Comparing the rheology of native spider and silkworm spinning dope

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Glossary

Convergent Evolution:	The process whereby organisms not closely related, independently evolve similar traits as a result of having to adapt to similar environments or ecological niches.
Silk Gland:	The organ responsible for producing and spinning silk proteins (dope) into fibres
Oscillation Test:	Applying a sinusoidal stress wave to the material and measuring its strain response
Elastic Modulus (G'):	Energy stored through the deformation of molecular backbones
Viscous Modulus (G"):	Energy lost through through friction in intermolecular passing events
Viscometry Test:	Applying a linear stress to a material and measuring its internal resistance to flow
Shear Thinning:	Describes a reduction in a material's viscosity with an increasing shear rate

Introduction

Silks are a group of **structural proteins** that have **evolved independently** many times and been selected to perform functions ranging from protective cocoons to aerial webs.

Silk production is energetically efficient and functionally optimised, resulting in a material that **outperforms most industrial fibres** [1].

Spun fibres, natural and man-made, rely on the extrusion process to facilitate molecular orientation and bonding [2-3]. Hence a full comprehension of the **flow characteristics** of native spinning feedstock (dope) will be essential to not only **understand its evolution,** but in translating these findings to **artificial silk production.**

The Golden Orb Weaving spider Nephila edulis

The Chinese silkworm Bombyx mori

We compared the rheology of native dope taken straight from the silk glands of the spider and silkworm, without modification or dilution, in order to understand how silk is spun [4].

Stress induced phase transition

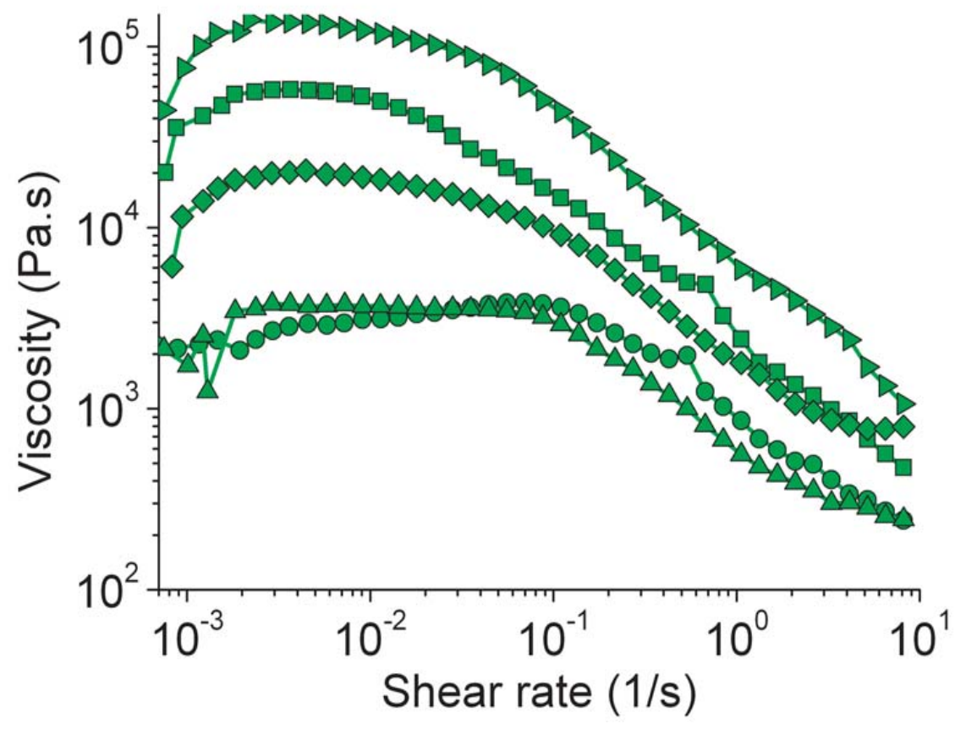
The spider's (and silkworm's) conversion of stored liquid dope to solid final fibre occurs through an **irreversible stress-induced phase transition** [5-6].

At present through **rheometry** we are able to reproduce the **shear forces** silk dope encounters in a gland *(although other forces such as extensional flow play an important role)* to samples *in vitro* thus providing a **window into the silk production process.**

Sensitive materials

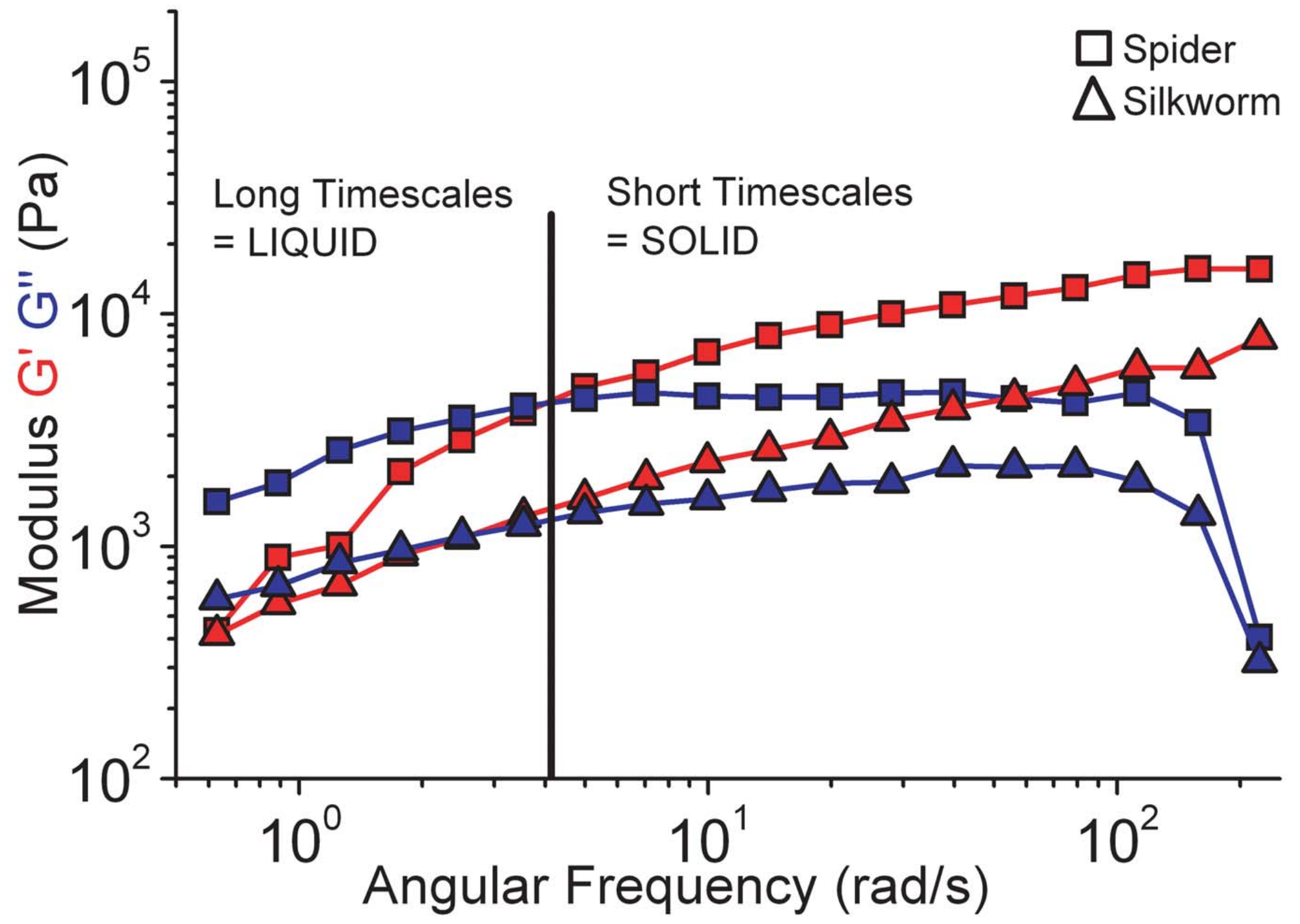
Simply **stretching or pinching** the dope during dissection or loading onto the rheometer produces **large variation** in rheological properties.

Upgrading our rheometer and increasing the number of samples tested allowed us to account for this and obtain the **'baseline' rheological parameters presented.**



Viscosity shear rate profiles of 5 samples of silk dope taken from the same silkworm silk gland shows that even the slightest mishandling affects the rheology

Similar Rheologies

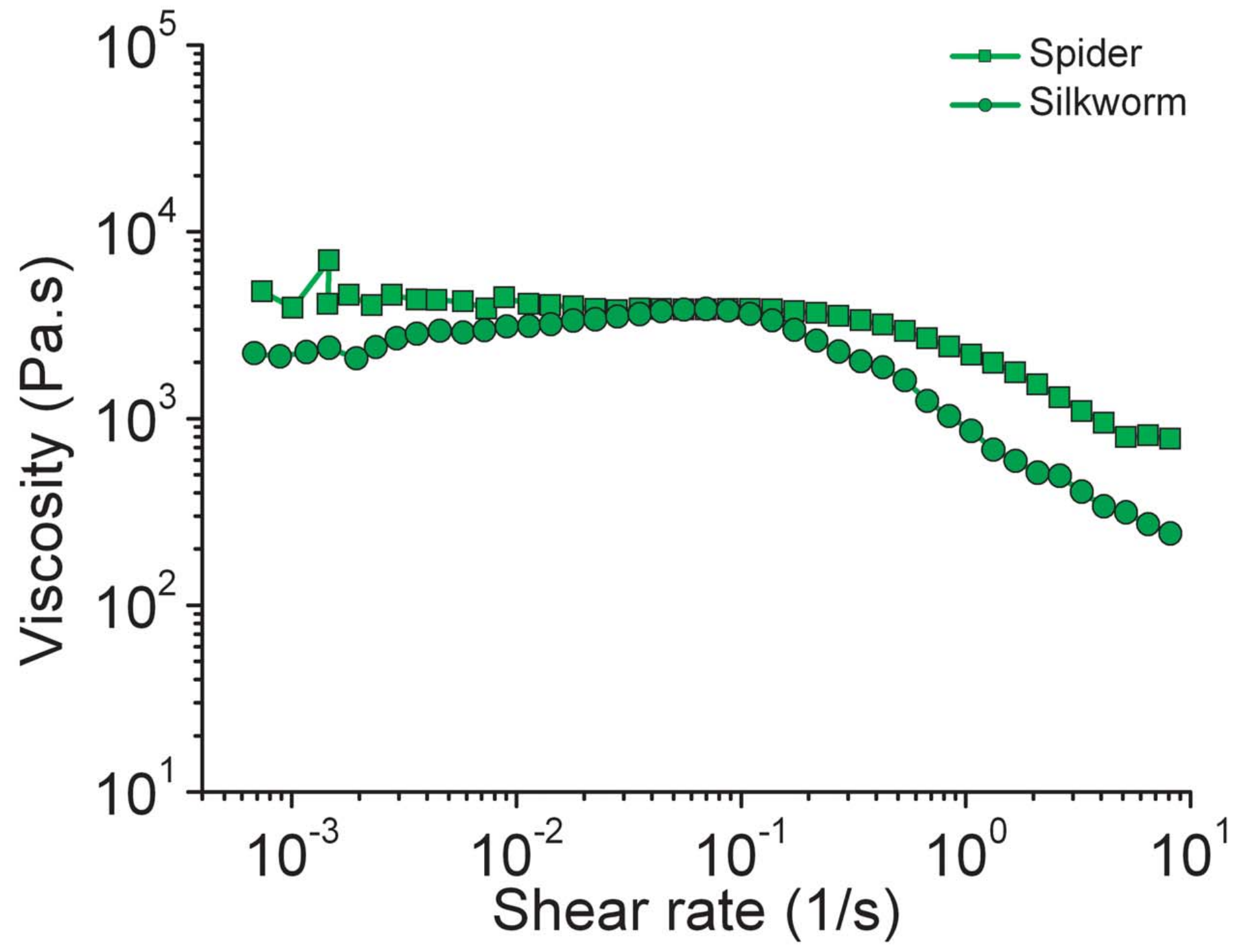


Oscillating the material over a range of frequencies at a fixed strain reveals how silk dope responds to shear over different timescales, determined by the ratio of G', (elastic storage) modulus to G", (viscous loss) modulus.

Oscillatory tests (right) on spider and silkworm dope reveal that despite being composed of **different proteins** they share a **similar rheological response** to shear.

Over long time scales (low frequency) they behave like a liquid and over shorter timescales (high frequency) like a solid.

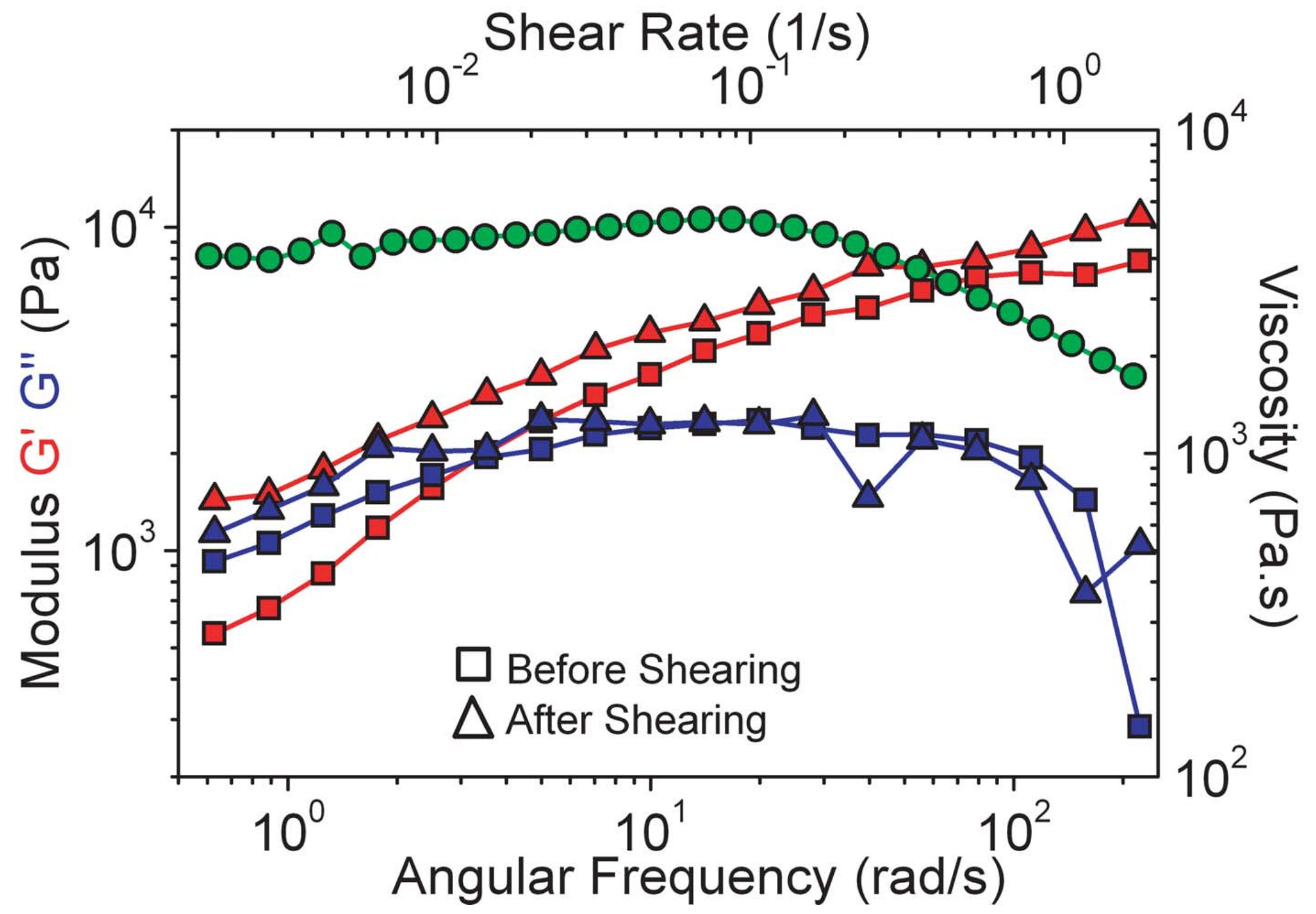
Hence standard polymer rheology would suggest both silks behave like **undiluted polymers of high molecular weight** acting as weak gels [7].



Subjecting the dope to shear flow in vitro allows us to collect viscosity measurements at different rates of shear, which can then be related to shear encountered in vivo as the dope moves through the spinning duct.

How silk proteins in the dope interact with one another **when forced to flow** at different rates is represented by viscosity measurements.

Again spider and silkworm dopes **behave like one another**, possessing a shear independent Newtonian flow at low shear rates followed by shear thinning at higher rates, also similar to the type of shear thinning and simplest power law models **observed in polymer melts** since the 1920's [7-8].



Coupling oscillation and viscosity tests indicates how the material has changed before and after it has been forced to flow.

By **coupling the two previous experiments** it is possible to characterise the dope before and after flow.

The results reveal silkworm dope to behave as a **weak gel before** being forced to **flow** and **like a solid afterwards.**

This is **seen *in vivo*** as the dope undergoes a stress induced phase transition from liquid dope to solid fibre.

Self Consistency

These materials have rheological properties that are **quantitatively self consistent** within a polymer modelling framework. Using the standard assumption $\eta_o = G_N \tau_p$, measured values from oscillatory tests can be used to accurately predict those obtained from viscosity tests.

This implies we may be able to **adapt standard polymer theory** to predict the properties of these **complex biological materials.**

	Relaxation time (τ_p, s)	Plateau modulus (G_N, kPa)	Calculated zero shear viscosity (η_o, kPa.s)	Measured zero shear viscosity (η_o, kPa.s)
Spider	0.21	17.5	3.8	4.0
Silkworm	0.15	8	1.2	1.5

Conclusions

Silk spinning dopes possess:

Extreme shear sensitivity

Convergent rheologies despite independent evolutionary origins

Seemingly standard shear rheologies, akin to molten polymers

Materials and methods

Extraction of gland contents: Final instar *N. edulis* and *B. mori* were dissected in distilled water for their silk glands. Once gland epithelium had been carefully peeled silk dope was removed and immediately subjected to rheological testing. *Rheological testing:* All tests were performed on a Bohlin Gemini HR nano constant stress rheometer with a cone and plate 1° 10mm at 25°C. Oscillatory tests were conducted at a target strain of 0.002 at frequencies between 0.1 and 100 Hz. Viscosity measurements were taken from a steady shear response between 0.0075 and 50 1/s.

The Bohlin Gemini HR nano

Acknowledgements

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