Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Dual Physically Crosslinked Double Network Hydrogels with High Toughness and Self-Healing Properties

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Gel preparation

Agar was added to a 250 mL, 3-neck, round flask to form a homogeneous solution at 65℃. Then AAc, ionic cross-linker $Fe(NO_3)_3 \cdot 9H_2O$ and ultraviolet (UV)-light initiator KA were added to the solution to form a mixed aqueous solution, which then was poured into a home-made, rectangular reaction-cell consisting of two glass plates of smooth surfaces separated with a hollow silicone-rubber spacer of ~2.6 mm in thickness. The sealed reaction-cell was allowed to stand at room temperature (air-conditioned at 30℃) for 1 h, then the AAc subsequently was polymerized and meanwhile cross-linked physically upon UV-light irradiation at room temperature for 5 h, in the presence of KA as a UV initiator and ferric ion as ionic cross-linker.

Measurements

For mechanical property measurement, uniaxial tensile tests of as-prepared gels (40 mm in length, 10 mm in width, and 2.6 mm in thickness) were carried out using a universal tensile tester equipped with a 1 kN load cell with a variety of crosshead speed of 50 $mmmin^{-1}$. For hysteresis measurement, gel specimens were first stretched to a maximum strain ε_1 and then unloaded. After returning to the original length, the specimens were reloaded and stretched to an increased maximum strain ε_2 at the same velocity rate as the first loading and unloaded again. Tearing testing was performed using commercial test machine. The gel samples were cut into a trousers shape (40 mm in length, 10 mm in width, and 2.6 mm in thickness) with an initial notch of 20 mm. The two arms of the samples were clamped, in which the one arm was fixed, while the other one was pulled upward at velocity 50 $mmmin^{-1}$.

For self-healing tests, the cylindrical Agar/PAAc-Fe^{3+} gel samples were cut using a knife, and then the two freshly cut surfaces were placed together (without adding any chemicals) within the plastic syringes (the same size of the as-prepared gel sample). To avoid water evaporation, the plastic syringes were wrapped with polyethylene films, and then stored in a sealed polyethylene bag at the prescribed temperatures or times. After the allotted time, the healed hydrogels were subjected to mechanical measurements at ambient temperature to study the self-healing properties of the Agar/PAAc-Fe^{3+} gel.

Results and discussion

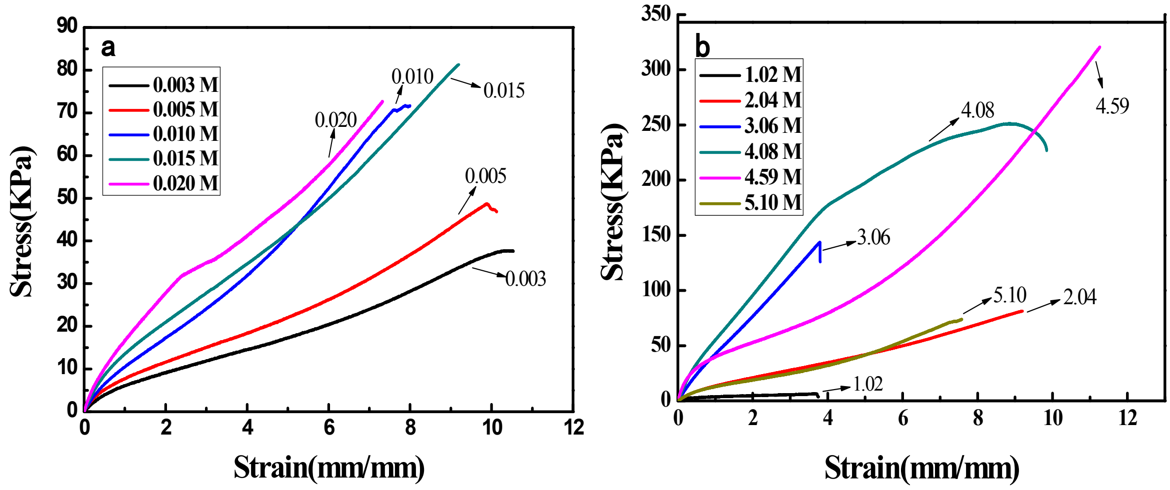

Fig. S1 Mechanical property characterization of the Agar/PAAc-Fe^{3+} gels. Dependence of the tensile strength and maximum elongation of mole ratio of Fe^{3+} concentration (a), AAc concentration (b).

Fig. S1a shows that variation of the ferric ion concentration highlights the key role that they play in the outstanding mechanical properties of the Agar/PAAc-Fe^{3+} gels. An improvement in the tensile strength at break with the gradual increase of Fe^{3+} content from 0.003-0.015 molL^{-1}. And then a decline of mechanical properties was observed for the gels with higher Fe^{3+} content than 0.015 molL^{-1}. At a moderate content of ferric ions, its increase could facilitate the polymerization of PAAc and increase the crosslinking density of the gels, which ensured more stress to be sustained by the gel sample. However, with a further increase of the ferric ion content, it may retard the radical polymerization and reduce the molecular weight of PAAc and degrade the mechanical properties of the gels. [1-3] The mechanical properties of the gels exhibit a trend of first increase and then decrease with the increase in ferric content.

As shown in Fig. S1b, the AAc concentration was also found to be important, as variation in the water content was found to significantly influence the elastic modulus, tensile strength of the Agar/PAAc-Fe^{3+} gels. An improvement in the tensile strength, elastic modulus and elongation with the gradual increase of AAc concentration from 1.02-4.59 $molL^{-1}$. Agar/PAAc-Fe^{3+} gels of AAc concentration 4.59 $molL^{-1}$ was found to have good deformation characteristics and manage an elongation more than eleven times their initial length, with the AAc concentration 5.10 $molL^{-1}$ which managed less than eight-fold elongation. When the AAc concentration was 4.59 $molL^{-1}$, the stress-strain curve of Agar/PAAc-Fe^{3+} gels showed yielding areas at strain 100%. This phenomenon can be ascribed to the interactions between the PAAc chains and Fe^{3+} ions. Increase of AAc content resulted in decrease of water content. The movement of the PAAc chain becomes easy, and the PAAc chains are sufficiently extended when increasing the water content. Moreover, the polymer concentration for per unit cross-sectional area decreases, resulting in the higher applied stress on each of the PAAc chains. Meanwhile, the break-recombination of the reversible ionic and hydrogen bonding crosslinking during deformation should be slow at lower AAc concentration. Consequently, it is not efficient to bear the applied stress. Therefore, it exhibits a relatively low strain at higher water content. Besides, the macromolecular weight should be influenced by the monomer and ferric ion concentrations during the polymerization. Therefore, the Agar/PAAc-Fe^{3+} gels with a moderate PAAc content exhibits a balanced mechanical performance

Video S1 shown the large elongation of Agar/PAAc-Fe^{3+} gels. The uniaxial tensile testing was carried out using a universal tensile tester equipped with a 1kN load cell with at velocity rate of 50 mm/min. The gel samples were cut into a rectangle shape (40 mm in length, 5 mm in width, and 2.6 mm in thickness) without an initial notch.

Video S2 shown the notch-insensitivity of Agar/PAAc-Fe^{3+} gels. Tearing testing was performed at tensile rate of 50 $mmmin^{-1}$. The gel samples were cut into a trousers shape (40 mm in length, 10 mm in width, and 2.6 mm in thickness) with an initial notch of 20 mm. The two arms of the samples were clamped, in which the one arm was fixed, while the other one was pulled upward at velocity rate of 50 $mmmin^{-1}$. As shown in Video S2, the sample can be stretched to manage a more than ten-fold elongation and the breakage occurred on intact part rather than the notch, exhibiting the notch-insensitivity of Agar/PAAc-Fe^{3+} gels.

Video S3 shown the excellent self-healing property of Agar/PAAc-Fe^{3+} gels. Without adding any chemicals, by simply placing three hydrogel portions together (yellow-blue-yellow) allowing enough time for physical interactions to reestablish the network at the interface. The blue part was stained by methyl blue. As shown in Video S3, methyl blue have diffused to the non-stained part, self-healing sample possess great toughness and can be stretched to more than 7 times of the initial length.

Notes and References

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