

## Electronic Supplementary Information for

### **One-Step Mild Preparation of Tough and Thermo-reversible Poly(vinyl alcohol) Hydrogels Induced by Small Molecules**

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## Materials and methods

### Materials

Caffeic Acid (CA), Protocatechuic acid (PA) 3, 5-Dihydroxybenzoic acid (DHBA), 5-Hydroxyisophthalic acid (HIPA), and Gallic acid (GA) were purchased from Aladdin Biochemical Technology Co, Ltd. (Shanghai, China). Ferulic Acid (FA) was purchased from J&K. Polyvinyl alcohol 1799 were purchased from Sinopharm Chemical Reagent Co., Ltd. (Ourchem). All chemicals were of analytical pure and used without further purification.

### Methods

**Preparation of SM hydrogels.** We take Ferulic Acid (FA) as an example to show the preparation of hydrogel with crystallization induced by small molecule. PVA (25 g) was dissolved in deionized water (100 mL) under stirring and heating at 100 °C for three hours followed by cooling down to 80 °C to prevent the oxidization of -OH group of FA. Then varied FA (from 1 mmol to 15 mmol) was added, making the concentration of PVA 25% and the FA concentration 0.01 to 0.15 mol/L. The mixture was kept for 30 minutes under 80 °C to obtain a homogeneous solution. By pouring the PVA-FA solution into different molds, the FA hydrogels could be obtained. Other small molecule hydrogels were prepared as the same matter.

**Preparation of FT hydrogel.** PVA (25 g) was dissolved in deionized water (100 mL) under stirring and heating at 100 °C for three hours. Then, the solution was cooled down and poured into different molds, and hydrogel samples were obtained after freezing at -20 °C for 16 h and thawing at room temperature for 3 h

### **Characterizations**

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 6700

instrument with attenuated total reflection (ATR) accessories. All of the spectra were acquired at a resolution of  $4\text{ cm}^{-1}$  with four scans.

Ultraviolet–visible (UV–vis) spectra were recorded on an UV-1902- II (Shanghai AUCY Science Instrument Co. Ltd) spectrophotometer in the wavelength range from 380 to 780 nm, with a resolution of 1 nm and a quartz plate as the substrate. Certain amount of PVA and SM homogeneous solutions were poured into a mold and kept for 3 hours to obtain a film state hydrogel with a thickness of about 2.5 mm.

The hydrogels were characterized by wide-angle X-ray diffraction (XRD) with a Bruker AXS D8 using Cu K $\alpha$  radiation in the  $2\theta$  range of  $5\text{--}50^\circ$  with a scan rate of  $5^\circ/\text{min}$ .

The morphologies of hydrogels were studied by scanning electron microscopy (SEM) on a HITACHI S-4800 scanning electron microscope. To make measured samples, the hydrogels were freeze-dried, and quenched under liquid nitrogen to expose their inner cross-section and sputtered with gold.

Tensile experiments were performed at room temperature ( $25^\circ\text{C}$ ) with a loading rate of  $50\text{mm}/\text{min}$  on an Illinois Tool Works 5967X. The hydrogel samples were cut into dumbbell-shaped samples (length 15 mm, width 4 mm, and thickness 2 mm). The maximum compression strength was defined at 60% of compression strain. Compress samples were made into a cylinder (height 12 mm, diameter 15.4 mm).

The viscoelasticity was measured by rheological testing on a TA DHR-3 rheometer with an 8 mm parallel-plate geometry under the oscillation mode. The frequency sweep was scanned from 0.1 to 100 rad/s at  $25^\circ\text{C}$  with a constant strain of 1%. The temperature sweep was measured from 25 to  $75^\circ\text{C}$  ( $5^\circ\text{C}/\text{min}$ ) with a constant strain of 1% and a fixed frequency of 10 rad/s. Through the measurements, the specimens were coated with a thin layer of mineral oil to prevent water evaporation.

The nonisothermal measurement of the PVA hydrogel was performed with a Netzsch 204 F1 differential scanning calorimetry (DSC) (Germany). Granulated samples of 3 mg were heated from 50 to  $250^\circ\text{C}$  at  $20^\circ\text{C}/\text{min}$  under nitrogen atmosphere.

The stability of water erosion was performed in deionized water. The samples was

cut into small pieces of the round shape. Then all those samples were weighed to get the initial weight. Followed by putting them in water for two weeks. Before weighing again, wipe off residual water on the surface of samples with filter papers. The strength of those samples were also characterized.

**Table S1.** Influence of FA concentrations for gelation.

PVA concentration (%)	Small molecule concentration (mol/L)	State
25	0.01	solution
25	0.02	solution
25	0.03	hydrogel
25	0.04	hydrogel
25	0.05	hydrogel

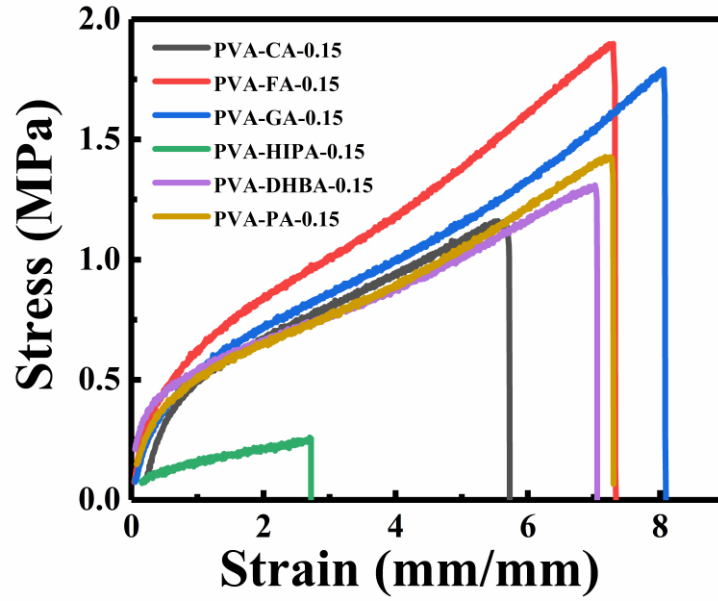
**Table S2.** Physical properties, gelation time, and crystallinity of various kinds of SM hydrogels.

Samples	Small molecular concentration (mol/L)	Crystallinity (%)	Gelation time (min)	Maximum stress (MPa)	Strain-at-break (%)	Compression modulus (MPa)
FT	0	32.81	960	0.74	515	0.17
PVA-FA-0.05	0.05	26.93	29	0.58	610	0.74
PVA-FA-0.1	0.10	38.88	11	1.53	730	1.54
PVA-FA-0.15	0.15	51.49	3	1.98	800	1.88
PVA-CA-0.15	0.15	55.15	3	1.15	640	1.05
PVA-PA-0.15	0.15	52.67	48	1.49	650	0.86
PVA-GA-0.15	0.15	49.75	3	1.84	830	1.75
PVA-HIPA-0.15	0.15	40.42	250	0.61	660	0.70
PVA-DHBA-0.15	0.15	46.60	850	1.38	700	1.24

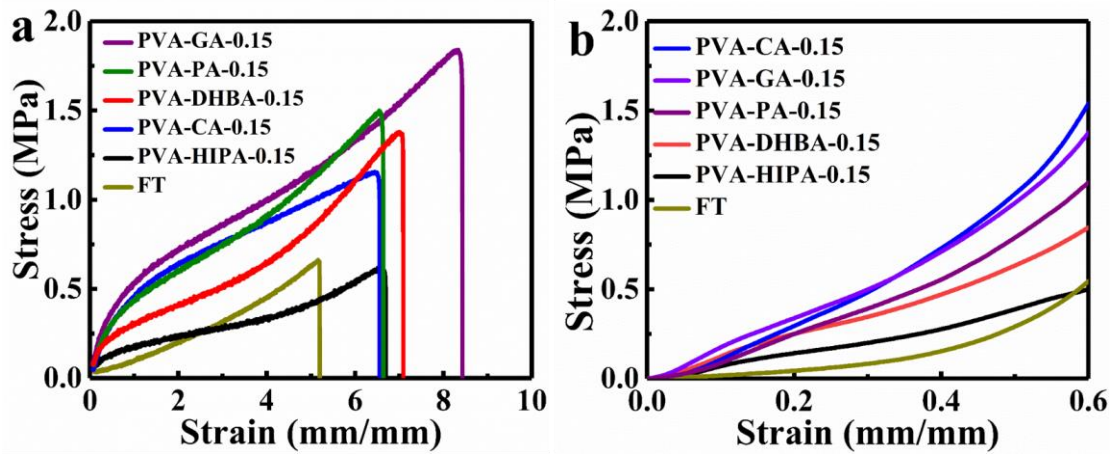
**Table S3.** Weight and strength of SM hydrogels before and after two weeks in water.

Samples	Initial weight (g)	Weight after two weeks in water (g)	Weight change ratio (%)	Initial strength (g)	Strength after two weeks in water (g)
PVA-FA-0.15	0.2078	0.2076	0.096	1.98	1.89
PVA-CA-0.15	0.2103	0.2114	0.523	1.15	1.16
PVA-GA-0.15	0.2069	0.2077	0.386	1.84	1.80
PVA-PA-0.15	0.2033	0.2049	0.787	1.49	1.46
PVA-DHBA-0.15	0.2104	0.2129	1.01	1.38	1.33
PVA-HIPA-0.15	0.2135	0.3685	72.6	0.61	0.26

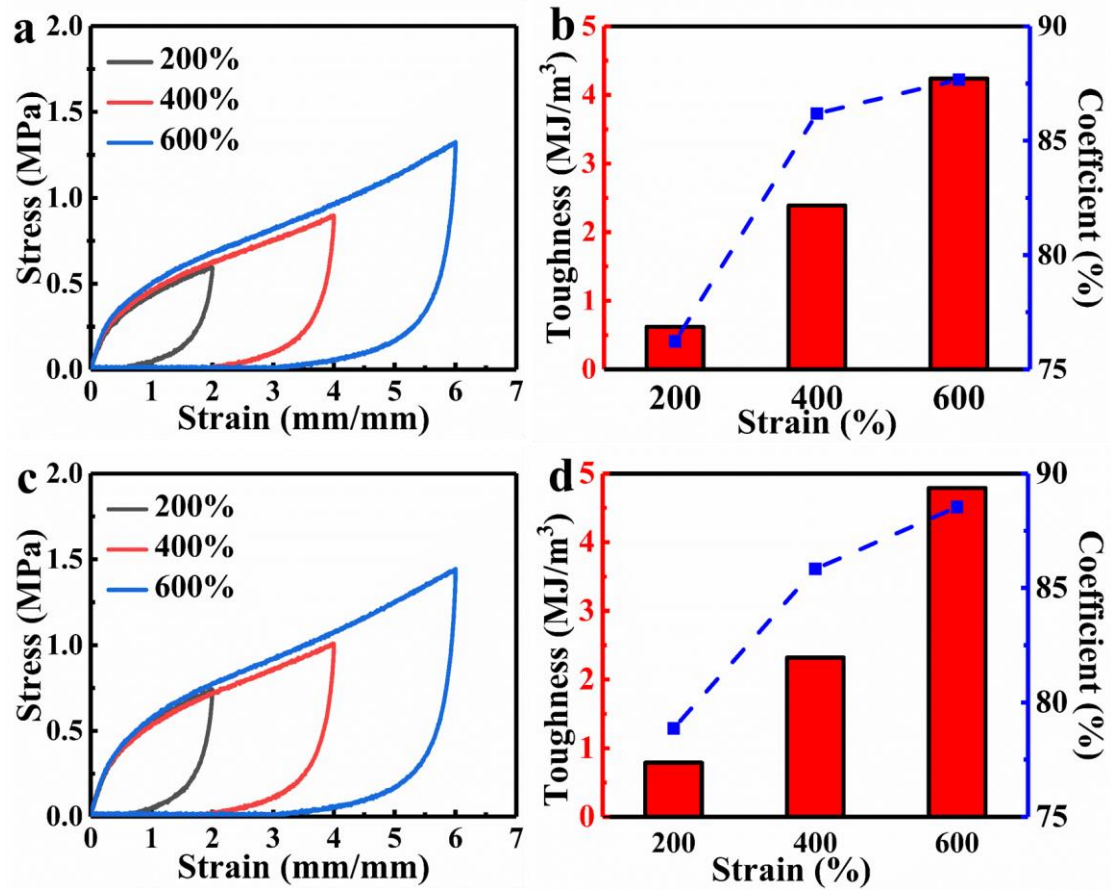
As small molecules are directly mixed with PVA to prepare the SM hydrogels, it is important to investigate the water erosion of the hydrogel. The six SM hydrogels were immersed into excess water for two weeks and weight and strength were then tested. All SM hydrogels except PVA-HIPA-0.15 showed negligible weight changes (less than 1%) after two weeks. Moreover, the strength of the hydrogels after soaking showed almost same value as the original one, indicating the weight stability was not due to the water invasion but good stability of the hydrogels. However, for the PVA-HIPA-0.15 hydrogel, it showed the lowest values of  $G'$  and crystallinity (Fig. S6 and Fig. S8b), indicating the lowest crosslinking density in PVA-HIPA-0.15. Thus, the chains in PVA-HIPA-0.15 might be loosed and the hydrogel swelled in water, resulting in large weight and strength changes. Accordingly, most of the SM hydrogels had good stability under water erosion. This result also confirmed the stable crystal structure induced by the small molecules.



**Fig. S1** Tensile strain and stress curves of different SM hydrogels at a concentration of 0.15 mol/L after soaking in water for two weeks.

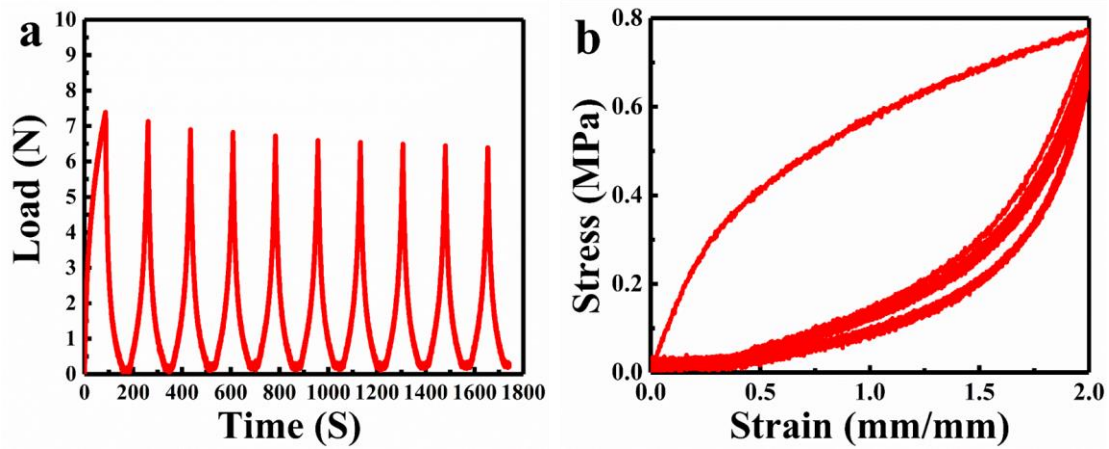


**Fig. S2** a) Tensile and b) compress strain and stress curves of FT hydrogel and different SM hydrogels at a concentration of 0.15 mol/L.



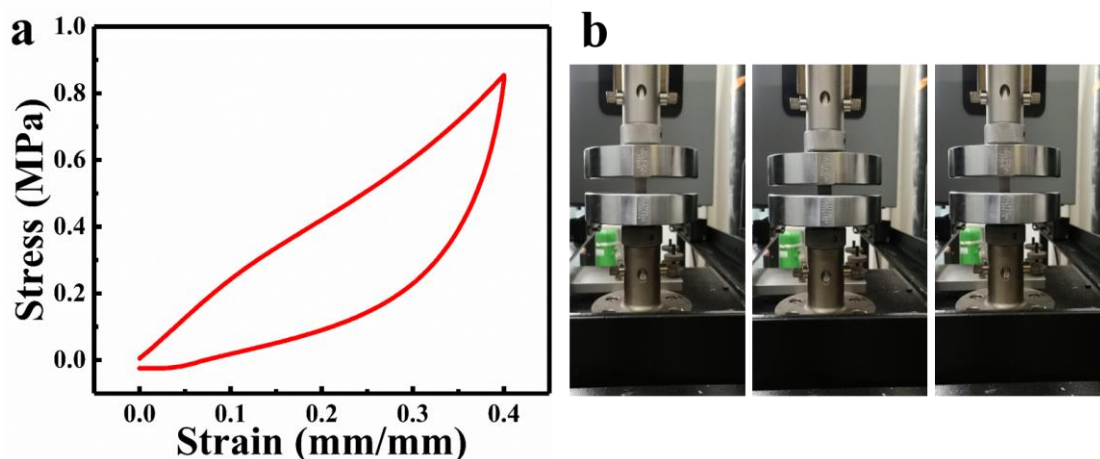
**Fig. S3** a) Loading–unloading curves at different strains and b) the corresponding dissipated energies of the PVA-FA-0.1 hydrogel. c) Loading–unloading curves at different strains and d) the corresponding dissipated energies of the PVA-FA-0.15 hydrogel.





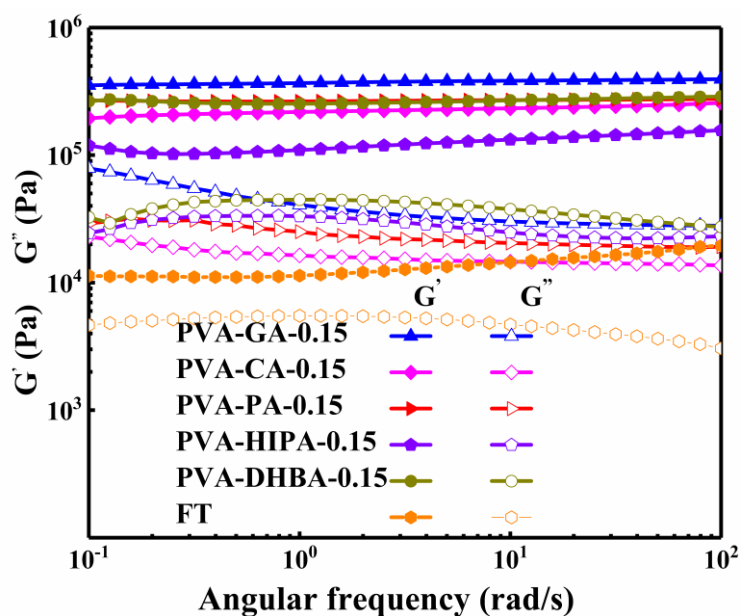
**Fig. S4** a) The load–time curve and b) stress–strain curve of ten successive tensile–relaxation cycles of PVA-FA-0.15 hydrogel under 400% deformation.

To further investigate the energy dissipation, PVA-FA-0.15 hydrogel was chosen as an example to detect the energy dissipation under 200% deformation. As shown in Fig. S4a, the maximum force decreased from 7.2 to 6.4 N in the force–time curve, 88.4% of its initial value after ten cycles of loading–unloading. The PVA-FA-0.15 hydrogel dissipated massive energy during the first cycle as shown in Fig. S4b, because the slip of the crystalline phase cannot be immediately restored. Whereas, the following nine cyclic curves almost overlapped and displayed similar hysteresis energy, which was dedicated by the instantaneously healable hydrogen bonding in SM hydrogels.

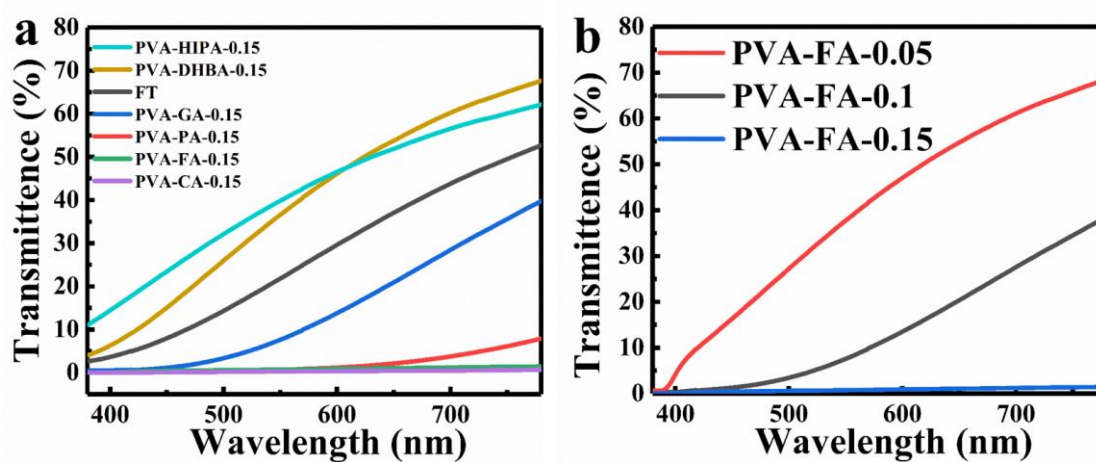


**Fig. S5** a) Compression–relaxation curves of PVA-FA-0.15 hydrogel. b) Photographs of PVA-FA-0.15 hydrogel before, during and after compression.

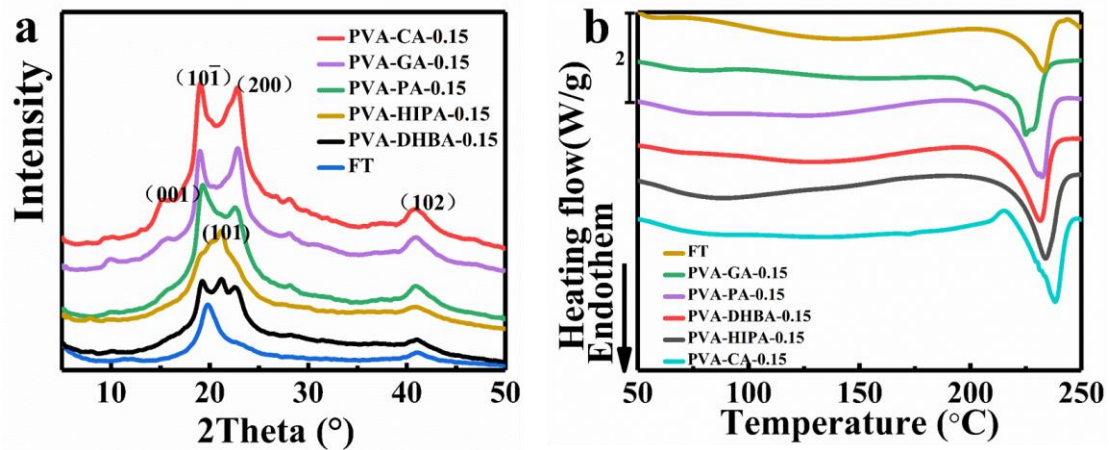
The recovery properties of SM hydrogels are very important to the application of the hydrogel, and PVA-FA-0.15 was chosen as an example to be tested under 40% of compress deformation. As it shown in Fig. S5a, the PVA-FA-0.15 hydrogel was compressed to 60% of strain and retained near 6% permanent deformation after unloading. The whole procedure could also be observed from Fig. S4b. It was clear that the PVA-FA-0.15 hydrogel did not show significant deformation after 40% of compress deformation, indicating the good compress recovery property.



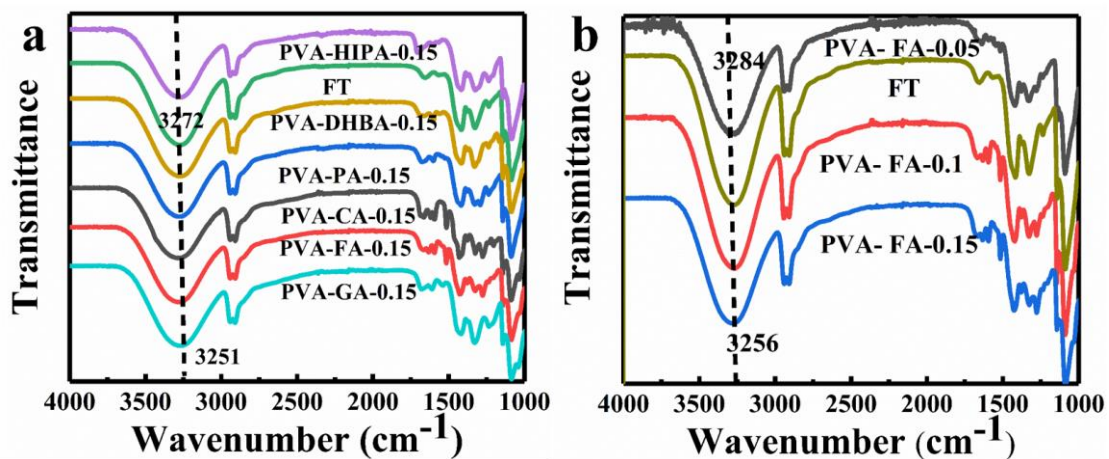
**Fig. S6**  $G'$  and  $G''$  as a function of frequency for FT hydrogel and different SM hydrogels at a concentration of 0.15 mol/L.



**Fig. S7** UV-vis spectra of a) FT hydrogel and different SM hydrogels at a concentration of 0.15 mol/L. b) PVA-FA-0.05, PVA-FA-0.1, and PVA-FA-0.15 hydrogels.



**Fig. S8** a) XRD patterns of FT hydrogel and different SM hydrogels at a concentration of 0.15 mol/L. b) Representative DSC thermographs of FT hydrogel and different SM hydrogels at a concentration of 0.15 mol/L.



**Fig. S9** ATR-FTIR spectra of a) FT hydrogel and different SM hydrogels at a concentration of 0.15 mol/L. b) FT hydrogel and PVA-FA hydrogels at different concentrations.