Supporting Information

Tough Protein Organohydrogels

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Experimental Section:

***Materials*:** Gelatin (250 bloom, microbiology grade) and Glycerol (AR grade, 99%)were purchased from Shanghai Aladdin Biochemical Technology Co. Ltd. and Shanghai Macklin Biochemical Co. Ltd, respectively. Deionized (DI) water (18 MΩ·cm^{-1}) was used unless stated otherwise.

Synthesis of gelatin organohydrogels: 15 g gelatin was dissolved in 85 ml DI water by stirring for 40 min at 50 °C. To remove air bubbles from the gelatin solution, it was treated with reduced pressure in a desiccator for about 5 minutes. Finally, the transparent gelatin solution was poured into an acrylic mold and maintained at 4°C for 1 h to form the pristine gelatin gel. To synthesize the gelatin organohydrogel, the obtained gelatin gels were balanced and soaked in glycerol (8 times mass of gel) at room temperature. The soaking time was varied between 10 min and 24 h. Afterwards, the soaked gels were removed from the container and excess solvent on the gel surface was blotted with filter paper.

***Characterization of the liquid retention*:** The liquid retention was probed by placing the glycerol-mediated tough organohydrogels into a container, which was maintained at constant temperature (20 °C) and humidity (50 %). At the beginning and at each time interval, the tough organohydrogels were balanced and the retained wt% calculated by Equation S1.

$$\text{wt\%}=\left(\frac{current\ weight}{original\ weight}\right) \qquad \text{S1}$$

Characterization of the anti-freezing property: The anti-freezing property of the glycerol-mediated organohydrogels was scrutinized in terms of freezing behavior at two temperatures (-45 °C and -60 °C). The cooled and/or frozen hydrogels were subjected to optical analysis as well as deformation by hand/tweezers to ascertain their state.

***Characterization of the mechanical properties*:** Tensile tests of the gelatin organohydrogels were carried out by using a tensile testing machine (CMT6103, SANS). Cuboid gels were cut for the measurement with dimensions of: length = 20±2mm, width = 17±2 mm and thickness = 2.5 ± 0.5mm. Both ends of the sample were fixed with clamps. The rate of elongation was fixed to 20 mm/min for the tensile test. The elastic modulus was determined from the average slope (0-15 %) of the stress-strain curve. The fracture energy was calculated by Equation S2

$$\Gamma = \frac{U(L_C)}{a_0 b_0} \qquad \text{S2}$$

,in which L_c is the length of the gel at fracture strain, $U(Lc)$ denotes the area beneath the force-displacement curve from zero to the distance Lc, and a_0 and b_0 are the width and thickness of the sample, respectively.

To determine the recovery ability of the organohydrogel, a gelatin organohydrogel (immersion time 6h) was stretched to 200% strain. Then, the organohydrogel was relaxed (0 % strain). After a relaxation time (idle time) of 0 min, 5 min, 15 min, 30 min or 1h a second loading-unloading cycle was started.

Topological-healing of gelatin organohydrogels: The as-made gelatin organohydrogels were cut into halves. The cut surface areas were soaked in hot water (60 °C)for different activation times: 5 s, 10 s, 15 s, and 20 s. Subsequently, the soaked segmentswere pressed against each other. The organohydrogel segments immediately adhered to each other. Finally, the cured organohydrogels were stored either at room temperature or in a refrigerator (4 °C) for different healing-times.

Thermal plasticizing and recycling of the gelatin organohydrogels: Method A: Organohydrogels, which had been tested in the tensile test machine, were collected in a container. The organohydrogels were heated to 70 °C to melt. The melted organohydrogels were poured into molds and stored at room temperature to form recycled organohydrogel. Method B: The collected organohydrogels were swelled in water and heated 1h (70 °C) to melt again. Subsequently, the melted gelatin solution was poured into molds and cooled down to room temperature. Finally, the as-made gelatin hydrogel was immersed in glycerol (*vide supra*) for 6h to form tough protein organohydrogel.

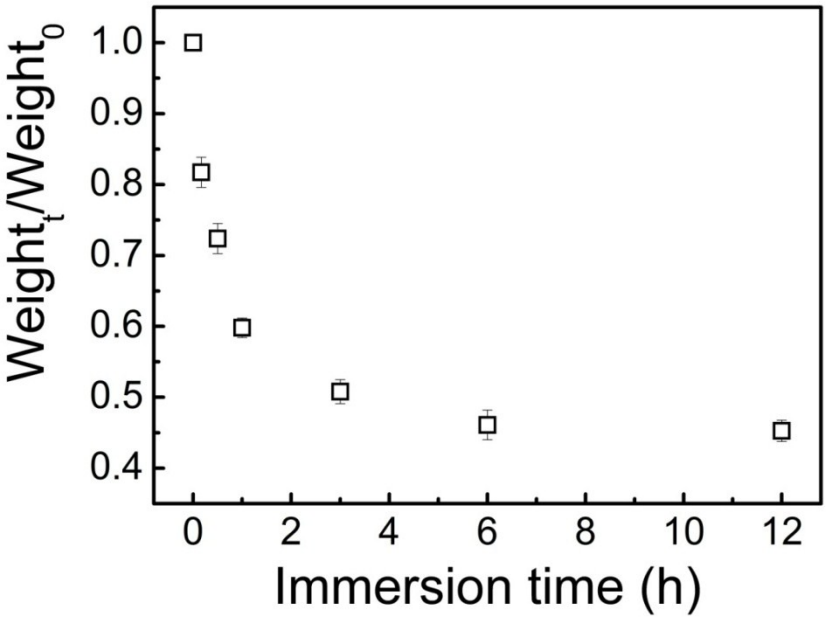

Figure S1. Reduction of the weight of the hydrogel due to immersion in glycerol. To denote the weight loss, the ratio between weight of the hydrogel after (weight$_t$) and weight of the hydrogels before (weight$_0$) immersion in glycerol versus the immersion time is plotted.

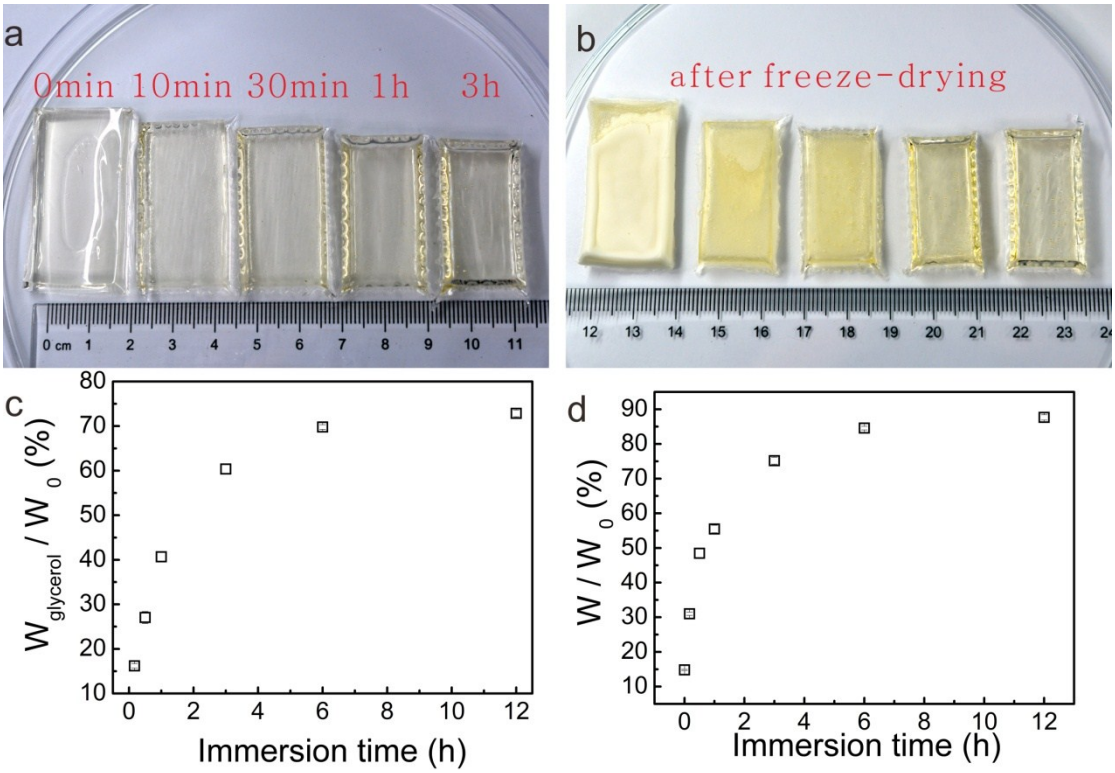

Figure S2. Digital images of the hydrogel and organohydrogels (different immersion times in glycerol) before a) and after b) freeze-drying. c) Weight fraction of glycerol in the as-made organohydrogels after different immersion times. The $W_{glyerol}$ denotes for the weight of glycerol and the W_0 for the weight of

the organohydrogels. d) Retained mass percentage after freeze-drying of the gels from c). Here, W is the mass of the hydrogels after freeze-drying and W_0 is the hydrogels original weight.

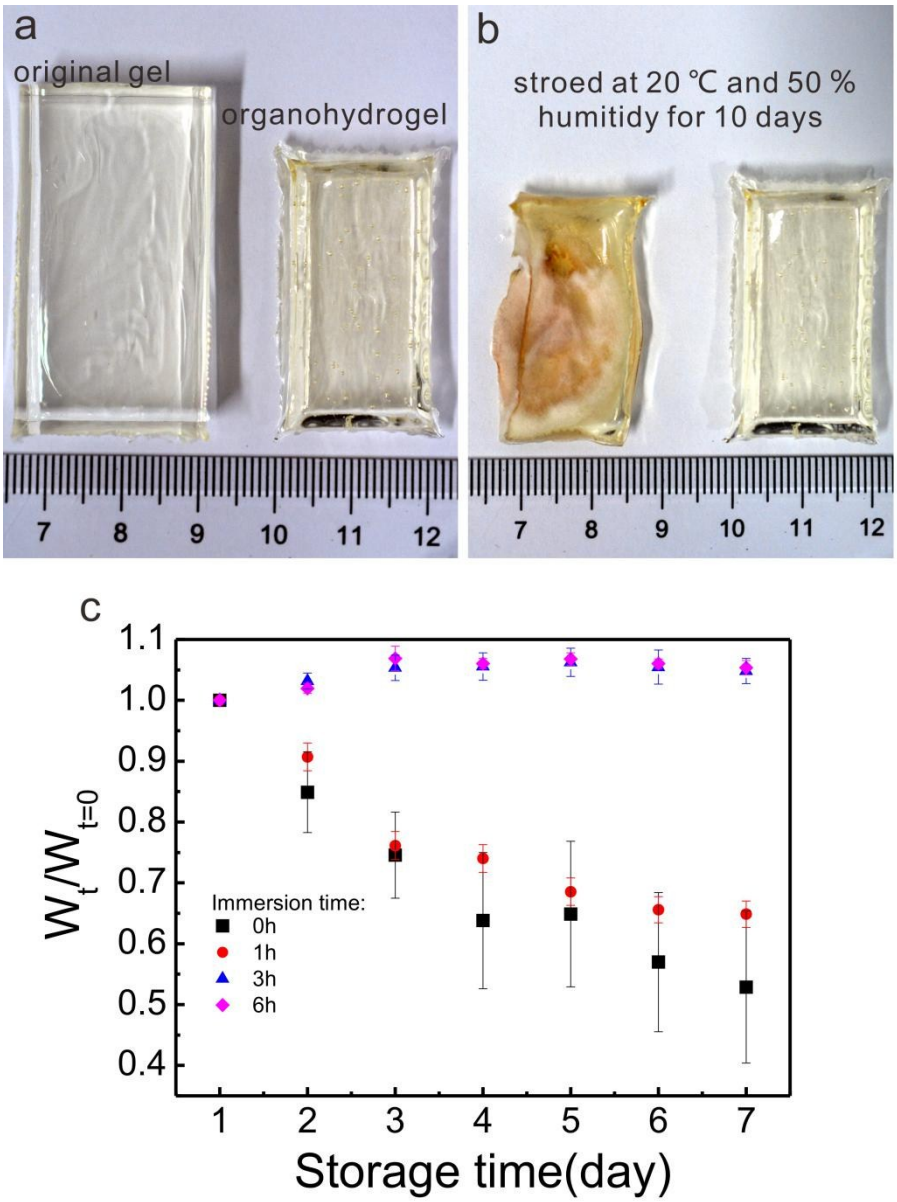

Figure S3. Non-drying performances of organohydrogels. Digital image of the original gel (a) and organohydrogel (immersion time 6h) (b) before and after storage (20 ℃ and 50% humidity) for 10 days. (c) Weight retention of the glycerol organohydrogels upon storing at 20 °C and 50 % humidity. $W_{t=0}$ and W_t denote for the weight of the gel before storage and after storage time t, respectively.

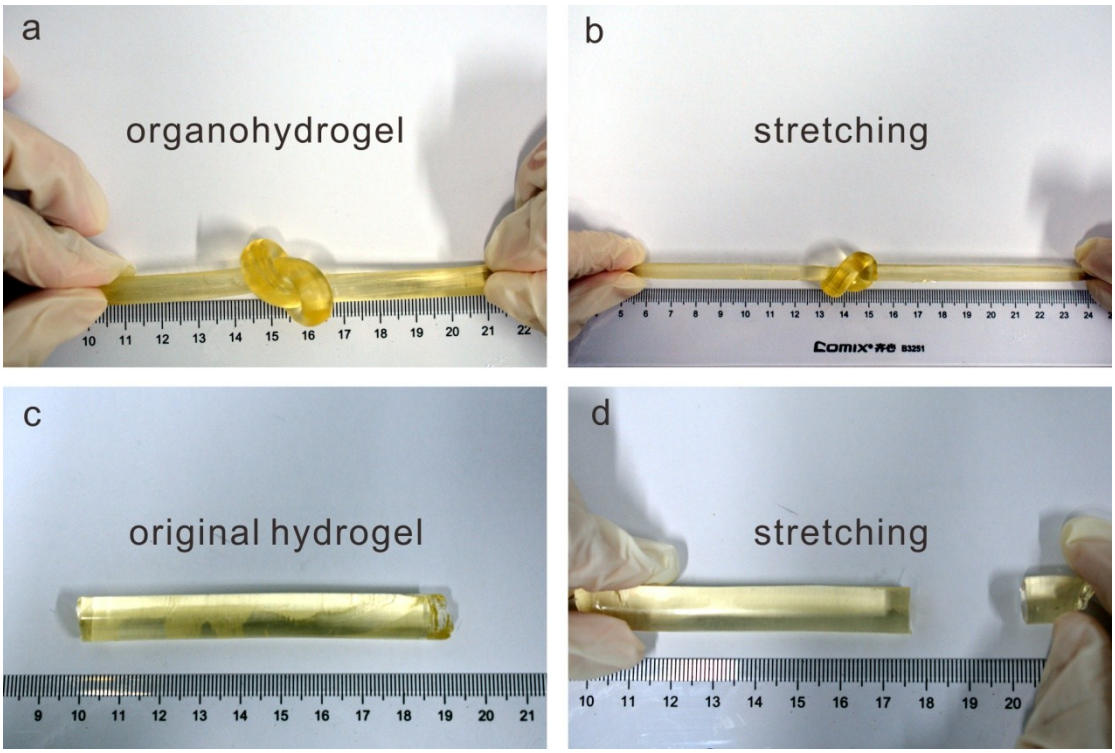

Figure S4. Digital image of an organohydrogel with a knot in its relaxed a) and b) stretched state. Digital image of a straight (water-based) gelatin hydrogel in its relaxed c) and stretched d) state, showing that the water-based hydrogel breaks easily.

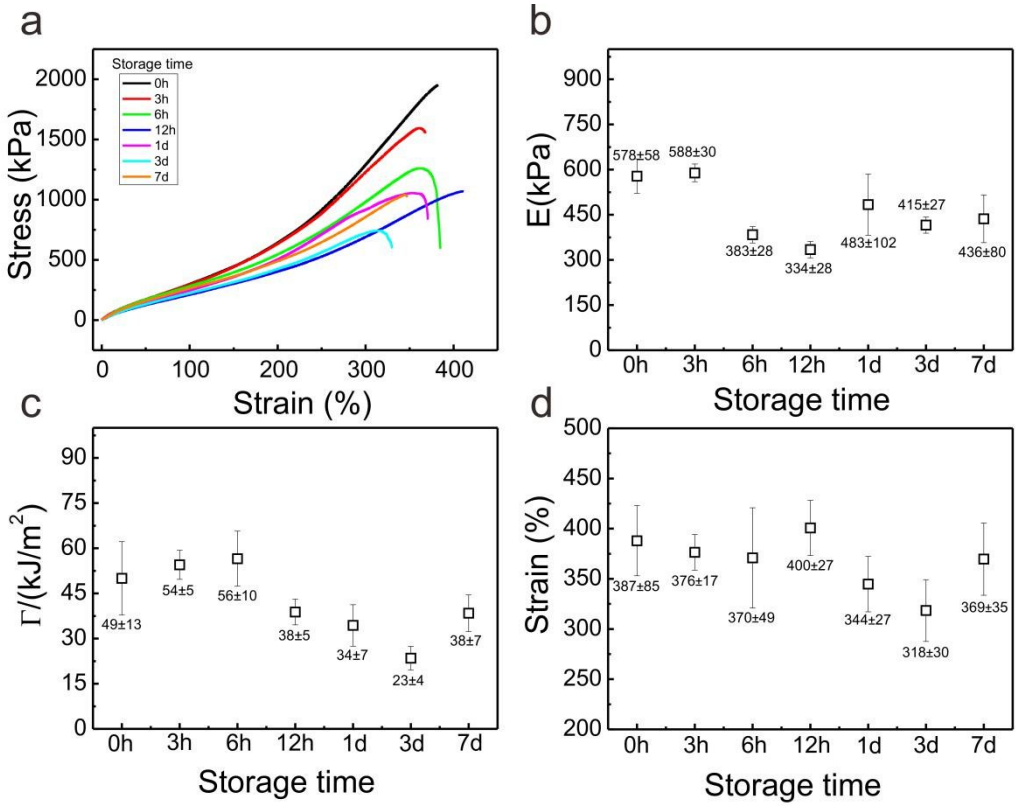

Figure S5. Development of strain-stress curve a), elastic modulus b), fracture energy c) and maximum sustained tensile strain with storage time of as-made organohydrogel (immersion time 6h).

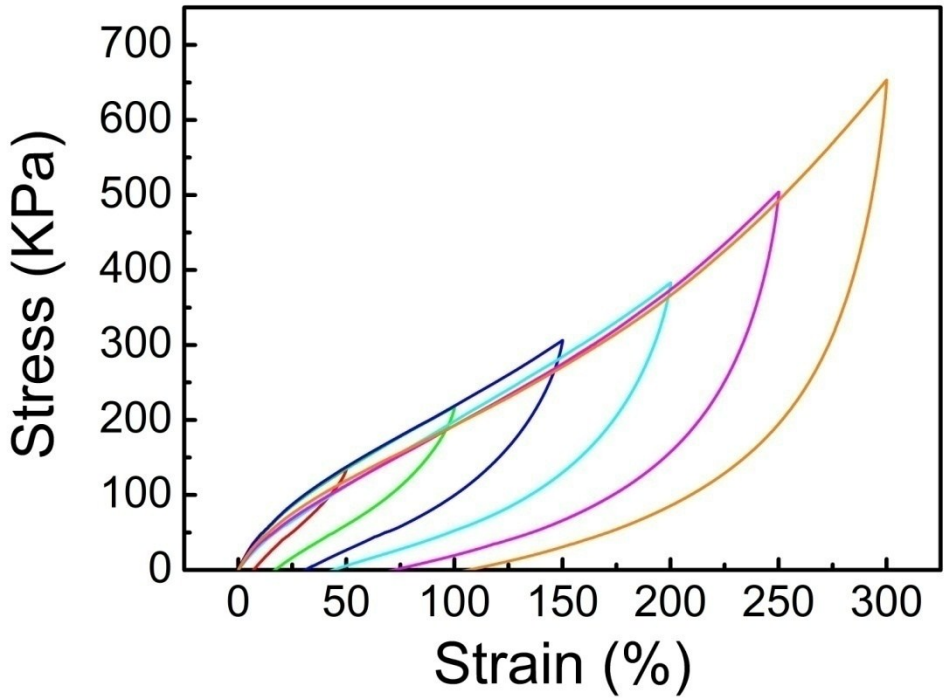

Figure S6. Loading-unloading curves of as-made organohydrogel (immersion time 6h) for different tensile strains (50%, 100%, 150%, 200%, 250% and 300%).

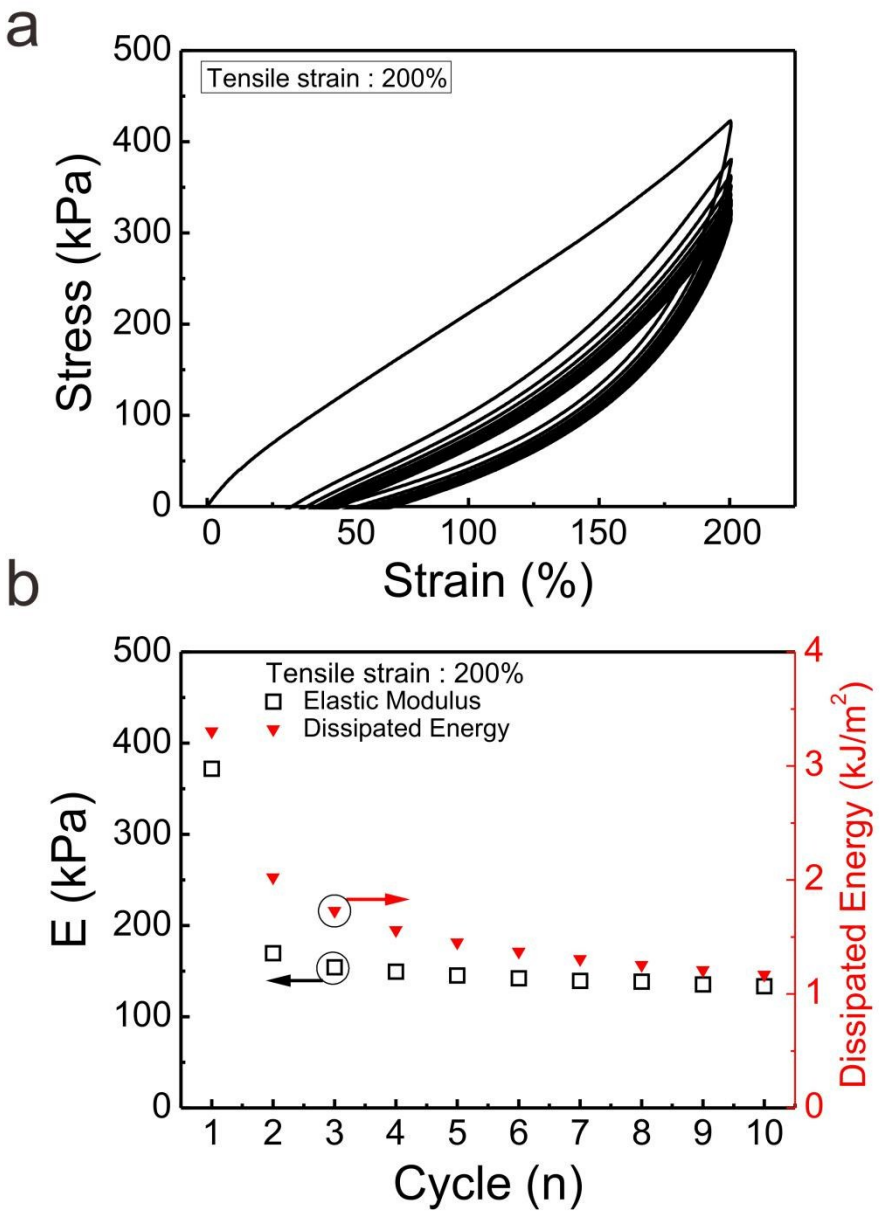

Figure S7. a) Stress-strain diagram of an organohydrogel (immersion time 6h). 10 loading-unloading cycles at 200 % tensile strain were executed. b) Elastic modulus and dissipated energy versus cycle number. The values were obtained from a).

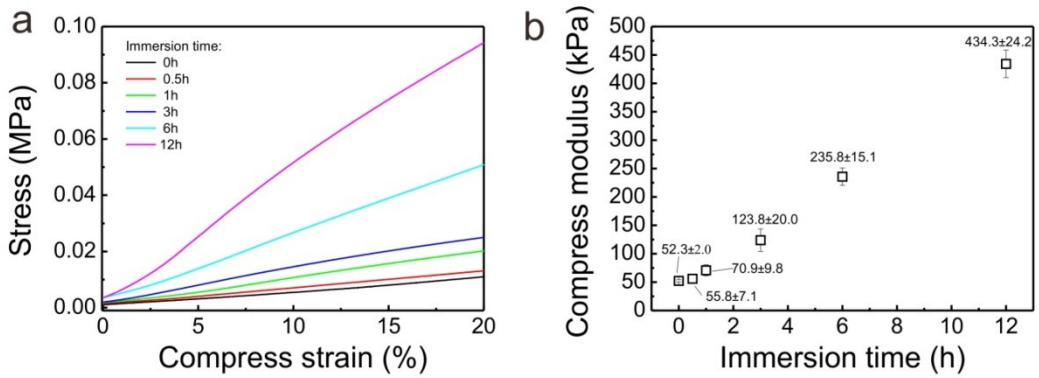

Figure S8. Compressive stress versus strain diagrams (a) and compressive modulus (b) at different immersion times.

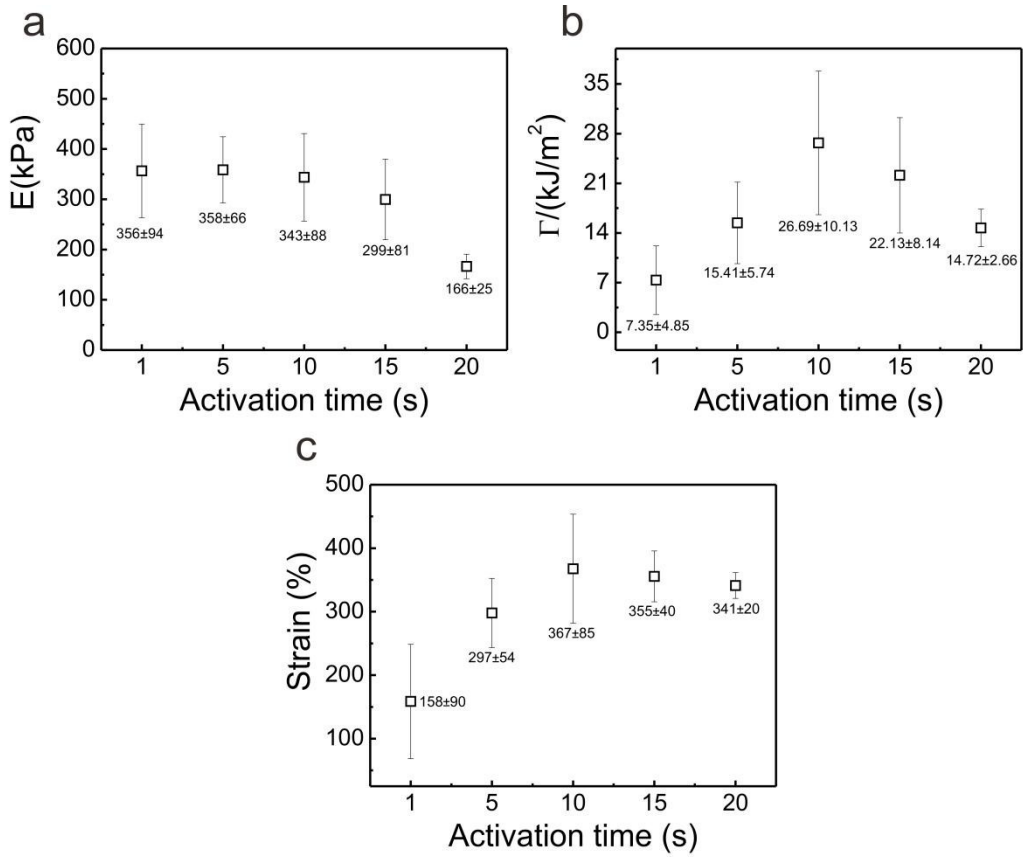

Figure S9. Mechanical properties of healed organohydrogels. Healing was conducted by immersing in hot water (60 °C) for activation times of 1 to 20 seconds. Dependence of (a) elastic modulus, (b)fracture energy and (c) tensile strain on activation time.

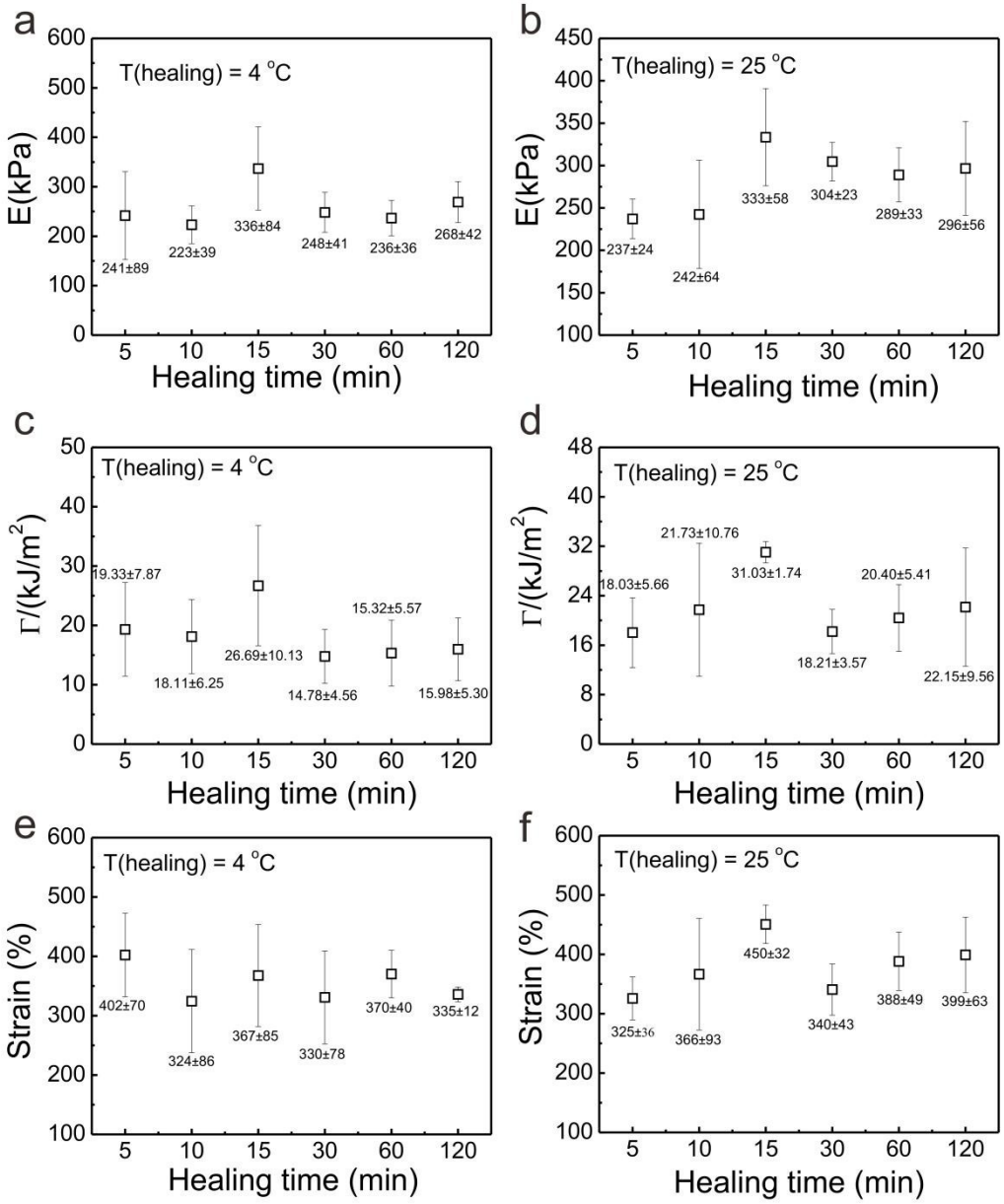

Figure S10. Dependence of mechanical properties of the organohydrogels (immersion time 6 h) on the healing time. Healing was conducted either at 4 °C or 25 °C. (a) Elastic modulus versus healing time (4 °C). (a) Elastic modulus versus healing time (25 °C). (c) Fracture energy versus healing time (4 °C). (d) Fracture energy versus healing time (25 °C). (e) Tensile strain versus healing time (4 °C). (f) Tensile strain versus healing time (25 °C).