Biomimetic supramolecular fibers exhibit water-induced supercontraction

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Supplementary Materials

S1. Materials and general methods.

S2. Preparation of supramolecular polymer-colloidal hydrogel H1.

S3. Preparation of supercontracted fibre.

S4. Mechanical test of the supercontracted fibre.

S5. Correlation of SCF to relative humidity (Video S1).
S.1 Materials and general methods

All starting materials were purchased from Alfa Aesar and Sigma Aldrich and used as received unless stated otherwise. CB[7] and CB[8] were prepared as documented previously.\textsuperscript{1,2}

\textsuperscript{1}H NMR (400 MHz) spectra were recorded using a Bruker Avance QNP 400. ATR FT-IR spectroscopy was performed using a Perkin-Elmer Spectrum 100 series FT-IR spectrometer equipped with a universal ATR sampling accessory. UV-vis studies were performed on a Varian Cary 4000 UV-vis spectrophotometer. Transmission electron microscopy (TEM) characterisation was carried out on a FEI Philips Tecnai 20 TEM under an accelerating voltage of 80 kV. Samples were prepared by applying one drop of the as-synthesised microspheres onto a Holey R carbon coated copper TEM grid (400 mesh) drying overnight. Dynamic light scattering (DLS) and zeta potential (ZP) measurements were performed on Malvern Zetasizer NS90 instrument. Microscopic images and fluorescence images were obtained using an Olympus IX81 inverted optical microscope coupled with a camera of Andor Technology EMCCD iXonEM\textsuperscript{p} DU 897. \(M_w\), number average molecular weight (\(M_n\)) and polydispersity (\(M_w/M_n\)) were obtained by aqueous or THF-GPC. The aqueous GPC setup consisted of a Shodex OHpak SB column, connected in series with a Shimadzu SPD-M20A prominence diode array detector, a Wyatt DAWN HELEOS multi-angle light scattering detector and a Wyatt Optilab rEX refractive index detector. The THF GPC setup consisted of two 30-cm PLgel Mixed-C columns in series, eluted using THF and calibrated against a series of 12 near monodisperse PMMA standards (\(M_p\) from 690 to 1,944,000 g/mol\textsuperscript{−1}). The polymers were analyzed in THF at a concentration of 5.0 mg ml\textsuperscript{−1}. All calibrations and analysis were performed at 35 \(^\circ\)C at a flow rate of 1mlmin\textsuperscript{−1}. Scanning electron microscopy (SEM) images were obtained using a FEI Verios 460 variable pressure SEM using and InLens detector. The samples were sputter coated with a thin layer of platinum and palladium metals prior to imaging.
S.2 Preparation of supramolecular polymer-colloidal hydrogel H1

Figure S1: Schematic representation of a supramolecular polymer-colloidal hydrogel H1 prepared through addition of CB[8] to a mixture of polymer-grafted silica P1 (functionalised with MV) and a linear Np-HEC-MA P2 in water.

To prepare P2, synthetically acquired HEC-Np (1 g) was dissolved in 50 mL of water. Dimethylformamide (DMF, 30 mL) was added and the solution stirred until it was homogeneous. The polymer solution was then cooled to 5°C in an ice/water bath and methacrylic anhydride (740 µL, 5.00 mmol) added dropwise over a period of 15 min. The reaction mixture was removed from the ice bath and the pH maintained between 8 and 10 for 4 h by the addition of 0.5 M NaOH(aq) before being left to stir overnight. The reaction mixture was then transferred directly to dialysis tubing (MWCO 15 kDa) and dialyzed against water for 5 days. The P2 was then obtained by lyophilization in yields upward of 70% and functionalization with methacrylate observed by 1H NMR (Figure S3).

Figure S2: Synthetic scheme of Np-HEC-MA (P2).
H1 was prepared by first dissolving P1 polymers in water (20 mg mL\(^{-1}\)) with stirring followed by addition of CB[8] (5 mg mL\(^{-1}\)). P2 polymer was then dissolved in water (20 mg mL\(^{-1}\)) with addition of a aqueous solution of Irgacure 2959 (100 µL, 1 mg/mL). P1 polymer solution (0.2 mL) and P2 polymer solution (0.2 mL) were then added together and mixed well by vortex in dark. The rheological characterisation was shown in Figure S4.
Figure S4: a) Rheological strain oscillatory rheology of H1 (2 wt%) from 0.1% to 400% at 20°C ($\omega = 10$ rad/s). The materials expressed broad viscoelastic regimes and resisted yielding up to 100% strain. b) Frequency dependent oscillatory rheology of H1 (2 wt%) indicating gel-like behaviour. c) Rheological strain oscillatory rheology of H1 (2 wt%) after UV treatment from 0.1% to 200% at 20°C ($\omega = 10$ rad/s), the value of $G'$ increases dramatically to more than twice its original state, indicating additional crosslinks inside the hydrogel composite. d) Frequency dependent oscillatory rheology of H1 after UV treatment (2 wt%) indicating a large increase in $G'$ across the whole range of frequencies.

S.3 Preparation of supercontracted fibre

Fibres were prepared by drawing hydrogel filaments from H1 at a steady speed (ca. 1 cm/min). After the fast dehydration process, the fibre was mounted on a pre-cut paper board, the pre-treated fibre was then exposed to the UV light (360 nm) for 15 min to initiate the crosslinking between P2 as illustrated in Figure S5 and S6.
Figure S5: Schematic representation of the network of pre-treated fibre before UV light (350 nm) treatment.

Figure S6: Schematic representation of the network of UV-treated fibre (wavelength = 350 nm).

Figure S7: Stability test of fibres in water a) pre-treated fibre with collapsed fibre matrix in water; b) UV-treated fibre in water illustrating the effective cross-linking within the fibre matrix.
**Figure S8:** The distribution of and correlation between fibre diameter and their contraction percentage in water (n = 15). There was no correlation ($R^2 = 0.002$) between fiber diameter and draw length.

<table>
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**Figure S9:** Photographs indicating SCF could not contract after it is immersed in toluene.
S.4 Mechanical test of the supercontracted fibre

Fibre mechanical testing was conducted as described in previous work\(^4\). Sample preparation for testing of filaments involved, firstly drawing filaments to lengths between 25 and 250 mm (Figure S10). Segments of around 50 mm were then carefully obtained using tweezers from the middle section, ensuring the filament was not stretched. These segments were placed on and attached to laser-cut card frames using a cyanoacrylate adhesive. The frames set the test gauge length at 10 mm. Before testing, the average diameter of each sample was obtained from three measurements along the gauge length using an optical microscope. Based on a circular cross-section, as supported by SEM images, an average cross-section area was obtained for each sample.

For testing, the frames were first loaded onto an Instron tensile testing machine equipped with a calibrated 5 N load cell. Upon clamping the card frame between the grips, the sides of the frame were cut, and the filament was subjected to specific loading regimes:

i) Quasi-static tests to failure at an extension rate of 1 mm/min. UF (n = 50), SCF1 (n = 12) and SCF2 (n = 13) fibre types were tested in their virgin state in ambient conditions (T = 20°C, RH = 55%). In addition, the SCF1 fibre type was tested at various humidity levels: at 75-80% RH (n = 8), 65-70% RH (n = 7), and 60% RH (n = 8). An EasyLog temperature and humidity data logger (Lascar Electronics Limited, UK) was used to monitor conditions. Humidity was regulated by placing the fibre in the test chamber and spraying water into the chamber, followed by air drying for a specified time. Ambient air conditions were controlled to T = 20°C and RH = 55%. Figure S11 and Figure S12 present the data exploring the effects of cross-linking and water on tensile mechanical properties, respectively.

ii) Multiple (five) load-unload cycles to ca 5% applied strain at a constant extension rate of 1 mm/min, with a 5 min dwell period between every reload cycle. UF (n = 8) and SCF1 (n=5) fibres were tested in their virgin state. In addition, the SCF1 fibre type was tested at 65-70% RH (n=5), where the fibre was wetted by spraying water onto it at the end of its unloading cycle and was air dried in ambient conditions during the 5 min dwell period before reloading. Furthermore, tests were done (n=3) where the SCF1 fibre was wetted-and-dried in alternate reloading cycles. Load-displacement curves were obtained, where displacement was determined from the crosshead displacement. Thereafter, engineering stress-strain plots were produced and used to determine initial elastic modulus (in the strain range of 0-1%), failure strength and strain. For cyclic tests, for each cycle, damping capacity was determined from the ratio of the damping energy (area between the loading and unloading curve) to the stored energy (area below the loading curve).
**Figure S10**: Schematic of fiber testing method: a) card frame with mounted fiber is clamped between grips on a testing machine, and then b) sides of the frame are cut, and c) the fiber is thereafter tested in tension.

**Figure S11**: Tensile behaviour a) and properties b-d) of three supramolecular fibre varieties. UF are uncrosslinked fibres, which solubilise in contact with water. The crosslinked fibres (SCF1 and SCF2) maintain their fibre structure, but exhibit supercontraction. SCF2 fibres were crosslinked over a shorter duration. Box plots show maximum and minimum (whiskers), upper and lower quartiles (box range), median, and mean (unfilled square).
Figure S12: a) An envelope of stress-strain profiles is obtained by varying the level of humidity, and therefore the degree of hydration of the fibre. Significant differences in initial modulus, b) tensile strength c) and failure strain d) are observed for fibres with different degrees of hydration. Box plots show maximum and minimum (whiskers), one standard deviation (box range), median, and mean (unfilled square).

Figure S13: The evolution of supercontraction induced pre-stress as a function of time (n=8). The equilibrium compressive stress (reached typically after 4 min) was measured to be 20.0±8.4 MPa.
Movie S1 | ESEM Video of the SCF at changing relative humidity, the diameter of SCF varies correspondingly.

References


