Electronic Supplementary Information for

Stiff, strong, and tough hydrogels with good chemical stability

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Mechanical properties and equilibrium water content

The equilibrium water content of hydrogels greatly affects their mechanical properties. Figure S1a and S1b illustrate the accessible range of stiffness, and toughness versus the equilibrium water content, respectively. Polyvinyl alcohol gels can be prepared with freeze-thaw method (as labeled by FT PVA gel) and dry-anneal method (as labeled by DA PVA gel). The hybrid gel prepared in this work absorbs more water than the dry-anneal PVA gel, and exhibits higher stiffness and toughness than other hydrogels.

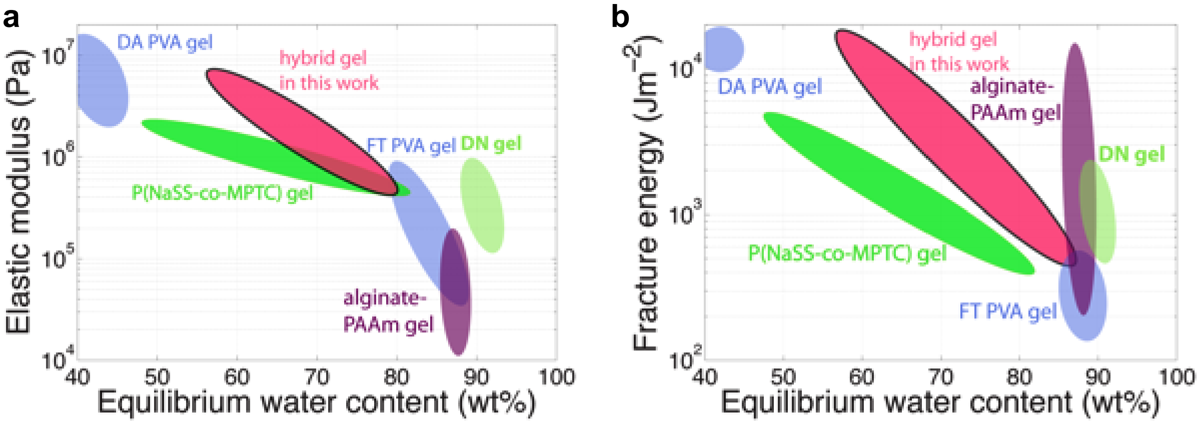
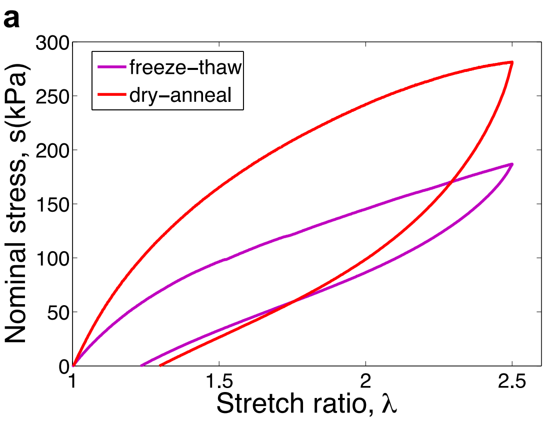


Figure S1. Material property charts for various hydrogels. a, Elastic modulus versus equilibrium water content. **b**, Fracture energy versus equilibrium water content. Materials include the hybrid gel prepared in this work, polyvinyl alcohol gel (PVA) prepared with freeze-thaw or dry-anneal method, double network gel (DN), alginate-polyacrylamide hydrogel and polyampholyte hydrogels (sodium p-styrenesulphonate-co-3-(methaacryloylamino)propyl-trimethylammonium; NaSS-co-MPTC).

Comparison of dry-anneal and freeze-thaw hybrid gels

The higher density of PVA crystallites is inferred qualitatively from tensile test results that show that the dry-anneal hybrid gel has higher stiffness and dissipates more energy than the freeze-thaw hybrid gel (Fig. S2a), indicating a higher density of physical cross-links in the dry-anneal hybrid gel. This observation is further supported by confocal microscopy, which demonstrates that the dry-anneal hybrid gel has a much finer PVA network structure as shown below (Fig. S2b and S2c).



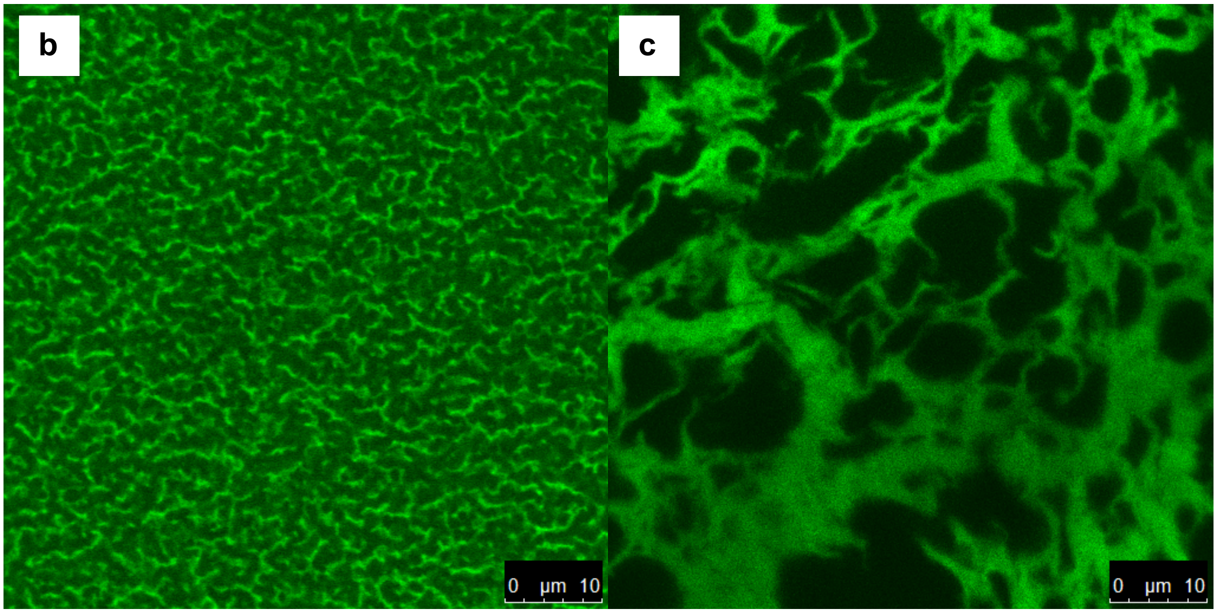


Figure S2. Comparison of dry-anneal and freeze-thaw PVA-PAAm gels. Tensile test curves of the freeze-thaw and dry-anneal hybrid gels (**a**), and confocal microscope images of the dry-anneal hybrid gel (**b**), and the freeze-thaw hybrid gel (**c**).

Phase separation of dry gels

Phase separation occurs in the binary mixture of polyvinyl alcohol (PVA) and polyacrylamide (PAAm): PVA-rich phase and PAAm-rich phase. The pure PVA gel looks translucent. The dry hybrid gel is opaque, because the phases with different diffraction indexes scatter the light. The opaqueness decreases with decreasing content of PAAm component (Fig. S3).

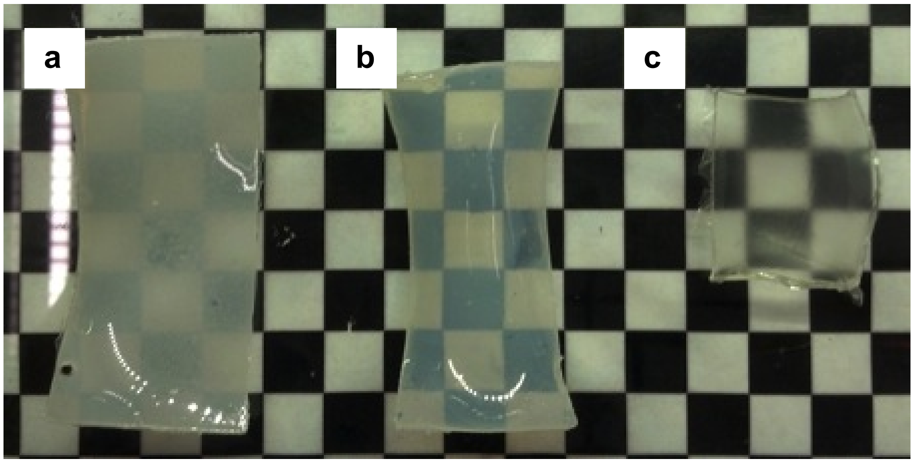


Figure S3. Phase separation of dry gels. Optical photographs of dry gels containing different ratios of polyacrylamide to (polyvinyl alcohol plus polyacrylamide), 70 wt% (**a**), 50 wt% (**b**) and 0 wt% (**c**).

X-ray diffraction measurement

We characterized the dry PVA-PAAm gels with the X-ray diffraction technique. The mass ratio of AAm to PVA in the hybrid gel was fixed at 1:1. The spectrum of the dry gel contains diffraction peaks at the *2Θ* angles of 19°, 23° and 41°, indicating the formation of PVA crystallites.

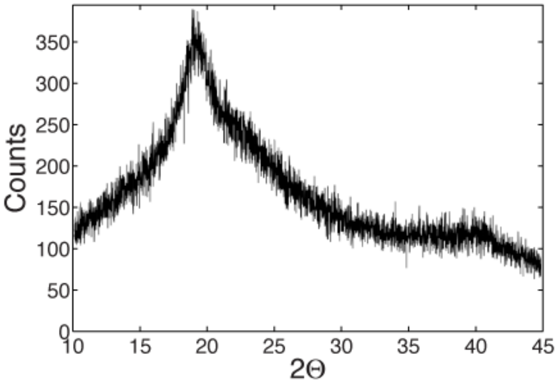


Figure S4. X-ray diffraction spectrum of dry PVA-PAAm gel.

Fourier transform infrared measurement

We measured the Fourier transform infrared spectrum (FTIR) of three gels (PVA, PAAm and PVA-PAAm hybrid gels) with Perkin Elmer FT-IR. The mass ratio of AAm to PVA in the hybrid gel was fixed at 1:1, and its water content was 70.8%. Distilled water was used as reference. A broad peak around 3390 cm^{-1} refers to stretching of N-H and O-H bonds, 2946 cm^{-1} of C-H stretch, 1666 cm^{-1} of C=O stretch and 1641cm^{-1} of O-H bend. Those peaks below 1400 cm^{-1} are the fingerprint regions related to C-C, C-O and C-N bonds. The spectrum of the hybrid gel is a superposition of those of PAAm and PVA gel, indicating the two polymers have no additional interaction.

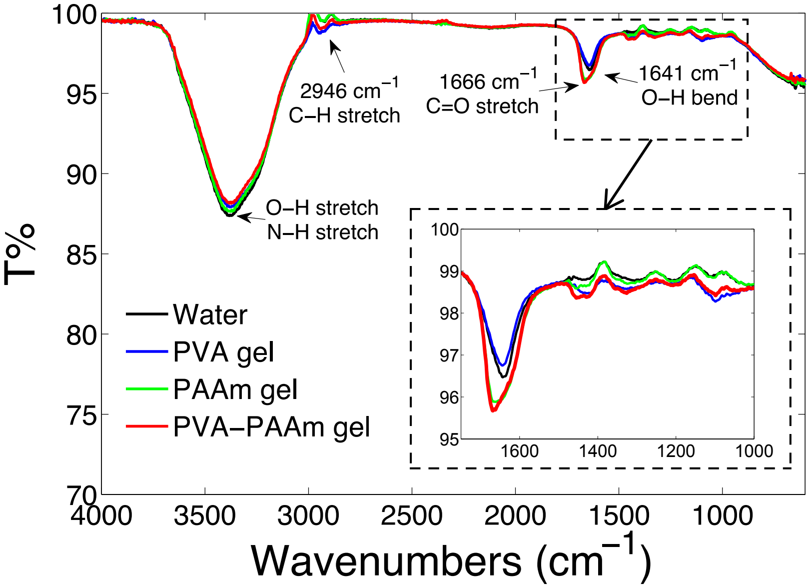


Figure S5. Fourier transform infrared spectrum (FTIR) of three gels and water. The inset shows the enlarged spectrum between 1750 cm^{-1} to 1000 cm^{-1}. Attenuated total reflectance (ATR) correction has been applied.

Confocal image of gels swollen after deformation

To show crystallite unzipping in deformed gels, we used the confocal microscope to map the morphology of the re-swollen gels after deformation. The fluorochrome dyes (5-DTAF) link with -OH groups on PVA chains. We excited the dyes with an Argon laser of 488nm band, and recorded images of 520nm band (Fig. S6). Evidently, the PVA-rich phases are the bright regions in the images.

When the gel is deformed, crystallites unzip, and the cross-link density decreases. The deformed gel was submersed in distilled water and showed anisotropic swelling in the loading direction. As revealed by confocal microscopy, the microstructure of deformed gels elongates along the stretching direction.

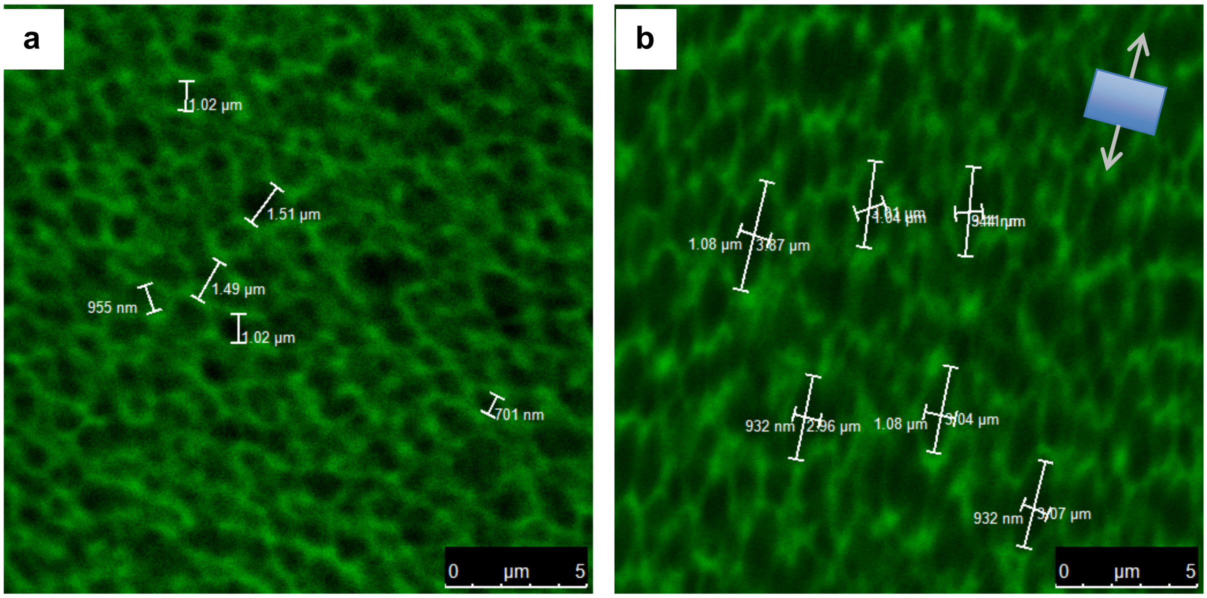


Figure S6. Morphology change of deformed gels. **a**, Undeformed gel. **b**, deformed gel after stretching. The inset indicates the stretching direction of specimen.

Stability in concentrated electrolyte solutions

We soaked the hybrid gels in electrolyte solutions containing different concentrations of calcium chloride ($CaCl_2$), and then performed tensile tests with an Instron machine. All stress-stretch curves overlapped (Fig. S7) indicating the PVA-PAAm hydrogels are stable even in concentrated electrolyte solutions ($CaCl_2$ 1.0 M).

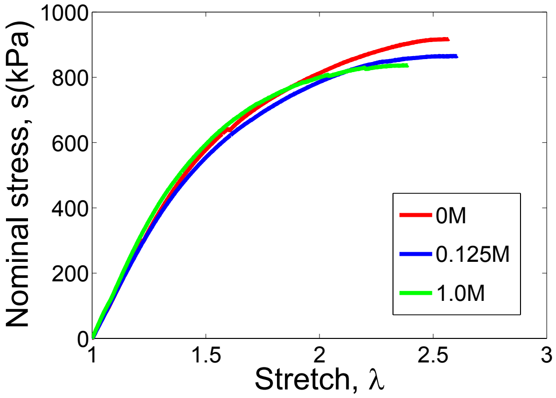


Figure S7. Stability of the PVA-PAAm hydrogels in $CaCl_2$ solutions. Stress-stretch curves of the gels that have been soaked in electrolyte solutions containing different $CaCl_2$ concentrations, as labeled.

Effects of covalent cross-links on recovery

We prepared hybrid gels with and without covalent cross-links and performed compression tests with an Instron machine. The samples were cylindrical in shape with a diameter of 12 mm. The loading curves of both gels overlapped in the first cycle (dashed lines, Fig. S8a). Immediate reloading revealed that the gel with covalent cross-links (0.05% MBAA/AAm) recovered more than the gel without covalent cross-links (solid lines, Fig. S8a). The recovery ratio, defined as the ratio of the work of the first loading versus that of the second loading, is plotted against the storage duration of the gel at room temperature (Fig. S8b). The covalent cross-links reduce viscous behavior and generate a retractive force in the deformed gel, which restores the undeformed shape, and enhances recovery.

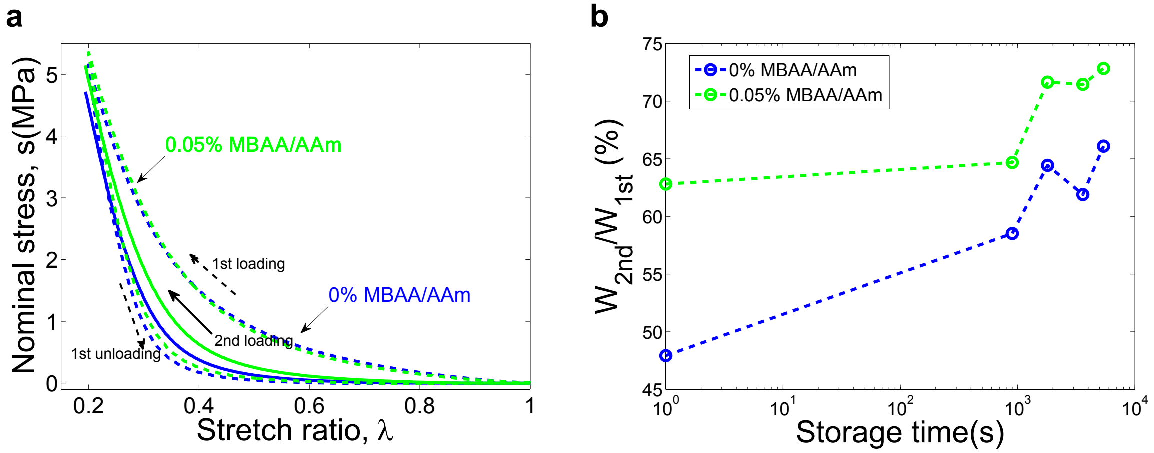


Figure S8. The covalent cross-links greatly affect the recovery process. **a**, First loading-unloading cycle and second intermediate loading of the PVA-PAAm hydrogels with and without covalent cross-links (MBAA). The samples are compressed to a stretch ratio of 0.2 (compressive strain 80%). **b**, The work of the second loading, W_{2nd}, divided by that of the first loading, W_{1st} as a function of storage duration at room temperature.

Phase separation of entangled PVA-PAAm gels

We prepared and performed tensile tests on two entangled PVA-PAAm hydrogels. Both samples were stretched to rupture (Fig. S9). The as-prepared gel was fully transparent; the gel that had stored at room temperature for 4 days was opaque (Inset of Fig. S9). Accompanied with the transparency changed, the elastic modulus increased form 132 kPa to 257kPa, indicative of increasing density of crystallites. These results confirm that the PVA and PAAm are incompatible; with the freeze-thaw or dry-anneal process, the two phases separate slowly with time; PVA crystallites are formed at room temperature.

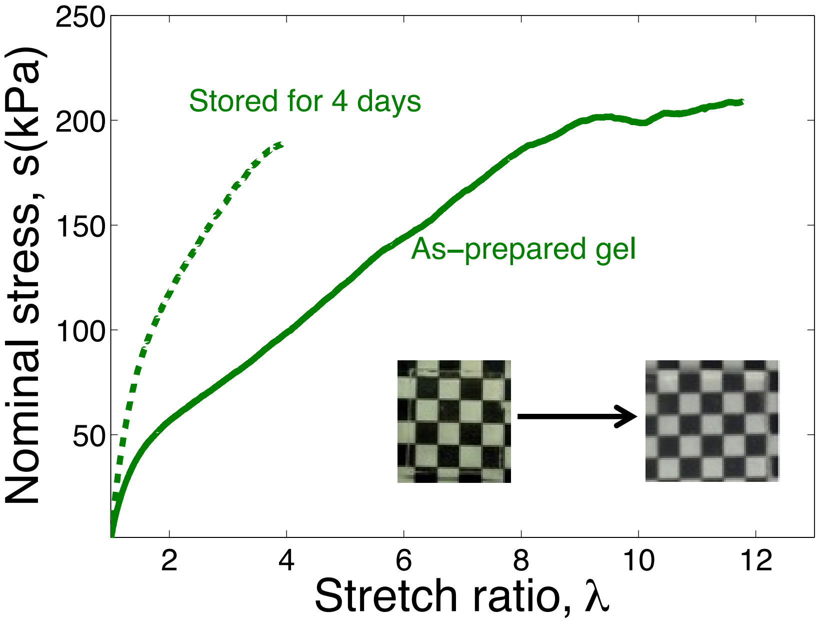


Figure S9. Phase separation of entangled PVA-PAAm gels. Stress-stretch curves of the two entangled PVA-PAAm gels. The inset shows the gel, which is transparent initially, becomes opaque after storage at room temperature for 4 days.

Rule of mixture

We used the rule of mixtures to fit the data. The results show that the elastic modulus and fracture energy can be expressed as a series additon of the PVA and PAAm networks (Fig. S10). The PVA-rich and PAAm-rich phases are assumed to have constant contents of water. The equilibrum water content of the whole gel can be expressed as

$$EWC = 1 - \frac{1}{1 + ax + b(1-x)},$$

where x refers to the ratio of AAm to (AAm plus PVA), a and b refer to the weight ratio of water to polymer in the PAAm-rich and PVA-rich phases, respectively. This equation fits the *EWC* data well (Fig. S10b), indicating that the PAAm-rich phase contains ~81wt% water and the PVA-rich phase contains ~41 wt% water.

Then we applied the rule of mixtures (Fig. S10c and S10d). With known water contents in the two phases, the weigth ratio of the PVA-rich phase to the whole gel, designated as *A*, can be caculated. By assuming the PVA-rich and PAAm-rich phases have a similar density (1.0 gcm^{-3}), the rule of mixtures indicates

$$E = AE_{PVA} + (1 - A)E_{PAAm} \, ,$$

$$\Gamma = A\Gamma_{PVA} + (1 - A)\Gamma_{PAAm} \, ,$$

where the subscripts PVA and PAAm refer to the PVA-rich phase and PAAm-rich phase, respectively.

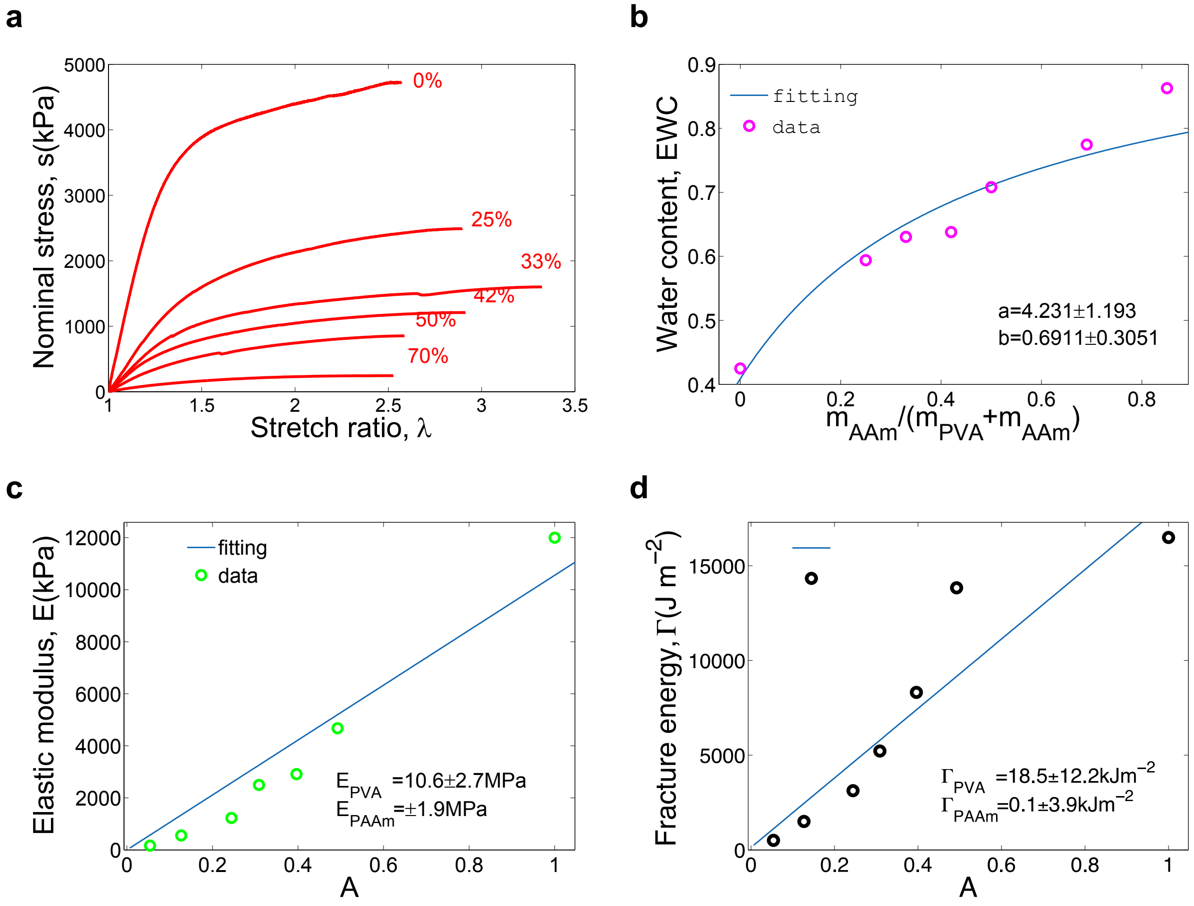
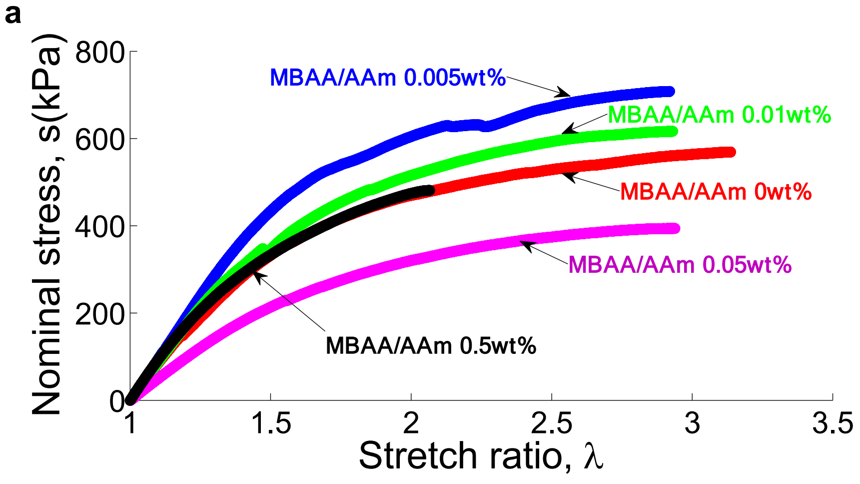


Figure S10. The properties of the hybrid gel follow the rule of mixtures. **a**, Stress-stretch curves of gels of various weight percentages of acrylamide to (acrylamide plus polyvinyl alcohol), as labeled. **b**, Fitting of equilibrium water content and the acrylamide content. **c**,**d**, Elastic modulus and fracture energy were fitted with respect to the weight ratio of PVA-rich phase to the whole gel, *A*.

Effect of covalent cross-links on mechanical properties

To evaluate the effect of covalent cross-links on the properties of the crystallized PVA-PAAm gel, we prepared a series of hydrogels with various ratios of MBAA to AAm, and performed tensile tests and pure shear tests. Interestingly, the elastic modulus of the hybrid gel first decreases, and then increases with increasing density of covalent cross-links. This trend can be understood as follows. A lightly cross-linked PAAm network acts as a physical obstacle that limits the crystallization of PVA, and thus decreases the elastic modulus; when the density of covalent cross-link is high, it contributes a net positive effect to the elastic modulus of the hybrid gel.



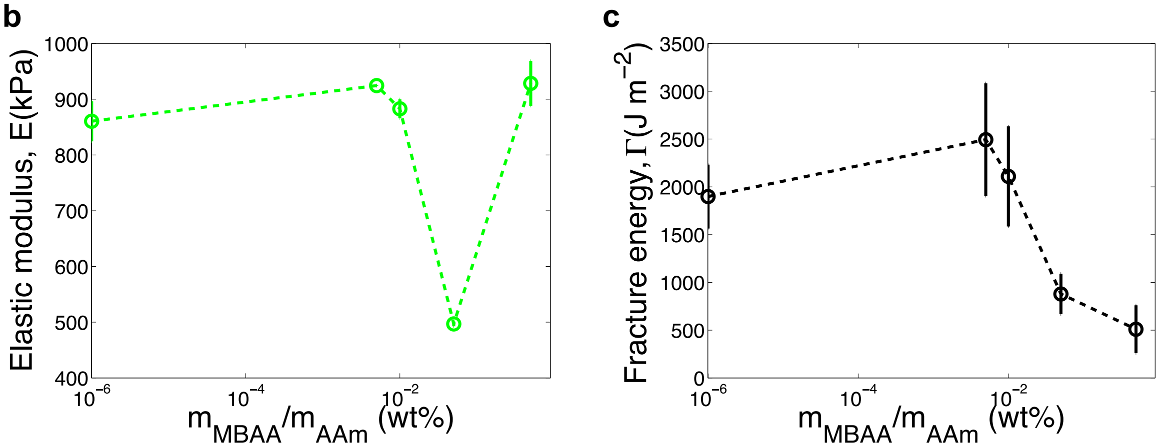


Figure S11. The amount of covalent cross-links affects mechanical properties of the hybrid gel. **a,** Stress-stretch curves were measured using unnotched samples of gels of various values of MBAA/AAm (wt%). **b,** Elastic modulus were calculated from stress-stretch curves. **c,** Fracture energy varies with the amount of covalent cross-links. (Error bars, S.D.; n=3). The ratio of PVA to AAm was fixed at 1:1, equilibrium water content was around 70wt%.

Effect of charge density on swelling behavior

We copolymerized sodium acrylate with acrylamide, to form a charged hydrophilic network in the hybrid gel. To study the effect of charge density, we varied the fraction of charged segments, Ac/(Ac+AAm). As the fraction of charged segments increases, the equilibrium water content increases due to increasing ion osmosis. The ratio of PVA to (AAm+AAc) was fixed 3:1.

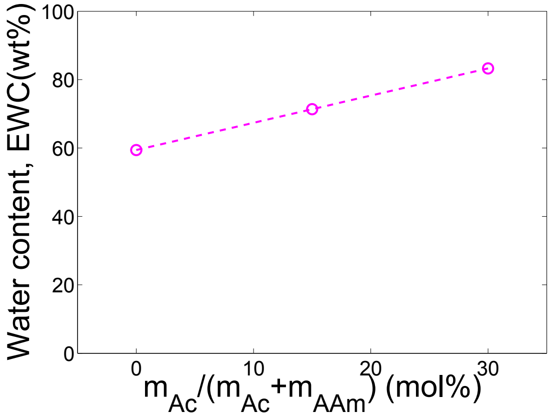


Figure S12. The ion osmosis affects the equilibrium water content. The ionic osmotic pressure was varied with the fraction of charged segment, $m_{Ac}/(m_{Ac}+m_{AAm})$.