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Supercontraction forces in spider dragline silk depend on hydration rate

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Abstract

Spider dragline silk is a model biological polymer for biomimetic research due to its many desirable and unusual properties. 'Supercontraction' describes the dramatic shrinking of dragline silk fibers when wetted. In restrained silk fibers, supercontraction generates substantial stresses of 40–50 MPa above a critical humidity of ∼70% relative humidity (RH). This stress may maintain tension in webs under the weight of rain or dew and could be used in industry for robotics, sensor technology, and other applications. Our own findings indicate that supercontraction can generate stress over a much broader range than previously reported, from 10 to 140 MPa. Here we show that this variation in supercontraction stress depends upon the rate at which the environment reaches the critical level of humidity causing supercontraction. Slow humidity increase, over several minutes, leads to relatively low supercontraction stress, while fast humidity increase, over a few seconds, typically results in higher supercontraction stress. Slowly supercontracted fibers take up less water and differ in thermostability from rapidly supercontracted fibers, as shown by thermogravimetric analysis. This suggests that spider silk achieves different molecular configurations depending upon the speed at which supercontraction occurs. Ultimately, rate-dependent supercontraction may provide a mechanism to tailor the properties of silk or biomimetic fibers for various applications.
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Introduction

Spiders use dragline silk for a variety of functions, including lifelines and the frames of webs. Dragline silk is a high-performance material that exhibits a strength to weight ratio five times greater than steel (Griffiths and Salanitri, 1980; Gosline et al., 1999; Smith et al., 1999). At high humidity, dragline silk can also supercontract (Work, 1981; Guinea et al., 2003). Unrestrained silk shrinks up to 50% of its original length while constrained fibers, such as in webs, generate substantial forces during supercontraction (Work, 1981). Water absorbed during supercontraction is hypothesized to plasticize silk fibers by disrupting hydrogen bonding between proteins, thereby allowing an entropy-driven

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re-orientation and coiling of silk molecules (Jelinski et al., 1999; van Beek et al., 1999; Yang et al., 2000; Guinea et al., 2003; Savage et al., 2004; Guinea et al., 2005; Schafer et al., 2008). Supercontraction may function as a mechanism that maintains tension in webs loaded by dew or rain (Guinea et al., 2003; Elices et al., 2004). Controlled supercontraction may also be exploited as a mechanism to tailor the properties of spider silk for different biomimetic applications (Pérez-Rigueiro et al., 2003; Guinea et al., 2005).

Some authors argue that supercontraction is ephemeral and that silk loses tension through time when humidity remains high (Bell et al., 2002). In contrast, others demonstrated that supercontraction tension can be sustained for long periods of time, suggesting that it results from a permanent transformation in molecular structure (Guinea et al., 2003). However, the stress generated during supercontraction varied widely between these studies (by an order of magnitude), which may account for some of the discrepancies. Resolving this controversy depends upon developing a better understanding of the interplay between the rate of water uptake by silk and ultimately how water molecules produce supercontraction forces.

Here we show that the force of supercontraction in spider dragline silk depends on the rate at which the critical humidity causing supercontraction is achieved, and that rapidly supercontracted fibers can generate stresses exceeding 100 MPa.

Materials and methods

We sampled silk from nine specimens of the golden silk orbweaver *Nephila clavipes* (Araneae: Nephilidae) from Florida and Costa Rica. Spiders were housed individually in cages at room temperature (about 23 °C), fed crickets two to three times per week, and misted daily with water. We first collected fibers by forcible silking and then glued the fibers across 10.7 mm gaps in cardboard mounts using Super Glue® (cyanoacrylate), as described by Blackledge et al. (2005a). This allowed us to collect samples consisting purely of major ampullate dragline silk. The diameter of each silk sample was determined prior to testing by averaging six measurements taken along the length of the fiber using polarized light microscopy. This method has been shown to be as accurate as scanning electron microscope (SEM) photography, and accounts for intra-individual variation in silk diameter (Blackledge et al., 2005b). We also collected bulk samples of 1–6 mg of silk by spooling forcibly silked fibers onto test tubes mounted on a rotating mandrel. We used portions of the bulk samples to examine changes in silk weight during supercontraction and for thermogravimetric analysis (TGA).

Stress response of silk to humidity

To examine how humidity affected silk, we fastened samples of dragline silk to the grips of a Nano Bionix tensile tester (Agilent Technologies, Oakridge, TN, USA). The tensile tester was equipped with a custom-designed environmental chamber that allowed precise and rapid control of humidity from ~1% to 95%, while maintaining constant temperature. We mounted silk at room humidity (13% for most of the experiments, range 13–40%) and temperature (22 °C throughout). Temperature was held constant at $\pm 0.1\,°C$ throughout the experiment. We relaxed the silk fibers and then pulled them slightly until they were 'just taut' (Savage et al., 2004), to standardize their starting tensions. Initial tension varied somewhat between 5 and 20 MPa, but with a few fibers stressed up to 50 MPa. Thus, fibers were usually mounted at ~ 5–10% of their yield stress.

We utilized two different protocols to increase humidity to the critical threshold for supercontraction. We rapidly cycled from room humidity to >90% RH as fast as the environmental chamber allowed, typically achieving the complete range within ~60 s. For other samples, we slowly reached the critical humidity for supercontraction by increasing humidity in 10% increments every 5–10 min. This novel combination of approaches allowed us to test for rate-dependent effects with silks experiencing increases in humidity ranging from 0.2% to 1.3% per second. To verify that stationary stress had been reached (i.e. 'full supercontraction'), tests were left at >90% for periods of up to 20 min. Stress never increased beyond the initial, rapid supercontraction.

For both methods, we continuously measured the force generated by silk and then calculated engineering stress by normalizing to the cross-sectional area of the sample. Increased stress indicated that the fiber was pulling (contracting). We calculated the exact rate of humidity increase during supercontraction by measuring the time, in seconds, for humidity to increase by 5% when supercontraction forces were first evident. We then used regression analysis to examine the relationship between rate of humidity increase and the force of supercontraction.

Water uptake by dragline silk

To measure water uptake during supercontraction by dragline silk fibers we used two approaches. First, we weighed bundles of virgin silk to the nearest 1 μg using an automatic electrobalance (Cahn25, Cahn Instruments, Madison, WI, USA). We then affixed the ~2 mg bundles of silk to the nano mechanical actuating transducer (NMAT) head of the Nano Bionix tensile tester in the environmental chamber and exposed the

silk bundles to supercontraction humidity. For four bundles we rapidly increased humidity while for another three bundles we slowly increased humidity as described above. We then dried the silk by returning the chamber to a room humidity of 13% for at least 10 min. Subsequently, the dried supercontracted fiber bundles were again weighed on the microbalance to measure weight gain during supercontraction.

Care was taken to handle the bundles minimally so that no material was lost while transporting silk between the balance and the tensile tester, since loss of material would bias against detecting weight gain (see below). Handling did not have any effect on one silk bundle that was transported back and forth between the Nano Bionix and microbalance three times without changes in humidity (control bundle). Furthermore, the Nano Bionix tensile tester could measure instantaneous changes in the mass of the silk within the environmental chamber as changes in load. We therefore continuously recorded the load exerted upon the NMAT head by the silk bundle before supercontraction, during supercontraction, and post-supercontraction after drying. The load translates into proportional changes in the mass of silk resting upon the NMAT head. We then converted those proportional changes to absolute mass by normalizing to the change in mass, before and after supercontraction, measured by the microbalance.

Thermogravimetric analysis

We performed thermogravimetric analysis (TGA) on bundles of virgin silk as well as the dried supercontracted silks from the above weight experiment. TGA exposes materials to gradual increases in tempera-ture (from room temperature to approximately 500 °C) and measures the relative weight loss of the materials as specific molecular compounds boil off at different critical temperatures. This provides a highly sensitive mechanism to determine if samples differ in their molecular structures. All tests were conducted in a nitrogen environment. We compared data from two samples of virgin silk, two samples of rapidly super-contracted silk and two samples of slowly supercon-tracted silk.

Results

Response of silk to slow versus rapid changes in relative humidity

The stress generated by supercontraction in *Nephila* dragline silk ranged from ~10 to 140 MPa, encompass-ing most of the range in the published literature (30–140 MPa in Work, 1985; Guinea et al., 2003; Savage et al., 2004), although higher values were reported by Bell et al. (2002) to the point that fibers yielded during supercontraction. Variation in supercontraction stress depended, to a considerable degree, on the rate of increase in relative humidity. Slower increases in humidity generated lower supercontraction stresses. Extremely rapid humidity increase ($>1\%$/s) sometimes generated much higher supercontraction stresses that approached the yield stress of dragline silk (Fig. 1). In our tests, approximately 30% of variation in super-contraction stress was explained by the rate of humidity increase alone (Fig. 2A; $R^2 = 0.284$, $P < 0.001$, $N = 37$). Relatively low rates of increase ($<0.6\%$/s) achieved an
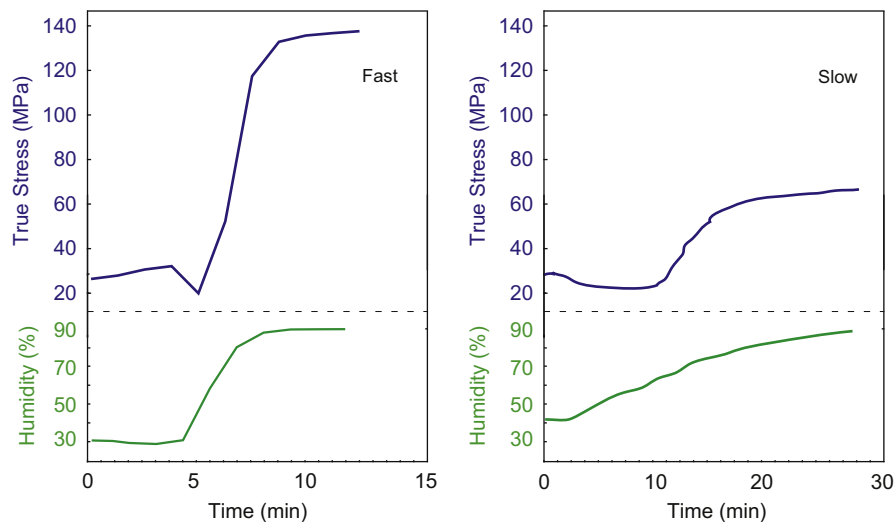

Fig. 1. Representative supercontraction stress curves in response to rapid (left) or slow (right) increase in humidity. Rapid increase in humidity leads to greater supercontraction forces than slow humidity increase. The initial relaxation of the fiber in response to humidity below the critical level (~70%) likely represents slight softening or swelling of the silk in response to humidity and was consistent across all samples. Note the difference in magnitude of the time axes between the left and right panels.

even more predictable effect on supercontraction, explaining 60% of the variation in supercontraction stress (Fig. 2B; $R^2 = 0.59$, $P < 0.001$, $N = 20$). At higher rates, variation in supercontraction was much greater, although many of the outliers were due to silk from two individual spiders (Fig. 2A). Yet strong supercontraction (above 50 MPa) never occurred at rates below 0.4%/s (0 out of 18), but frequently at higher rates (12 out of 19), a significant difference according to Fisher's exact test ($p < 0.001$).

Uptake of water by dragline fibers

The three slowly supercontracted bundles of silk gained $0.95 \pm 0.17\%$ (mean $\pm$ SE) mass during supercontraction, compared with $1.60 \pm 0.47\%$ for the four bundles of rapidly supercontracted silk. Change in load measured by the tensile tester confirmed a permanent increase in mass simultaneous with supercontraction, which was maintained when fibers were dried, and also indicated lower weight gain by slowly versus rapidly supercontracted silk.

Thermogravimetric analysis

TGA demonstrates differences in the molecular organization of supercontracted versus virgin silk, particularly in the decomposition of the material at 350–400 °C. Moreover, slowly supercontracted fibers differ from both virgin and rapidly supercontracted fibers in decomposition at lower temperatures of 200–300 °C (Fig. 3). Curves for the two virgin silk fibers were nearly identical, as were the two curves for fast supercontracted silk, demonstrating the repeatability of the process (Fig. 3). Decomposition of slowly supercontracted silk, however, was more variable at 350–400 °C. The behavior of one sample was strikingly similar to that of virgin silk, at 350–400 °C, and the other to that of rapidly supercontracted silk.

Discussion

Supercontraction in spider dragline silk is clearly a complex phenomenon (Blackledge et al., 2009). For instance, it varies widely among species (Work and Morosoff, 1982; Work, 1985), likely in relation to differences in content of critical amino acids such as proline (Liu et al., 2008; Savage and Gosline, 2008a). Supercontraction also depends in part upon the effect of spinning conditions on fiber orientation (Liu et al., 2005a). Here, we demonstrate that external factors also control variation in supercontraction such that the phenomenon depends upon the rate at which silk is exposed to water. When humidity slowly increases to the
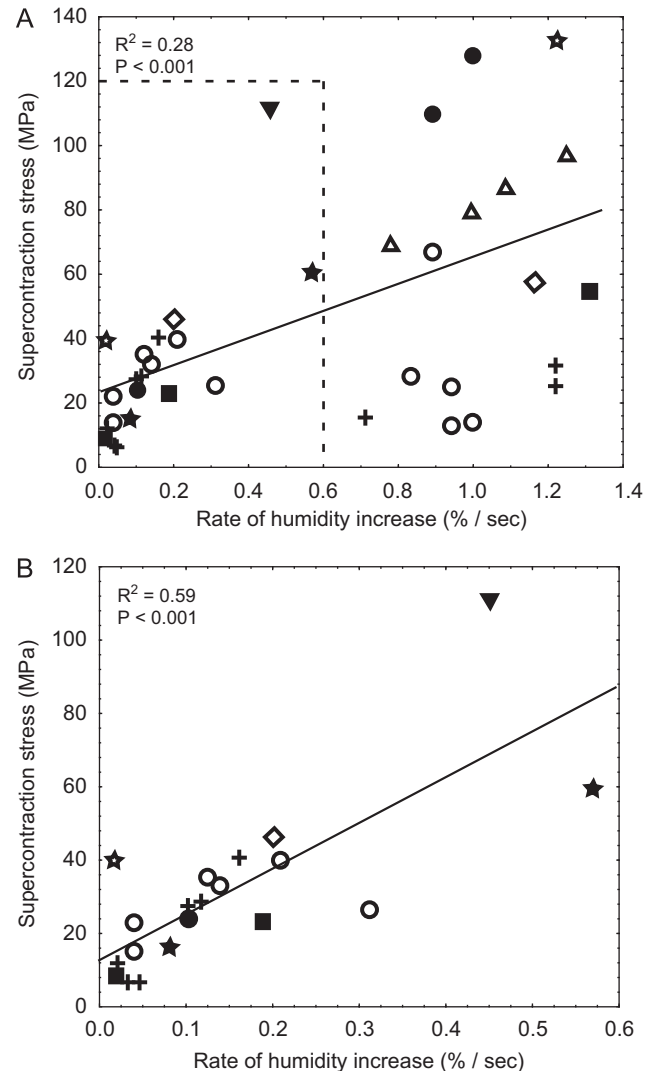

Fig. 2. (A) Relationship between rate of humidity increase and the force of supercontraction in constrained spider silk. Symbols separate nine individual spiders (open and full symbols of the same shape are different spiders). Note that all major outliers in the lower right were from only two individual spiders. Dashed box indicates the range of slowly supercontracted fibers shown in detail in panel B. (B) Relationship between rate of humidity increase and the force of supercontraction during slow increase in humidity (0.02–0.6%/s). Symbols denote the same spiders as in panel A.

critical threshold causing supercontraction, less water is permanently bound to the silk than when humidity rapidly reaches that threshold. This difference in the binding of water is associated with lower supercontraction forces (Figs. 1 and 2) during slower changes in humidity, as well as changes in the thermodynamic stability of the silk (Fig. 3). Thus, manipulating the rate of humidity increase may allow some control of the supercontraction phenomenon itself.

The rate at which supercontraction occurs provides a likely explanation for some of the enormous range in
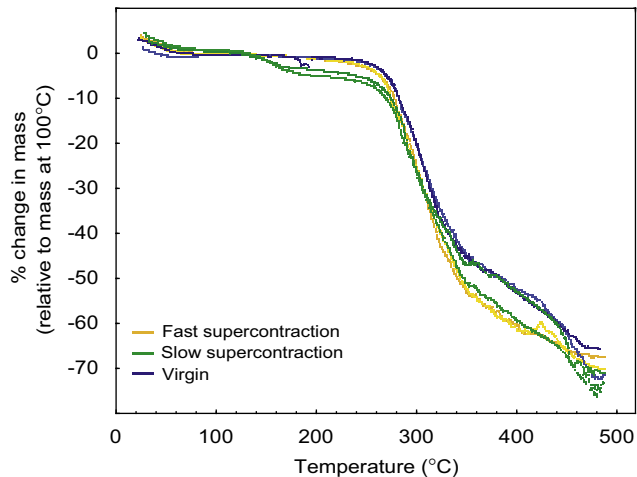
Fig. 3. Thermogravimetric analysis (TGA) of silk. The thermostability of slowly supercontracted fibers differs from both virgin silk and fast supercontracted fibers. Two tests are shown for each type of silk.

supercontraction forces reported in the literature (typically 30–140 MPa; Work, 1977, 1981; Bell et al., 2002; Guinea et al., 2003; Savage et al., 2004). Especially at relatively high rates of humidity increase, variation in supercontraction is quite large (Fig. 2A). This variation is not correlated with differences in mounting tension and fibers were typically mounted at 5–10% of yield stress, well within the range of prior studies (Work, 1985). However, it is worth noting that six out of seven points that exhibit unusually low supercontraction stress at high hydration rates (the rapidly supercontracted fibers with less than 50 MPa supercontraction in Fig. 2) were mounted at low tension (much less than 20 MPa) such that it is possible that some of the stress generated by supercontraction could have been undetected if excess slack needed to be removed first. Instead, variation between individual spiders' silk may be important – all seven high-rate outliers came from only two individual spiders. However, even within some individual spiders, different samples of silk also varied greatly if supercontracted at high rates. Such intra-individual variability has been found in many other studies of spider silk structure and performance (Madsen et al., 1999; Blackledge and Zevenbergen, 2007; Boutry and Blackledge, 2008; Savage and Gosline, 2008b). Presumably other factors that are difficult to control also play a role, such as spinning effects resulting from variation in forces applied to the fiber by the spider during artificial silking (Ortlepp and Gosline, 2004), as found in studies examining variability in the maximum magnitude of shrinking that occurs during supercontraction (Liu et al., 2005a). Future work should examine if native silk (e.g. sampled from the spider's web) shows the same rate dependence.

Spider dragline silk is a composite of highly structured β-sheet crystals embedded within less organized "amorphous" protein regions (Gosline et al., 1986; Hayashi et al., 1999). The degree of orientation of molecules within the amorphous region is determined in large part by the processing of liquid silk proteins as they pass through the spinning duct (Liu et al., 2005b). In dry silk, the amorphous region exhibits significant axial organization. Both the orientation within the amorphous region and the axial alignment of the β-sheet crystals are greatly reduced when silk physically supercontracts (Work and Morosoff, 1982; Fornes et al., 1983; Grubb and Ji, 1999; Shao and Vollrath, 1999). The organization within the amorphous region is maintained by hydrogen bonding between amino acids, which thereby freezes the orientation of the β-sheet crystals. Plasticization of these amino acids by water plays a crucial role in mobilizing protein chains during supercontraction (Jelinski et al., 1999; Liu et al., 2005a). The proteins now act as a rubber, and entropy drives them into a less ordered state (Gosline et al., 1984), shrinking unrestrained silk or generating significant forces in restrained silk, such as in our study. Thus, both the relative secondary structure of fibers and the degree to which fibers can become plasticized interact in determining supercontraction (Holland et al., 2008; Savage and Gosline, 2008a).

We hypothesize that it is in part the difference in the amount of water taken up during slow versus rapid supercontraction that accounts for the order of magnitude variation in stresses generated. Previous studies hypothesized that supercontraction might involve permanent uptake of water that changed both mechanical and thermodynamic properties of the fiber (Jelinski et al., 1999; van Beek et al., 1999; Yang et al., 2000; Guinea et al., 2003; Savage et al., 2004; Guinea et al., 2005; Vollrath and Porter, 2006; Schafer et al., 2008). However, to our knowledge this study is the first to demonstrate empirically that water permanently binds to the silk and that this binding alters the molecular organization of the silk. The molecular conformation of completely supercontracted, and hence relaxed, wet silk presumably represents a lower free energy state, at equilibrium, compared with the more organized structure of dry silk. Supercontraction is therefore a thermodynamically driven response to water, during which silk reconfigures toward this lower free energy state. In our experiment, silk was restrained such that it could not reach this equilibrium state, thereby generating force. This suggests at least two possible alternative explanations for why supercontraction stress is affected by the rate of humidity increase. First, slowly and rapidly supercontracted silks may represent different stages toward reaching the same preferred equilibrium state, with different rates of humidity change capable of "trapping" silk at intermediate levels of entropy.

This requires that the rate of plasticization of amino acids by water determines the ability of silk molecules to reconfigure, but the mechanisms for this effect are unclear. On the other hand, we found that different amounts of water permanently bound to silk during fast versus slow supercontraction. Because these tests were conducted using bundles of unrestrained silk, we assume that the molecules completely reconfigured to their preferred equilibrium states during supercontraction. This suggests that the chemical changes in the silk mediated by water uptake resulted in subtly different materials post-supercontraction that may in fact have different equilibrium states. This interpretation is at least weakly supported by our finding that fast and slowly contracted silks differed in thermostability (Fig. 3). Thus, the lower supercontraction force generated by slow humidity increase could indicate that the initial organization of the dry fibers (identical between methods) was closer to the equilibrium state of the slowly supercontracted silk. Ultimately, both hypotheses could be tested in part by comparing the structural organization of the amorphous regions of fast and slowly supercontracted silk. However, such differences are likely to be small compared with the clear contrast in the structure of native and fully relaxed supercontracted silk explored in previous studies.

The molecular reorganization that occurs within silk fibers during supercontraction results in permanent changes in the tensile mechanics of the silk (Pérez-Rigueiro et al., 2003). Thus, supercontraction provides a mechanism that can be used to tailor silk properties for various biomimetic applications (Pérez-Rigueiro et al., 2003; Guinea et al., 2005; Liu et al., 2005a). Our discovery of the rate-dependent nature of supercontraction therefore provides an important degree of control over this potential mechanism for processing silk fibers, as well as insight into the potential molecular mechanism causing supercontraction.

Acknowledgements

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