Electronic Supplementary Information

Super-strong and tough poly(vinyl alcohol)/poly(acrylic acid) hydrogels reinforced by hydrogen bonding

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Experimental Section

Fracture Energy Determination. To measure the fracture energy of the stretchable hydrogels, a method adapted by Suo et al. was used.[1] As shown in Figure E1, two samples of the same hydrogels were pulled. Noticeably, one sample was unnotched and the other was notched. When the samples were undeformed, the initial state of each sample was of width a_0 = 15 mm and thickness $b_0 \approx 1$ mm, and the distance between the two clamps was 5 mm. The unnotched sample was used to plot the force-displacement curve. (It is not necessary to pull the unnotched sample to rupture.) When the two clamps moved to a displacement *L*, the area beneath the force-displacement curve gave the work done by the applied force, $U(L)$. The notched sample was notched by a blade to form a 5 mm-long notch. (The precise length of the notch was insignificant for fracture energy test.) The clamp speed of the Instron 3366 electronic universal testing machine was 100 mm·min^{-1}, and the testing machine recorded the critical displacement of the clamps, L_c, when the notch turned into a running crack. The fracture energy was calculated by Equation (1):

$$\Gamma\ (\mathrm{KJ \cdot m^{-2}}) = \frac{U(L_c)}{a_0 b_0} \tag{1}$$

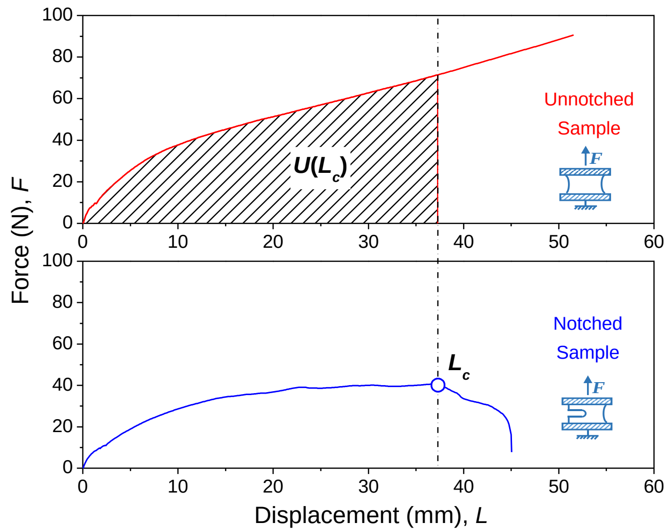

Figure E1. The force-displacement curve of the PVA/PAA-48 hydrogel. One sample was unnotched and the other was notched.

Supplementary Figures

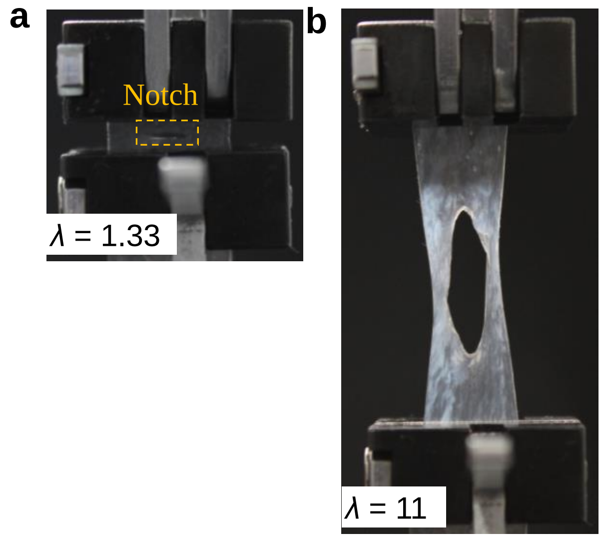

Figure S1. Highly stretchable and notch-insensitive properties of the PVA/PAA-48 hydrogel. (a) A 5 mm-long notch was cut in the PVA/PAA-48 hydrogel sample with a blade. A small stretch (λ) of 1.33 was applied to make the notch visible. (b) The PVA/PAA-48 hydrogel with a notch was stretched to 11 times its initial length. C_{PVA}=14 wt.%. The stretch (λ) is defined as the distance between the two clamps when the gel is deformed, divided by the distance when the gel is undeformed.

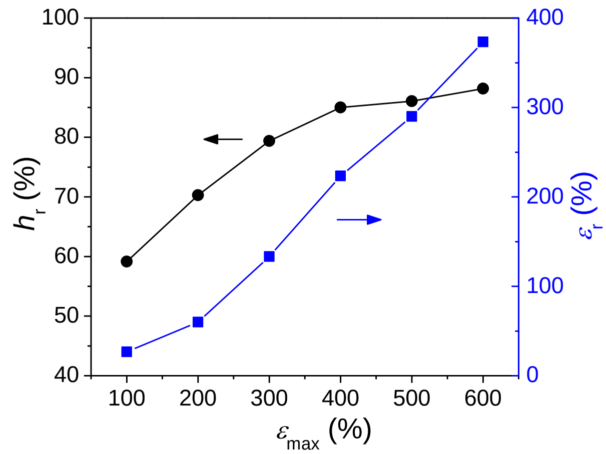

Figure S2. The hysteresis ratios (h_r) and residual strains (ε_r) of the PVA/PAA-48 hydrogel strings to different maximum tensile strains (ε_{max}). C_{PVA}=10 wt.%.

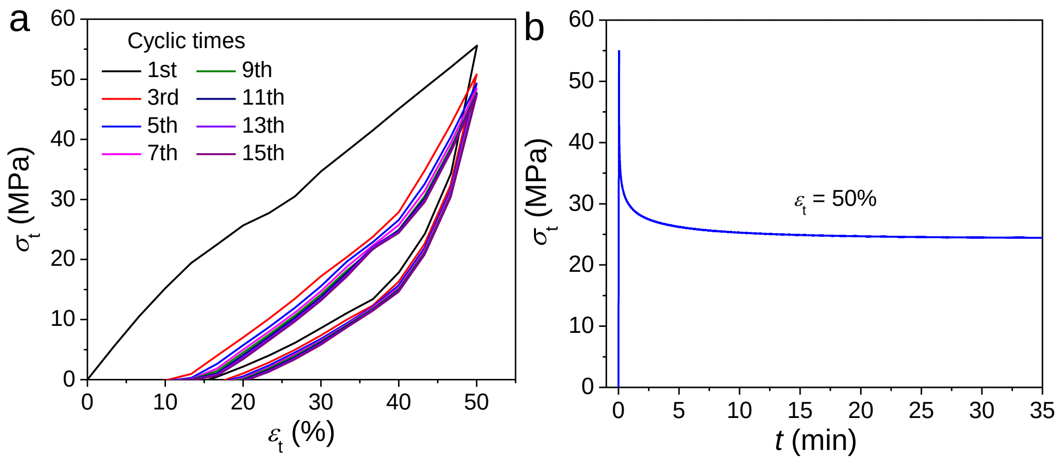

Figure S3. (a) Cyclic tensile curves and (b) stress-relaxation curves of the cold-drawn PVA/PAA-48 hydrogel strings with *n* of 240% at 50% strain.

A large hysteresis is present in the first loading-unloading cycle (Fig. S3a). In the following cycles, the loading curves are far from the loading curve in the first cycle, while the unloading curves are very close to the first unloading curve, and the maximum tensile stress (residual strain) decreases (increases) slightly with increasing cycle number, suggesting the physical cross-linking nature and poor recoverability of the PVA/PAA hydrogels.

Due to the physical cross-linking nature (H-bonding), the cold-drawn hydrogel string shows a remarkable relaxation in stress-relaxation tests like other tough physically cross-linked hydrogels (Fig. S3b). In the first 1 min, σ_t decreases dramatically from 55 to 29.5 MPa. The relaxation rate gradually decreases with time, and the σ_t keeps almost constant at 24.7 MPa after 20 min. Under an applied force, partial H-bonds in the PVA/PAA-48 hydrogel string can be broken, leading to the decrease in σ_t with time.

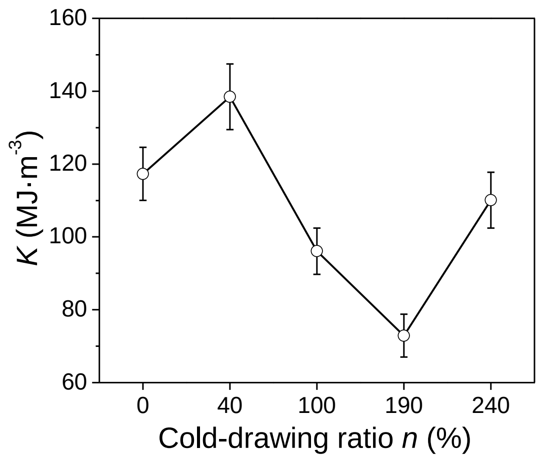

Figure S4. Toughness (*K*) of the cold-drawn PVA/PAA-48 hydrogel strings prepared with different *n*. C_{PVA}=14 wt.%. Error bars represent standard deviations.

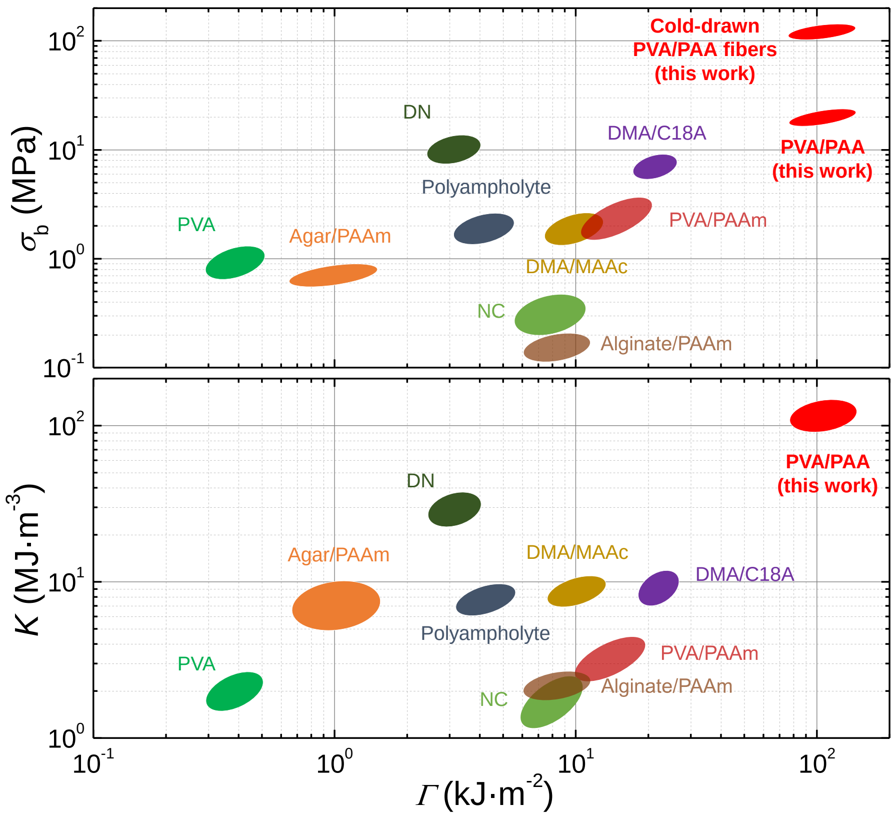

Figure S5. A comprehensive comparison of the tensile strength (σ_b), toughness (K) and fracture energy (Γ) of the PVA/PAA hydrogel strings and cold-drawn hydrogel strings with other toughest hydrogels, including double network hydrogel (DN), N,N-dimethylacrylamide/methacrylic acid hydrogel (DMA/MAAc), poly(vinyl alcohol) hydrogel (PVA), N,N-dimethylacrylamide/n-octadecyl acrylate hydrogel (DMA/C18A), poly(vinyl alcohol)/polyacrylamide hydrogel (PVA/PAAm), alginate/polyacrylamide hydrogel, polyampholyte hydrogel, nano-composite hydrogel (NC), and agar/polyacrylamide hydrogel.

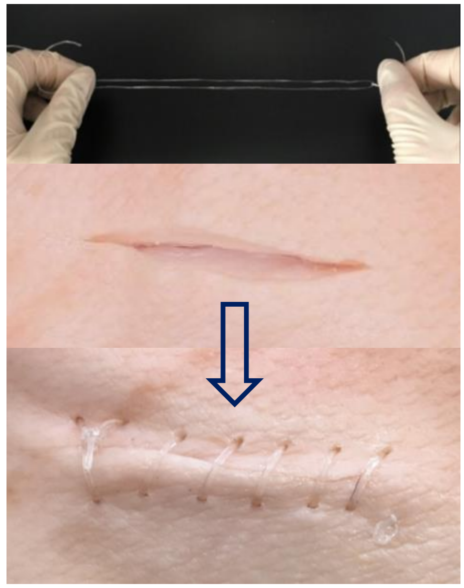

Figure S6. Sewing up a wound using a PVA/PAA hydrogel string as a surgical suture. A piece of pigskin was used and a 4 cm-long wound was notched by a blade.

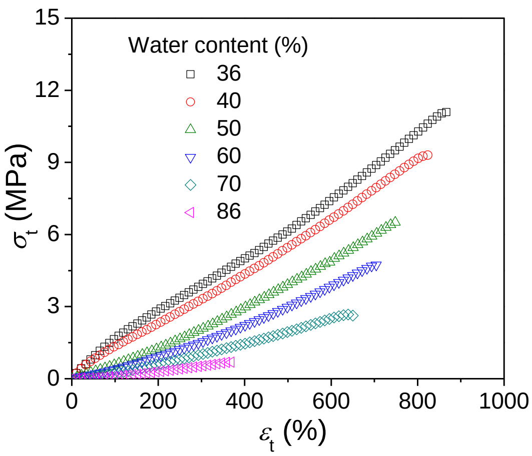

Figure S7. Tensile stress-strain (σ_t-ε_t) curves of neat PVA hydrogels (C_{PVA}=14 wt.%) dried to different water contents. σ_t refers to nominal stress.

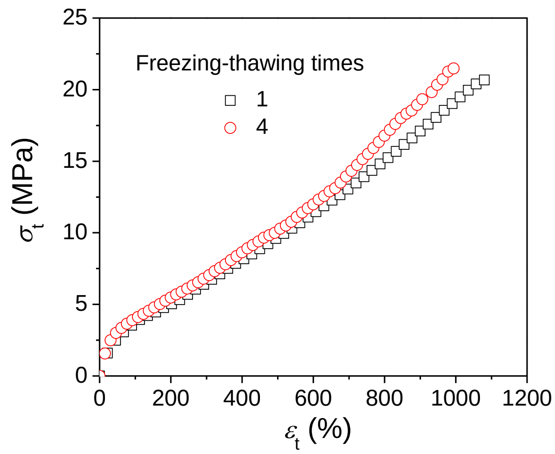

Figure S8. Typical tensile σ_t-ε_t curves of the PVA/PAA-48 hydrogel strings prepared with different freezing-thawing times. C_{PVA}=14 wt.%. σ_t is referred to as nominal stress.

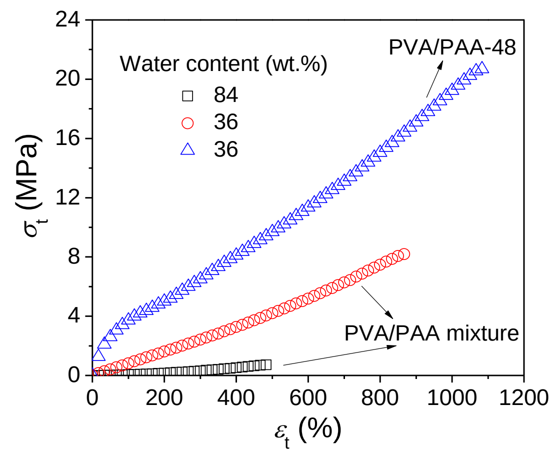

Figure S9. Typical tensile σ_t-ε_t curves of the PVA/PAA mixture hydrogels and the PVA/PAA-48 hydrogel. The PVA/PAA mixture hydrogel with a water content of 84 wt.% were formed by direct freezing-thawing a PVA/PAA aqueous mixture. The mass ratio of PVA to PAA is consistent with that in the PVA/PAA-48 hydrogel. Then the PVA/PAA mixture hydrogels were dried to a water content of 36 wt.%. Therefore, the PVA/PAA mixture hydrogel has the same water content (36 wt.%) and the same mass ratio of PVA/PAA as those of the PVA/PAA-48 hydrogel. σ_t is referred to as nominal stress.

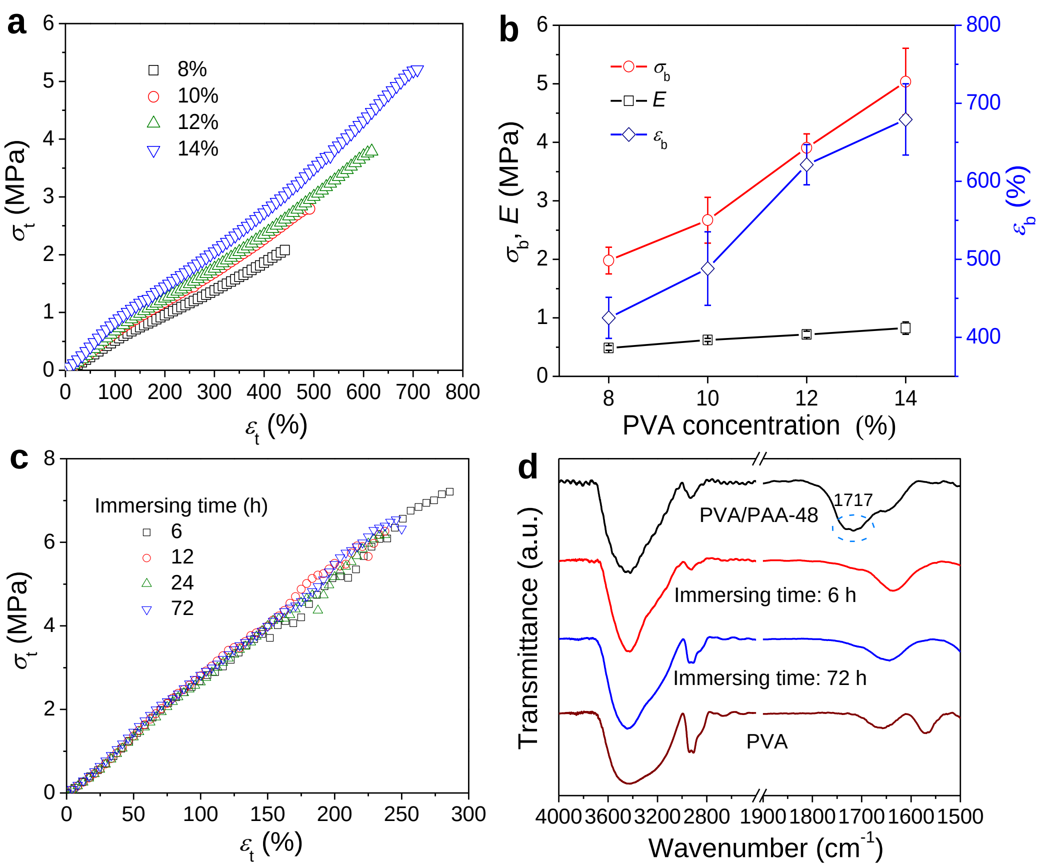

Figure S10. (a) Tensile σ_t-ε_t curves of the PVA/PAA-48 hydrogel strings prepared with different PVA concentrations after being immersed in deionized water for 72 h. (b) The tensile strengths (σ_b), elastic moduli (E) and elongations (ε_b) of the same samples as in (a). Error bars represent standard deviations. (c) Tensile σ_t-ε_t curves of the cold-drawn PVA/PAA-48 hydrogel strings (C_{PVA}=14 wt.%) with n of 100% after being immersed in deionized water for different periods. (d) FT-IR spectra of the PVA and PVA/PAA-48 hydrogel strings (C_{PVA}=14 wt.%) with n of 100% after being immersed in deionized water for different periods. σ_t is referred to as nominal stress.

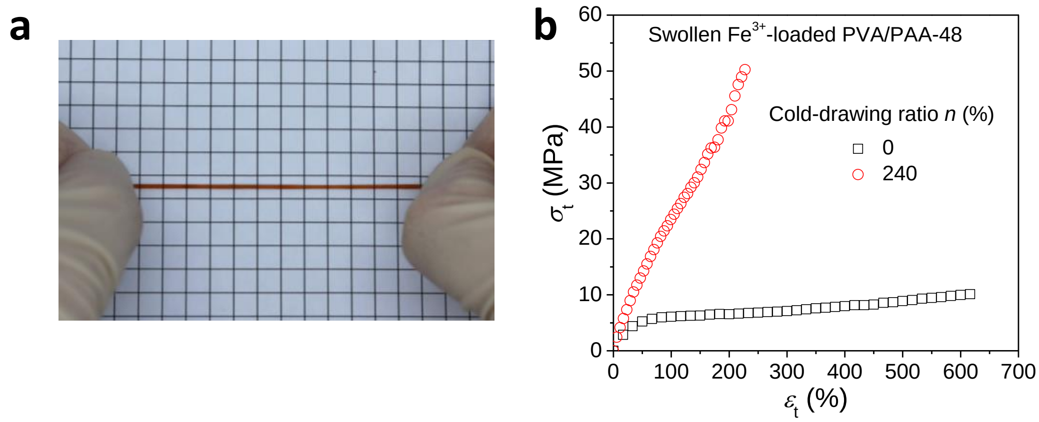

Figure S11. (a) A photograph of the swollen Fe^{3+}-loaded PVA/PAA-48 hydrogel string with *n* of 240%. (b) Tensile σ_t-ε_t curves of the swollen Fe^{3+}-loaded PVA/PAA-48 hydrogel strings with *n* of 0 and 240%. C_{PVA}=14 wt.%. σ_t is referred to as nominal stress.

Supplementary Tables

Table S1. The contents of PVA, PAA and water in the PVA/PAA-48 hydrogel strings prepared with different PVA concentrations.

C_{PVA} (wt.%)	PVA (wt.%)	PAA (wt.%)	H_2O (wt.%)
8	45.1	14.7	40.2
10	49.1	13.6	37.3
12	53.5	10.3	36.2
14	54.0	10.1	35.9

Table S2. The mechanical properties of solid engineering plastics.[2, 3]

Code of Plastics	σ_b (MPa)	ε_b (%)	E (MPa)
Polyamide-66 (nylon-66, PA-66)	62.1-77.2	200-300	3300
Polystyrene (PS)	30-60	1-4	3200-3400
Polymethyl methacrylate (PMMA)	48-76	2-10	3180
Polycarbonate (PC)	65.5	110	2380
Polyethylene (HDPE)	10-60	18-40	60-290
Polyvinyl chloride (PVC)	56.6	85	3000
Polypropylene (PP)	30-40	100-600	1100-2000
Acrylonitrile-butadiene-styrene copolymer (ABS)	30-50	15-30	2000-2800
Polyethylene terephthalate (PET)	50	180	1700
Polytetrafluoroethylene (PTFE)	17.5-24.5	200-600	340

Table S3. The equilibrium water contents (EWC) of the PVA/PAA-48 hydrogels prepared with different PVA concentrations after being immersed in deionized water for 72 h.

C_{PVA} (wt.%)	EWC (wt.%)
8	75.8
10	72.9
12	70.0
14	69.1

Table S4. The equilibrium water contents of the cold-drawn PVA/PAA-48 hydrogel strings with cold-drawing ratio (*n*) of 100% after being immersed in deionized water for different periods.

Immersing Time (h)	EWC (wt.%)
6	63.6
12	64.5
24	63.3
48	64.1
72	63.7

Table S5. The mechanical properties of biological tissue materials.[4-7]

Materials	σ_b (MPa)	ε_b (%)	E (MPa)
Articular Cartilage	4.7 ± 2.1	113.8 ± 25.1	3.4
Ligament	49.1 ± 31.0	22.2 ± 5.6	294.6 ± 190.4
Tendon	64.7 ± 15.0	14 ± 6	660 ± 266
Muscle Tissue	0.163 ± 0.0757	50.5 ± 22.2	0.447 ± 0.0977

Movie S1. A movie showing that a cold-drawn PVA/PAA-48 hydrogel string (*n* of 240%) with a diameter of 0.5 mm holds up a load of 3.5 kg without breakage.

Movie S2. A movie showing that the soft and strong PVA/PAA hydrogel strings can be used to knit a hydrogel textile by a traditional manual method.

Movie S3. A movie showing that the PVA/PAA hydrogel strings can be used as surgical suture to sew up a wound.

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