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Self-tightening of spider silk fibers induced by moisture

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Abstract

Spider dragline silk has a unique combination of desirable mechanical properties—low density, high tensile strength and large elongation until breaking—that makes it attractive from an engineering perspective [Nature 410 (2001) 541]. Nevertheless, this outstanding performance is threatened by the way mechanical properties are affected by a wet environment, particularly if the stress of these fibers can relax when exposed to moisture. Tests on spider dragline silk (*Argiope trifasciata*) performed by the authors have shown that when the fiber is clamped and exposed to a wet enough environment non-vanishing supercontraction forces develop. When the moisture is removed the residual stresses increase, and this effect has proven long lasting, as the fiber remains stressed for hours. In addition, the tensile properties of the fiber remain unaffected by the residual stresses build up after removing the moisture or after a wetting and drying cycle. These tests give support to the thesis that supercontraction helps to keep the spider webs tight and opens new applications for synthetic analogs.

Keywords: Spider silk; Supercontraction; Residual stress

Supercontraction is a very large shrinkage in water at room temperature of major ampullate silk (MAS) fibers of orb-web-building spiders [1], first observed by Work [2,3]. It was noticed that fibers retract to about one-half their original lengths when they were wetted in an axially unrestrained condition [3]. When restrained, stress is induced—due to restricted supercontraction—and amounts to up to 4.7% of the breaking strength [2,4]. It has been suggested that wetting-induced supercontraction of MAS takes up the slack in webs and restores web shape and tension after prey capture [2,3,5].

MAS fibers from *Argiope trifasciata* spiders were collected by forced silking at a drawing speed of 1 cm/s at 20 °C and 35% relative humidity (RH) [6]. Samples were stored at nominal conditions 20 °C and 35% RH until the time of the test. Adjacent samples were used to ensure the reproducibility of fiber properties [7]. In addition, one out of every five samples was taken as control, and it was tensile tested at nominal conditions (20 °C and 35% RH) to check the fiber variability. Control samples were also used to measure the fiber cross-sectional area by scanning electron microscopy. No significant differences were observed in the tensile properties or fiber diameter between control samples.

The experimental procedure to measure the stress developed by the restrained supercontraction of the fibers is shown in Fig. 1. Loose silk fibers were cut and glued onto aluminium foil frames with a nominal gauge length of 20 mm. Following a well-established procedure [8], samples were fixed in the grips of the testing machine (Instron 3309-622/8501) which was appended to an environmental chamber (Dycometal CCK-25/300). Forces were measured by a 100 mN load cell with 0.1 mN resolution (HBM 1-Q11). Before exposing the samples to moisture, the environmental chamber was driven to the initial conditions of 20 °C and 35% RH. Temperature and moisture control was achieved within ±0.2 °C and ±1% RH. Once stabilized at the initial conditions, the samples were lengthened up to zero force length—i.e. the length at which the fiber is fully extended but no appreciable loads are exerted on their ends—and fixed in this position. A moist environment of 50, 60, 90, and 100% RH (saturation by immersion in water) was applied to the samples for a period of 24 h, with a final step of 35% RH during at least 5 h. All these tests were carried out at 20 °C. At the end of the test, the samples were unloaded and tensile tested at

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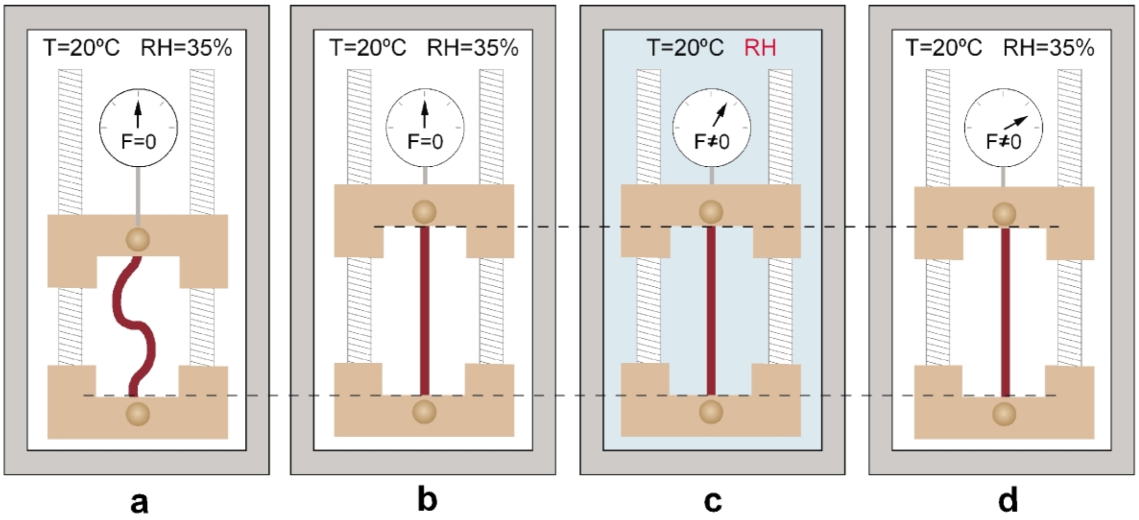

Fig. 1. Measurement of the fiber stress developed due to restrained supercontraction: (a) initial set up, with loose fiber; (b) clamping the fiber at maximum length with zero force; (c) surrounding the fiber with a controlled moist environment during 24 h; (d) last step, drying the environment (up to 35% RH) at least, 5 h.

1 mm/min strain rate while keeping constant temperature and humidity at 20 °C and 35% RH.

The reproducibility was checked by at least three tests in each condition. Additionally, and to make certain that no spurious effects were taken into account—moisture condensation, load cell accuracy and performance—all the tests were repeated using a completely different experimental setup using a balance to measure forces (Instron 4411 machine and Precisa 6100C balance, with resolution ±0.1 mN).

Fig. 2 shows the evolution in time of the stresses generated by supercontraction at different moisture conditions. Stresses were calculated by dividing the supercontraction force by the initial area of the cross-section. For an environment of 50% RH, no noticeable stresses due to supercontraction were measured (Fig. 2(a)). These stresses start to build up in moist environments about 60% RH (Fig. 2(b)). Specimens subjected to 90% (Fig. 2(c)) and 100% RH (Fig. 2(d)) experienced maximum supercontraction stresses close to 60 MPa. These stresses were found to relax during 24 h by only 20–25%. This 1-day period can be taken as a typical value for the spider web life cycle [9]. In all the tests, supercontraction stresses proven to be irreversible, maintaining their values or even increase them to some extent when the humidity was reduced to the initial value of 35%. Similar results—not shown here—were found in *Nephila clavipes* dragline silk, whereas in *Bombyx mori* silkworm cocoon silk, used as control, no supercontraction stresses were observed, which confirms previous reports [10]

It is assumed that supercontraction is due to hydrogen bonds breaking caused by water, which acts as a plasticizer, and the subsequent chain re-orienting and coiling driven by the entropic restoring force of the chains [11–14]. In this context, disruption of hydrogen bonds would allow a limited re-orientation of the initially pre-stressed chains, thereby originating tensile stresses at the fibers grips. The subsequent drying process would prompt the creation of hydrogen bonds that stabilize the new conformation. The attractive character of hydrogen bonding would tend to shrink the fiber, justifying the increase in the tensile stresses during drying.

The stress–strain curves obtained for fibers after a moisture-drying process and for control samples mantained at 35% are shown in Fig. 3. All the tests were performed at 20 °C and 35% RH. Stress and strain values were computed using the initial cross-sectional area and length at zero force. A striking repeatability is shown in Fig. 3 for all the specimens; control samples and samples subjected to different conditioning process. Results from this figure show that a wetting–drying cycle applied to restrained fibers seems to have no effect on their tensile behaviour, which closely mimics the stress–strain response of control fibers

This fact suggests that all the fibers tested could share the same microstructure, and chain re-orientation and coiling promoted by supercontraction [11]—that leads to higher compliance—has been prevented by the zero deformation condition imposed to the samples (steps (b), (c) and (d) in Fig. 1). The values reached by the supercontraction stresses (≈60 MPa)—which amount to approximately 5% of the breaking strength of the fiber, a figure close to the value of 4.7% quoted by Work [2]—are well inside the initial linear elastic range (see Fig. 3) and, hence, no irreversible behaviour should appear.

The fact that supercontraction stresses develop similarly—within the usual scatter bands—for 90 and 100% RH environments, whereas for dry enough atmosphere (50%) they do not appear, suggest the existence of a moisture threshold for supercontraction to take place. Looking for this threshold, restrained silk fibers were exposed to

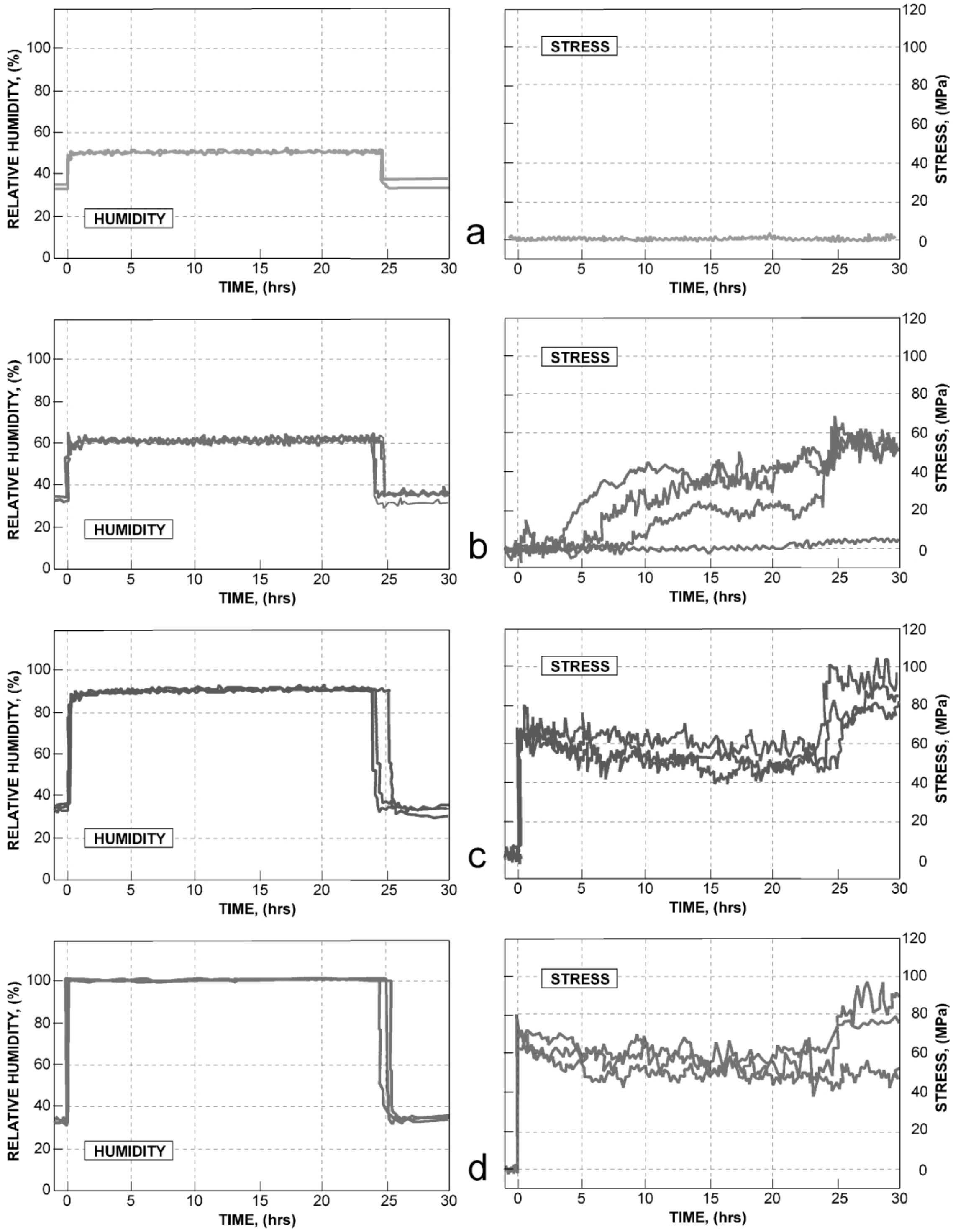

Fig. 2. Stresses generated by supercontraction at different moisture environments: (a) 50% RH; (b) 60% RH; (c) 90% RH; (d) 100% RH. Notice that the average tensile strength is about 1500 MPa (see Fig. 3) and maximum values of supercontraction stresses are 60 MPa.

monotonically increasing moisture content while carefully measuring the fiber stress. Fig. 4 shows the development of supercontraction stresses from dry (35%) to wet (90%) atmosphere in about 60 s as a function of the RH. From the figure, it is immediately apparent that a transition occurs between 70 and 75% RH, where stresses quickly build up in the fiber. This behaviour has been confirmed in all the samples tested, and seems to be connected to fiber geometry (due to water diffusion processes).

In addition, the presence of this moisture threshold at 70–75% RH could explain the large scatter shown in Fig. 2(b) for fibers tested at nominal 60% RH environments.

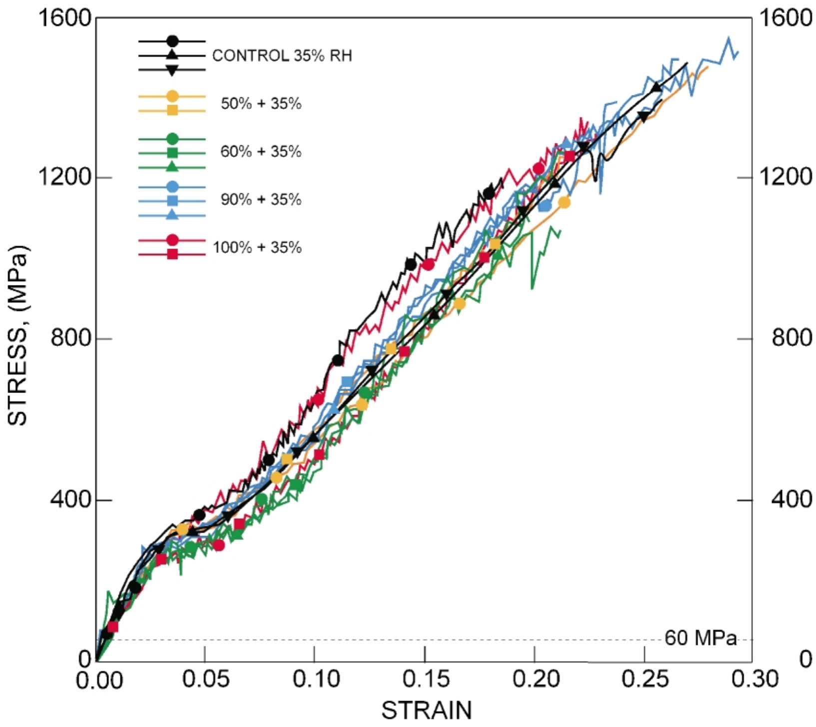

Fig. 3. Stress–strain curves of spider silk fibers; control samples and fibers subjected to different moisture environments (50, 60, 90, and 100% RH) and subsequently dried (at 35%).

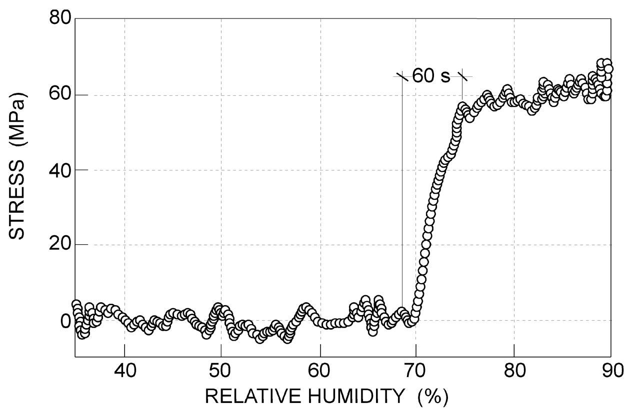

Fig. 4. Stresses in spider silk fibers due to supercontraction under different moisture environments.

These differences are probably due to the fact that chamber turbulences can produce local fluctuations of moisture in the air surrounding the fiber, exceeding temporarily the threshold value and resulting in a partial development of supercontraction stresses.

The results shown in this paper give additional support to the hypothesis that wetting-induced supercontraction helps in tightening spider webs [2,4], and provide quantitative measurements of the supercontraction stresses.

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