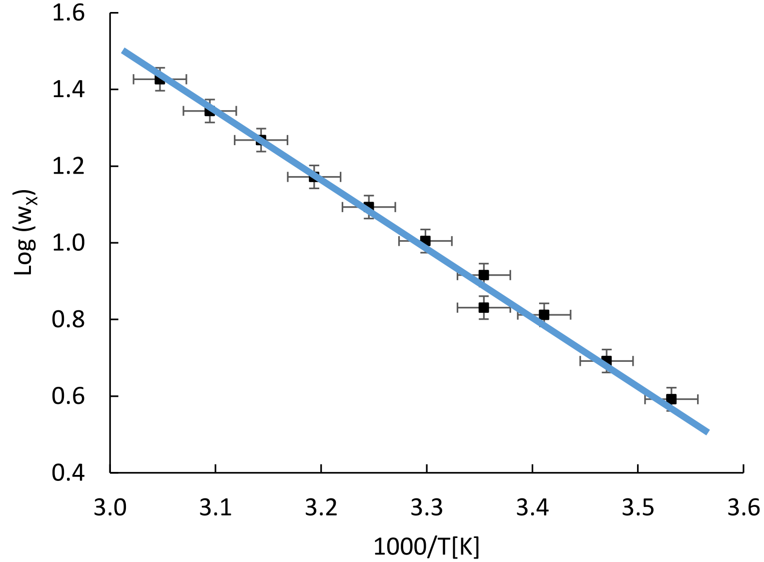
Perhaps due to narrow MWD of native silk feedstock?



(Laity, P. Holland, C. (2016) *Biomacromolecules* DOI:10.1021/acs.biomac.6b00709)

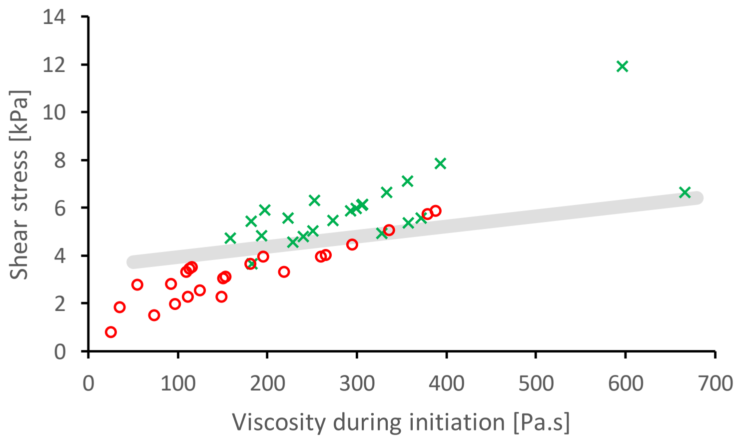
Polymer approach: Thermal response





Time Temperature Superposition can now be applied to native silk

Arrhenius plot (of log(ω_X) vs. 1/T) suggests an activation energy of flow

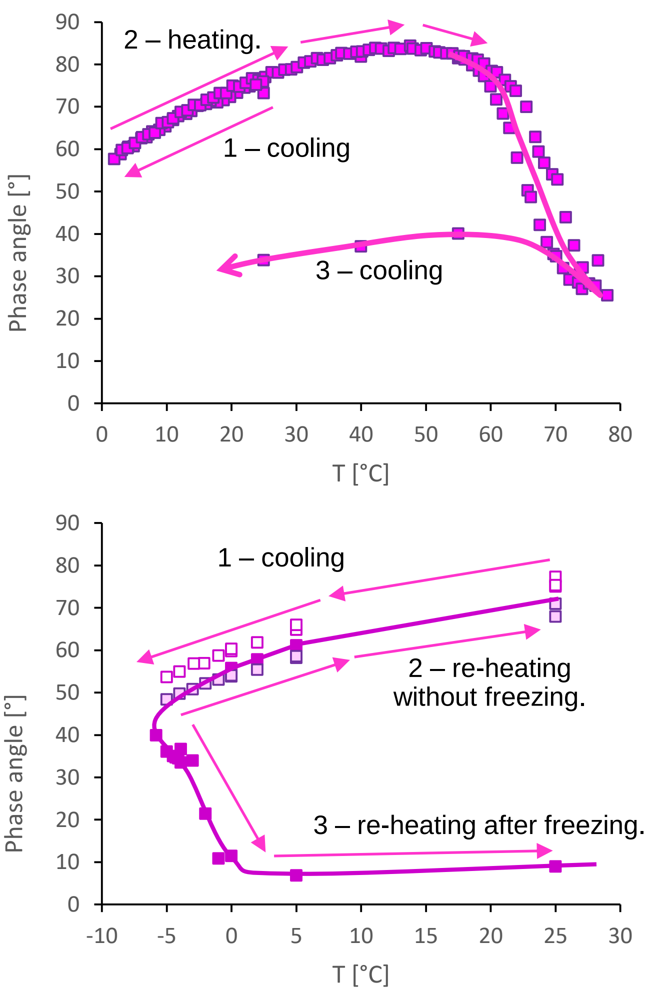


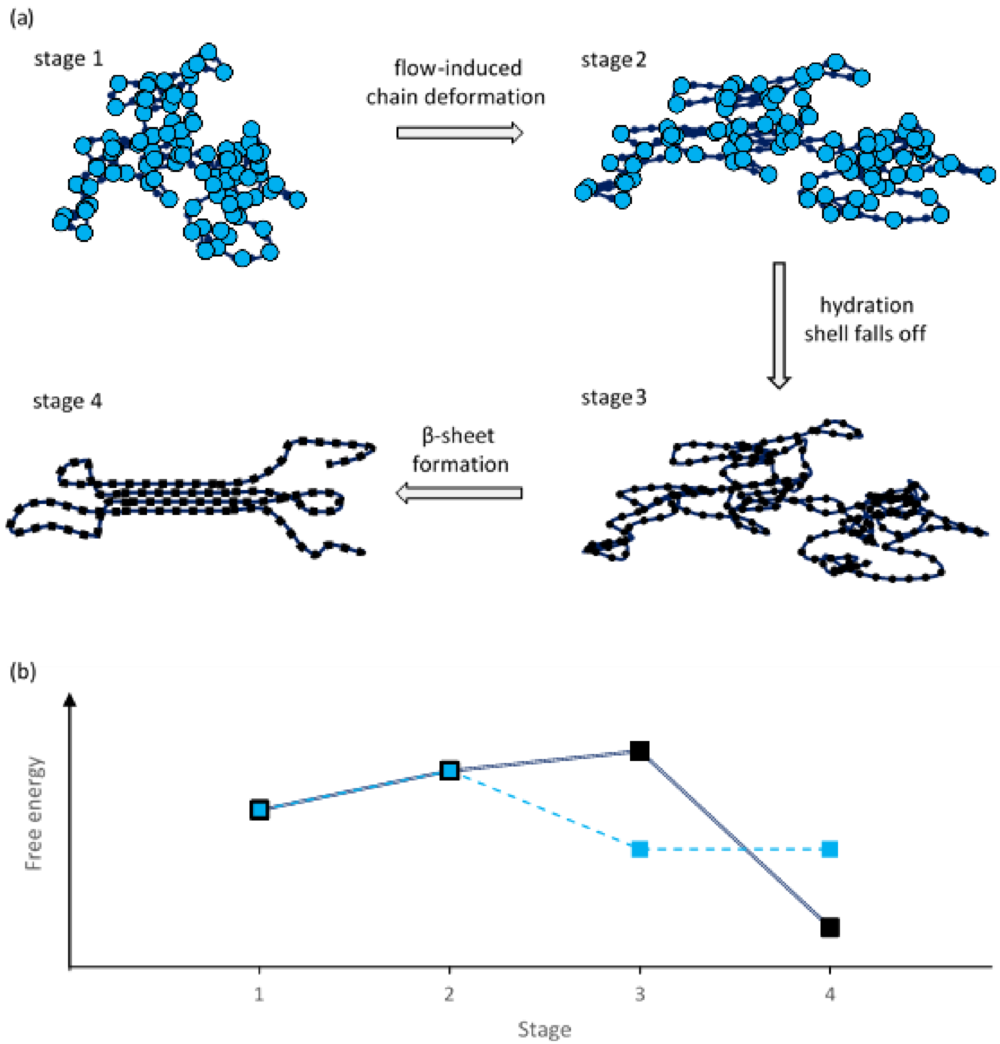
Current work is investigating stress induced solidification

(Laity, P. Holland, C. Submitted, *European Polymer Journal and IJMS*)

Thermal response and silk hydration

Phase angle of native silk feedstock at 0.1 Hz





(Laity, P. Holland, C. Submitted, *European Polymer Journal and IJMS*)

Silk is more than a fibre

Photo credit Carnifex82 CC Flikr

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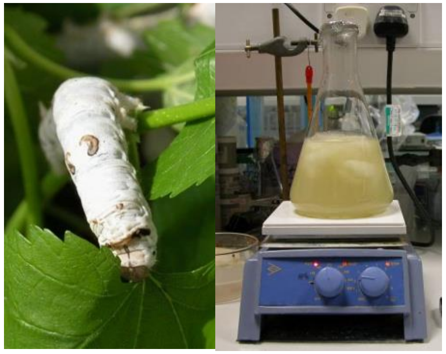
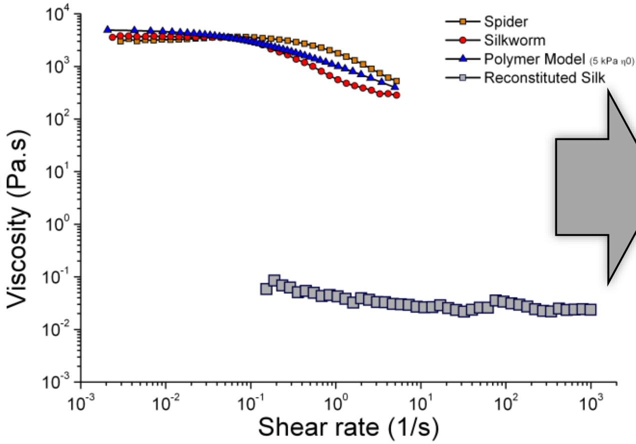
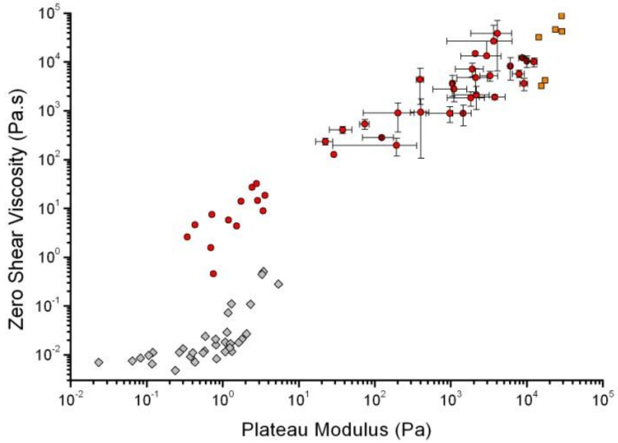
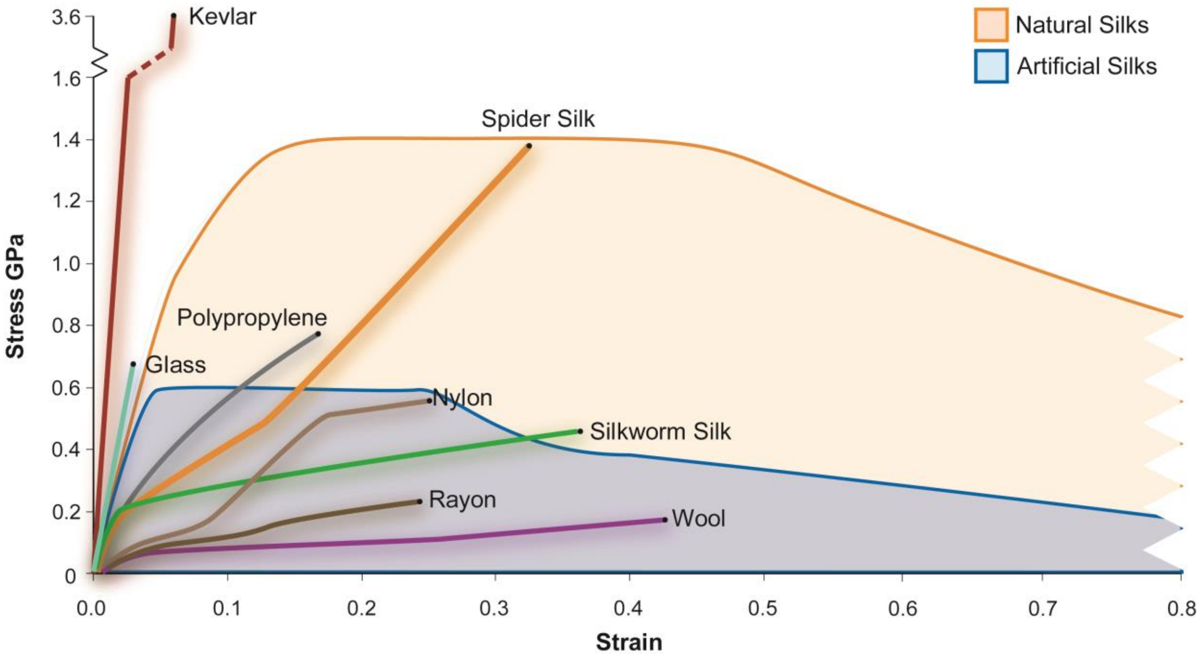
Comparing regenerated silk to the model native silk









Constraints to criteria

Damaging the silk proteins during processing

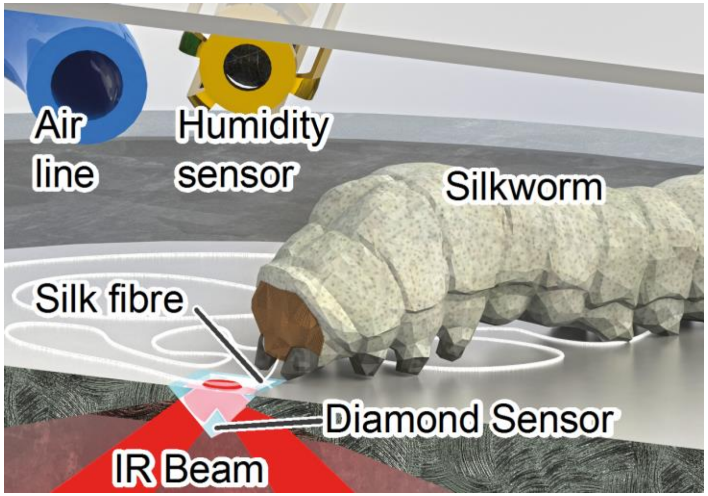
Spinnability indicators

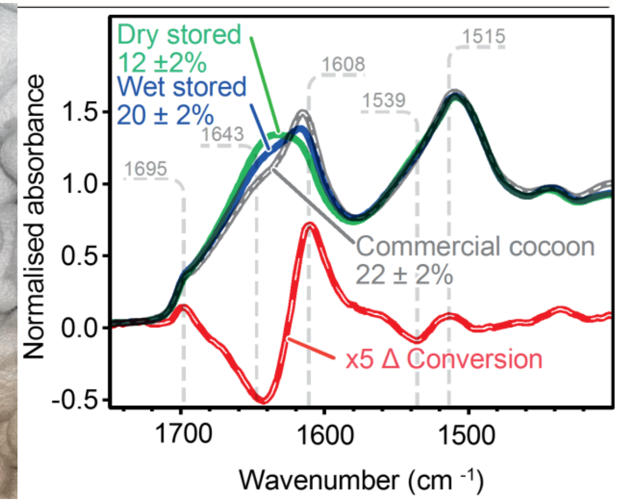
Fibre = feedstock + processing

(Holland *et al* (2007) *Polymer* 48 3388-3392, Vollrath et al (2011) *Soft matter* 7 (20) 9595-9600)

Understanding processing to make better silks

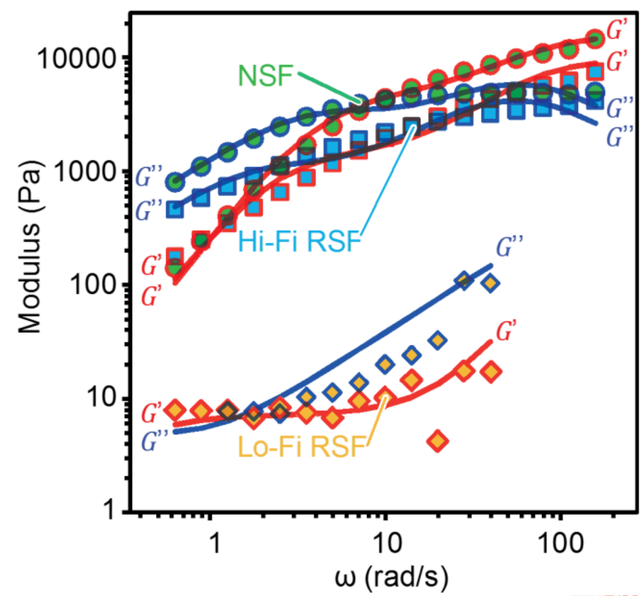
With Maxime Boulet-Audet Imperial College, Tom Gheysens Ghent, Fritz Vollrath Oxford





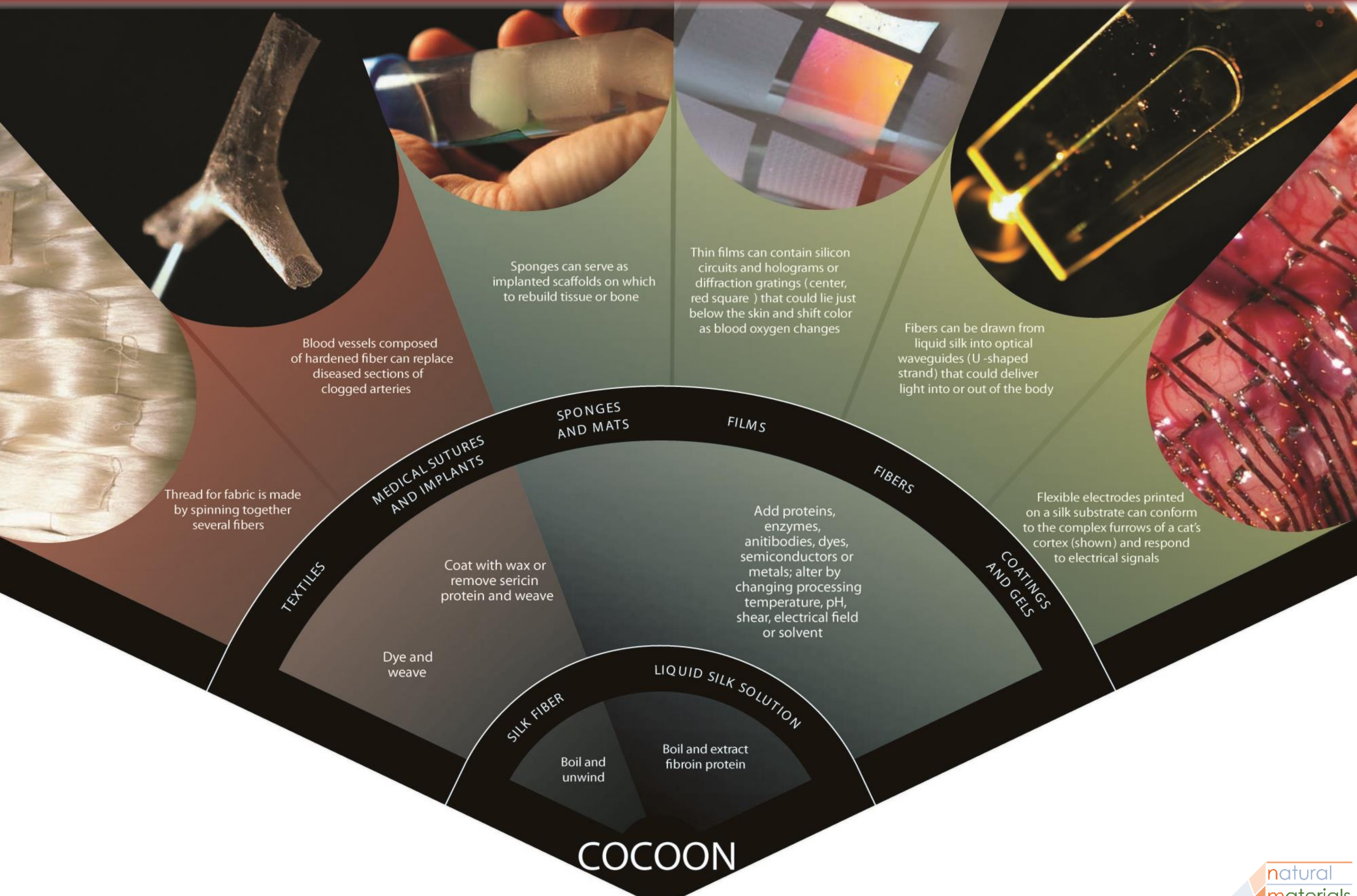
How does silk change after it is spun?

- Rapid crystallization in high RH
- Crystallization prevented by spinning and storing at low RH
- Majority of commercial silks = high crystallinity
- Low crystallinity silks make high quality regenerated silks (Hi-Fi RSF)



(Boulet-Audet *et al* (2016) *Biomacromolecules*)

Silk Applications



Omenetto, F. Kaplan, D. *Scientific American* **2010,** November, 76-77

Biodiversity = significance of silk

Variability = challenge of silk

Fibre = processing + feedstock

Silk is more than a fibre

Photo credit Carnifex82 CC Flikr

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