Supporting Information

Anisotropic Tough Multilayer Hydrogels with Programmable Orientation

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Materials and methods

Materials. Filter paper (ADVANTEC, Toyo Roshi Kaisha Ltd., Japan) was used as the cellulose source. Lithium chloride (LiCl), *N,N′*-dimethylacetamide (DMAc), and ethanol were used as received from Duksan Pure Chemicals Co., Ltd., Korea. Ultrapure deionized water was used to prepare all of the hydrogels.

Preparation of cellulose hydrogels. Physical cellulose hydrogels were prepared according to a previously reported procedure with slight modifications.[S1,S2] To purify the cellulose, cut filter paper sheets were sequentially washed with water, ethanol, and DMAc, and then vacuum dried at 60 °C. A 1.5 wt% cellulose solution was prepared by dissolving 1.5 g of purified cellulose paper in 98.5 g of a DMAc/LiCl (92:8) solvent. This solution was used to prepare the physical cellulose gel and also to facilitate self-welding of the multilayered hydrogels. To prepare hydrogels of different thicknesses, the cellulose solution was poured into glass molds of different depths (0.3, 0.5, 1, 3, and 5 mm) and left in ambient conditions (temperature: ~25 °C; humidity: 30–50%) for 1 d to induce gelation of the cellulose through H-bond formation. The solvent of the as-prepared organogel was then replaced first with ethanol and then with water to obtain the desired water-equilibrated hydrogels (with thicknesses of ~0.1, ~0.25, ~0.5, ~1.6, and ~2.6 mm). Stress-induced anisotropic cellulose hydrogels were prepared by applying different degrees of prestretching along the length direction of the physical cellulose hydrogel (thickness: ~0.5 mm; width: 30 mm; length: 30 mm). The gel was kept under stretched conditions in air for 15 min, and during that time, external water was frequently applied to the gel surface to prevent drying. The stress was removed after 15 min. The hydrogels obtained through prestretching by 50%, 100%, and 125% were denoted as 50-, 100-, and 125-prestretched hydrogels, respectively.

Self-welding. To explore the possibility of fabricating multilayered hydrogels using thin anisotropic films, two cofacially joined 100-prestretched samples were prepared using our welding method to determine their shear adhesive strengths by a standard lap shear test. The gels were initially equilibrated in DMAc. The portion of the organogels that we planned to weld was soaked in a cellulose/LiCl/DMAc solution for ~30 s, and the cellulose-soaked gels were cofacially joined over a length of 5 mm with slight pressing. The gel was then left in ambient conditions for 1 d. During this time, the gels bonded through strong cellulose-mediated H-bond formation. The solvent of the bound gel was sequentially replaced with ethanol and water. A tensile test was performed at 500% of the initial length (distance between clamps) per min (500%/min) with an initial length of ~10 mm, and the gel's adhesive strength was determined by dividing the maximum force required for interfacial failure by the shear area.

A cut physical cellulose hydrogel (thickness: ~1.6 mm) was also bound side-to-side using the method described above. A tensile test was performed on the bound hydrogel, and the result was compared with that of the pristine hydrogel to evaluate the hydrogel's self-welding efficiency.

Preparation of self-welded multilayered hydrogels. A 100-prestretched hydrogel (thickness: ~0.25 mm) was used to prepare the multilayered hydrogels. First, the 100-prestretched hydrogel was equilibrated in DMAc. Each layer of the 100-prestretched organogel was soaked in the cellulose/LiCl/DMAc solution for 30 s before it was used to prepare multilayered gels. The 6-parallel-laminate (6PL) and 6-orthogonal-laminate (6OL) gels were prepared by stacking six layers of cellulose-soaked 100-prestretched gels in parallel (i.e., the polymers in each layer were oriented in the same direction) and orthogonally (i.e., the polymers in adjacent layers were oriented perpendicular to each other), respectively. The stacked gels were then kept in air for 1 d. All the adjacent layers connected with each other through strong cellulose-mediated H-bond formation. The solvents of the self-bound multilayered gels were then sequentially replaced with ethanol and water to obtain the final 6PL and 6OL hydrogels, which were used for all the characterizations. Axially rolled (AR) and concentrically rolled (CR) hydrogels were prepared by rolling a layer of cellulose-soaked 100-prestretched organogel along the width (the dimension in which the cylindrical axis is aligned with the polymers of the layer) and length (the dimension in which the polymers of the layer are arranged concentrically around the cylindrical axis) directions of the sample, respectively. The rolling state was maintained by hand for ~10 min to prevent any unrolling during the initial welding process. Next, the gel was kept in ambient conditions for 1 d, and the solvent was sequentially replaced with ethanol and water to obtain the final AR and CR hydrogels. To measure the electrical conductivity, we prepared a 12-parallel-laminate (12PL) hydrogel because such gels have a thickness (~3 mm) that facilitates connection with LED (light-emitting diode) lights.

Structural observations. The structure, birefringence, and orientation patterns of the hydrogels were observed using polarizing optical microscopy (POM; BX53, Olympus, Japan). The optical retardation was measured quantitatively using a Berek compensator (U-CBE, Olympus, Japan) in the microscope. The birefringence was determined by dividing the retardation value by the thickness of the sample. The structure was further examined by scanning electron microscopy (SEM; S-4700, Hitachi, Japan). To prepare samples for SEM, the gel was freeze-dried for 1 d and coated with platinum. The cross-sectional surface was exposed by breaking the sample, which was frozen under liquid nitrogen and used for observing the layer interfaces. The fiber morphology of hydrogel was observed from its dried cross-sectional surface using atomic force microscopy, AFM (XE-100, PSIA Advanced Scanning Probe Microscope).

X-ray diffraction (XRD) measurements. X-ray spectra of hydrogels were measured using a PANalytical EMPYREAN X-ray diffractometer with CuKα-radiation source ($\lambda = 0.1541874$ nm) operating at 40 kV and 30 mA. The range of diffraction angle (2 theta) was from 10° to 60° with a scanning rate of 8.5°/min and step size of 0.026°.

Thermogravimetric analysis (TGA). Thermal property of the gel was evaluated using a thermogravimetric analyser (TGA2, METTLER TOLEDO, SWISS). TGA was measured from 30° to 500° at a heating rate of 10°/min under a nitrogen atmosphere.

Water content measurements. The hydrogels' water contents were determined by measuring the difference between the gels' weights when they were water-saturated (W_o) and when they were completely dried (W_d) after drying at 120 °C overnight. The following equation was used:

$$\text{Water content} = [(W_o - W_d)/W_o] \times 100 \text{ wt\%}$$

Mechanical characterization. A commercial tensile test machine (model TO-100-1C, TESTONE Co. Ltd., Korea) was used for mechanical characterization. All tests were performed in ambient conditions (at ~25 °C). Water-equilibrated cellulose hydrogels were used for all mechanical tests. Depending on a sample's mechanical strength, either a 10-kgf or a 100-kgf load cell was used.

Tensile tests. The rectangular (3 mm in width) and cylindrical (~2 mm in diameter) hydrogels were clamped along the length direction in the tensile test machine, and an initial length of ~10 mm between the clamps was maintained. Tensile tests were conducted by pulling the upper clamp upward at a constant deformation rate of 500%/min until the material fractured. Three tests were performed on each sample. During the cyclic tensile tests, loading and unloading up to 5% strain were performed at a deformation rate of 100%/min. To prevent air-drying during prolonged measurement periods, water was sprayed on the hydrogels' surfaces from an external source.

Compression tests. A cylindrical (~2 mm in diameter and ~1.5 mm in thickness) sample was set coaxially on the lower plate of the tensile test machine, and a compression test (with up to 90% compression) was performed by pressing with the upper plate, which was connected to a load cell, at a deformation rate of 20%/min. The plate surfaces were coated with a thin layer of silicone oil to reduce the friction between the samples and the metal plates. Three tests were performed on each sample. Throughout the cyclic compression testing, loading and unloading with compressions of up to 5% were performed at a strain rate of 20%/min. To prevent air-drying during prolonged measurement periods, water was sprayed on the hydrogels' surfaces from an external source.

Conductivity measurements. The 12PL hydrogel (length: 15 mm; width: 5 mm; thickness: 3 mm) was used for resistance measurements (LCR-819 meter, GW Instek, Taiwan). The resistance was measured both parallel and perpendicular to the polymer direction. The hydrogel resistivity ρ (Ω m) and conductivity σ (S m^{-1}) were calculated using the following equations:

$$\rho = RA/l$$

$$\sigma = \rho^{-1}$$

Here, R is the measured resistance (Ω), A is the cross-sectional area (m^2), and l is the length (m) of the sample.

Supporting figures

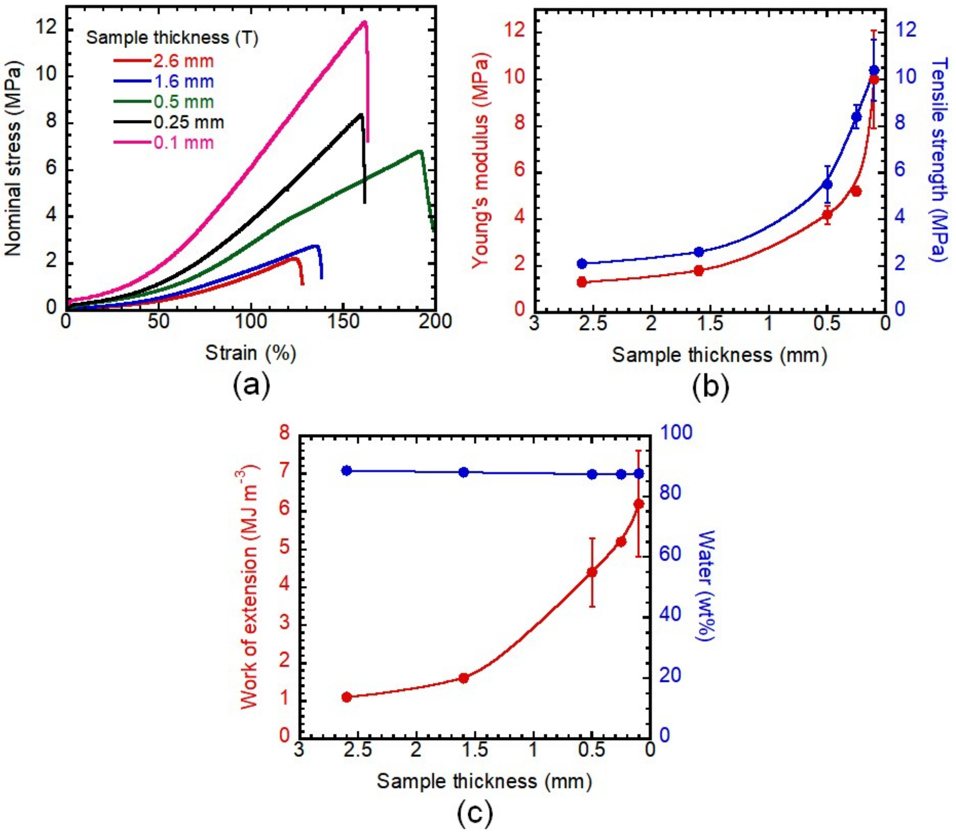

Figure S1. (a) Tensile stress–strain curves of physical cellulose hydrogel samples of different thicknesses. (b) Young's modulus and tensile strength and (c) work of extension and water content versus the hydrogel thickness.

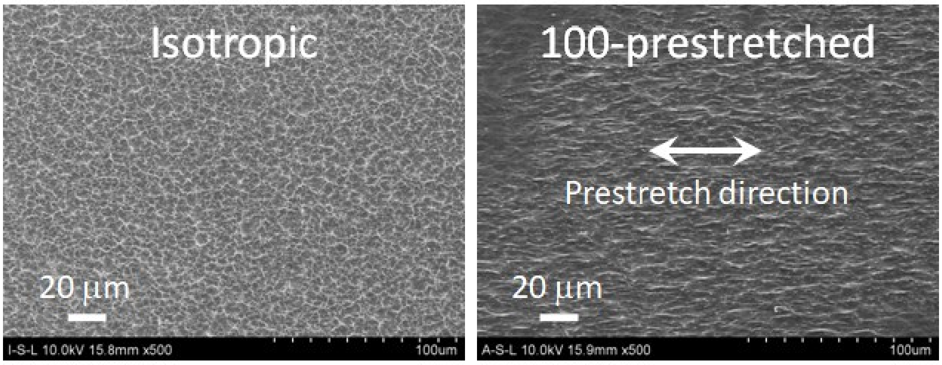

Figure S2. SEM images of the surfaces of isotropic gel (0.5 mm in thickness) and the corresponding 100-prestretched cellulose hydrogel.

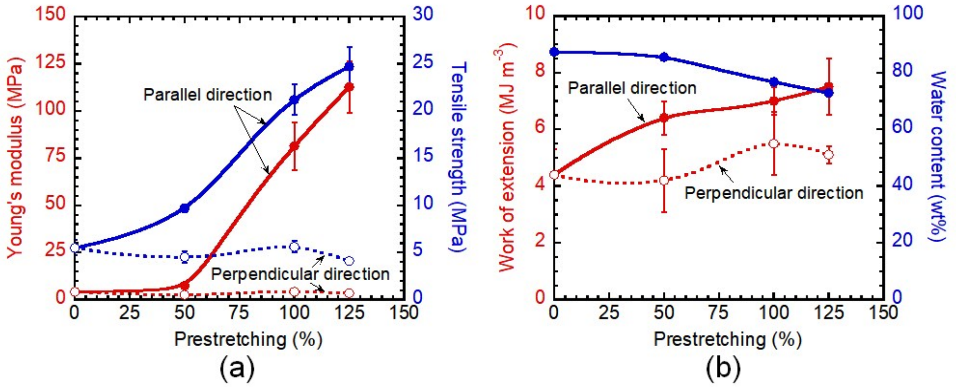

Figure S3. (a) Young's modulus and tensile strength and (b) work of extension and water content of anisotropic cellulose hydrogels versus degree of prestretching.

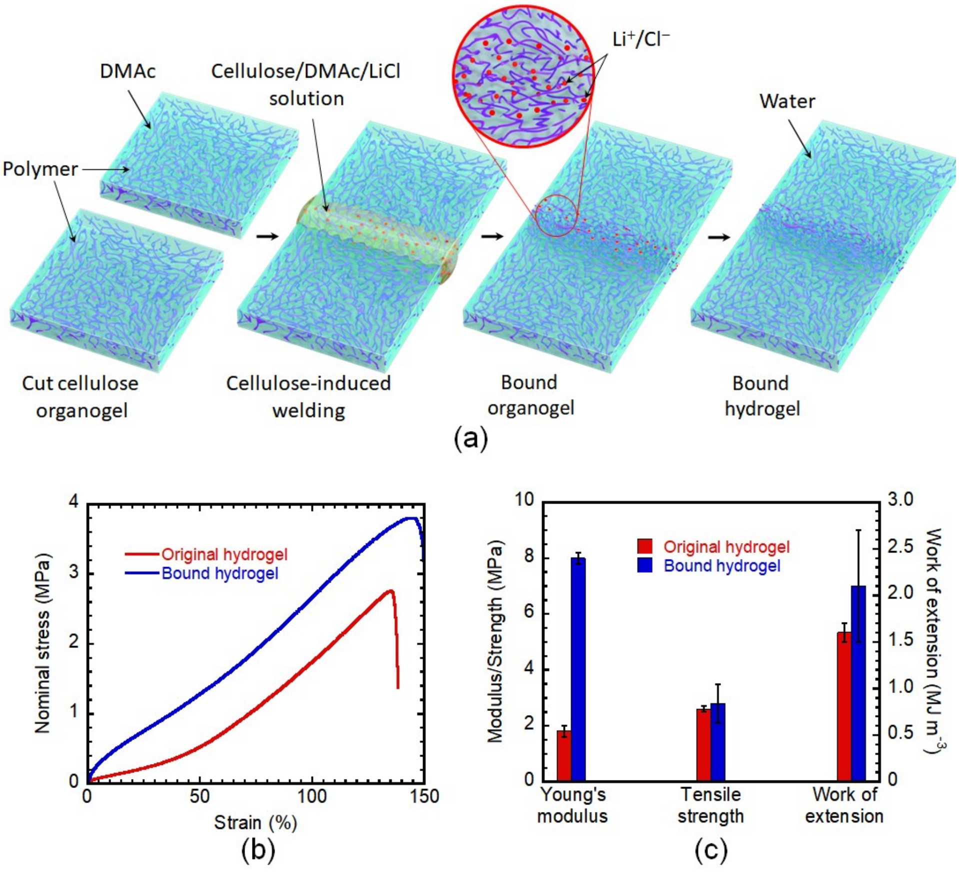

Figure S4. (a) Illustrations of cellulose/DMAc/LiCl-solution-induced self-welding of the cellulose hydrogel. (b) Tensile stress–strain curves of pristine and self-bound cellulose hydrogels. (c) Comparison of the Young's modulus, tensile strength, and work of extension values of pristine and self-bound cellulose hydrogels.

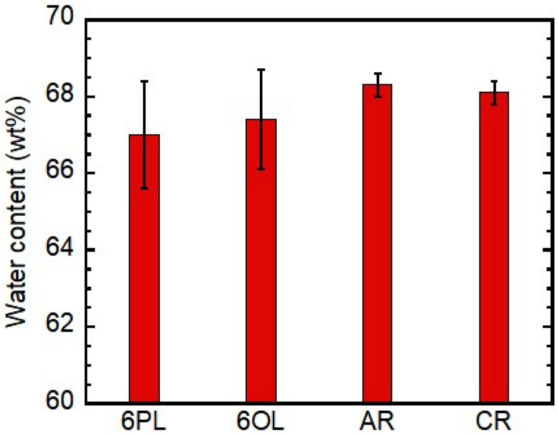

Figure S5. Water content of 6PL, 6OL, AR, and CR hydrogels.

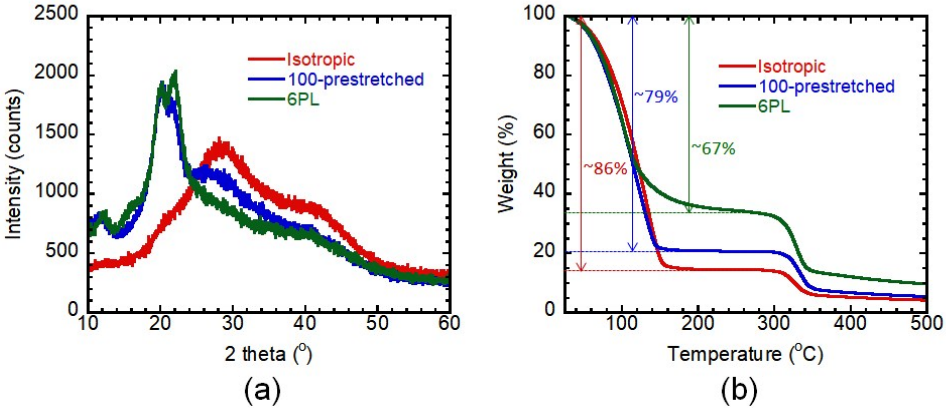

Figure S6. (a) XRD and (b) TG curves of isotropic, 100-prestretched, and 6PL cellulose hydrogels.

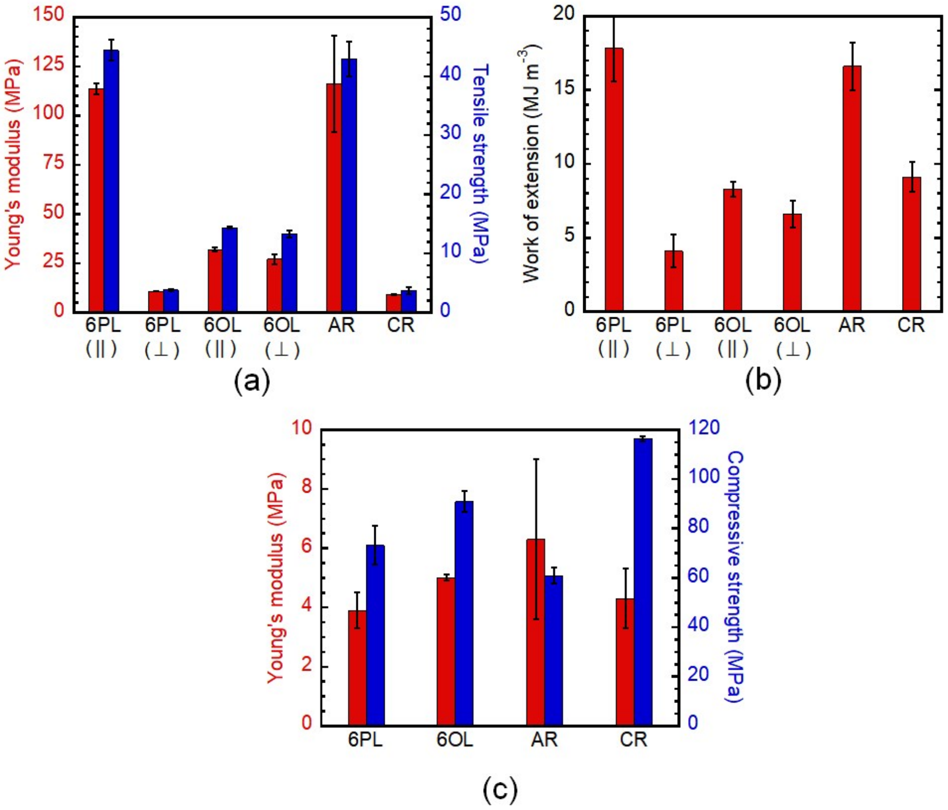

Figure S7. (a) Young's modulus (derived from tensile testing) and tensile strength and (b) work of extension of 6PL, 6OL, AR, and CR hydrogels. (c) Young's modulus (derived from compression testing) and compressive strength (at 90% compression) of the investigated multilayered hydrogels.

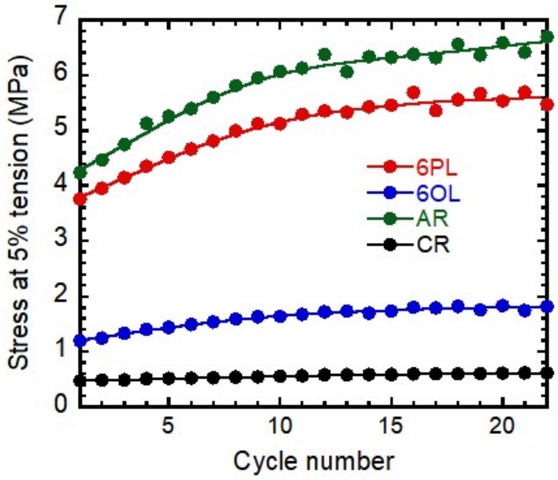

Figure S8. Stress (at 5% tension) of multilayered gels throughout 22 cycles of tensile loading–unloading test.

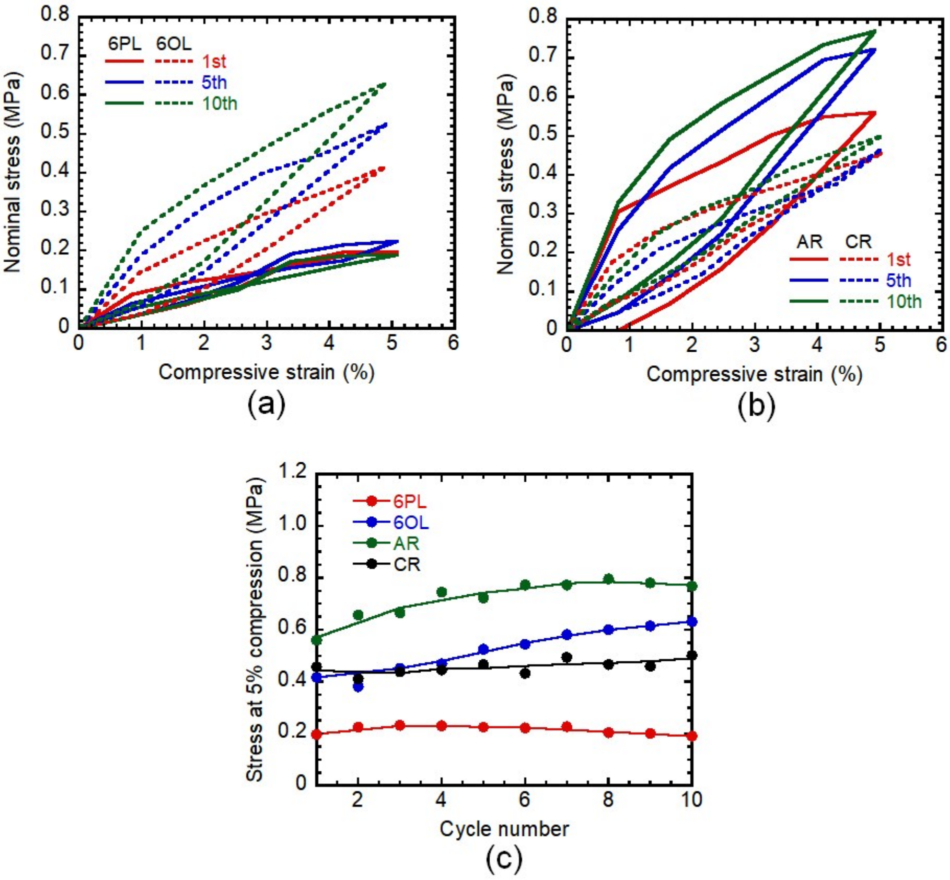

Figure S9. (a, b) Results of repeated compressive loading–unloading tests (at a deformation rate of 20%/min) for 6PL, 6OL, AR, and CR hydrogels up to 10 cycles. The waiting time between consecutive cycles was 1 min. Only the 1st, 5th, and 10th cycles are shown here. (c) Stresses (at 5% compression) of the gels throughout 10 cycles.

Supporting table

Table S1. Comparison of the tensile properties and water contents of various reported hydrogels[S3–S9] with those of our hydrogel.

Hydrogel	Tensile strength (MPa)	Young's modulus (MPa)	Fracture strain (%)	Work of extension (MJ m^{-3})	Water content (wt%)
Anisotropic cellulose[S3]	8	37.9	26.4	1.1	85 ± 0.5
Wood/PAAm[S4]	36	310	~10	-	65
P(AAc-co-AAm)/Fe^{3+}[S5]	5.9	2	748	27.8 ± 1	70
P(DMAAm-co-MAAc)[S6]	2	28	800	-	70
P(AN-co-AAm-co-AMPS)[S7]	8.3 ± 0.4	5.6 ± 0.2	684 ± 58	-	78
DN (PAMPS/PAAm)[S8]	1–10	0.1–1	1000–2000	-	~90
Alginate/PAAm[S9]	0.1–0.5	0.1–1	700–2400	-	~90
This study	~47	~140	~60	~20	~68

PAAm: polyacrylamide; AAc: acrylic acid; AAm: acrylamide; DMAAm: *N,N'*-dimethylacrylamide; MAAc: methacrylic acid; AN: acrylonitrile; AMPS: 2-acrylamido-2-methyl-1-propanesulfonic acid; DN: double network; PAMPS: poly(2-acrylamido-2-methyl-1-propanesulfonic acid)

Supporting movies

Movie S1. Dehydration–rehydration-induced shape change (in thickness direction) of the 6PL hydrogel (length: 10 mm; width: 2 mm; thickness: 1.5 mm). The gel was dehydrated by air drying for 15 min, and its rehydration was monitored for 10 min after external water was supplied to it. The movie is played at 50× normal speed.

Movie S2. Dehydration–rehydration-induced shape change of the 6OL hydrogel (length: 10 mm; width: 2 mm; thickness: 1.5 mm). The experiment was conducted using the method used for the 6PL gel, and the movie is played at 50× normal speed.

Movie S3. Reversible switching of an LED electrical circuit (at 24 V) using dehydration–rehydration-induced actuation of the 6OL hydrogel (length: 10 mm; width: 5 mm; thickness: 1.5 mm). The gel was dehydrated by air drying for 6 min, and its rehydration was monitored for 4 min after external water was supplied to it. The movie is played at 25× normal speed, except that the addition of the water is shown at 5× normal speed.

References

[S1] W. Gindl, J. Keckes, *Polymer* **2005**, *46*, 10221.

[S2] Md. T. I. Mredha, Y. Z. Guo, T. Nonoyama, T. Nakajima, T. Kurokawa, J. P. Gong, *Adv. Mater.* **2018**, *30*, 1704937.

[S3] D. Ye, P. Yang, X. Lei, D. Zhang, L. Li, C. Chang, P. Sun, L. Zhang, *Chem. Mater.* **2018**, *30*, 5175.

[S4] W. Kong, C. Wang, C. Jia, Y. Kuang, G. Pastel, C. Chen, G. Chen, S. He, H. Huang, J. Zhang, S. Wang, L. Hu, *Adv. Mater.* **2018**, *30*, 1801934.

[S5] P. Lin, S. Ma, X. Wang, F. Zhou, *Adv. Mater.* **2015**, *27*, 2054.

[S6] X. Hu, M. Vatankhah-Varnoosfaderani, J. Zhou, Q. Li, S. S. Sheiko, *Adv. Mater.* **2015**, *27*, 6899.

[S7] Y. Zhang, Y. Li, W. Liu, *Adv. Funct. Mater.* **2015**, *25*, 471.

[S8] J. P. Gong, *Soft Matter* **2010**, *6*, 2583.

[S9] J. Li, W. R. K. Illeperuma, Z. Suo, J. J. Vlassak, *ACS Macro Lett.* **2014**, *3*, 520.