Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Multi-responsive polyethylene-polyamine/gelatin hydrogel induced by non-covalent interactions

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Table S1. The concentration of gelatin and PPA in PPA-gelatin hydrogel

			PPA Concentration (wt.%)			Gelatin Concentration (wt.%)
P50/G0.1			50			0.1
P50/G0.25			50			0.25
P50/G0.5			50			0.5
P50/G1			50			1
P50/G2			50			2
P50/G4			50			4
P10/G6	P30/G6	P50/G6	10	30	50	6
P50/G8			50			8

Table S2. Storage modulus of PPA/gelatin, PPA/BSA and PPA/RSF (degummed by Na_2CO_3 and $NaHCO_3$, respectively) hydrogels (Mass fraction of PPA is 50%)

Mass fractions of protein (%)	**Storage modulus (kPa)**			
	Gelatin (Mw~80 kDa)	BSA (Mw~66 kDa)	RSF(Na_2CO_3) (Mw~140 kDa[1])	RSF($NaHCO_3$) (Mw~225 kDa[1])
0.5	20.8±0.8	19.1±0.6	16.7±1.1	22.4±1.4
1	39.7±1.2	24.8±0.9	28.2±1.5	38.4±1.8
2	49.2±1.3	44.6±1.2	81.0±3.4	173.6±7.4

From Table S2, G' mainly relied on the molecular weight of protein when protein concentration was increased to 2 wt.%. In such protein concentration, integrated hydrogel network could be formed through intermolecular conformation of protein molecules. Thus higher molecular weight of RSF induced more hydrogen bonding cross-linkers, resulting in much stiffer hydrogel. As a matter of fact, it is impossible to fabricate RSF/PPA hydrogels with higher protein content (above 2%) in such a case, because of the extremely high tendency of RSF becoming aggregates during mixing, not to mention the high temperature (60 °C) during fabrication.[1] BSA reveals poor mechanical properties because of its spherical molecular conformation, where most of the amine groups are embedded, and could hardly form hydrogen bonding cross-linkers with PPA. Therefore, we would choose PPA/gelatin hydrogel for the controllable hydrogel modulus.

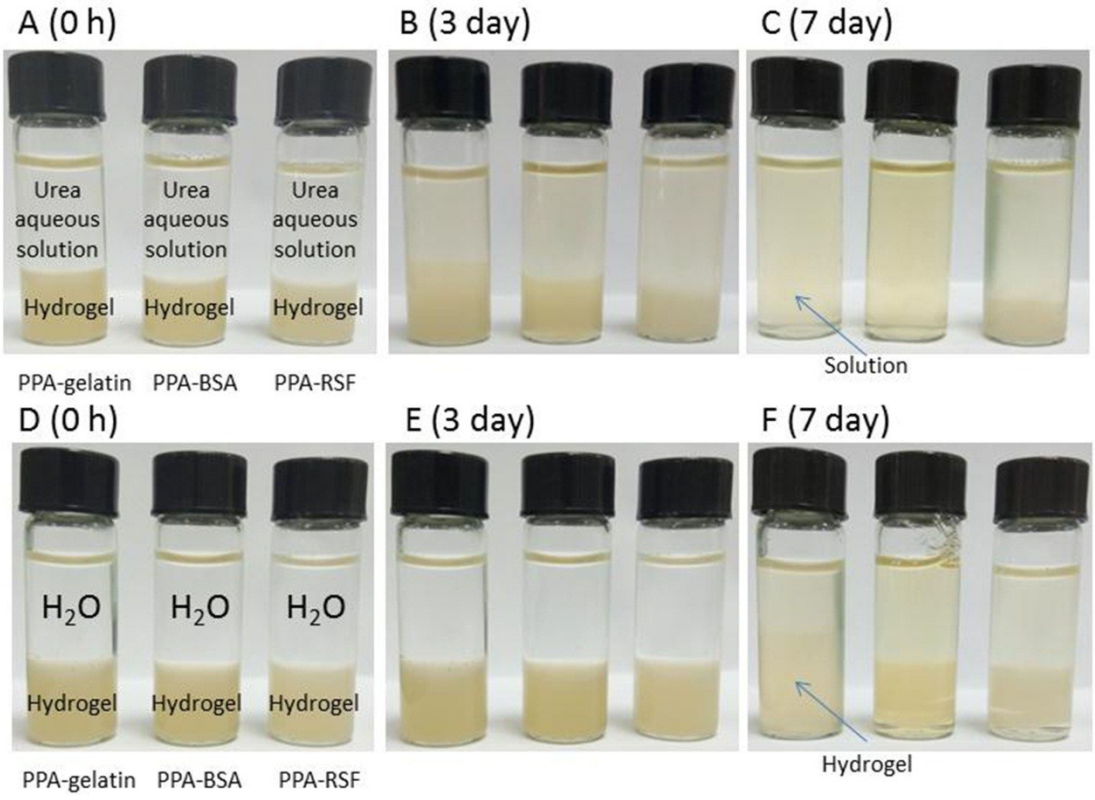

Fig.S1 Stability of PPA/protein hydrogel in 5 mol/L urea aqueous solution (A, B, C) and H_2O (D, E, F) after shaking. The mass fraction is 50 wt.% PPA/6 wt.% gelatin, 50 wt.% PPA/6 wt.% albumin from bovine serum (BSA) and 50 wt.% PPA/3 wt.% regenerated silk fibroin (RSF), respectively. pH=7. Legend is the same for all pictures.

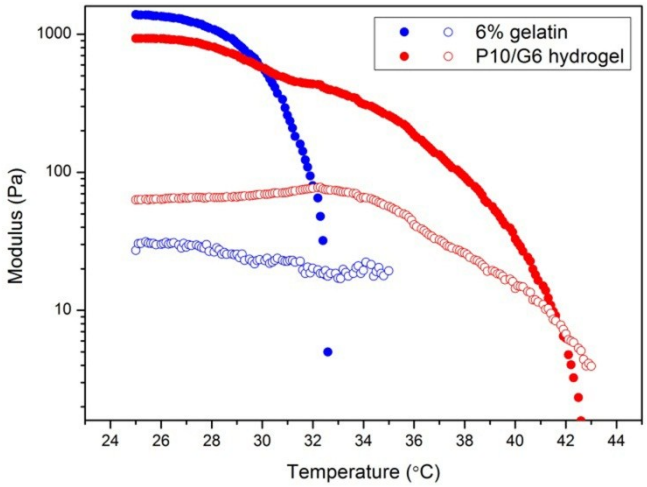

Fig.S2 Rheological storage modulus (G', filled symbols) and loss modulus (G'', open symbols) of P10/G6 hydrogel and pure gelatin hydrogel versus temperature.

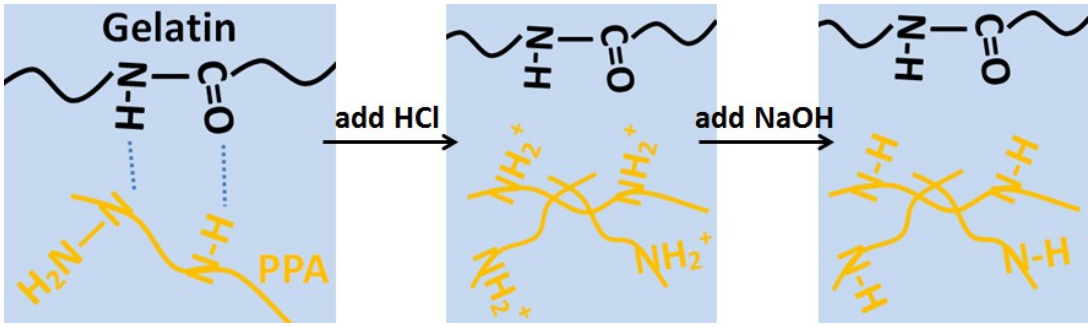

Fig.S3 Illustration of pH-induced gel-sol transition of PPA/gelatin hydrogel.

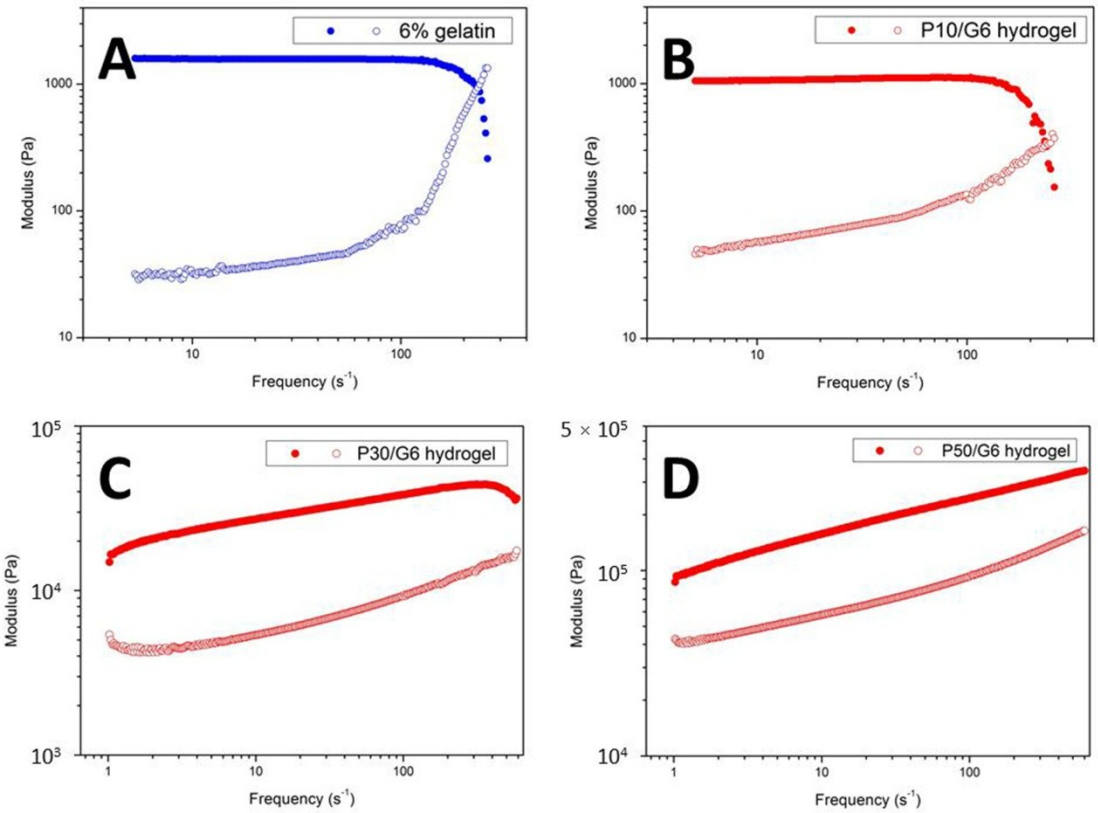

Fig.S4 Rheological storage modulus (G', filled symbols) and loss modulus (G'', open symbols) of gelatin involved hydrogel versus frequency. (A) 6% gelatin hydrogel. (B) P10/G6 hydrogel. (C) P30/G6 hydrogel. (D) P50/G6 hydrogel.

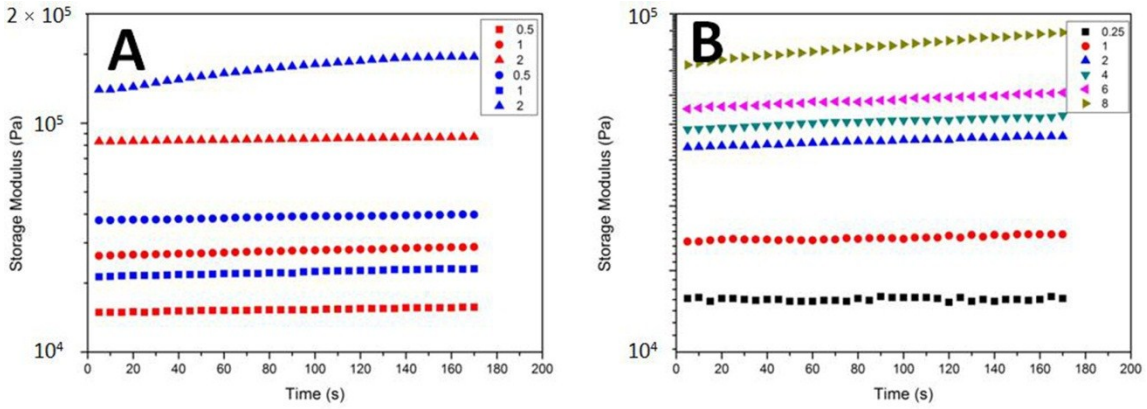

Fig.S5 (A) Rheological storage modulus (G') of PPA/RSF hydrogel with different concentrations and molecular weights of RSF, versus time. Red dots represent the RSF obtained via Na_2CO_3 degumming process (Mw~140 kDa[1]), while blue dots represent RSF obtained via $NaHCO_3$ degumming process (Mw~225 kDa[1]). (B) Rheological storage modulus (G') of PPA/BSA hydrogel with different concentrations of BSA. Mass fraction of PPA is 50%, and mass fractions (%) of RSF and BSA are listed in the legends.

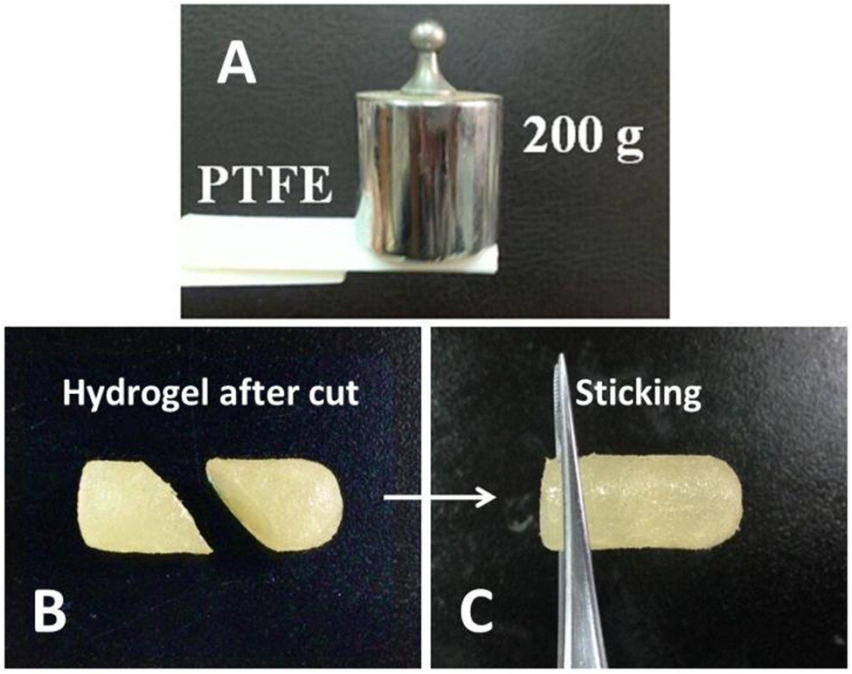

Fig.S6 P50/G6 hydrogel sticks PTFE pieces to resist weight of 200 grams (A) and its self-healing behavior is illustrated by photographs of B and C.

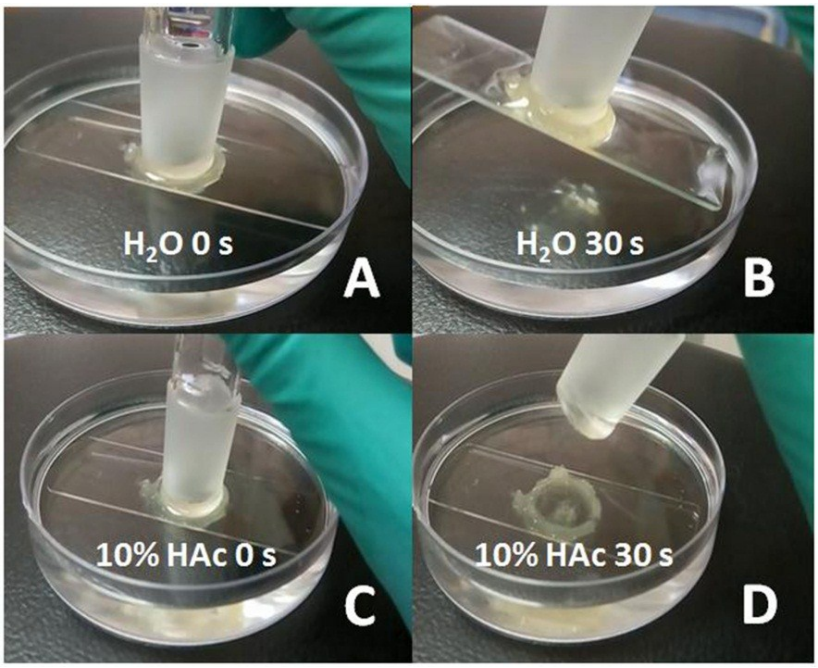

Fig.S7 Illustration photographs of P50/G6 hydrogel adhesive stability in H_2O (pH=7) and 10% HAc aqueous solution (pH=2).

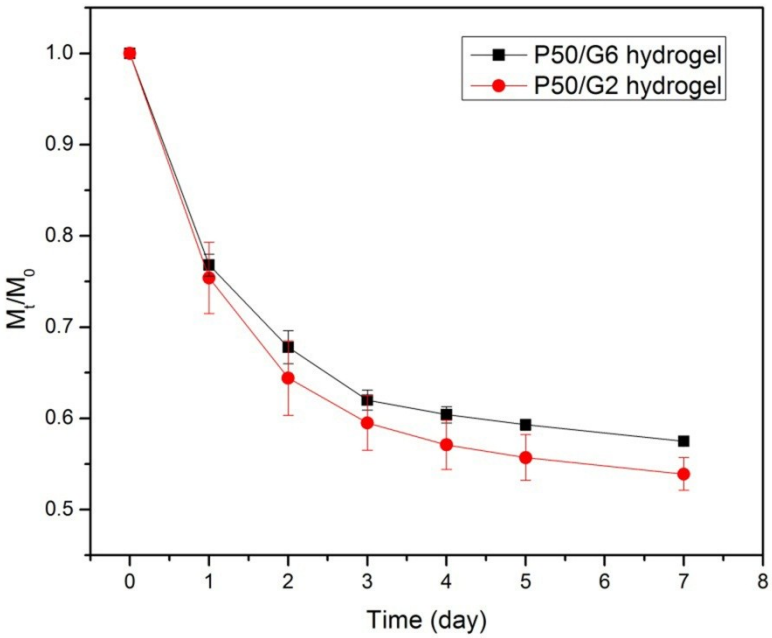

Fig.S8 Drying experiment of P50/G6 and P50/G2 hydrogel. M_0 represents the original weight of the hydrogel, while Mt represents the weight of the hydrogel stabilized in dryer after a period of time.

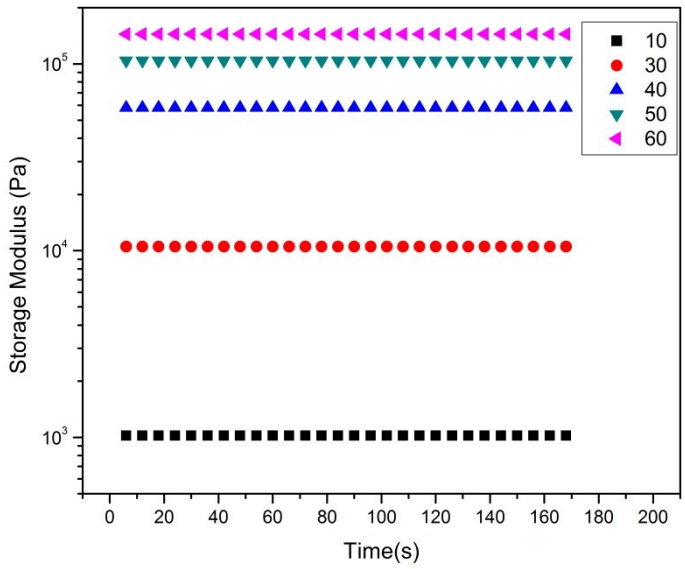

Fig.S9 Rheological storage modulus (G') of PPA/gelatin hydrogel with different PPA concentrations, versus time. Mass fraction of gelatin is 6%, and mass fractions (%) of PPA are listed in the legends.

From Fig.S9, the mechanical property could be adjusted by the content of PPA, however further increasing amount of PPA (above 50 wt.%) could not promote G' significantly. On the other hand, a high PPA concentration would greatly suppress the dispersion of gelatin as the viscosity increases, resulting in the inhomogeneous hydrogels. Therefore, P50/G6 is the optimum condition for both relatively high storage modulus and homogeneous dispersion of gelatin in the hydrogel.

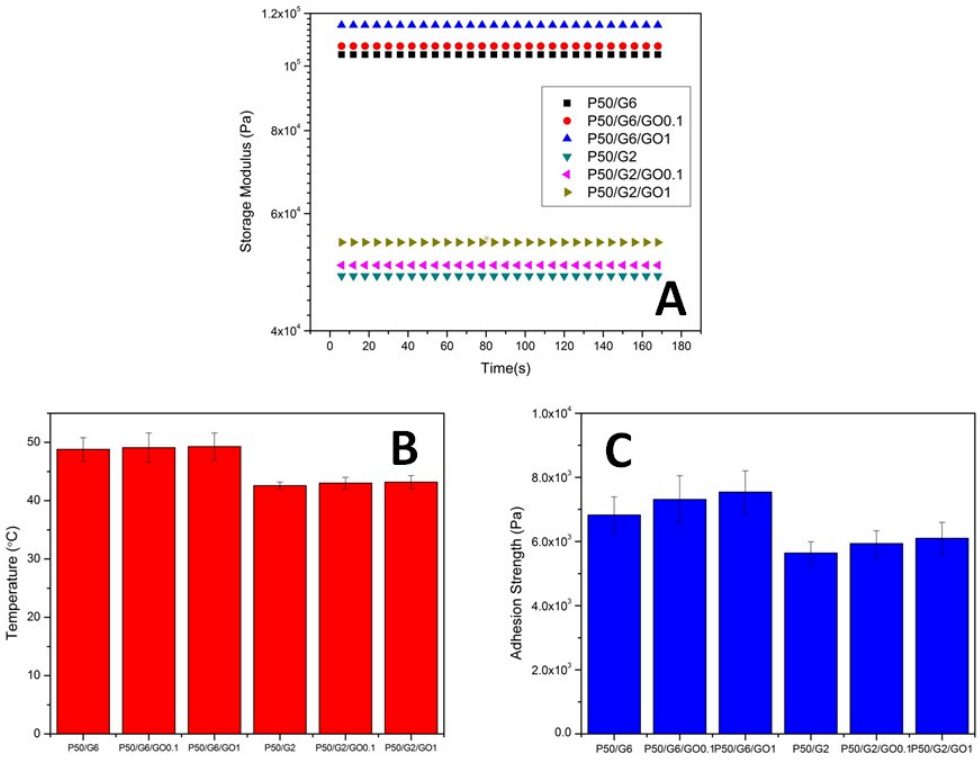

Fig.S10 Rheological storage modulus (A), gel-sol transition temperature (B) and adhesion strength (C) of P50/G6/GO(0.1/1) and P50/G2/GO(0.1/1) hydrogels (0.1 wt.%/1 wt.% GO in P50/G6 and P50/G2 hydrogels, respectively), compared to P50/G6 and P50/G2 hydrogels.

From Fig.S10, rheological storage modulus, gel-sol transition temperature and adhesion strength of P50/G6/GO(0.1/1) and P50/G2/GO(0.1/1) hydrogels were of little difference compared to P50/G6 and P50/G2 hydrogels. On the other hand, P50/G6/GO0.1 hydrogel revealed the controllable photo-thermal conversion at a relatively low GO concentration compared to P50/G6/GO1 hydrogel. Meanwhile, PPA/gelatin/GO hydrogel might be restricted in practical adhesive use owing to complex process and high expense in GO preparation and unstable gel-sol transition induced by sunlight or visible light.[2-4]

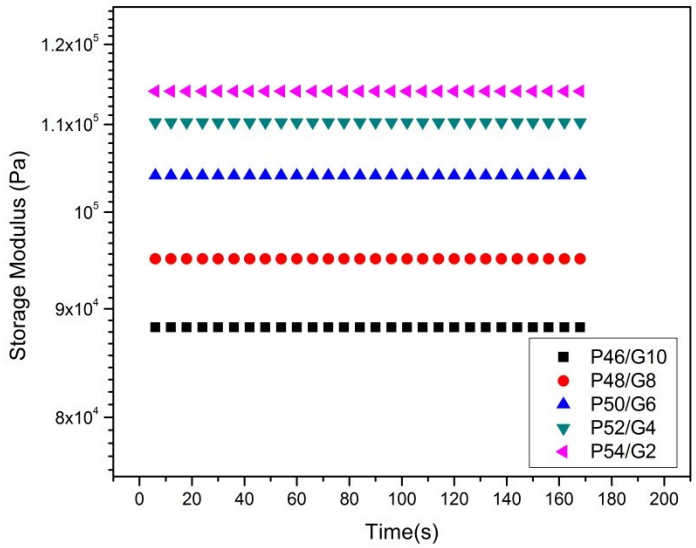

Fig.S11 Rheological storage modulus (G') of PPA/gelatin hydrogel with different PPA/gelatin proportions, versus time. Mass fractions (%) of gelatin and PPA are listed in the legends.

As we have assumed that hydrogen bonds between PPA and gelatin are the dominant crosslinking points, the amount of which will significantly affect the mechanical strength of PPA/gelatin hydrogel. As shown in Fig.S11, when keeping the solid content of hydrogels constant, the G' could increase corresponding to the increase of PPA content. It was speculated that PPA molecules acted as cross-linkers of gelatin chains, thus inducing the increase of crosslinking density and G'.

Notes and references:

1. Q. Wang, Q. Chen, Y. Yang and Z. Shao, *Biomacromolecules*, 2013, **14**, 285.
2. P. V. Kumar, M. Bernardi and J. C. Grossman, *ACS Nano*, 2013, **7**, 1638.
3. D. Kim, H. S. Lee and J. Yoon, *RSC Advances*, 2014, **4**, 25379.
4. D. Kim, E. Lee, H. S. Lee and J. Yoon, *Scientific Reports*, 2015, **5**, 7046.