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Controlled supercontraction tailors the tensile behaviour of spider silk

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Abstract

The interest in the production of fibres that mimic the behaviour of natural silks has been boosted by the first successful attempts of spinning fibres based on spider drag line silk proteins. However, both the processing of biomimetic silk fibres and the basic studies on silk are hampered by the large variability of the fibre properties. Here we show that the tensile behaviour of spider silk can be predictably and reproducibly tailored by controlling the supercontraction effect, a large shrinkage of the longitudinal dimension of the fibre if unrestrained by its ends and immersed in water. This procedure allows to reproduce the tensile behaviour of natural drag line fibres and offers the possibility of obtaining silk fibres with predictable tailored properties in large quantities for experimental use. These results can be interpreted in the frame of the molecular model of drag line silk, as the result of re-orientation of the protein chains, leading to an explanation for the observed variability of natural drag line fibres.

Keywords: Spider silk; Supercontraction; Tensile Properties

1. Introduction

Silk produced in the major ampullate glands of spiders (MAS) shows a striking combination of tensile strength and elongation [1–3]. Attempts to mimic such outstanding properties is one of the major challenges in the field of biomimetics [4]. Tensile tests of spider silk fibres display a vast range of stress–strain curves. This variability could be related either to the state of the spider or to the method of silk collection [5,6], and it has been suggested that the production of silk with different tensile properties would increase the survival ability of the spider [7]. The active control on the properties of the fibre during spinning [8,9] would allow an adaptation of the properties of silk to both the usual environment of the species (interspecific variability) and to the immediate requirements of the spider (intraspecific and intraindividual variabilities). Parallel arguments indicate that it would be desirable to maintain the possibility of tailoring the properties of artificial silk to match a variety of intended uses.

In contrast to the benefits of its biological function, the large variability of the tensile properties of spider silk fibres has been a major hindrance in the characterization of the mechanical properties of natural spider silk, since most conclusions have been blurred by the large scatter in the tests [5,7,10]. Consequently, consideration of variability as either a positive or a negative characteristic of spider silk depends on the extent to which control can be exerted on the design of the mechanical properties of the fibre. The interest in controlling the variability of spider silk extends to the biomimetic production of artificial silk, since the tensile properties of the first artificial silk fibres have shown significantly low reproducibility [4].

When an unrestrained (MAS) fibre is submerged in water its length shortens substantially, a phenomenon known as supercontraction [11]. Research done by Gosline [12] revealed that the existence of the supercontraction effect had profound implications on the mechanical behaviour of spider silk, even suggesting a possible theoretical relationship between the variability of the tensile properties and supercontraction [13,14]. Based on this hypothesis, we have found that the variability of the tensile behaviour of natural spun spider silk can be controlled and reproduced through a supercontraction process by monitoring the supercontracted length.

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2. Experimental

Silk fibres from *Argiope trifasciata* spiders were used in this study. *A. trifasciata* is a common orb-web-building species in the Mediterranean coast that can be breed in captivity and whose size allows an easy manipulation of the spider. Silk fibres are collected using two different procedures; *naturally spun* fibres are either retrieved from the spider web or from the safety line, and *forcibly silked* fibres are obtained by pulling the silk fibre from the spider at controlled speed. Both procedures are described in detail elsewhere [9,15,16].

Adjacent samples were used to ensure reproducibility [11] of the tensile properties of the fibres before supercontraction. Reproducibility was checked by testing one out of every five samples, as a control sample; no significant deviation was observed in the tensile properties of the control samples.

The controlled supercontraction of silk fibres was achieved as illustrated in Fig. 1. Samples were glued on perforated aluminium foil frames by their ends, as explained elsewhere [17]. The gauge length of the samples before supercontraction, L_0, was measured (with a precision of ± 0.1 mm) by reckoning the maximum length between the glued ends of the fibre with no force exerted on the fibre. Controlled supercontraction was attained in the following way: The gauge length was decreased a value Δ (see Fig. 1), then samples were immersed in water for 30 min and allowed to dry overnight (nominal conditions $T = 20$ °C, relative humidity 35%). Once dried, the gap between grips was decreased Δ_r (see Fig. 1) until the force built up during supercontraction vanished (this force is about 5% of the breaking strength of the fibre). The distance between the glued ends of the fibre, L_C, was taken as the base length of the supercontracted samples.

Some selected control and supercontracted samples were metallised after tensile testing, and observed in a scanning electron microscope to measure the cross sectional area. Force–displacement curves were re-scaled as stress–strain curves by dividing the force by the cross sectional area (engineering stress) and the displacement by the base length, L_C, (engineering strain). We gave a detailed description of this experimental procedure elsewhere [18].

3. Results and discussion

The range of stress–strain curves displayed by MAS fibres from a single *Argiope trifasciata* spider, retrieved either from the mooring lines of the web [16] or from the safety line [9], is illustrated in Fig. 2. At present there is a very limited knowledge on the microstructural origin of variability, although the systematic description of the range of tensile properties exhibited by naturally spun spider silk [19] has allowed to establish its limits.

Fig. 3 shows the evolution of the stress–strain curves of supercontracted fibres with different percentages of supercontraction. The percentage of supercontraction is defined as $100 \times (\Delta + \Delta_r)/L_0$. Clearly there is a monotonous decrease in the stiffness of the fibre as supercontraction increases. The reproducibility of the process was checked by at least four tests for each percentage of supercontraction. All the curves showed differences below 5% in stress at a given strain, except for the large scatter in the values of tensile strength. The poor reproducibility of the tensile strength appears to be a characteristic of spider silk as it has been indicated by previous studies on naturally spun silk fibres [16,18].

Representative stress–strain curves of naturally spun and forcibly silked fibres are included in Fig. 3 for comparison. Forcibly silked fibres are stiffer than naturally spun ones. However, controlled supercontraction reduces the stiffness of forcibly silked fibres to the point that the stress–strain curves of fibres with supercontraction from 7.5 to 25% present similar stress–strain curves to those of naturally spun fibres. Supercontraction above 25% gives stress–strain

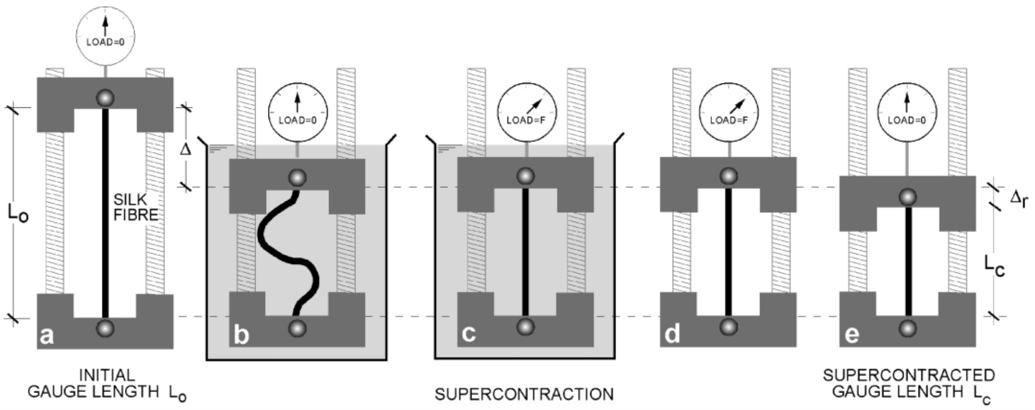

Fig. 1. Experimental procedure of the controlled supercontraction process. (a) A silk fibre with a base length L_0 is mounted on a frame to fix the distance between the grips. (b) The controlled supercontraction is achieved by lowering the upper grip a distance Δ from the initial position L_0, and by immersion in distilled water. (c) The fibre shortens and becomes stressed. (d) The frame is removed from the water after 30 min, and the fibre is allowed to dry overnight. (e) The fibre is unloaded a distance Δ_r until the forces built up during supercontraction vanish. The length of the sample after supercontraction is L_C.

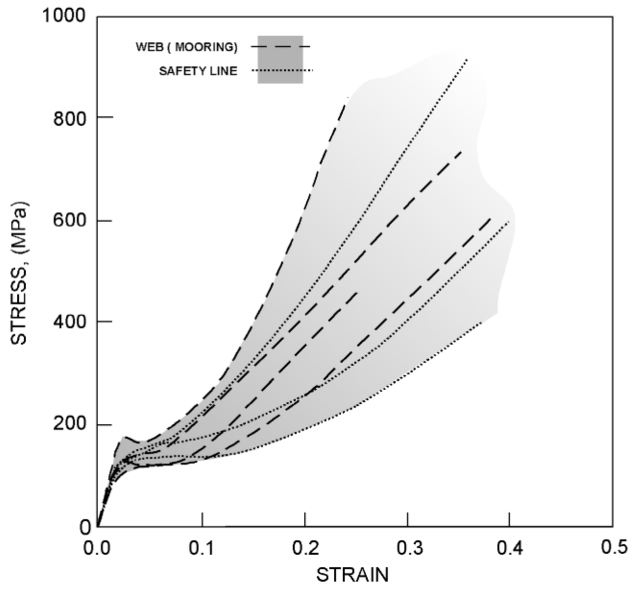

Fig. 2. Stress–strain curves of naturally spun *Argiope trifasciata* silk fibres. Stress–strain curves of naturally spun silk fibres retrieved either from the mooring lines of the web or from the safety line of a spider crawling on a horizontal surface are compared. The shadowed area illustrates the large variability observed in the tensile properties of naturally spun fibres.

curves that are more compliant than those of naturally spun fibres. The label maximum applied to a percentage of supercontraction of 60%, indicates that the silk fibre did not supercontract beyond this limit.

The combination of forced silking and controlled supercontraction offers the possibility of obtaining spider silk fibres with tailored properties including -but not restricted to- those of naturally spun fibres. This procedure should mark a significant improvement in the experimental study of spider silk. Moreover, if artificial silk fibres should show a comparable supercontraction effect, it is likely that controlled supercontraction could be introduced as a post-spinning treatment to tailor their final tensile properties, adapting them to their intended uses. However, the successful use of controlled supercontraction during the processing of artificial fibres will require that the tensile properties of the fibres prior to controlled supercontraction display a reproducibility comparable to that observed in spider forcibly silked fibres

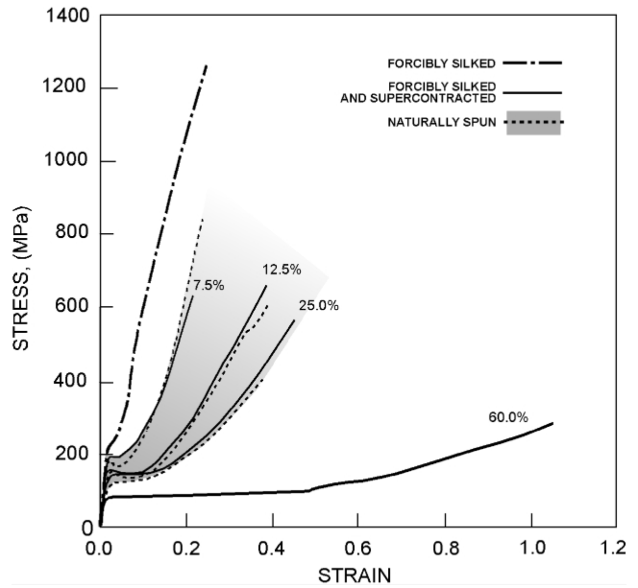

Fig. 3. Influence of the controlled supercontraction length on the stress–strain curves of spider silk. Stress–strain curves of forcibly silked fibres subjected to controlled supercontraction processes are compared with curves obtained from naturally spun fibres. Each controlled supercontraction fibre is labelled by the percentage of supercontraction (defined as $100 \times (\Delta + \Delta_r)/L_0$, see Fig. 1). The shadowed area shows the range of stress–strain curves obtained from naturally spun fibres. (Nominal test conditions: $T = 20$ °C; RH = 60%; strain rate = 0.0002^{-1}).

The influence of controlled supercontraction on the tensile properties can be justified within the frame of the molecular model of spider silk [13,14]. In this context, the hydrogen bonds established between the silk proteins would be disrupted by water molecules (water molecules exert a similar plasticising effect on silkworm silk [17]), and the initially pre-stressed silk proteins would re-orient themselves driven by the entropic restoring force. Re-orientation would lead to a decrease in the alignment of the proteins and a subsequent decrease in the longitudinal dimension of the fibre. The drying process would prompt the creation of hydrogen bonds that stabilize the new conformation. Consequently, the variability observed in natural fibres would correspond to different degrees of alignment of the polypeptide chains. The possibility of characterising the stress–strain curves of naturally spun fibres at high strains using a single parameter [19] suggests the interpretation of this parameter as a measurement of the alignment of the chains.

3. Conclusions

(1) The stress–strain curves of forcibly silked fibres and *maximum supercontracted fibres* represent the limits of the tensile behaviour of *A. trifasciata* spider silk. In particular, the maximum supercontraction condition can be considered as a reference state, since it can be reached independently of the previous history of the sample.
(2) Stress–strain curves similar to those of naturally spun fibres can be predictably obtained by a controlled supercontraction process on forcibly silked fibres.
(3) The combination of forced silking and controlled supercontraction provides the first source of silk fibres from a spider species, whose properties can be predictably tailored, including—but not restricted to—those of naturally spun fibres. The ubiquitous character of the supercontraction effect in MAS fibres of orb-web spinning spiders suggests that the controlled supercontraction process could be extended to silk fibres from other species.

(4) These results can be interpreted in the frame of the molecular model of spider silk assuming that with controlled supercontraction the alignment of the polymer chains is changed in a predictable way.

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