

Supplementary Materials

Strong and tough polyvinyl alcohol hydrogels with high intrinsic thermal conductivity

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CHARACTERIZATIONS

Fourier transform infrared (FT-IR) Spectroscopy: The samples were characterized using an attenuated total reflection accessory of a Tensor 27 FT-IR spectrometer from Bruker, Germany.

X-ray diffraction (XRD): The crystalline structure of the samples was analyzed and characterized using a D8 Advance X-ray diffractometer equipped with a Cu-targeted radiation source from Bruker, Germany. The scanning speed was 10°/min with the diffraction angle of $2\theta = 10^\circ$ to 60° . The step size was 0.02°/step.

Small angle X-ray scattering (SAXS): The micro-structure of the hydrogels was analyzed using a Xeuss type small angle X-ray diffractometer from Xenocs SAS, France. The 2D-SAXS images were obtained by processing through the test software (XSACT) at the end of the shooting. The 2D-SAXS images were processed by FIT 2D software to obtain the corresponding intensity-azimuth curves and intensity-scattering vector curves in the orientation direction, respectively. The degree of orientation of the hydrogel was calculated by:

$$\Pi = \frac{180 - FWHM}{180} \quad (S1)$$

where Π is the degree of orientation; $FWHM$ is the full width at half height in the intensity-azimuth curve of the sample, which is the width of the diffraction peak where the intensity is half of the peak intensity, and the value was calculated by peak fitting the intensity-azimuth curve of the sample using Origin software.

The spacing of crystal domains along the orientation direction of the hydrogel was calculated by:

$$L = \frac{2\pi}{q_{max}} \quad (S2)$$

where L is the crystal domain spacing; q_{max} is the scattering vector value at the peak in the modified intensity-scattering vector curve in the orientation direction of the sample.

Differential scanning calorimetry (DSC): The crystallinity of the samples was analyzed using a DSC1 calorimeter from Mettler-Toledo, Switzerland. The temperature range of the test was 50~250°C under a nitrogen atmosphere. The temperature increase and decrease rate was 20°C/min. Hydrogels were pretreated as follows prior to testing: hydrogels were immersed in a mixture of 10 mL of glutaraldehyde, 0.5 mL of hydrochloric acid, and 50 mL of deionised water for 6 h. The samples were then immersed in deionized water for 24 hours to remove unreacted glutaraldehyde and hydrochloric acid, and were placed in a 50°C oven to dry for 24 hours. The crystallinity

of the hydrogel in the dried state was calculated by:

$$X_d = \frac{\Delta H_m}{\Delta H_c} \times 100\% \quad (\text{S3})$$

Where X_d is the crystallinity of the PVA hydrogel in the dry state, ΔH_m is the enthalpy of melting of the PVA hydrogel in the dry state, and ΔH_c is the enthalpy of melting when the PVA is a 100% crystalline structure, which is $138.6 \text{ J} \cdot \text{g}^{-1}$.

The crystallinity of the hydrogel was calculated by:

$$X_w = X_d(1 - C_w) \quad (\text{S4})$$

where X_w presents the crystallinity of the original hydrogel; X_d represents the crystallinity of the hydrogel in the dry state; and C_w is the water content of the hydrogel.

Scanning electron microscopy (SEM): The micro-morphology of the samples was characterized using a Verios G4 SEM from FEI, USA. The samples were treated as follows before testing: the hydrogel was fixed on a PTFE plate and freeze-dried, and then placed in liquid nitrogen for 10 minutes for brittle fracture along the orientation direction.

Polarized optical microscope (POM): The crystal structure of the hydrogel samples was characterized using a POM (WMP-6880) from Shanghai Wumo Optical Instrument, China equipped with a hot-stage. The operation was as follows: the POM was adjusted to the cross-polarization mode, in which the polarizer and the analyzer were perpendicular to each other. The sample orientation was adjusted so that the sample was oriented at 0° or 45° to the polarizer.

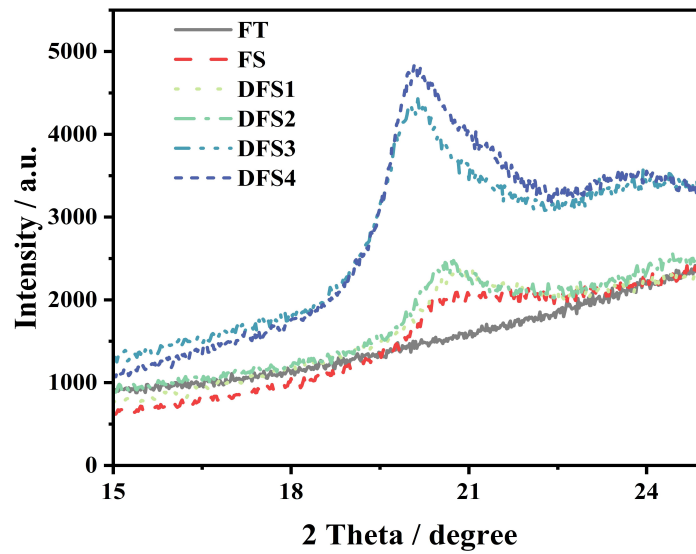
Infrared thermography: A Ti300 infrared thermal imager from Fluke, USA was used to record the temperature changes on the surface of the test samples.

Thermal conductivity: The thermal conductivity (λ) of the hydrogels was tested using the flat module by a thermal constant analyzer (TPS2200) from Hot Disk, Sweden.

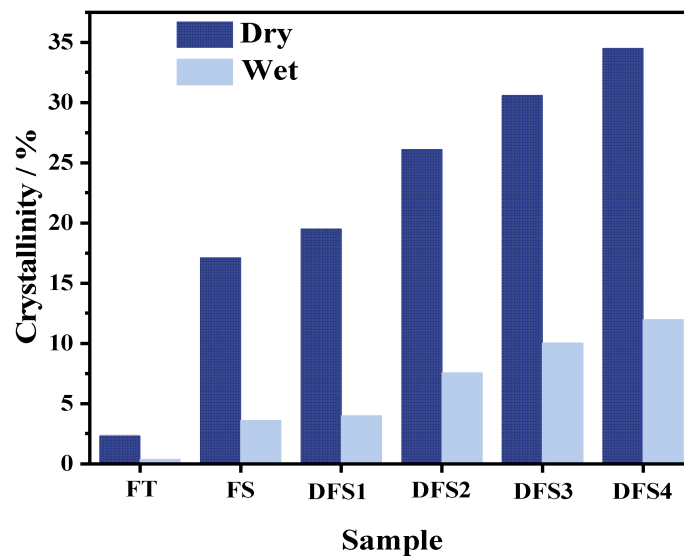
Mechanical properties: The tensile strength, elongation at break, toughness, and modulus of elasticity of the hydrogels were tested using a ST-D200 universal mechanical tester equipped with a 200 N loading element from SYSTEX Instruments Co. Ltd. of China. The tensile speed was 10 mm/min. The specific conditions were as follows: the hydrogel was cut into dog-bone shaped specimens with a width of 2 mm for the conventional tensile test. The thickness of individual specimen was measured with a vernier caliper, usually around 2 mm.



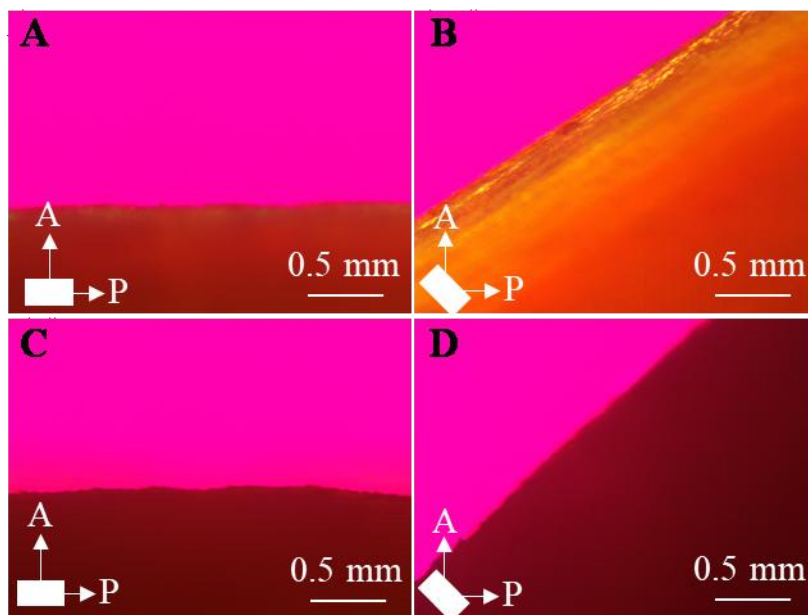
Supplementary Figure 1. Digital image of DFS PVA hydrogel with the stretching ratio of 4.



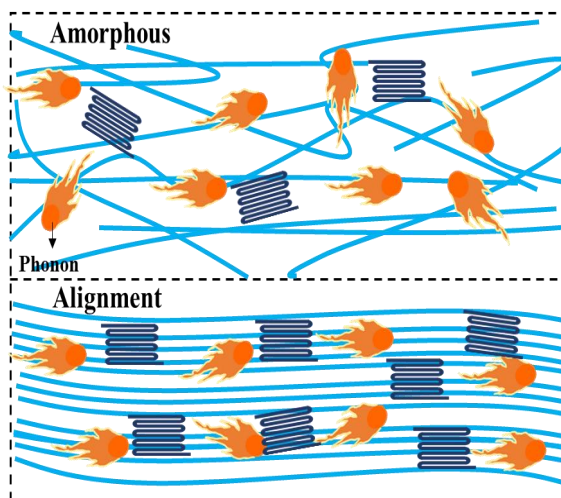
Supplementary Figure 2. Zoomed in XRD curves between 15~25° of FT PVA, FS PVA, and DFS PVA hydrogels with different stretching ratios.



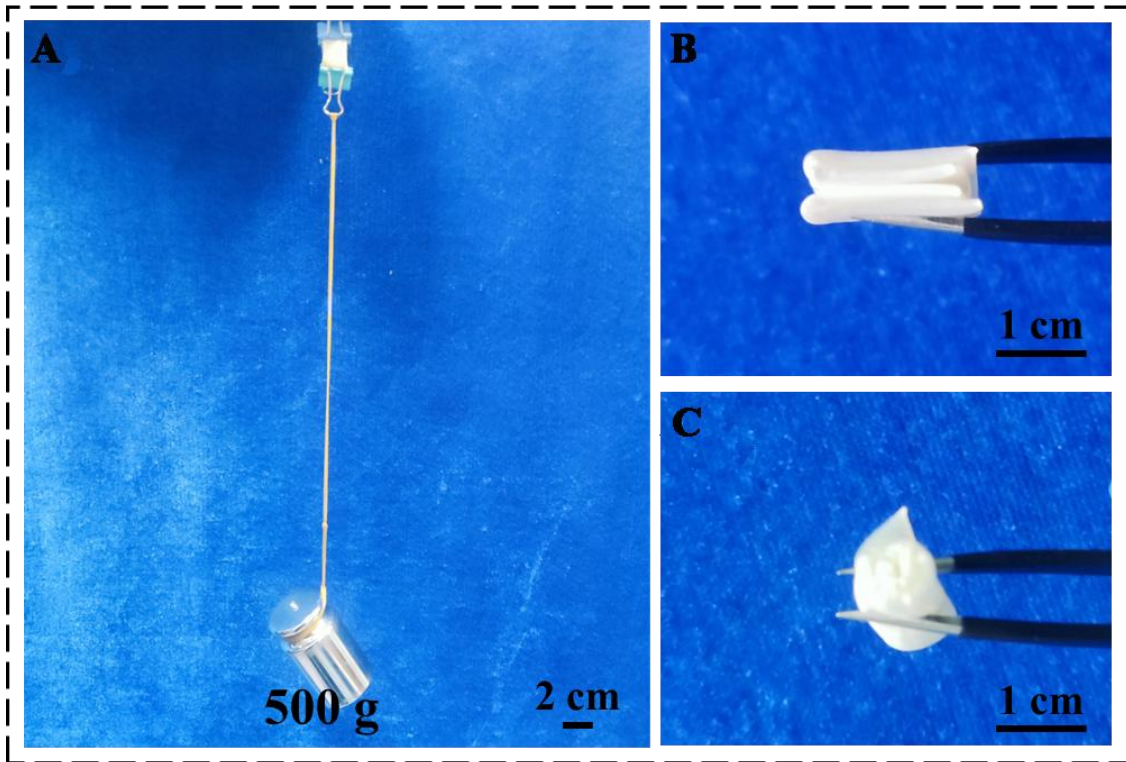
Supplementary Figure 3. Calculated crystallinity in dried and wet state of FT PVA, FS PVA, and DFS PVA hydrogels with different stretching ratio.



Supplementary Figure 4. POM images of DFS1 (A and B) and FS (C and D) PVA hydrogels (taken in cross-polarization mode; A: analyzer; P: polarizer).



Supplementary Figure 5. Schematic diagram of the thermal conduction mechanism for DFS PVA hydrogels.



Supplementary Figure 6. Digital images of DFS4 PVA hydrogel with 15 wt% PVA carrying a 500 g weight (A), the folded (B), and curled (C) state.

Supplementary Table 1. Comparison of the thermal conductivities and mechanical properties of FT PVA and DFS4 PVA hydrogels

Properties	FT PVA hydrogel	DFS4 PVA hydrogel
λ (W/(m·K))	0.52	1.25
Tensile strength (MPa)	0.4	27.1
Toughness (MJ·m ⁻³)	0.32	25.3
Elastic modulus (MPa)	0.07	21.5