Biomimetic Supramolecular Fibers Exhibit Water-Induced Supercontraction

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Spider silk is a fascinating material, combining high strength and elasticity that outperforms most synthetic fibers. Another intriguing feature of spider silk is its ability to “supercontract,” shrinking up to 50% when exposed to water. This is likely on account of the entropy-driven recoiling of secondary structured proteins when water penetrates the spider silk. In contrast, humidity-driven contraction in synthetic fibers is difficult to achieve. Here, inspired by the spider silk model, a supercontractile fiber (SCF), which contracts up to 50% of its original length at high humidity, comparable to spider silk, is reported. The fiber exhibits up to 300% uptake of water by volume, confirmed via environmental scanning electron microscopy. Interestingly, the SCF exhibits tunable mechanical properties by varying humidity, which is reflected by the prolonged failure strain and the reversible damping capacity. This smart supramolecular fiber material provides a new opportunity of fabricating biomimetic muscle for diverse applications.

Natural systems frequently exploit intricate multiscale and multiphasic structures to generate properties which exceed those generally achievable by man-made systems.\(^1,2\) For example, spider dragline silk tends to outperform other natural fibers and most man-made filaments.\(^3,4\) More interestingly, spider silk is able to “supercontract” at high humidity, with contraction >50% of its original length.\(^5-7\) Supercontraction is thought to be induced by the entropy-driven recoiling of molecular chains.\(^8-12\) In analogy, most man-made fibers undergo thermal-induced shrinkage leading to changes in mechanical properties.\(^13,14\) Humidity-driven contraction in synthetic fibers is rarely seen on account of a “frozen” molecular network in the fiber. Recently, we reported drawing a supramolecular fiber from a self-assembled multiphase hydrogel at high water content (98 wt%).\(^15\) The fiber exhibits a good combination of tensile properties as well as damping capacity. More importantly, its underlying structure can be readily manipulated to produce novel fiber materials with a range of properties.

We report a supercontractile fiber (SCF) that is capable of contracting up to 50% of its original length at high humidity, comparable to spider silk. In comparison to the previously reported supramolecular fiber where the polymer chains were held together solely through dynamic, physical interactions, the SCF is imparted with a second network of covalent crosslinks (Figure 1). The resulting SCF is not only resilient to water, but also shows stimuli-responsiveness with humidity. The fiber exhibits up to 300% uptake of water by volume at high humidity, confirmed by environmental scanning electron microscopy (ESEM). Moreover, the SCF undergoes a cyclic relaxation–contraction response to wetting and drying, similar to spider silk. This type of fiber material provides a new opportunity of fabricating biomimetic muscle for diverse applications, ranging from humanoid robots and prosthetic limbs to exoskeletons.

The fabrication of SCF was accomplished in two steps. Fibers were initially drawn from a hydrogel composite, followed by a UV treatment at room temperature. The hydrogel is primarily formed by host–guest interactions with cucurbit[8]uril (CB[8]), consisting of methyl viologen (MV)–functionalized polymer (P1, 1 wt%) grafted onto silica nanoparticles, napthol (Np)-functionalized hydroxyethyl cellulose (P2, 1 wt%), CB[8] [0.5 wt%], and photoinitiator (0.1 wt%, see Figures S1–S3 in the Supporting Information for synthetic procedures). The constituents serve different purposes: the CB[8] is a supramolecular macrocycle, crosslinking P1 and P2 in aqueous media by forming a dynamic heteroternary complex with the pendant guest molecules on both polymers. This induces the desired viscoelastic behavior required for directly drawing fibers with high aspect ratio from the hydrogel.\(^13\) In addition, P2 is functionalized with methacrylic anhydride (MA) for further UV crosslinking in the fiber matrix. The resulting fiber is imparted with a double network, including the physical interactions between P1 and P2 and covalent crosslinks within P2.

The efficacy of UV crosslinking was studied in both hydrogel and fiber states. The mechanical properties of the hydrogels were characterized through rheological measurements. Strain-dependent oscillatory rheology of the hydrogel before UV treatment displays a broad linear viscoelastic region (storage
moduli $G' > G''$, $\tan \delta \approx 0.75$; Figure S4a, Supporting Information). After UV treatment, the value of $G'$ increases dramatically to more than twice its original state ($\tan \delta \approx 0.66$), indicating additional crosslinks inside the hydrogel composite (Figure S4c, Supporting Information). This is correlated with a decrease in the elasticity of the hydrogel as it cannot yield high aspect ratio fibers. Similarly, in the frequency-dependent oscillatory rheology, a large increase in $G'$ across the whole range of frequencies was observed in the hydrogel before and after the UV treatment (Figure S4b,d, Supporting Information). In terms of the fiber state, the success of UV crosslinking was clearly demonstrated by a stability test of the fiber in water. Fibers that were produced from the hydrogel without further crosslinking could be easily solubilized upon rehydration on account of the fiber network being held together solely by dynamic interactions. In comparison, the fiber after UV treatment remained stable without any collapse in the fiber matrix (Figure S7, Supporting Information). This further confirmed that the SCF was reinforced by the additional covalent crosslinks.

Interestingly, the SCF was observed to contract at high humidity, similar to spider silk. As shown in Figure 2a,b, upon introducing high humidity, the SCF contracts from an original length of 2 to 1.1 cm. The contraction could achieve values up to 50% (average $42 \pm 7\%$), and it is independent of fiber diameter (Figure S8, Supporting Information). ESEM was used to further investigate the SCF with respect to humidity variation in an effort to explain its unique contraction behavior. As polymeric materials are usually assumed to be incompressible, we expect no volumetric change, and therefore changes in length

Figure 1. a) Photograph of the supercontractile fiber (SCF). b) Schematic illustration of SCF undergoing supercontraction at high humidity. Water molecules penetrate into the fiber matrix and interact with the hydrophilic moieties. The covalent crosslinks ensure the stability of wet fiber, while the dynamic crosslinks enable the movement of polymer chains. Thus, water induces the polymer chains to reconfigure toward higher entropy and cause the entire fiber to contract.

Figure 2. a,b) Photographs of SCF undergoing supercontraction at high humidity, RH > 70%. c–e) Environmental SEM images of the SCF at different humidity levels, difference in diameter indicating different amounts of water uptake inside the SCF.
(supercontraction) must be twinned with changes in diameter (swelling). Figure 2c depicts a section of the fiber \( (D = 6.53 \mu \text{m}) \) at a relative humidity of 53%. As the humidity increased (relative humidity \( \text{RH} = 97\% \)), the diameter expanded significantly to 14.82 \( \mu \text{m} \). By calculating the net volume of the fiber, we could estimate the volume of water uptake \( (1.4 \text{ nL} \text{ cm}^{-2}) \). This represents a large amount of water that rapidly penetrated into the fiber matrix without breaking the network. Furthermore, as the relative humidity dropped, the diameter of the swollen fiber decreased accordingly, indicating an entirely reversible process of water uptake and release (see Video S1 in the Supporting Information). This is possibly on account of the co-existence of dynamic network inside the fiber, including polymer chains’ entanglement, slipping, and host–guest interactions of CB[8]. In addition, the SCF did not contract when immersed into a nonpolar solvent such as toluene, even though organic solvent also causes the SCF to swell (Figure S9, Supporting Information). Therefore, contraction of the SCF could be attributed to its uptake of water at high humidity. When water molecules penetrate into the fiber matrix, they disrupt the hydrogen bonding within the polymer chains. This disruption does not cause any collapse or breakage in the SCF on account of the crosslinked polymer network. Yet it is sufficient to allow the polymer chains to reconfigure gaining in entropy and causing the entire fiber to suddenly contract in length while expanding in diameter. The SCF now behaves like a filled rubber with a relatively low modulus, which is confirmed by the following mechanical tests. A similar model has also been proposed in spider silks.[8]

The UV crosslinking of the fibers prevents them from dissolving in water and also substantially alters their dynamic-mechanical behavior. Tensile tests reveal that the SCF has significantly lower modulus and strength in comparison to the uncrosslinked fibers, with the failure strain remaining unchanged (Figure S11, Supporting Information). An increase in crosslink density, resulting from varying UV crosslinking duration, leads to similar observations (Figure S11, Supporting Information). The drop in modulus and strength with crosslinking is presumably a result of multiple factors. First, crosslinks may have a defect-trapping effect.[16–18] Defects, such as internal voids,[15] may be locked during the formation of the covalent crosslink network and act as microcracks during tensile loading, leading to premature failure. Second, crosslinking may cause initial decrease in crystallinity of the system and introduce flexible moieties. This has been identified as a cause of reduction in the modulus of crosslinked polyvinyl alcohol.[19] a semicrystalline polymer that can be used as an alternative to the semicrystalline hydroxyethyl cellulose (HEC) used here to produce supramolecular fibers.[15] Third, it is envisaged that the formation of a second chemical network through covalent crosslinks may alter the molecular stretching behavior within the fiber, for example, by restricting some of the dynamic mechanisms associated with the purely noncovalent interactions of the uncrosslinked fiber. Nevertheless, the degree of crosslinking can be viewed as a tool to tune the mechanical behavior of the fibers, as is evidenced by the range of stress–strain profiles that can be generated (Figure S11, Supporting Information).

Most interesting were our observations on the effects of humidity on fiber properties. We have already shown that, like spider silks, our crosslinked supramolecular fibers exhibit substantial supercontraction in water. Moisture substantially alters fibers’ mechanical properties: while “dry” fibers tested at RH = 55% (SCF1-virgin fibers) have stiffness, strength, and failure strain of 2.1 ± 0.6 GPa, 110 ± 27 MPa, and 19.8 ± 4.7%, respectively, “wet” fibers (at RH = 75–80%) exhibited very low stiffness of 0.17 ± 0.07 GPa, low strength of 30 ± 11 MPa, and high failure strains of 31.1 ± 9.4% (Figure 3; Figure S12, Supporting Information). Furthermore, in comparison to the classic linear elastic region at low (<2%) strains observed for the “dry” fibers, the “wet” fibers present an extended region (up to 25% applied strain) in which the fiber deforms substantially for minute increases in applied stress. The “J-shaped” stress–strain curve of the latter is similar to elastomers, and biomaterials such as human skin and muscle tissue. Indeed, a family of stress–strain profiles are observed with varying levels of relative humidity (Figure 3, Figure S12, Supporting Information). Moreover, by re-drying fibers from RH = 80% to RH = 60%, we found that the effects of humidity were reversible, with the fiber stress–strain profiles returning to their virgin dry state (at RH = 55%).

Intriguingly, the humidity response of our supramolecular fiber mimics the behavior of major ampullate spider silks.[8,20] Major silks generate an envelope of stress–strain plots when spun under different conditions, namely humidity level and spinning rate. A number of studies have computationally simulated this behavior by using structure-defining parameters such as the degree of supercontraction, also referred to as the coefficient of shrinkage, and the order/disorder fraction, also known as the alignment parameter.[8,20] It has been proposed that water, and other polar solvents like ethanol, “plasticize” the silk, leading to an increase in the internal free volume and thereby increasing mobility and dispersion of and damage to inter- and/or intramolecular hydrogen bonds. Eventually, plasticization increases the disordered fraction (and decreases the ordered fraction) of the biopolymer, which consequently affects supercontraction.[8,20–23] We envisage that as in spider silks, water disrupts noncovalent interactions, particularly hydrogen bonding, in our supramolecular fibers.

![Figure 3. Tensile engineering stress–strain response of supercontractile fibers produced with 1 h UV crosslinking duration (SCF1) tested a various humidity levels. SCF1-virgin identifies the stress–strain curve for an as-produced fiber at 55% RH. SCF1 tested at various humidity levels; see Figure S12 in the Supporting Information for comparison between initial modulus, strength, and failure strain.](image-url)
The cyclic response and damping behavior of the supramolecular fibers were evaluated through multiple load-unload-reload tests (Figure 4). When tested at RH = 55%, the crosslinked fiber exhibited a damping capacity of 74.1 ± 3.6%, measured by the ratio of the damping energy to the stored energy in each load-unload cycle (Figure 4a,b). This was even higher than the impressive initial damping capacity of the uncrosslinked fiber of 67.2 ± 5.3%, both of which exceed spider silks and viscose (Figure 4c).[15] However, we observe that similar to spider silks, substantially lower damping capacities were registered for subsequent cycles, 44.3 ± 9.4% by the fifth cycle for the crosslinked fiber, and 31.2 ± 2.8% for the uncrosslinked fiber (Figure 4c).[15] This is likely due to molecular rearrangement upon loading and unloading,[15] and the manifestation of a permanent set from plastic deformation. Excitingly, we observed that water-induced supercontracture enables elimination of any permanent set from the loading history. In essence, exposing the fiber to a high moisture environment (RH > 75%) “reset” the fiber properties, presumably by resetting the molecular organization. Upon subsequent equilibration of the fiber at RH = 65–70% (during a 5 min dwell period in the unload-reload cycle), we were able to obtain a consistent damping capacity of 75.4 ± 4.9% for every load-unload cycle, Figure 4c). Comparing the load-unload-reload stress-strain plots for the crosslinked fiber without (Figure 4a) and with (Figure 4b) the high-moisture environment resetting step clearly shows the removal of any permanent set, and a stable hysteresis response with a larger, constant hysteresis loop, for the latter. This further reflects the improved and stabilized damping performance. Figure 4d shows the ability to exercise control over the damping behavior by resetting the properties every alternate cycle. It is well known among silk experts that proteinaceous spider silk dragline fibers also exhibit such tunability and control in static and dynamic properties through interactions with water.[8,21–23] While the evolutionary function and advantage of this is not known for spider silks,[23,24] applications of such smart functional materials can be envisioned in sensors and biomedical applications.

SCF exhibits an average prestress of 20.0 ± 8.4 MPa (Figure S13, Supporting Information). To demonstrate an analogy of our SCF fibers with muscle fibers, multiple SCFs were aligned and joined as a fiber bundle to conduct weight lifting experiments (Figure 5a,b). As shown in Figure 5c, the hanging weight is 5 mg, and after spraying water on the fiber bundle, it contracted and lifted the weight 0.5 cm (12.5%) within a second. This represents an ≈10 MPa in stress. In addition, the weight lifting can be repeated for multiple cycles (Figure 5d), after resetting the length of the fiber bundle.

Water is a key resource and tool in nature. Spider silks, for instance, are produced from a dope where water is the solvent, and water is also used by the spider to control properties for a range of functions. Learning how to effectively use water to produce such low-energy, high-performance fibers will be key in future sustainable fiber processing. Development of supramolecular fibers formed from hydrogels (with 98 wt% water) with emergent properties including supercontracture is important and pioneering scientific step changes in material science.

In conclusion, we demonstrated the supercontractile fiber by introducing a double network, consisting of a dynamic network governed by polymer chain entanglement and CB[8] host-guest interactions as well as a covalent network that enhances resilience against water penetration. The underlying dynamic interactions allow the reconfiguration of polymer chains within the fiber matrix. The penetrated water molecules induce contraction of the SCF up to 50%, which is comparable to spider silk. Moreover, similar to spider silk, the mechanical properties of SCF is tunable according to the humidity level. The SCF is a good example for developing emerging fiber materials, such as sensors and artificial muscles. We envision that the alteration of chemistry and processing technology offer limitless opportunities toward biomimetic materials.
Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

biomimetic, supercontraction, supramolecular fibers

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Figure 5. a–c) Microscopy image of the SCF bundle, imitating a muscle fiber to lift weight (5 mg). d) Recyclability diagram of the fiber bundle showing weight lifting can be repeated in multiple cycles.

[1] P. Egan, R. Sinko, P. R. Leduc, S. Keten, Nat. Commun. 2015, 6, 7418.
[2] J. C. Nawroth, H. Lee, A. W. Feinberg, C. M. Ripplinger, M. L. McCain, A. Grosberg, J. O. Dabiri, K. K. Parker, Nat. Biotechnol. 2012, 30, 792.
[3] M. Heim, D. Keerl, T. Scheibel, Angew. Chem., Int. Ed. Eng. 2009, 48, 3584.
[4] R. Ene, P. Papadopoulos, F. Kremer, Soft Matter 2009, 212, 4568.
[5] T. A. Blackledge, C. Boutry, S.-c. Wong, A. Baji, A. Dhinojwala, V. Sahni, I. Agnarsson, J. Exp. Biol. 2009, 2, 1981.
[6] I. Agnarsson, A. Dhinojwala, V. Sahni, T. A. Blackledge, J. Exp. Biol. 2009, 212, 1990.
[7] C. Boutry, T. A. Blackledge, J. Exp. Biol. 2010, 213, 3505.
[8] Y. I. Liu, Z. Shao, F. Vollrath, Nat. Mater. 2005, 4, 901.
[9] Z. Qin, M. J. Buehler, Nat. Mater. 2013, 12, 183.
[10] Y. Zheng, H. Bai, Z. Huang, X. Tian, F.-q. Nie, Y. Zhao, J. Zhai, L. Jiang, Nature 2010, 463, 640.
[11] X. Huang, G. Liu, X. Wang, Adv. Mater. 2012, 24, 1482.
[12] I. Agnarsson, C. Boutry, S.-c. Wong, A. Baji, A. Dhinojwala, A. T. Sensenig, T. A. Blackledge, Zoology 2009, 112, 325.
[13] C. S. Haines, M. D. Lima, N. Li, G. M. Spinks, J. Foroughi, J. D. W. Madden, S. H. Kim, S. Fang, M. J. Andrade, F. Göktepe, Ö. Göktepe, S. M. Mirvakili, X. Lepró, J. Oh, M. E. Kozlov, S. J. Kim, X. Xu, B. J. Swedlove, G. G. Wallace, R. H. Baughman, Science 2014, 343, 868.
[14] C. S. Haines, N. Li, G. M. Spinks, A. E. Aliev, J. Di, R. H. Baughman, Proc. Natl. Acad. Sci. USA 2016, 113, 11709.
[15] Y. Wu, D. U. Shah, C. Liu, Z. Yu, J. Liu, X. Ren, M. J. Rowland, C. Abell, Proc. Natl. Acad. Sci. USA 2017, 114, 8163.
[16] X. Liu, Y. Won, P. X. Ma, Biomaterials 2006, 27, 3980.
[17] S. Dong, B. Zheng, F. Wang, F. Huang, Acc. Chem. Res. 2014, 47, 1982.
[18] X. Yan, F. Wang, B. Zheng, F. Huang, Chem. Soc. Rev. 2012, 41, 6042.
[19] R. Benavente, C. Mijangos, J. M. Peren, M. Krumova, D. Lo, Polymer 2000, 41, 9265.
[20] F. Vollrath, D. Porter, Soft Matter 2006, 2, 377.
[21] J. Perez-Rigueiro, M. Elices, C. Guinea, Polymer 2003, 44, 3733.
[22] M. Elices, C. R. Plaza, J. Exp. Biol. 2005, 208, 25.
[23] Z. Shao, F. Vollrath, Polymer 1999, 40, 1799.
[24] M. Elices, G. R. Plaza, J. Pérez-rigueiro, J. Mech. Behav. Biomed. Mater. 2011, 4, 658.