## **Electronic Supplementary Information (ESI)**

# A general strategy for strengthening and toughening physical hydrogels

### via anti-Hofmeister sequence solid salting-out

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#### **Experimental section**

#### Differential scanning calorimetry (DSC) analysis

DSC analysis was conducted on a Mettler Toledo DSC3. Before DSC measurement of hydrogels, the amorphous PVA polymer chains in the hydrogel were crosslinked with excessive glutaraldehyde, which reduced the further crystallization during drying. Hydrogels were placed in a Tzero pan and heated from 50°C to 250°C at 10°C min–1 under a nitrogen atmosphere. The integration of the endothermic transition from 200°C to 250°C gives the enthalpy for the melting of the crystalline domains per unit mass of the dry samples. Therefore, the mass of the crystallinity (m<sub>crystalline</sub>) can be calculated according to the following formula:

$$mcrystalline = Hcrystalline/H0crystalline$$
(1)

where  $H_{crystalline}$  is the integration of the endothermic peaks of the DSC curve from 200°C to 250°C for melting the crystalline domains per unit mass, and  $H^0_{crystalline}$  is the thermodynamic enthalpy of fusion for 100 wt% crystalline PVA (138.6 J g<sup>-1</sup>).

#### Small-angle x-ray scattering (SAXS)

SAXS measurements were performed on Anton paar Saxsess MC2 with an X-ray of  $\lambda = 0.154$  nm. The momentum transfer (*q*) range was 0.003–0.185 Å<sup>-1</sup>, and the exposure time was set as 300 s. To identify the location of the scattering peak more clearly, this study multiplied the scattering intensity (*I*) with the square of *q* and plotted it as  $Iq^2$ . The average distance between adjacent crystalline domains (*L*) can be estimated using the Bragg expression:

$$L = 2\pi/qmax \tag{2}$$

where  $q_{\max}$  is the critical vector corresponding to the peak intensity.

#### Wide-angle x-ray scattering (WAXS)

WAXS testing was performed on a Xenoc 2.0 instrument with an X-ray of  $\lambda = 0.154$  nm, operated at 40 kV and 200 mA. WAXS profiles were collected in the 2 $\vartheta$  range of 5° to 35° with a speed of 2°/min. The average size of crystalline domains (*D*) can be estimated using the Scherrer equation:

$$D = k\lambda/(\beta \cos\theta)$$
(3)

where the dimensionless shape factor (k) is set as 1 if the shape of the crystalline domain is approximated as a sphere and  $\lambda$  is the wavelength of X-ray diffraction. Moreover,  $\vartheta$  is the Bragg angle, and  $\beta$  is the full width at half maximum of the peak.

#### Water vapor permeability testing (WVP)

The WVP of the hydrogel film was measured according to the ASTM E96 standard (ASTM, 1995). First, 1.5 g of CaCl<sub>2</sub> (0% relative humidity) was added to glass bottles. The circular hydrogel films were then placed over the glass bottles, which were placed in a desiccator containing saturated NaCl solution (75% relative humidity) at 25°C. The glass bottles were periodically weighed on a scale with a 0.0001 g resolution. The WVP was calculated according to the following formula:

$$WVP = \Delta m \times L/\Delta t \times A \times \Delta p$$

where  $\Delta m$  (g) is the increase in the weight of the test bottle, *L* (m) represents the average film thickness,  $\Delta t$  (s) represents the duration of the increase in weight of the test bottle, *A* (m<sup>2</sup>) represents the permeation area of the hydrogel film sample, and  $\Delta p$  (Pa) represents the partial vapor pressure.

(4)

#### Molecular dynamics simulation

The diffusion/aggregation behavior of PVA chains at 30%, 60%, and 90% moisture content was simulated using Materials Studio software. The 3D Atomistic Doctumnt module was established to create water molecules and PVA monomers, and set the polymerization degree of PVA. The Forcite Geometry Optimization module was used to optimize the structures of each component separately. The Forcefield was selected as COMPASS III, and the Algorithm was selected as smart. Construct boxes with a density of 1g/cm<sup>3</sup> using the Amorphous Cell construction function (with the same density but different molecular ratios and box sizes), and then fill the boxes with water molecules (H<sub>2</sub>O) and PVA in proportion using the Amorphous Cell-packing function. Using the Forcite-Dynamics module, perform molecular dynamics simulations on the constructed model to investigate the diffusion/aggregation behavior of PVA chains at 30%, 60%, and 90% moisture content. Among them, the temperature is maintained at

298K, the pressure is maintained at 1 bar, the ensemble is selected as NVT, and the electrostatic force and van der Waals force are selected as atom based and ewald, respectively.



Before solid salting out

After solid salting out

Fig. S1 AHSS-PVA with good shape designability.



Fig. S2 The transmittance of PVA hydrogel and AHSS-PVA.



Fig. 3 Variation in hydrogel surface area during six solid salting-out cycles.



**Fig. S4** Atomic force microscope images of (a) PVA hydrogel cross-section and (b) AHSS-PVA cross-section.



**Fig. S5** (a, b) After the thickened PVA hydrogel was completely solid salting-out, the SEM image showed a dense structure.



**Fig. S6** Molecular dynamics simulation of diffusion and aggregation states of PVA molecular chains at different moisture contents.



**Fig. S7** Preparation of AHSS-PVA by solid salting-out and layer-by-layer self-assembly of PVA molecular chains induced by aqueous phase separation.



**Fig. S8** The photographs of PVA hydrogels prepared by solid salting-out at different times.



Fig. S9 (a) Tensile stress-strain curves and (b) toughness of PVA hydrogel after solidsalting-outatdifferenttimes.

![](_page_13_Picture_0.jpeg)

**Fig. S10** The photographs of PVA hydrogels prepared by solid salting-out at different temperatures.

![](_page_14_Figure_0.jpeg)

**Fig. S11** (a) Tensile stress–strain curves and (b) toughness of PVA hydrogel after solid salting-out at different temperatures.

![](_page_15_Figure_0.jpeg)

**Fig. S12** (a) Tensile stress–strain curves and (b) toughness of natural dry PVA hydrogel with low moisture content (27.16%). (c) Tensile stress–strain curves and (b) toughness of liquid salting-out PVA hydrogel.

![](_page_16_Figure_0.jpeg)

**Fig. S13** (a) Tensile stress–strain curves, (b) toughness and tensile modulus of AHSS-PVA and AHSS-PVA<sub>15%</sub>. (c-d) SEM images of AHSS-PVA<sub>15%</sub> cross-section after fracture.

![](_page_17_Figure_0.jpeg)

**Fig. S14** (a) Solid salting-out enhanced (a) stress-strain curves and (b) comparison of toughness and tensile modulus of  $AHSS-PVA_{15\%}$  and  $AHSS-C_{3.5\%}$  PVA.

![](_page_18_Figure_0.jpeg)

**Fig. S15** (a) The recyclability of solid salting-out strategy reduces resource waste. (b) Mass changes of solid salt blocks during 6 cycles of solid salting-out.