Soft Matter

Supplementary Information

Extensional flow behaviour and spinnability of native silk

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Surface tension measurements

The pendant drop method was used to determine the surface tension of oil as well as the interfacial tension of the water-oil system. The surface tension of water was determined as a control and reference to check the suitability and accuracy of the pendant drop method. The curvature of pendant drops at equilibrium (drop is about to fall off) can be analysed and with the density difference the surface tension can be calculated according to the Young-Laplace equation[1] (see equation (1)).

$$\gamma\left(\frac{1}{R_1}+\frac{1}{R_2}\right) = \Delta P \equiv \Delta P_0 - \Delta\rho g z \qquad (1)$$

where R_1 and R_2 are the radii of curvature, ΔP is the Laplace pressure across the interface and $\Delta\rho$ is the density difference to air in case of surface tension or another media for calculating the interfacial tension. In our case, the surface tension was determined from images of pendant drops with an ImageJ plugin by Dearr and Mogne.[2] (see Figure S1)

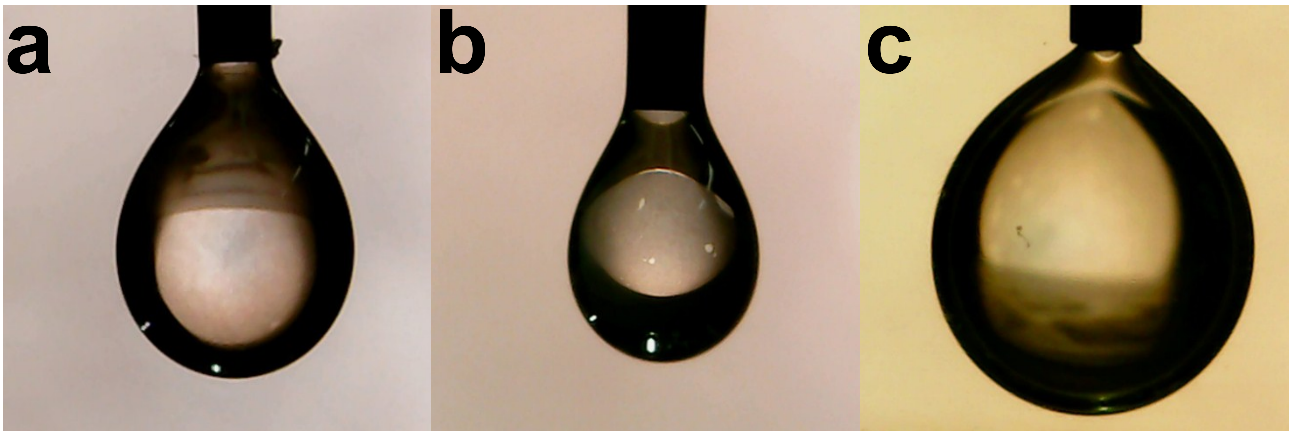


Figure S1: Pendant drops of **a** water in air, **b** oil in air and **c** water in oil were analysed to determine the values for the surface/interfacial tension of these systems.

The density of water and oil was determined by weighing a volume of 10 ml that was pipetted in a weighing boat. The average of 10 measurements was taken for the calculation of the surface tension. The gravitational acceleration g was taken as 9.81 m/s^{-2}. The results of the measured density differences and the surface/interfacial tensions are shown in Table S1.

Table S1: Results of the surface/interfacial tension measurements of water, oil and oil in water.

	$\Delta\rho$ / g cm^{-3}	γ / mN m^{-1}
water-air	0.9976 $\pm$ 0.0004	71.8 $\pm$ 0.8
oil-air	0.9161 $\pm$ 0.0027	31.2 $\pm$ 1.7
oil-water	0.0815$\pm$ 0.0031	22.4 $\pm$ 1.2

At 24˚C, the surface tension of water was calculated to be 71.8 ± 0.8 mN/m which is in good agreement with the value reported in literature for 25˚C (72.0 ± 0.1 mN/m).[3] The surface tension of rapeseed oil with 31.2 ± 1.7 mN/m and the interfacial tension of oil-water with 22.4 ± 1.2 mN/m are also in accordance with values reported in literature.[4, 5]

Table S2: Results of the contact angle measurements for air and oil to the silk surface as well as results for the surface tension of silk and its dispersive and polar components. The average was taken from 10 measurements.

θ_O / °	θ_A / °	γ_{SA}^d / mN m^{-1}	γ_{SA}^p / mN m^{-1}	γ_{SA} / mN m^{-1}
23.2	42.6	33.0	28.9	61.9
42.1	52.0	28.4	25.7	54.1
38.3	51.0	28.4	26.2	54.6
27.7	43.8	32.7	28.4	61.1
32.3	51.7	26.6	26.6	53.2
37.3	60.7	20.3	24.6	44.9
34.7	37.7	40.2	28.9	69.1
32.2	59.1	20.7	25.3	46.0
45.4	63.1	19.9	23.4	43.3
40.0	52.4	27.5	25.8	53.3
35.3 ± 6.4	51.4 ± 7.8	27.8 ± 6.1	26.4 ± 1.8	54.2 ± 7.8

Calculation of the lowest and highest extension rates during natural silk spinning in *Bombyx mori*

The lowest and highest extension rates during natural silk spinning in the converging silkworm duct were estimated by equation 2.[6]

$$\dot{\varepsilon} = \frac{4\dot{Q}}{\pi L}\left(\frac{1}{d^2} - \frac{1}{D^2}\right) \tag{2}$$

where $\dot{Q}$ is the flowrate of the silk proteins within the silkworm duct, L is the length of the converging duct, D and d are the duct diameters before and after the converging section, respectively.

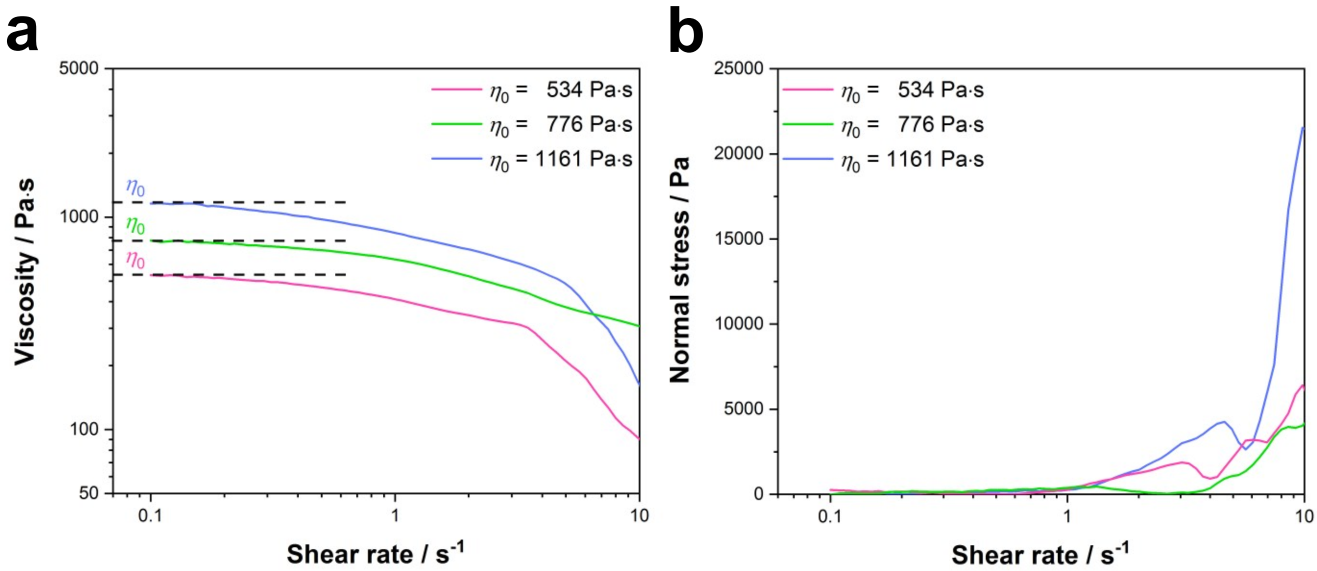
The natural spinning speeds in silkworms range from around 5-15 mm/s[7] and the dimensions of the spinning duct where taken from Asakura and co-workers.[8]

Therefore, the lowest extension rate within the silkworm duct occurs at a spinning speed of 5 mm/s. At this speed a fibre volume of 0.0016mm^3/s is spun which is equal to the flowrate due to the principle of conservation of mass. This results in an minimum extension rate of 0.036 s^{-1} for L=22 mm, D=0.4 mm and d=0.05 mm.[8] At 15 mm/s the extension rate within the duct equals to 0.11 s^{-1}.

The highest extension rates, however, occur at the draw-down taper where fibre is pulled from the silk gland. At this position the diameter converges from D=0.04 mm to d=0.02 mm over a length L=3 mm. For the lowest and highest spinning speeds (5 and 15 mm/s) this results in extension rates of 0.625 and 1.88 s^{-1}, respectively.

Video 1:

Video 2:



Shear rheology results of native silk proteins

Figure S2: Shear rheology results of different native silk protein samples with different zero-shear viscosities (< 1500 Pa·s). **a** The native protein samples from the posterior middle part of the *Bombyx mori* silk gland have similar concentrations (534 Pa·s: 19.6 wt.%, 776 Pa·s: 20.2 wt.% and 1161 Pa·s: 22.1 wt.%) but show a highly variable zero-shear viscosity due to the formation of salt bridges induced by metal ions.[9] All protein samples show pronounced shear-thinning similar to synthetic polymer melts. **b** Starting from a shear rate of 1 s^{-1} a significant increase in the normal stress can be observed due to the elastic nature of the native silk proteins. The drop in the normal stress around 4 and 5 s^{-1} for the 534 Pa·s and 1161 Pa·s sample, respectively, might indicate the occurrence of slippage which also effects the shear thinning behaviour in the viscosity curve starting from 4 s^{-1}.

References

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