

Supporting Information

3D Printing of Polyvinyl Alcohol Hydrogels Enabled by Aqueous Two-Phase System

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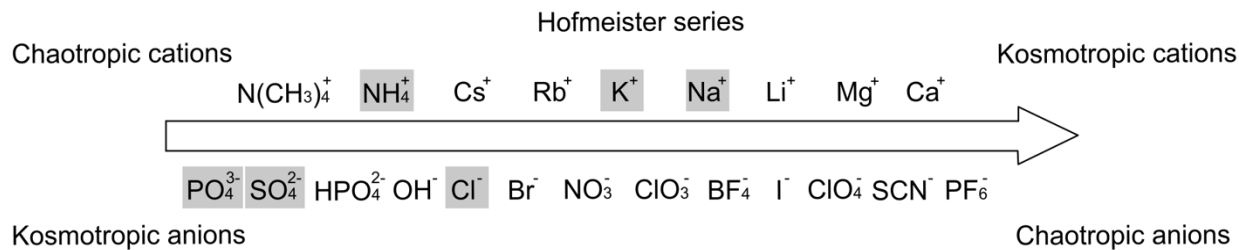


Figure S1. A Hofmeister series showing both anions and cations of growing size. The series provides a qualitative ranking of the ions according to their ability to solubilize (salting in) or precipitate (salting out) proteins in solutions. Kosmotropes are to make water structures, which enhance the hydrophobic interactions and exclude the hydrophobic substances from the aqueous solutions. In contrast, chaotropes are to break water structures, which increase the solubility of hydrophobic substances in water. The salts Na_2SO_4 , $(NH_4)_2SO_4$, K_3PO_4 , and $NaCl$ are selected to understand their effects on the salting out of PVA in this study.

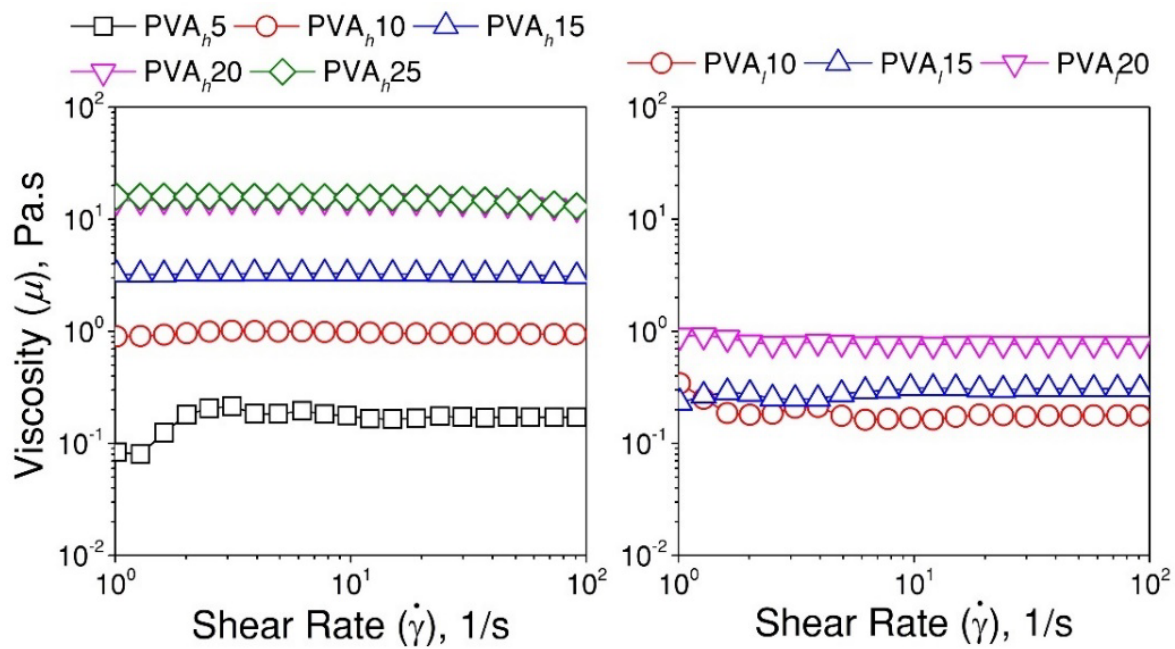


Figure S2. Rheological characterization of PVA inks. Plots showing viscosity (μ) as a function of applied shear rate ($\dot{\gamma}$) for high MW PVA (5 – 25% w/w) and low MW PVA (10 – 20% w/w).

Volume of PVA_h(25) - 2 mL

Na₂SO₄ (% w/w)

2 4 6 8



○ ○ ○ ○

K₃PO₄ (% w/w)

2 4 6 8



○ ○ ○ ○

(NH₄)₂SO₄ (% w/w)

2 4 6 8



○ ○ ○ ○

○ Soluble/delayed salting-out ○ *In situ* salting-out

Figure S3. Optical images showing the effect of concentration of Na₂SO₄, K₃PO₄ and (NH₄)₂SO₄ on *in situ* precipitation of PVA_h(25) solution.

PVA_h(25)-S/ Na₂SO₄(12)

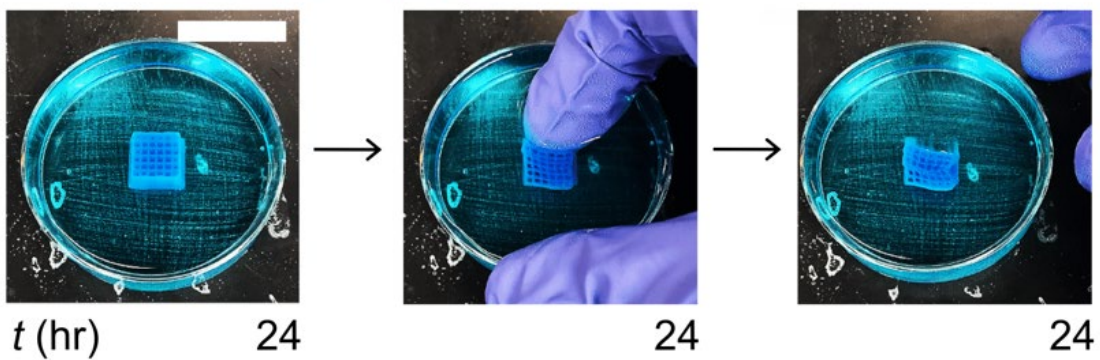


Figure S4. Photographs showing plastic deformations of the printed object of PVA_h(25)-S in Na₂SO₄(12) while detaching from the substrate. Scale bar = 1 cm.

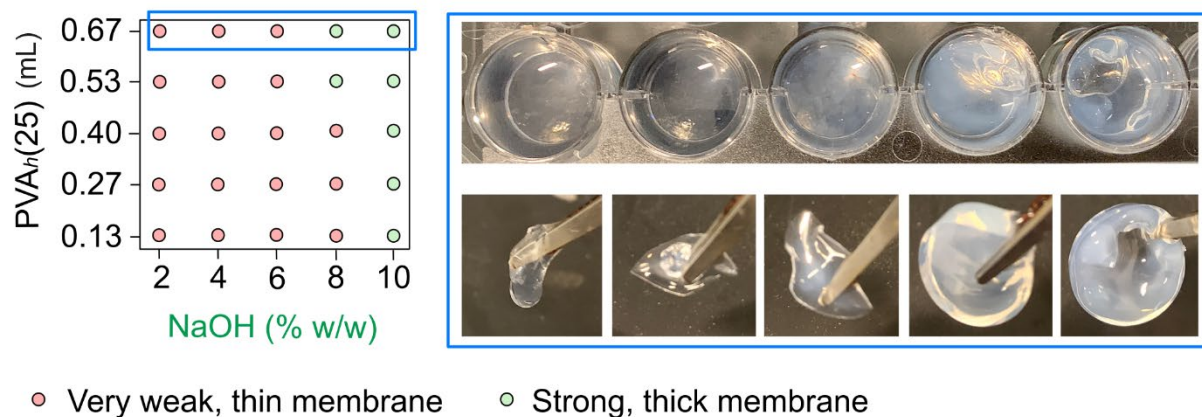


Figure S5. Effect of concentration of NaOH on gelation or physical crosslinking of PVA solutions.

PVA_h(25)-A/NaOH(20)

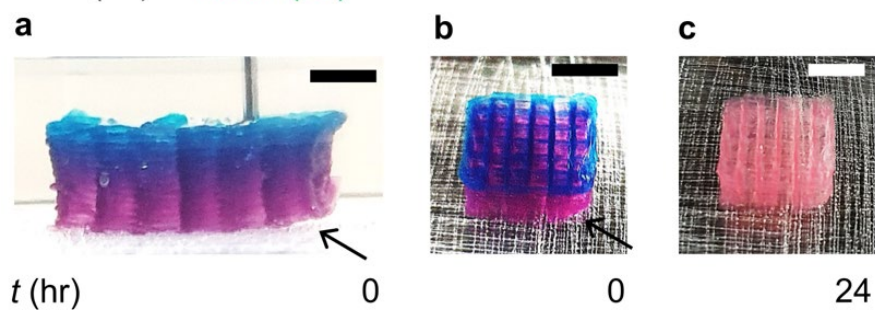
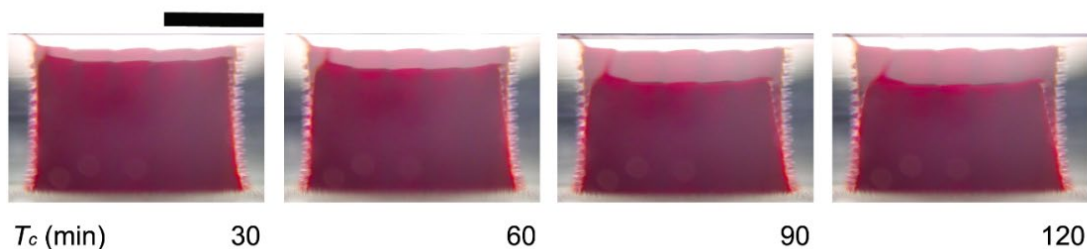


Figure S6. Warping and detachment of the printed object from the substrate: **(a)** during printing and **(b)** after printing. These deformations occurred during printing due to the fast crosslinking of PVA_h chains at high concentrations of NaOH in the embedding media (NaOH(20)). The black arrows show the detachment of the printed object from the substrate. The color of the dye mixed with PVA_h ink changed from blue to violet while printing, possibly due to the reaction of the dye with NaOH. The gradual color change was indicative of the progress of the physical crosslinking of PVA_h. **(c)** Optical image of the 3D printed object showing the change in the color to light violet after 24 hr of printing. Scale bars = **(a)** 2 mm, and **(b-c)** 5 mm.

a Sagging and spreading of PVA_h(20)-S/Na₂SO₄(8) after the completion of printing

Post-printing contact time, T_c

(Opaque image in the background is for $T_c = 0$, immediately after printing)



b Effect of T_c on the behaviour of the printed objects after dialysis (swelling/no swelling)

PVA_h(20)-Hy/Na₂SO₄(8)/NaOH(1) → ① $T_c = 10$ min, ② $T_c = 30$ min, ③ $T_c = 24$ hr

PVA_h(20)-Hy/Na₂SO₄(8)/NaOH(4) → ④ $T_c = 10$ min, ⑤ $T_c = 30$ min, ⑥ $T_c = 24$ hr

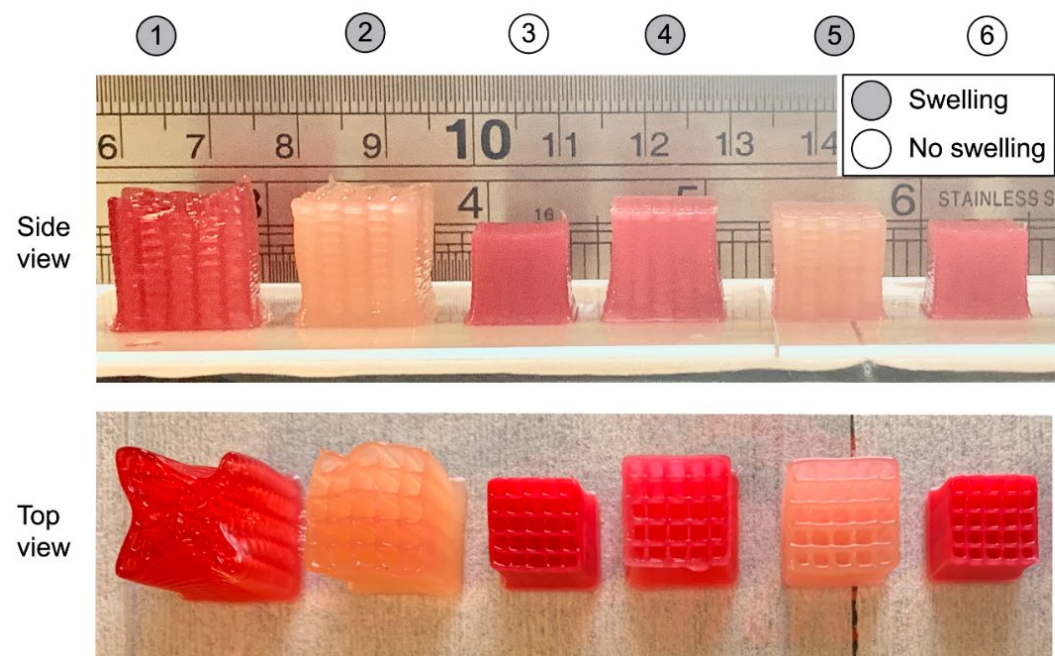


Figure S7. A proposed mechanism of formation of PVA-Hy when PVA ink was printed in an embedding media containing both salt and alkali. **(a)** Optical images showing spreading and sagging of PVA_h(20)-S after printing in Na₂SO₄(8) with the increase in post-printing contact time (T_c). **(b)** Optical images of printed objects of PVA_h(20)-Hy showing the effect of T_c on printed structures when the ink was printed in embedding media containing Na₂SO₄(8)/NaOH(1) and Na₂SO₄(8)/NaOH(4). Scale bar = **(a)** 5 mm.

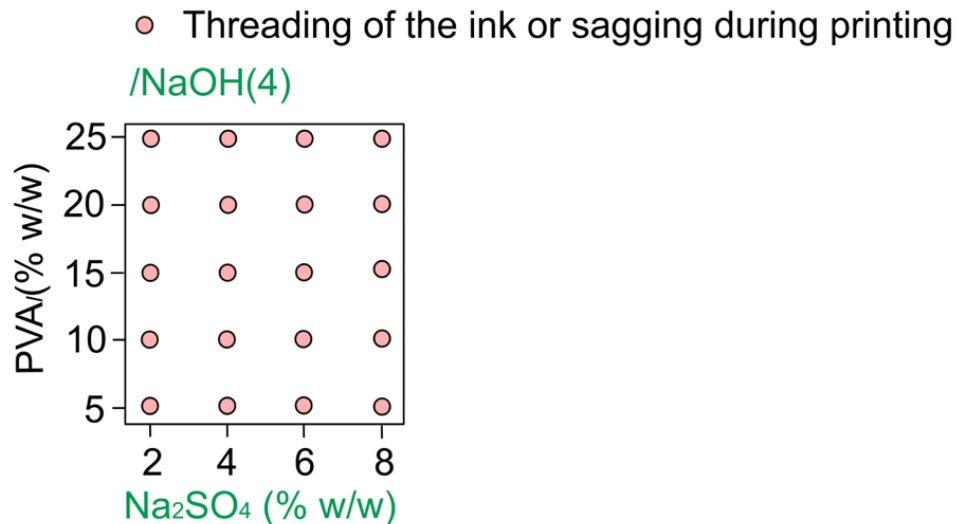


Figure S8. A plot showing fidelity of printing of PVA inks prepared with different concentrations of PVA₁ when printed in NaOH(4) with varying concentrations of Na₂SO₄ (2 – 8% w/w). Inks prepared with PVA₁ were not suitable for DIW 3D printing. Threading of the ink due to the attachment of the ink to the nozzle tip or spreading of the ink was observed during printing. The threading of the inks was mainly due to the low viscosity of PVA₁ inks.

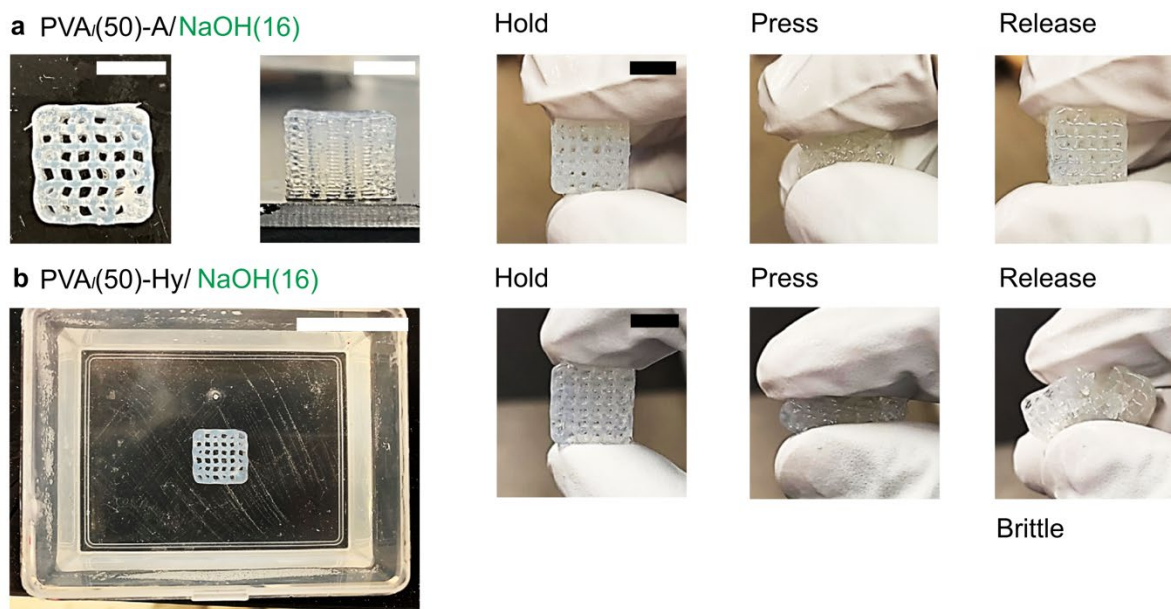


Figure S9. (a) Optical images showing top and side view of the 3D printed PVA_l(50)-A in NaOH(16), and its elastic and flexible nature. (b) Optical image showing washing of 3D printed PVA_l(50)-A in DI water to remove Na⁺ ions and its degradation after removing the Na⁺ ions. The printed object collapsed into pieces when compressed. Scale bar = (a) 1 cm, and (b) 2 cm (white) and 1 cm (black).

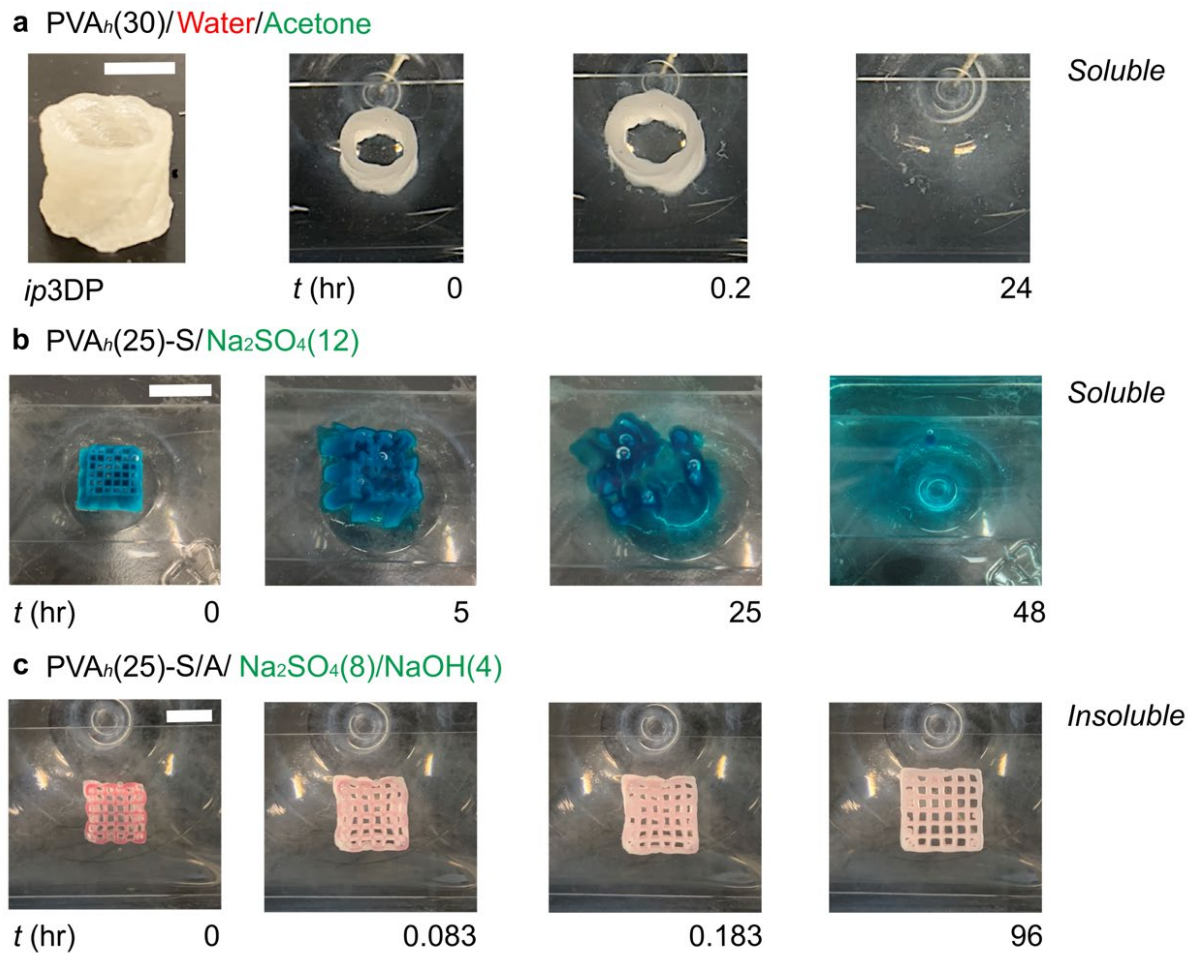
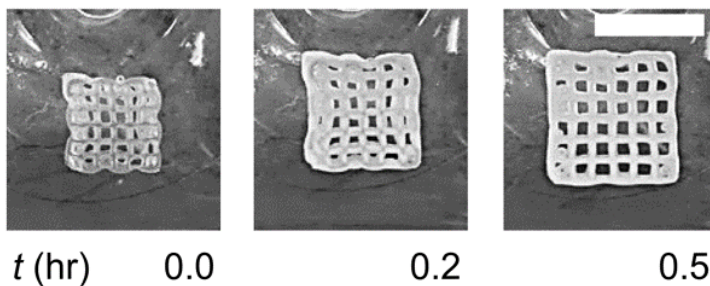


Figure S10. Optical images showing the dissolution of the 3D printed objects: (a) PVA_h(30), (b) PVA_h(25)-S and (c) PVA_h(25)-S/A in DI water. PVA_h(30): PVA_h dissolved in water and printed in acetone by *ip3DP*. PVA_h(25)-S: PVA_h dissolved in water and printed in Na₂SO₄(12). PVA_h(25)-S/Na: PVA_h dissolved in water and printed in Na₂SO₄(8)/NaOH(4). Scale bars = 5 mm.

a Dried PVA_h(25)-Hy in DI water



b Swollen PVA_h(25)-Hy in air

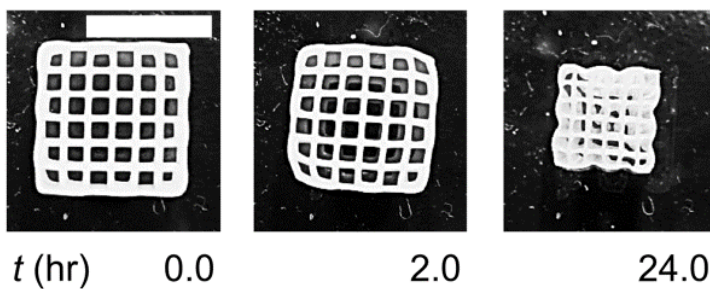
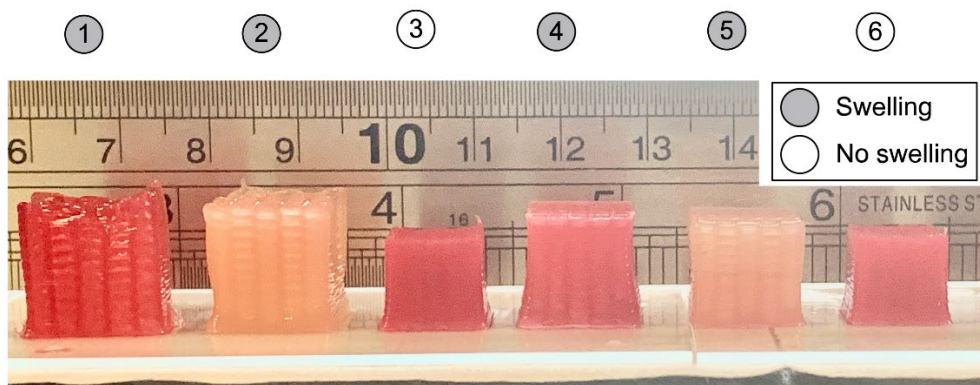


Figure S11. Optical images showing (a) swelling of the dried PVA_h-Hy in DI water at room temperature and (b) drying of the swelled PVA_h-Hy in air at room temperature. Scale bars = 1 cm.

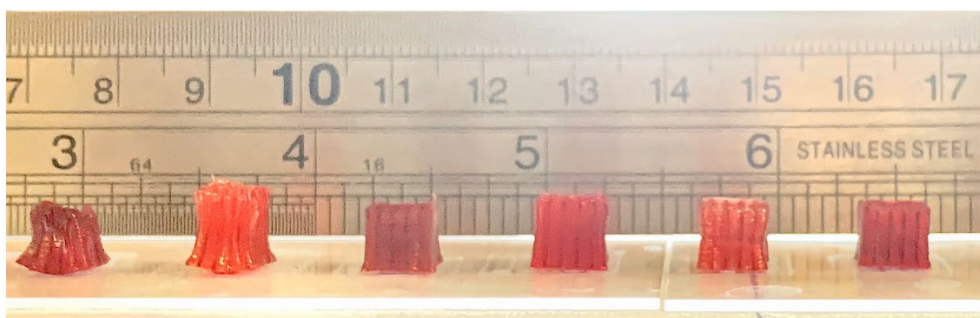
PVA_h(20)-Hy/Na₂SO₄(8)/NaOH(1) → ① T = 10 min, ② T = 30 min, ③ T = 24 hr

PVA_h(20)-Hy/Na₂SO₄(8)/NaOH(4) → ④ T = 10 min, ⑤ T = 30 min, ⑥ T = 24 hr

a 3D-printed objects of PVA_h(20)-Hy



b drying at room temperature for 5 days ↓



Volume Shrinkage (%)

~80.5

~75.3

Figure S12. The volume shrinkage (%) of PVA_h(20)-Hy observed after drying at room temperature for five days.

PVA_h(25)-Hy/ Na₂SO₄(8)/NaOH(4)



T (°C) 60 70 80

Figure S13. Thermal stability of the printed PVA_h(25)-Hy when immersed in water at 60 °C, 70 °C and 80 °C for 2 h. PVA_h(25)-Hy was stable below 70 °C, and no swelling was observed. PVA_h(25)-Hy dissolved entirely above 90 °C. Scale bar = 1 cm.

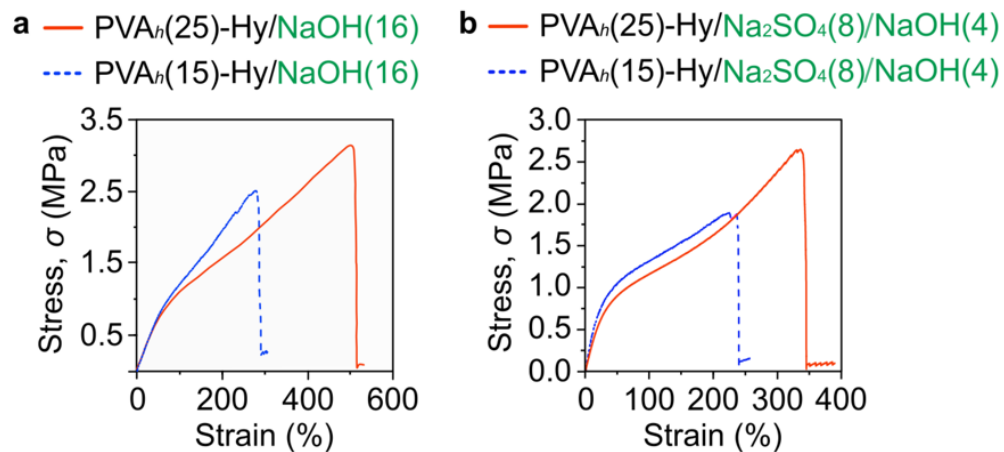


Figure S14. Stress-strain curves of PVA_h(25)-Hy and PVA_h(15)-Hy fabricated with NaOH(16) and Na₂SO₄(8)/NaOH(4), respectively.