Tough, Swelling-resistant, Self-healing and Adhesive Dual-Crosslinked Hydrogels Based on Polymer-Tannic Acid Multiple Hydrogen Bonds

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1. Experimental Section

1.1 Measurement of the water content of hydrogels

The water content of as-prepared DC hydrogels were calculated as:

$$Content_{water} = \frac{m_g - m_d}{m_g} \times 100\%$$

where m_g is the mass of hydrogel at as-prepared state, m_d is the mass of corresponding dried hydrogel.

The water content of equilibrium swollen DC hydrogels were calculated as:

$$Content_{water} = \frac{m_g - m_d}{m_g} \times 100\%$$

where m_g is the mass of hydrogel at swelling equilibrium state, m_d is the mass of corresponding dried hydrogel.

1.2 Measurement of the TA content of DC hydrogels

The TA content of as-prepared polymer-TA DC hydrogel was calculated as:

$$Content_{TA} = \frac{m_{TA}}{m_g} \times 100\% = \frac{m - m_0}{m_g} \times 100\%$$

where *m* is the mass of dried as-prepared polymer-TA hydrogel, m_0 is the mass of polymer aerogel before soak in TA solution, m_g is the mass of as-prepared polymer-TA gel. The TA content of equilibrium swollen polymer-TA DC hydrogel was calculated as:

$$Content_{TA} = \frac{m_{TA}}{m_g} \times 100\% = \frac{m - m_0}{m_g} \times 100\%$$

where *m* is the mass of dried equilibrium swollen polymer-TA hydrogel, m_0 is the mass of polymer aerogel before soak in TA solution, m_g is the mass of equilibrium swollen polymer-TA gel.

1.3 Measurement of crystallinity degree of PVA hydrogel

The crystallinity degree (X) of the PVA and PVA-TAx hydrogel samples were approximately evaluated as the ratio of the area of the crystalline reflection in the 20 range $18-21^{\circ}$ (A₁) and the area of whole diffraction profile of the gel sample (A₂):¹

$$X = \frac{A_1}{A_2} \times 100\%$$

Because the T_g of PVA is 85 °C, we ignored the formation of crystallization in PVA hydrogel during the freeze-drying process. Based on the XRD data of freeze-dried PVA gels and PVA-TA gels, the *X* of gel was calculated: X = 33-38%.

The degree of crystallinity (X) of the PVA hydrogel samples were also evaluated by density measurement, in which the densities of 100% crystalline and amorphous PVA were used.² The degree of crystalline, X, of PVA hydrogels is calculated as:²

$$\frac{1}{\rho_p} = \frac{X}{\rho_c} + \frac{1 - X}{\rho_a}$$

$$\frac{1}{\rho_h} = \frac{1 - W_{PVA}}{\rho_{H_2O}} + \frac{W_{PVA}}{\rho_p}$$

where ρ_c is the density of 100% crystalline PVA ($\rho_c = 1.345 \text{ g cm}^{-3}$), ρ_a is the density of 100% amorphous PVA ($\rho_a = 1.269 \text{ g cm}^{-3}$), ρ_p is the density of the PVA in dried state, ρ_h is the density of the hydrogel, W_{PVA} is the weight percentage of PVA in gel, and ρ_{H2O} is the density of water.

Based on the experiment data, the density of PVA in dried state ρ_p is 1.294 g cm⁻³, and the X of PVA gel was calculated: $X \approx 35\%$.

2. Supporting Figures

X-ray diffraction profiles of PVA and PVA-TA100 gels before and after freeze-drying were presented in Figure S1a and S1b. Strong crystalline reflections in the 2θ range of 18-20° and weak peaks around 41° corresponded to the diffraction reflections of crystalline PVA.³ Besides, introducing TA showed no influence on the crystallinity degree of PVA (Figure S1c).



Figure S1. XRD profiles of the PVA and PVA-TA100 hydrogels (a) and corresponding freeze-dried samples (b). (c) The crystallinity degree of PVA and PVA-TAx hydrogels. Error bars indicate standard deviation; N = 3. The numbers in abscissa are the concentrations of TA solution in the preparation of polymer-TA hydrogels.



Figure S2. Mass ratio as function of soaking time of polymer aerogels in different TA solutions. Error bars indicate standard deviation; N = 5.



Figure S3. The mass ratio of polymer-TA DC hydrogels immersed in water in different times. (a) PVA-TA100 hydrogels, (b) PAAm-TA100 hydrogels. Error bars indicate standard deviation; N = 5.



Figure S4. SEM images of freeze-dried hydrogels. (a) PVA hydrogel, (b) PVA-TA100 hydrogel, (c) PAAm hydrogel, and (d) PAAm-TA100 hydrogel. The polymer-TA DC hydrogels were prepared by soaking aerogels into TA solutions.



Figure S5. SEM images of freeze-dried PVA-TA hydrogels at boundary. (a) PVA-TA100 hydrogel,(b) PVA-TA200 hydrogel. The PVA-TA DC hydrogels were prepared by soaking PVA gels into TA solutions.



Figure S6. Mass ratio as function of soaking time of PVA hydrogels in different TA solution. The PVA-TA DC hydrogels were prepared by soaking PVA gels into TA solutions. Error bars indicate standard deviation; N = 5.



Figure S7. The time-dependent recovery efficiency of hysteresis loop for PVA-TA300(S) gel at different strains, (a) at strain of 100%, (b) at strain of 300%.



Figure S8. Adhesive strength of polymer-TA(S) hydrogels to stainless steel (SS), titanium (Ti), glass, polycarbonate (PC), poly(methyl methacrylate) (PMMA), and pork skin tissue. (a) PVA-TA300(S) gel, (b) PAAm-TA300(S) gel.

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