Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.


# Supporting

## 1. Fourier transform infrared (FTIR) spectra

4-arm-PEG-NHS and LZM were added into TA solution in a ratio of 1:1 respectively. The mixtures were freeze-dried into PEG+TA and LZM+TA powders. Pure 4-arm-PEG-NHS,LZM and TA powders were used as the control samples. Using a TENSOR-27 spectrometer (Bruker, German), we scanned the five samples in the frequency range of 4000-400 $cm^{-1}$ after the progress of the potassium bromide tableting.

## 2. Hydrogel composition analysis

In our experiment, the content of each component in the prepared hydrogels were analyzed by weighing method. PEG-LZM-TA 0 (DH) hydrogel was prepared through the solvent exchange method, and the weight of freeze-dried PEG-LZM-TA 0 (DH) was recorded as $W_a$. The weight of PEG-LZM-TA x (DH) hydrogel (x=20,30,40,50 mg/mL) was recorded as $W_b$, and the weight of freeze-dried gel was recorded as $W_c$. $W_t$ represents the original weight of TA in the DMSO solvent used to prepare hydrogel.

According to the following formulas (1.1)、(1.2 )and (1.3), TA retention ratio、TA content and water content of PEG-LZM-TA x (DH) hydrogels prepared by different TA concentrations of DMSO solutions were calculated.

$$\text{TA retention ratio}\ (\%) = \frac{(W_c - W_a)}{W_t} \times 100\% \tag{1.1}$$

$$Water\ content\ (\%) = \frac{(W_b - W_c)}{W_b} \times 100\% \tag{1.2}$$

$$TA\ content\ (\%) = \frac{(W_c - W_a)}{W_b} \times 100\% \tag{1.3}$$

TA contents of PEG - LZM - TA (H) hydrogels were also evaluated. The weight of freeze-dried PEG - LZM hydrogel was recorded as $W_d$, PEG-LZM-TA (H) hydrogel which was soaked in TA aqueous solution for 48h was recorded as $W_e$, and the freeze-dried PEG-LZM-TA(H) hydrogel was recorded as $W_f$.

$$TA\ content\ (\%) = \frac{(W_f - W_d)}{W_e} \times 100\% \tag{1.4}$$

Elemental analysis (EA) was performed to analyze the sulfur content with an Elementar, Vario ELIII. DMSO residues in PEG-LZM-TA(DH) hydrogel were calculated according to Equation (1.5)

$$c = \frac{78}{32} \times c_0 \times w_c \div w_b \tag{1.5}$$

where c is the DMSO residues in PEG-LZM-TA(DH) hydrogel and $c_0$ is the sulfur content of the freeze-dried gel.

**3.Volume shrinkage**

PEG-LZM-TAx (D) hydrogels with different TA contents were prepared, and the height($h_a$) and bottom radius($r_o$) of the cylindrical organogel were measured with vernier caliper. Next, after using our solvent exchange method, the height ($h_b$) and bottom radius($r_b$) of the PEG-LZM-TA(DH) hydrogel were measured. The volume shrinkage ratios of TA-reinforced hydrogels were calculated according to formula 2.1.

$$Volume\ shrinkage\ ratio\ （\%）= \frac{{r_b}^2 \times h_b}{{r_a}^2 \times h_a} \times 100\% \tag{2.1}$$

**4. Mechanical properties at 37°C**

The size of tensile test samples is 10 mm × 40 mm. Gently clamp the samples on the clamp of the ElectroForce® test instrument (Load Frame 3200 System, BOSE, USA), and stretch the samples at 37°C at a stretching rate of 50 mm/min.

Compression test was conducted by an ElectroForce® test instrument (Load Frame 3200 System, BOSE, USA) at 37 °C at a speed of 10 mm/min. PEG-LZM-TA (DH) and PEG-LZM-TA (H) hydrogels with different TA contents were prepared in cylindrical molds (10mm in diameter and 5mm in height) and treated with different method later. Photos of hydrogels before and after compression were taken. Compressive modulus was calculated through the initial slope of the stress-strain curve.

**5.Hardness of PEG-LZM-TA (DH)**

PEG-LZM-TA50 (DH) hydrogel film was fixed on the mouth of a cup which was filled with 37 ℃ water. And the hydrogel film was pressed against the water and covered with a layer of gauze. The whole set was placed into a chamber with 25°C and 50% humidity for 72h. The cup with water

was replaced at regular intervals in order to keep the temperature of water at 37 °C. The change of the hardness was detected by a Ta.XTplus Texture Analyser (Stable Microsystems) using probe 5. Probe 5 is placed on the surface of the PEG-LZM-TA (DH) film dropping at a speed of 5 mm/s. When the deformation of the film reaches 75%, the hardness is recorded

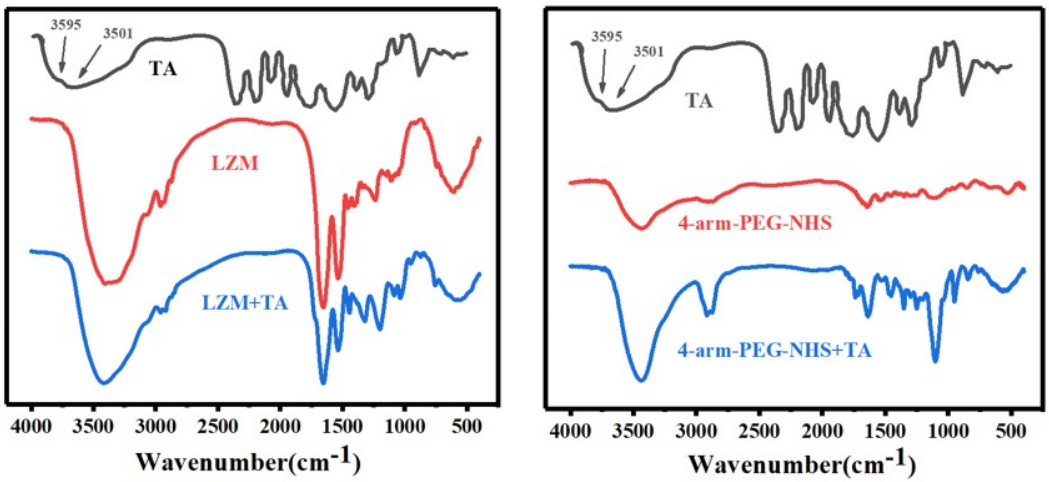


**Fig.S1** FTIR spectra of TA, LZM, TA+LZM (1:1) and TA, PEG, TA+PEG (1:1)

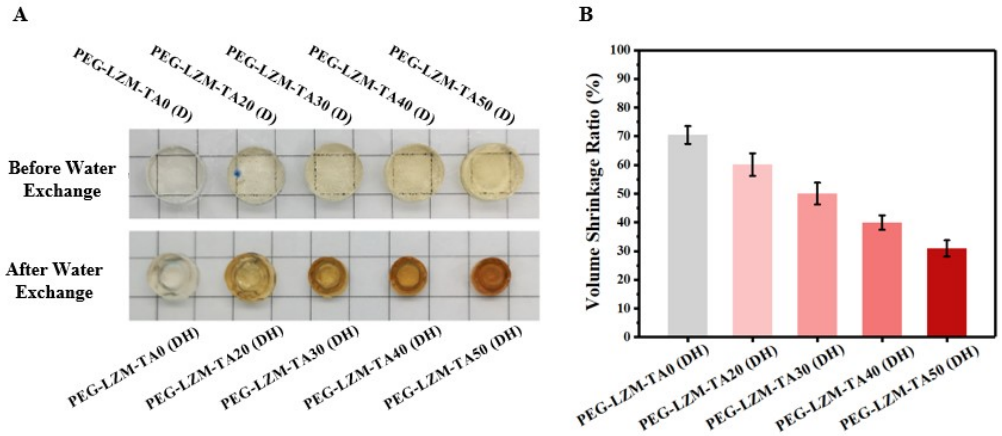


**Fig.S2** Photographs (A) and volume shrinkage ratio (B) of gels prepared with different TA concentrations.

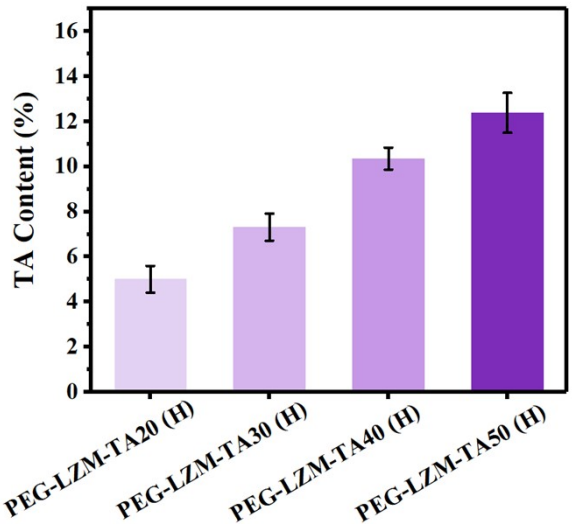


**Fig.S3** TA content of PEG-LZM-TA (H) hydrogels prepared by PI method.

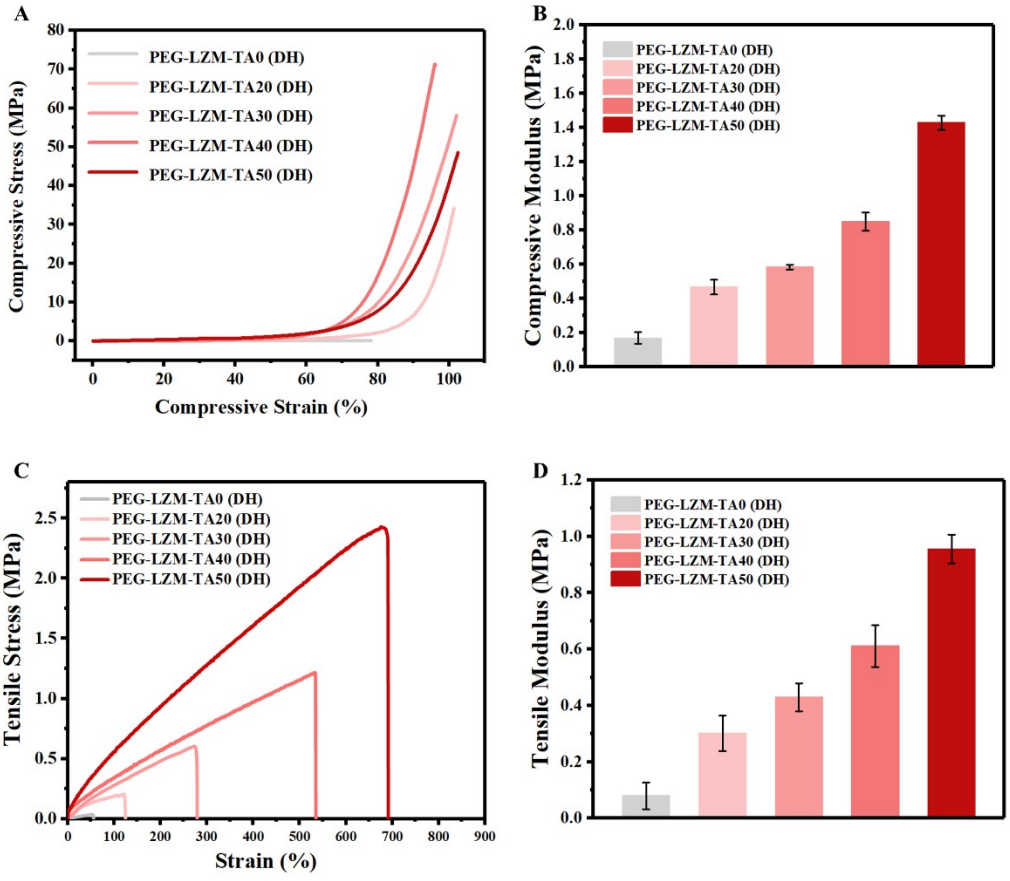


**Fig.S4** Mechanical properties of PEG-LZM-TA (DH) hydrogels at 37℃. (A) Compressive stress-strain curve, (B) compressive modulus, (C) tensile stress-strain curves, (D) tensile modulus.

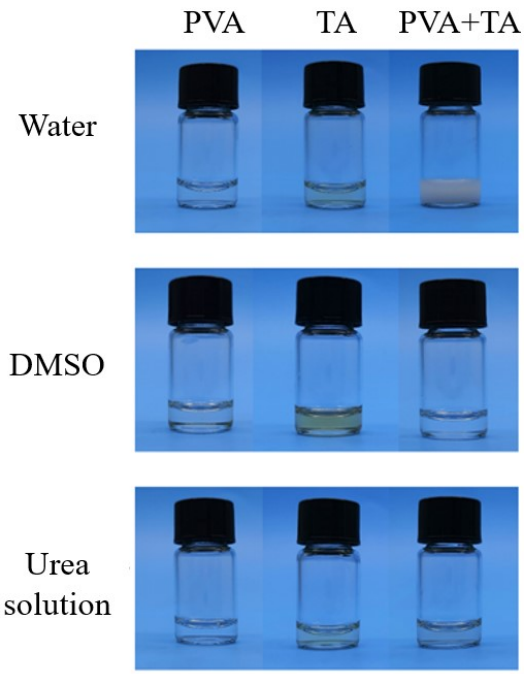


**Fig.S5** Photographs show that mixing tannic acid (TA) and PVA in phosphate buffer (PB) at pH 7.4 yields precipitates and precipitation is inhibited in DMSO or urea solvent, which indicates hydrogen binding is an important intermolecular interaction between TA-PVA, and DMSO can shield it.

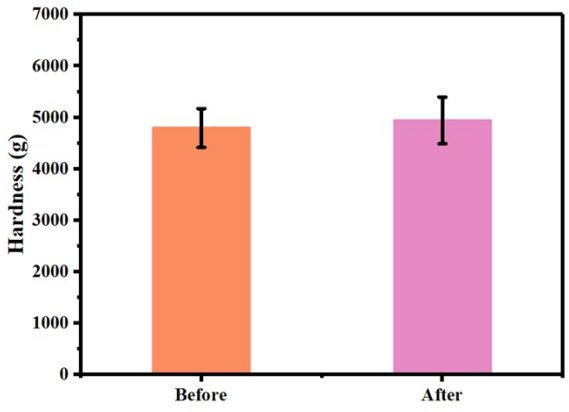


**Fig.S6** Hardness of PEG-LZM-TA50 (DH) hydrogel film before and after treatment (25°C and 50% humidity for 72 hours)