

Supporting Information of

**Understanding the Variability of Properties in
Antheraea Pernyi Silk Fibres**

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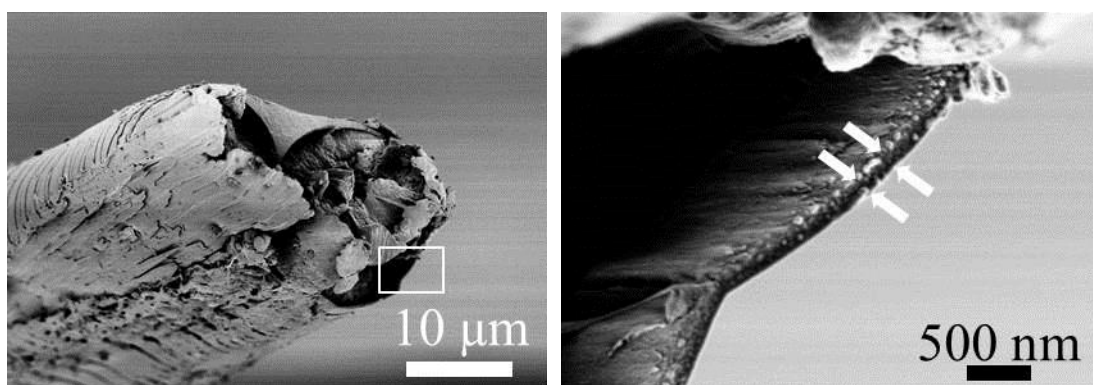


Figure S1. Fracture end of as-reeled *A. pernyi* silk from silkworm 1 broken in liquid nitrogen, the right image is the enlarged version of the rectangle in the left image. Arrows indicate the external sericin layer.

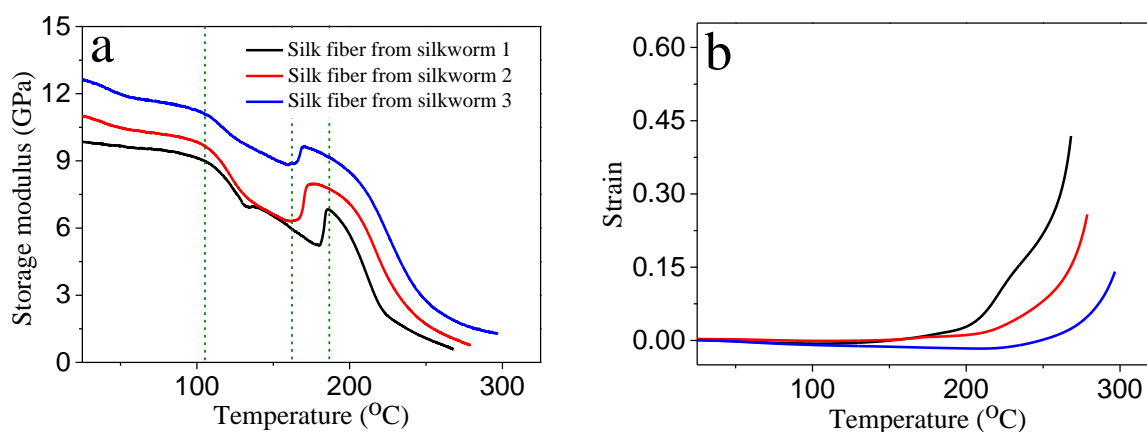


Figure S2. Storage modulus (a) and static strain (b) of as-reeled *A. pernyi* silks from different silkworms. Same legend for both (a) and (b).

Synchrotron FTIR (S-FTIR) Microspectroscopy

The S-FTIR experiments were performed at Beamline (BL01B) in the Shanghai Synchrotron Radiation Facility (SSRF). A relatively large $20 \times 20 \mu\text{m}$ square aperture was selected here due to the large width of flat as-reeled *A. pernyi* silk ($\geq 30 \mu\text{m}$). The square aperture was placed in the center of the silk in order to avoid the diffraction and scattering of the infrared light. All the FTIR microspectra were collected in the mid-infrared range of $800\text{--}4000 \text{ cm}^{-1}$ at a resolution of 4 cm^{-1} with 256 coadded scans. At least three different positions for each silk sample (1 cm long) were chose to obtain effective datum.

It should be noted that the band at about 1450 cm^{-1} (CH_3 in-plane bending vibration) was used as an intensity standard to compare all the three curves and the band at 965 cm^{-1} has been assigned to β -sheet conformation (C-N stretching, CH_3 rocking).¹

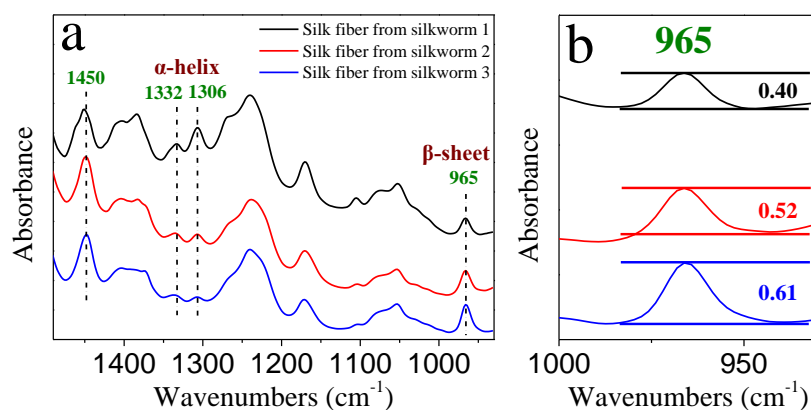
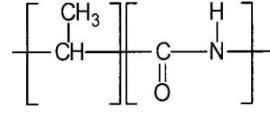


Figure S3. S-FTIR microspectra of as-reeled *A. pernyi* silk fibers from different individuals (a), with the enlarged image around 965 cm^{-1} shown in (b). Legend is the same for both (a) and (b).

Group Interaction Modelling of Silk

Group Interaction Modelling is a mean field approach to predicting the thermomechanical properties of polymers from their composition and structure. The model has been presented in detail for amorphous polymers,^{2, 3} and the model has been applied to semicrystalline silk structures to predict the full range of mechanical properties that are possible in silks.⁴ Here, we present for reference the latest form of the model that is appropriate for *A. pernyi* silk, which is very similar to the model initially developed for spider dragline silk, with only minor updates to the parameter values.

The parameter set for *A. pernyi* is the same as for the model poly(alanine) protein used as the simplified primary structure of silks, with specific model parameters given in Table ST1.



The model starts from the potential well function and its identity in energy, E , with the ensemble averaged energy terms at the mer unit level

$$E = E_{coh} \left(\left(\frac{V_o}{V} \right)^6 - 2 \left(\frac{V_o}{V} \right)^3 \right) = -E_{coh} + H_c + H_T \quad (\text{SI1})$$

where V is volume at energy, E , relative to its value, V_o , at the well minimum energy, E_{coh} , which has a value $V_o = 1.26 V_w$. The energy terms H_c and H_T are the zero point energy of vibrational entropy and the thermal energy of skeletal mode vibrations respectively. This allows volume to be calculated as a function of temperature (thermal expansion coefficient).

Properties are derived by mathematical processing of this potential energy function. First, a purely elastic reference elastic modulus is calculated as the bulk modulus, B , using

$$B \approx 18 \frac{E}{V} \quad (\text{SI2})$$

The cumulative loss through T_g is calculated using

$$\tan \Delta \approx 0.0085 \frac{E_{coh}}{N} \quad (\text{SI3})$$

and distributed as a normal distribution function with a standard deviation value of 20 degrees due to the distribution of structural units in the complex protein chain composition.

Tensile modulus, Y , is calculated from the effect of bulk modulus reducing with increased elastic energy dissipation with increasing temperature using the relation

$$Y = B \cdot \exp \left(- \frac{\int_0^T \tan \delta(T) dT}{A \cdot B} \right) \quad \text{where} \quad A = \frac{1.5 \cdot 10^5 L}{\theta \cdot M} = 1.6 \text{ GPa}^{-1} \quad (\text{SI4})$$

Finally, we can calculate the stress-strain response of the model polymer at the simplest level by taking the strain, ϵ_y , to be equivalent to the thermal expansion from ambient temperature to T and calculating stress at any T by integrating the product of

modulus and strain as function of temperature. Parameters for the three silkworm fibers are given in Table ST1, noting that only the values of cohesive energy and ordered fraction are different. Model stress-strain curves are plotted in Figure S4 in comparison with experimental observations. The failure stress is calculated using the energy to failure, presented in detail in reference 5 below.

Table ST1. Parameter values for GIM modelling of the stress-strain curves for the silkworm fibres. Only the cohesive energy, E_{coh} , and ordered fraction change for the three fibers.

Silkworm	V_w (cc/mol)	M (D)	θ (K)	N	L (Å)	E_{coh} (kJ/mol)	f_o
1	36.5	400	75	8	3.6	53	0.4
2	36.5	400	75	8	3.6	55	0.55
3	36.5	400	75	8	3.6	63	0.65

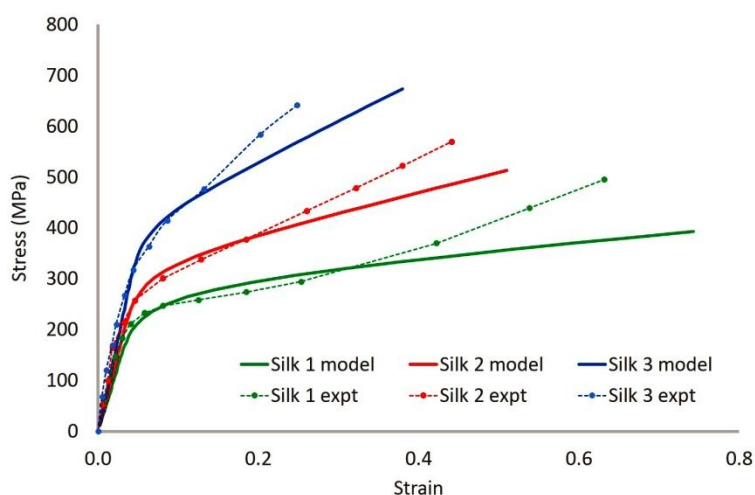


Figure S4. Comparison of experimental stress-strain curves for the three *A. pernyi* silkworm fibers with GIM predictions using the parameters give in Table ST1. See references below for details of the modelling method.

References:

1. S. J. Ling, Z. M. Qi, D. P. Knight, Y. F. Huang, L. Huang, H. Zhou, Z. Z. Shao, and X. Chen *Biomacromolecules*, 2013, 14, 1885–1892.
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5. C. J. Fu, D. Porter and Z. Z. Shao, *Macromolecules*, 2009, 42, 7877–7880.