Supporting Information

Assessment of the effect of drying and relaxation on byssal threads

To test the mechanical effect of the sample preparation procedure for the XAS study on *M. californianus* byssal threads, threads were stretched under wet conditions and rested in the strained state under wet or dry (i.e. approximately 5% rel. humidity) conditions. For this test, a tensile stage equipped with a climate chamber was used. The relative humidity of the climate chamber could be adjusted by flushing with water-saturated air and nitrogen. At maximum humidity, water droplets formed on the byssal thread, indicating that the thread was fully hydrated. This test was carried out for samples loaded to 10%, 25% and 40% strain (Fig. S1 A-C). Resting strained threads under wet conditions results in an approximate 50% decrease in stress over time for all three strain states. When strained wet to 25% or 40% and rested under dry conditions, the stress initially decreases due to a time delay until the relative humidity of the climate chamber has been adjusted to the set value, but is eventually outbalanced by drying effects with the stress increasing to a stable stress within 2 hours that is at or slightly above the stress before the drying process began. These results indicate that dried threads represent a stable equilibrium state with regards to stress and that they maintain a constant strain when dried and fixed.

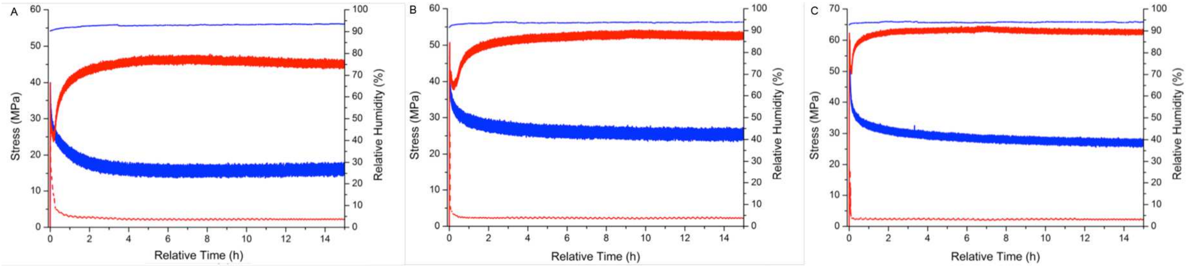

Figure S1. Thread stress under strain in the wet and dry state. Stress relaxation of a byssal thread under wet conditions after deformation to (A) 10% strain, (B) 25% strain and (C) 40% strain (blue curve) and stress increase of a thread stretched under wet conditions to (A) 10% strain, (B) 25% strain and (C) 40% strain and subsequently dried (red curve). The thick lines represent the mechanical data and the thin lines the corresponding relative humidity measured in the chamber. It should be emphasized that the maximum humidity that can be measured is 95%, and that threads were fully hydrated based on the observation of water droplets that formed on the thread.

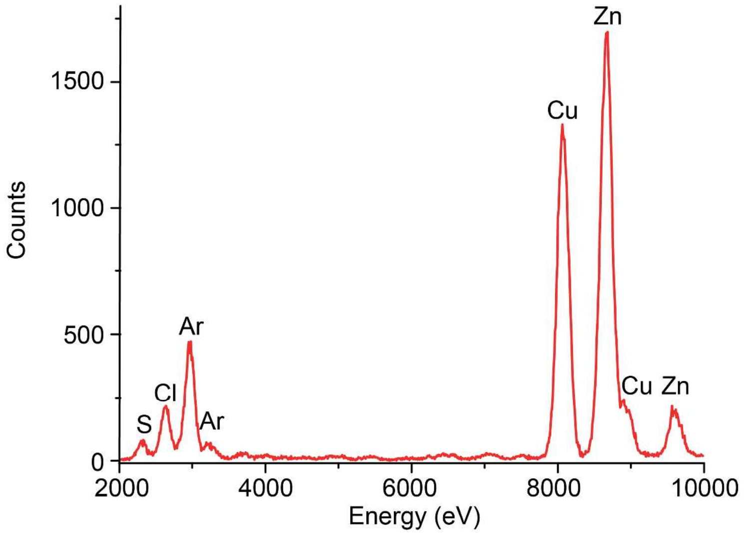

Figure S2. X-ray fluorescence (XRF) of byssal thread core. XRF measurements on thread sections with cuticle removed show dominant peaks for Cu and Zn, without Fe present.

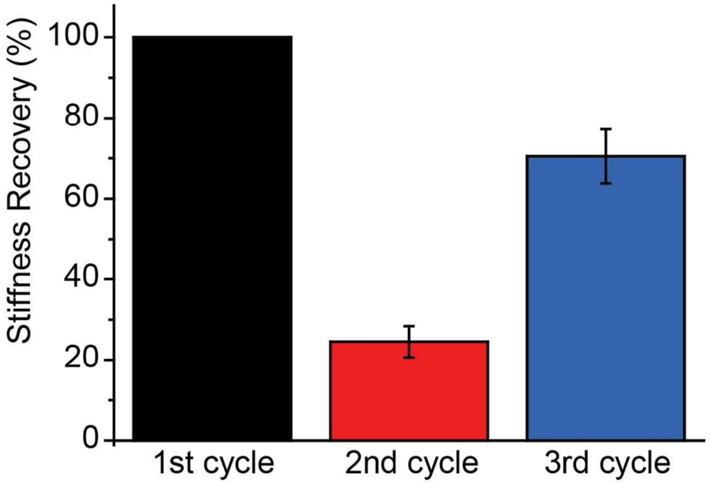

Figure S3. Self-healing of *M. californianus* threads rested in distilled water. The 2nd cycle is performed immediately following the 1st cycle, whereas the 3rd cycle was performed after resting the thread in distilled water for 24 hours following the 2nd cycle. Stiffness values of the 2nd and 3rd tensile loading cycles are given as a percentage (mean ± S.D.) relative to the stiffness of the first cycle.

Assessment of healing in distilled water

In order to avoid contamination by dried salts on threads during XAS measurements and to slow the thread aging process, threads were stored, mechanically tested and healed in distilled water. To test if storage in a low ionic strength medium (distilled water) has an effect on the threads ability to self-heal, we performed cyclic tensile loading on *M. californianus* threads that were stored in distilled water prior to testing and during healing. Threads (n = 5) were cycled at a strain rate of 0.0003 s^{-1} twice consecutively to 25% strain and then were rested for 24 hours before cyclically loading to 25% strain once more. Figure S3 shows percent recovery of the stiffness relative to the native state of the threads, indicating recovery to over 70% of the native value in 24 hours.

Table S1. EXAFS fitting of Zn K-edge XAS spectra with four first shell ligands.

EXAFS fitting results								
			1st coordination shell					
sample	s_0^2	E_0 (eV)	N/O_{long}			N/O_{short}		
			R (Å)	N	σ^2 (Å^2)	R (Å)	N	σ^2 (Å^2)
0% strain	1.13 f	5.02 f	2.01 (0.01)	2.0 (0.1)	0.010 (0.001)	1.95 (<0.01)	2.0 4-N/O_{long}	0.004 (<0.001)
10% strain	1.09 f	5.26 f	2.02 (0.02)	2.0 (0.2)	0.008 (0.002)	1.97 (<0.01)	2.0 4-N/O_{long}	0.003 (<0.001)
25% strain	1.12 f	5.26 f	2.05 (0.01)	2.5 (0.7)	0.006 (<0.001)	1.96 (<0.01)	1.5 4-N/O_{long}	0.006 (<0.001)
40% strain	1.15 f	5.46 f	2.01 (0.01)	3.8 (0.2)	0.006 (<0.001)	- -	- -	- -
relaxed (25%)	1.18 f	5.26 f	2.05 (0.02)	2.3 (0.5)	0.013 (0.002)	1.98 (<0.01)	1.7 4-N/O_{long}	0.004 (<0.001)
healed (25%)	1.11 f	5.37 f	2.04 (0.02)	1.6 (0.2)	0.008 (0.001)	1.96 (<0.01)	2.4 4-N/O_{long}	0.010 (<0.001)
			2nd coordination shell					
sample	s_0^2	E_0 (eV)	C_{long}			C_{short}		
			R (Å)	N	σ^2 (Å^2)	R (Å)	N	σ^2 (Å^2)
0% strain	1.13 f	5.02 f	2.89 (0.01)	3.9 2xN/O_{long}	0.014 (0.002)	2.57 (0.02)	1.0 ½xN/O_{short}	0.008 (0.002)
10% strain	1.09 f	5.26 f	2.92 (0.01)	4.0 2xN/O_{long}	0.007 (0.002)	2.58 (0.01)	1.0 ½xN/O_{short}	0.011 (0.003)
25% strain	1.12 f	5.26 f	2.95 (0.01)	3.5 (1.0)	0.012 (0.003)	2.66 (0.02)	2.0 (0.4)	0.004 (0.004)
40% strain	1.15 f	5.46 f	2.91 (0.02)	1.9 (1.1)	0.014 (0.005)	2.54 (0.02)	0.8 (0.3)	0.011 (0.005)
relaxed (25%)	1.18 f	5.26 f	2.85 (0.01)	3.7 (0.9)	0.015 (0.004)	2.52 (0.01)	1.0 ½xN/O_{short}	0.007 (0.004)
healed (25%)	1.11 f	5.37 f	2.90 (0.01)	3.2 2xN/O_{long}	0.003 (0.002)	2.58 (0.02)	1.2 ½xN/O_{short}	0.003 (0.002)

The overall degeneracy of 1st shell paths (N/O) was set to 4. s_0^2 was allowed to vary from the experimentally determined value from the fits of the standards. Numbers in parentheses are fit uncertainties. If no uncertainty is given, the formula for the calculation of the parameter is stated.

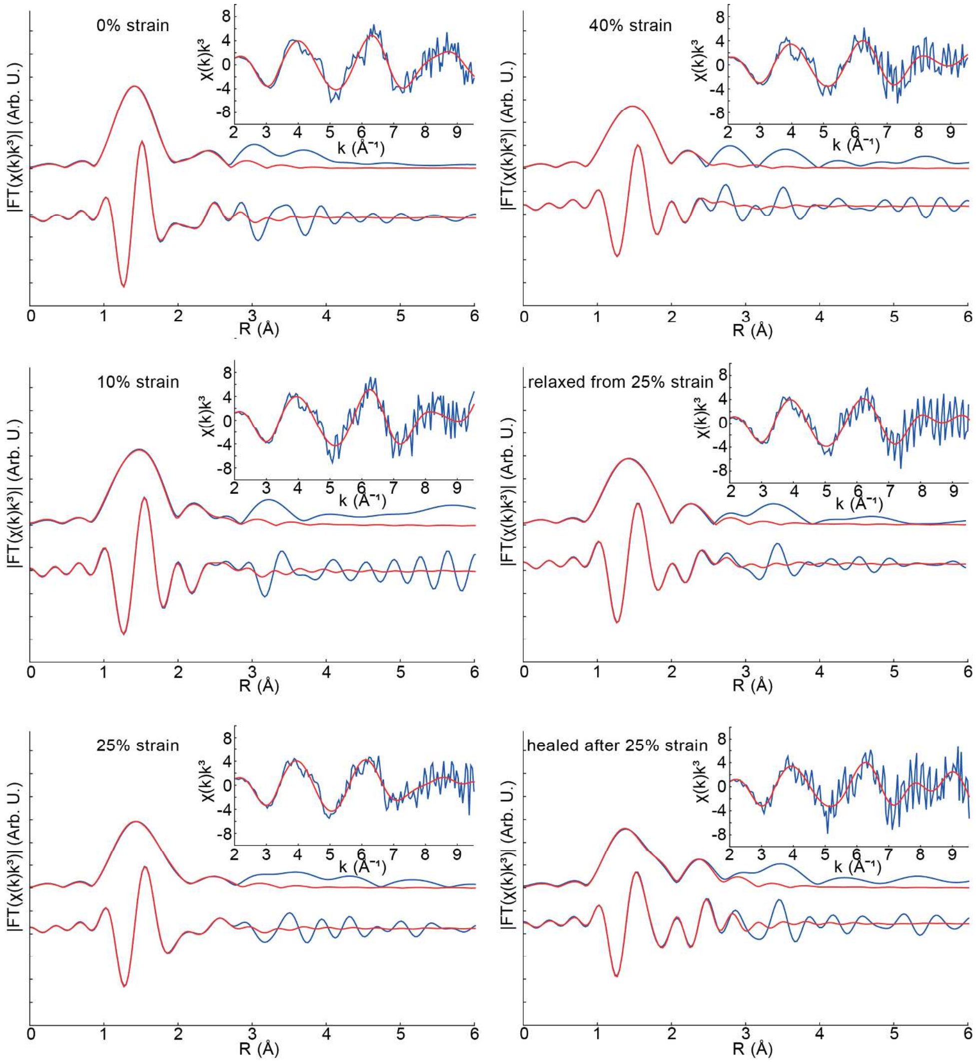

Figure S4. EXAFS fitting of Zn K-edge XAS spectra from byssal threads at various stages of mechanical straining and healing.