Thin, Tough, pH-Sensitive Hydrogel Films with Rapid Load Recovery

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SUPPORTING INFORMATION

Movie S1:

A knot was formed on a PU-D3/PAA hydrogel film equilibrated at pH 6 (WC 85 %), then the film was stretched.

Experimental Details

PU-D3 films. All PU-D3 hydrogel films were produced by solution casting of PU-D3 in EtOH:water (95:5) at room temperature. First, a stock solution of PU-D3 in EtOH:water was made by dissolving 4 g of PU-D3 in 36 ml of EtOH:water mixture. To produce PU-D3 films of desired thickness, various concentration of PU-D3 was obtained by further diluting the PU-D3 stock solution with the EtOH:water mixture. After casting the solution in plastic containers, the containers were covered by plastic wraps with small holes to prevent quick evaporation of EtOH from the system. This process allowed creating bubble-free and uniform PU-D3 films. Water was then added to the system to remove the films from the containers. This step was considered crucial to generate robust, free-standing PU-D3 hydrogel films. At this step water acted as a non-solvent, causing the hydrophobic segments of PU-D3 to collapse and form free-standing hydrogel films.

PU-D3/PAA hydrogel films. PAA was introduced to the system by placing the PU-D3 films in the AA monomer solution. Preliminary studies showed that PU-D3 films were soluble in AA. Hence, NaOH was added to the system to neutralise the carboxylic groups of AA. To make the AA monomer stock solution, 2.33 g of NaOH was fully dissolved in 36 ml of water, followed by adding 4 ml of AA monomer to the solution. Then, 42 mg of α-ketoglutaric acid (UV initiator) and 15 mg of *N*,*N'*-methylenebisacrylamide (crosslinking agent) were added to the neutralised AA solution. The AA stock solution was then diluted further (2:3) by adding 5 ml Milli-Q water to 10 ml of the stock solution. The PU-D3 films were kept in this solution in dark for at least 2 days. UV-initiated polymerization was performed by placing the PU-D3 films between two glass plates and exposing them to 300 nm UV light for 12 hours.

Swelling Ratio

Swelling ratio of PU-D3 and PU-D3/PAA hydrogels was measured as a function of pH by recording the mass of hydrogels equilibrated at different pHs (m_s) followed by recording their dry mass (m_d). The swelling ratio (Q) was then calculated from:

$$Q = \frac{m_s}{m_d}$$

The results obtained for swelling ratio as a function of pH is presented in Figure S1. While the swelling ratio of PU-D3 hydrogel did not change with pH, a clear pH-dependency was observed for PU-D3/PAA hydrogels. When below pH 4 (*i.e.* pH=1–3), PU-D3/PAA hydrogels had a swelling ratio of 2.75±0.25, which then increase to 5.63±0.66 when pH increased above 4 (*i.e.* pH=5–11).

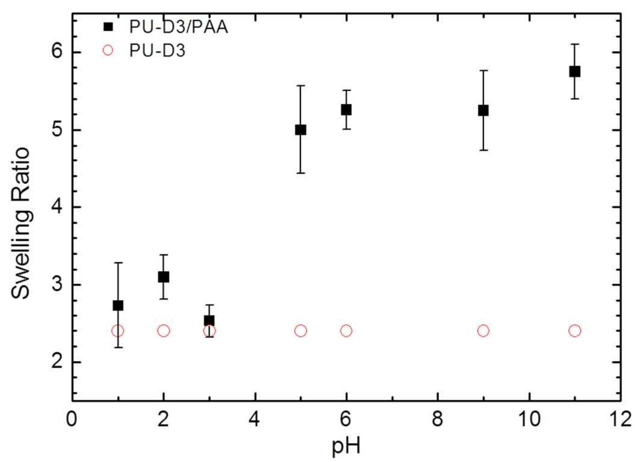

Figure S1. Swelling ratio of PU-D3 (open circles) and PU-D3/PAA hydrogels (filled squares) equilibrated at different pHs. Error bars indicate the standard deviation for three measurements.

Mechanical Performance Comparison of PU-D3/PAA Hydrogels with other Materials

Toughness vs. modulus

The toughness and modulus of PU-D3/PAA hydrogels equilibrated at pH 2 and pH 6 are presented in Figure S2 as a comparison with other hydrogels and classes of materials. Data were extracted from ref. 16 and ref. 27. As can be seen from Figure S2, the PU-D3/PAA hydrogels bridge between the DN hydrogels and rubbers.

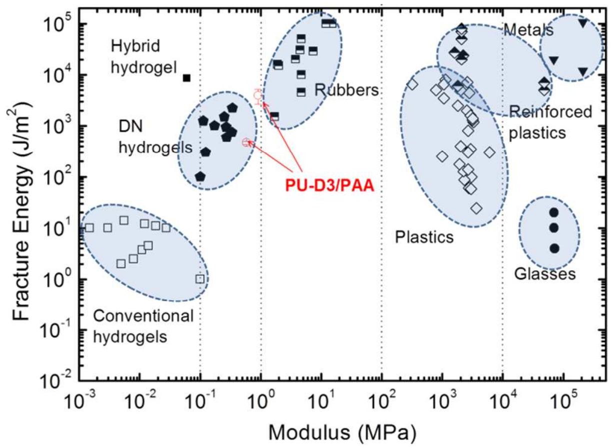

Figure S2. Fracture energy of various materials[16, 27] *vs.* their modulus compared with the PU-D3/PAA hydrogels developed here (open circles).

Tensile strength vs. elongation at break

The average tensile strength and elongation at break of PU-D3/PAA hydrogels equilibrated at pH 2 and pH 6 are compared with other hydrogels, including conventional hydrogels, DN hydrogels, nanocomposite (NC) hydrogels, homogeneous hydrogels (made by click chemistry) and alginate/PAAm hybrid hydrogels (Figure S3).[16, 27] The PU-D3/PAA hydrogels exhibit both high tensile strength and elongation at break, comparable with other tough hydrogel systems.

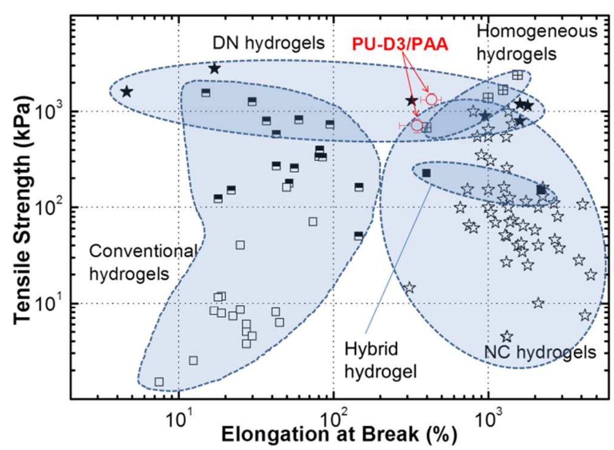

Figure S3. Tensile strength of various hydrogels *vs.* their corresponding elongation at break. Open circles represent the PU-D3/PAA hydrogels developed here and equilibrated at pH 2 and pH 6. The half-filled squares are hydrophilic-hydrophobic copolymer hydrogels used in contact lenses.[16] The filled squares represent the hybrid hydrogels.[27] Other types of hydrogels are as-labelled.

Work of extension vs. modulus and swelling ratio

Since the fracture energy values obtained from proper toughness tests are not readily available for all categories of hydrogels, work of extension can be used as a measure of toughness to compare the PU-D3/PAA hydrogels with different hydrogels. Figure S4 compares the work of extension of PU-D3/PAA hydrogels equilibrated at pH 2 and pH 6 with other hydrogels[16] as a function of their modulus. Figure S5 highlights the effect of swelling ratio of various hydrogels, including PU-D3/PAA, on their work of extension. The PU-D3/PAA hydrogels have higher modulus when compared with DN hydrogels and NC hydrogels, while their work of extension is comparable with tough hydrogels in both categories. The modulus of PU-D3/PAA hydrogels fall in the range of less swollen PHEMA-based copolymer hydrogels (Figure S4), while their swelling ratio is relatively higher than most of the PHEMA-based copolymer hydrogels presented in Figure S5.

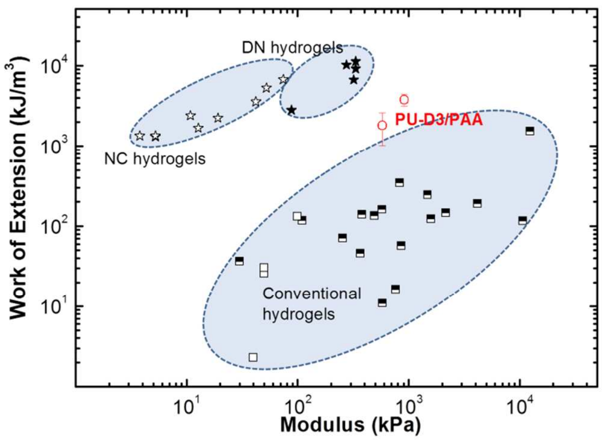

Figure S4. Work of extension of various hydrogels[16] and their corresponding modulus compared with the PU-D3/PAA hydrogels equilibrated at pH 2 and pH 6 (open circles). The half-filled squares represent hydrophilic-hydrophobic copolymer hydrogels with lower swelling ratio (see Figure S5) and higher modulus.

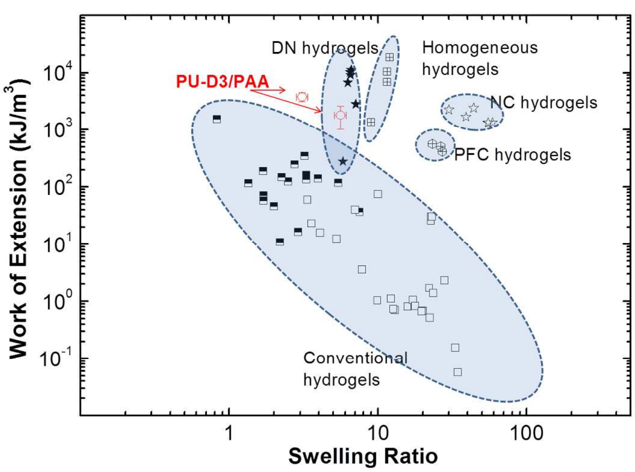

Figure S5. Work of extension and swelling ratio of various hydrogels[16] compared with those of PU-D3/PAA hydrogels equilibrated at pH 2 and pH 6 (open circles).