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A Novel Design Strategy for Fully Physically Linked Double Network Hydrogels with Tough, Fatigue Resistant, and Self-Healing Properties

Qiang Chen, Lin Zhu, Hong Chen, Hongli Yan, Lina Huang, Jia Yang, and Jie Zheng**

Double network (DN) hydrogels with two strong asymmetric networks being chemically linked have demonstrated their excellent mechanical properties as the toughest hydrogels, but chemically linked DN gels often exhibit negligible fatigue resistance and poor self-healing property due to the irreversible chain breaks in covalent-linked networks. Here, a new design strategy is proposed and demonstrated to improve both fatigue resistance and self-healing property of DN gels by introducing a ductile, nonsoft gel with strong hydrophobic interactions as the second network. Based on this design strategy, a new type of fully physically cross-linked Agar/hydrophobically associated polyacrylamide (HPAAm) DN gels are synthesized by a simple one-pot method. Agar/HPAAm DN gels exhibit excellent mechanical strength and high toughness, comparable to the reported DN gels. More importantly, because the ductile and tough second network of HPAAm can bear stress and reconstruct network structure, Agar/HPAAm DN gels also demonstrate rapid self-recovery, remarkable fatigue resistance, and notable self-healing property without any external stimuli at room temperature. In contrast to the former DN gels in both network structures and underlying association forces, this new design strategy to prepare highly mechanical DN gels provides a new avenue to better understand the fundamental structure-property relationship of DN hydrogels, thus broadening current hydrogel research and applications.

1. Introduction

Polymer hydrogels are soft and wet materials containing a large amount of water in their porous network structures, which have been widely used for many applications of superabsorbents,[1,2] wastewater treatment,[3] agriculture and food chemistry,[4–6] tissue scaffolds,[7,8] drug delivery carriers,[9,10] and biosensors.[11,12] However, most of polymer hydrogels suffer from low mechanical strength, poor toughness, and/or limited recoverability and self-healing property, due to their intrinsic structural heterogeneity and/or lack of efficient energy-dissipation mechanisms,[13] which greatly limit their uses for other applications requiring highly mechanical properties such as cartilage, tendon, muscle, and blood vessel.

Many efforts have been made to develop tough hydrogels with new microstructures and toughening mechanisms, such as double network hydrogels,[14] nanocomposite hydrogels,[15] sliding-ring hydrogels,[16] macromolecular microsphere composite hydrogels,[17] tetra-polyethylene glycol hydrogels,[18] hydrophobically associated hydrogels,[19,20] and dipole–dipole or hydrogen bonding enhanced hydrogels.[21,22] Among them, double network (DN) hydrogels have demonstrated their excellent mechanical properties. The existing knowledge of DN gels from synthesis methods, network structures, to toughening mechanisms mainly comes from chemically cross-linked DN gels.[23] Both networks with contrasting structures in DN gels are separately crosslinked by covalent bonds,[24] and the interpenetration of two contrasting networks makes the chemically linked DN gels both tough and soft, as evidenced by stiffness (elastic modulus of 0.1–1.0 MPa), strength (failure tensile stress of 1–10 MPa, strain 1000%–2000%, failure compressive stress 20–60 MPa, strain 90%–95%), and toughness (tearing fracture energy of 10^2–10^3 J m^{-2}).[23] Chemically linked DN gels have comparable toughness to cartilage and rubber. The toughening mechanisms are largely based on “sacrificial bonds” that break from the first network to effectively dissipate energy, protect the second network, sustain stress, and store elastic energy, thus to reinforce the gels. However, the fracture of the first network also causes irreversible and permanent bond breaks, making the gels very difficult to be repaired and recovered from damages and fatigues.[25] Thus, the internal fracture process of the first network is considered to be critical for toughness enhancement, because relatively large damage zones formed in the first network allow for more accumulated damage before macroscopic crack propagation occurs throughout whole networks.[26,27]

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To improve fatigue resistance and self-recovery property of chemically linked DN gels caused by permanent bond breakage, introduction of reversible, noncovalent bonds to replace sacrificial covalent bonds in the first network can be applied to form hybrid physically–chemically crosslinked DN gels. Upon loading/deformation, physically bonds in the first network break and dissipate energy, but these bonds can reform during unloading/resting, leading to the recovery of hybrid DN gels from damages and fatigues. Only several hybrid physically–chemically linked DN gels were developed recently, showing different effects of self-recovery and fatigue resistance properties. Haque et al. developed lamellar bilayer DN gels consisting of rigid, hydrophobic poly(dodecylglyceryl itaconate) (PDGI) lamellar bilayers and ductile, hydrophilic polyacrylamide (PAAm) matrix, both of which alternatively stack on top of each other.[28] Hysteresis loops also revealed multiple self-recovery or fatigue resistance of the PDGI/PAAm DN gels on several tens of successive loadings. Panhuis and co-workers developed a series of ionic-covalent DN gels using anionic polysaccharides (gellan gum and carrageenan) as the first ionically crosslinked network and poly(acrylamide) as the second, covalently crosslinked network.[29–31] The hybrid gellan gum/PAAm gels can recover ≈53% of the hysteresis of the first compressive cycle and ≈90% of subsequent cycles.[32] Suo and co-workers reported hybrid interpenetrating polymer network (IPN) hydrogels with Ca^{2+} crosslinked alginate as the first network and covalently crosslinked PAAm as the second network.[13,33,34] The loading–unloading tests showed that after storing the Ca^{2+}-Alg/PAAm IPN gel at 80 °C for 1 day, it can be slowly recovered to ≈74% of the initial work of the first loading, but this gel is soft with tensile strength of ≈160 kPa. We recently developed hybrid cross-linked agar/polyacrylamide (Agar/PAAm) DN hydrogels, consisting of two interpenetrating networks of a hydrogen-bond linked Agar network and a covalently cross-linked PAAm network.[35] The Agar/PAAm DN hydrogels exhibited high mechanical properties of hardness (elastic modulus of 123 kPa), strength (failure compression stress of 38 MPa, strain 98%; failure tensile stress of 1.0 MPa, strain ca. 2000%), and toughness (9 MJ m^{-3}), excellent extensibility (≈15–20 times longer relative to its initial length), and a unique free-shapeable property (formation of many complex geometrical shapes). More importantly, the gels can recover 90% of stiffness and 65% of toughness after 10 min of the first loading at 100 °C. But, no recovery effect was observed at temperatures below the T_m of agar gel (25 and 50 °C). High recovery temperatures of our Agar/PAAm gels could limit their uses for biomedical applications.

For the existing fully chemically linked or hybrid-linked DN gels, the second network is chemically and loosely linked by soft and ductile polymers (particularly PAAm-based DN gels). However, the inherent soft and ductile nature of the second network usually cannot bear large stress as the first network is fractured.[36] Such stress will be transferred from the second network to the fractured first network again, leading to further disruption of the first network. To better dissipate energy and bear stress via the second network to improve fatigue resistant, herein we proposed a new design strategy to construct the second network using a ductile gel with strong physical interactions, instead of a conventional soft, ductile chemically linked gel. We synthesized a new type of DN gels with both networks being physically crosslinked, consisting of a hydrogen bond-associated agar gel as the first network and a hydrophobically associated polyacrylamide gel (HPAAm gel) as the second network (named as Agar/HPAAm DN gels). We expect that the ductile and tough HPAAm second network will provide additional platform to dissipate energy, bear stress, and reassemble network structure upon deformation, thus to promote strength, toughness, fatigue resistance, and self-healing property simultaneously. As a result, Agar/HPAAm DN gels exhibited excellent mechanical strength (fracture stress of 0.267 MPa and fracture strain of 52.6 mm mm^{-1}) and toughness (dissipated energies of 9.35 MJ m^{-3} and tearing energies of 1000 J m^{-2}), comparable to conventional chemically linked or hybrid-linked DN gels. More importantly, Agar/HPAAm DN gels also demonstrated rapid self-recovery property (≈60% stiffness recovery and ≈40% toughness recovery within 2 min), remarkable fatigue resistance (40 times car crash without damage), and notable self-healing property (≈40% recovery of initial strength) without external stimuli at room temperature. To our knowledge, taking advantage of our simple one-pot method, we are the first to realize fully physically linked DN gels with highly mechanical strength, fatigue resistant, self-healing properties by introducing and tuning the second, physically linked network, not the first network. We believe that our new design strategy, along with the simple one-pot method and the gel system, could be generally applied to develop a new generation of tough hydrogel materials.

2. Results and Discussion

2.1. Synthesis of Agar/HPAAm DN Gels

Figure 1 shows a general procedure to prepare fully, physically crosslinked Agar/HPAAm DN gels using a "one-pot" method. All reactants of agar, AAm, stearyl methacrylate (SMA), and UV-initiator were first added to a sodium dodecyl sulfate (SDS)/NaCl aqueous solution, followed by a heating-cooling-photopolymerization process for synthesizing DN gels. Briefly, all reactants in a "one-pot" were added in the SDS/NaCl aqueous solution and then heated to 95 °C above a melting point of agar under magnetic stirring, forming a transparent solution. During the heating process, Agar formed linear macromolecules, while SMA was dissolved in the SDS micelles to form polymerizable micelles. The resulting solution was then gradually cooled down to room temperature, allowing the agars to form the first network via hydrogen bond-associated agar helix bundles. Once the first agar network was formed, the agar gel and other unreacted species in the same pot were photopolymerized to form the second physically crosslinked network of HPAAm via the micelle copolymerization of AAm and SMA. The second HPAAm network, interpenetrating with the first agar network, was mainly associated by strong hydrophobic interactions between SDS micelles and alkyl groups of SMA.

Completely different from other chemically linked and hybrid-linked DN gels, here we presented a fully physically linked Agar/PAAm DN gel, without any chemical links being formed in both networks. HPAAm single network (SN) alone

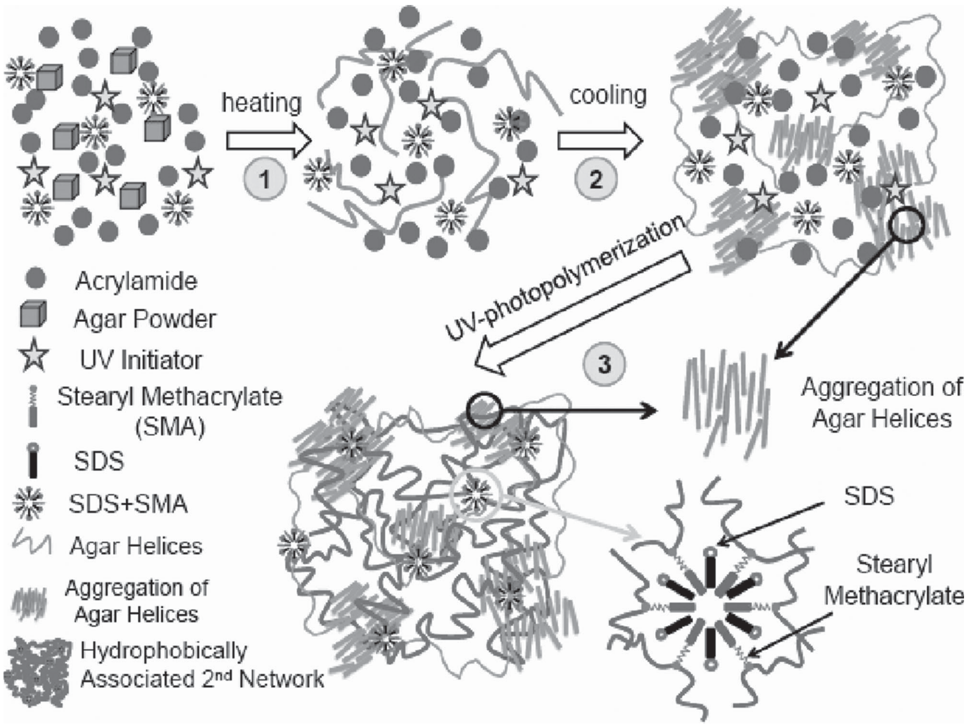

Figure 1. Preparation of fully physically crosslinked Agar/HPAAm DN gels using the one-pot method.

was very ductile and its strength was very weak.[20] However, when HPAAm network interpenetrates into the agar network to form double network structures, the second HPAAm network functions to not only enhance mechanical extensibility, strength, and toughness of the gels, but also introduce new self-recovery and self-healing properties via reversible hydrophobic interactions without external stimuli at room temperature. Strong and reversible hydrophobic interactions in the second HPAAm network allows to dissipate energy and bear stress as the first network is fractured, leading to reconstruct the networks after loading.[37] In contrast, PAAm gel alone did not show any self-healing property due to lack of significant energy dissipation upon cyclic loadings.[13,35] In addition, due to the strong hydrophobically associated HPAAm network, we found Agar/HPAAm DN gels did not dissolve in pure water for ≈1 month at room temperature. Even when heating temperature up to 95 °C (higher than melting point of agar gel) for 2 h, the gels still did not dissolve in pure water. These results indicated that our DN gels are very structurally stable. The preliminary swelling data indicate that the swelling ability of Agar/HPAAm DN gels is very limited and much weaker than that of HPAAm SN gels (data not shown).

2.2. Highly Mechanical Properties of Agar/HPAAm DN Gels

Figure 2 showed that Agar/HPAAm DN gels were very strong and flexible to withstand high-level deformation of ordinary stretching (a->b), knotted stretching (c->d), twisted stretching (e->f), and compression (Movie S1, Supporting Information). Upon removal of the deformation force, the gels can quickly recover to their initial shapes, indicating that the gels exhibit excellent shape-recovery property (Movie S1, Supporting Information). More importantly, Agar/HPAAm DN gels can be readily adapted to different shapes (g and h) and be fabricated in a large scale up to 12 cm in diameter and 1 cm in thickness (i and i′).

We compared tensile and tearing mechanical properties among HPAAm SN gel (phyiscally linked network), Agar/HPAAm DN gel (physically linked networks), Agar/PAAm DN gel (physically–chemically linked networks), and poly(2-acrylamido, 2-methyl, 1-propanesulfonic acid)/PAAm (PAMPS/PAAm) gel (chemically linked networks). As shown in **Figure 3**a, HPAAm gel with a single network exhibited good extensibility, but poor strength (E of 37 kPa, σ_f of 0.069 MPa, ε_f of 33.24 mm mm^{-1}, and W of 1.73 kJ m^{-3}). However, by adding a very small amount of agar biomolecules (≈0.7 wt%) to HPAAm gel, Agar/HPAAm DN gel can achieve excellent tensile properties (E of 106 kPa, σ_f of 0.267 MPa, ε_f of 52.6, and W of 9.35 kJ m^{-3}). Particularly, σ_f and W of Agar/HPAAm gels were ≈3.9 and ≈5.4 times higher than those of HPAAm SN gels. Agar/HPAAm DN gels also exhibited slightly better tensile properties than hybrid-linked Agar/PAAm DN gel (E of 63 kPa, σ_f of 0.267 MPa, ε_f of 44.89, and W of 6.65 kJ m^{-3}). Figure 3b showed that the tearing energy of Agar/HPAAm DN gel was ≈1000 J m^{-2}, comparable to that of chemically linked PAMPS/PAAm DN gel (10^2–10^3 J m^{-2}), cartilages (10^2–10^3 J m^{-2}), and rubbers (10^2–10^3 J m^{-2}), but higher than that of hybrid-linked Agar/PAAm DN gel (≈800 J m^{-2}) and HPAAm SN gel (≈350 J m^{-2}). Addition of a small amount of agar in the HPAAm gel also led to a significant increase in tearing energy (≈650 J m^{-2}), implying that the rigid and brittle agar can enhance the

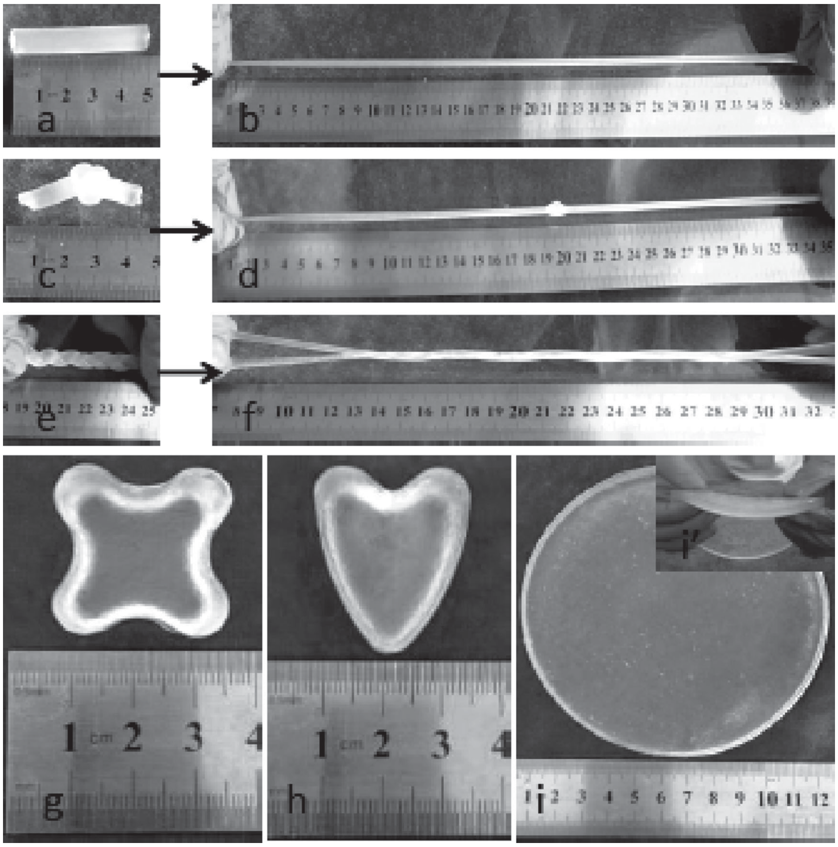

Figure 2. Agar/HPAAm DN gels exhibit extraordinary mechanical properties: a,b) ordinary stretching; c,d) knotted stretching; e,f) twisted stretching; and free-shapeable properties (g,h,i,i′).

fracture propagation resistance of the DN gels, consistent with the results in Figure 3a. Figure 3c showed that after a deformational loading, Agar/HPAAm DN gel can rapidly recover its original shape in 2 min without any observable residual strain, while HPAAm SN gel deformed seriously at both ends and cannot recover its original shape even after 1 h. We also examined the notch-dependence of tensile properties on our Agar/HPAAm DN gels. In Figure 3d, when Agar/HPAAm gel with a cut notch (≈10 mm) was stretched up to 7 times, the notch was dramatically blunted and remained stable, indicating that no stress concentrates in the front of the notch tip. To our knowledge, this is the first report of a fully physically linked DN hydrogel, showing comparable mechanical properties to chemically linked DN gels and self-recovery and notch-insensitive to hybrid-linked DN gels. In contrast to a conventional view of weak physically linked gels, our fully physically crosslinked Agar/HPAAm DN gel demonstrates that a combination of hydrophobic interactions and hydrogen bonds between and within the networks enables to achieve highly mechanical strength and toughness, comparable to conventional chemically linked and hybrid linked DN gels.

We further conducted a series of tensile tests to investigate three important parameters – total monomer concentrations of AAm and SMA (C_{total}), molar ratio of SMA to AAm, and agar concentration – on mechanical properties of Agar/HPAAm DN gels (Tables S1–S3, Supporting Information). With the increase of C_{total} at the fixed molar ratios of SMA/AAm, the gels showed prominent enhancement in elastic modulus (E), fracture stress (σ_f), and dissipated energy (W). Specifically, the gels achieved the best mechanical properties (E of 73 kPa, σ_f of 0.244 MPa, and W of 6.78 kJ m^{-3}) at $C_{\text{total}} >$ 30% w/v (Table S1, Supporting Information). Molar ratio of SMA:AAm is another parameter important for tough gels. The dissipated energy of Agar/HPAAm gels increased with SMA:AAm ratios ranged from 0.1 to 1.0 mol%. The gels achieved a maximal W of 9.35 kJ m^{-3} at 1.0 mol% of SMA:AAm, comparable to Agar/PAAm DN gels (W=9.0 kJ m^{-3}) and PAMPS/PAAm DN gels (W= 14 kJ m^{-3}), as well as the balanced mechanical properties (E of 134 kPa, σ_f of 0.203 MPa, and W of 7.86 kJ m^{-3}) at a very small SMA:AAm ratio of 0.3 mol% (Table S2, Supporting Information). Moreover, dependence of agar concentrations on the mechanical properties of Agar/HPAAm gels revealed that the gels showed superior mechanical properties (E = 106–113 kPa, σ_f = 0.26–0.37 MPa, ε_f = 33.9–52.6, and W = 7.16–9.96 MJ m^{-3}) at agar concentrations of >20 mg mL^{-1} (Table S3, Supporting Information), even exceed conventional chemically linked DN gels. Unless otherwise stated, below we mainly focused on Agar/HPAAm DN gels prepared at the optimal polymerization conditions (C_{total} of 30 w/v, %, SMA/AAm of 1.0 mol%, and agar concentration of 20 mg mL^{-1}).

2.3. Hysteresis and Softening of Agar/HPAAm DN Gel

Figure 4a compared the stress–strain curves of the three types of hydrogels during a loading–unloading cycle to reveal their energy dissipation capacity, another indicator to assess the mechanical property of gels. At λ = 10, both Agar/HPAAm DN gel and Agar/PAAm DN gel showed similar large hysteresis loops, while weak HPAAm SN gel only showed a very small hysteresis loop. Consistently, Agar/HPAAm and Agar/PAAm DN gels had comparable dissipated energies (U_{hys}) of 503 and 526 kJ m^{-3}, respectively, which were much higher than U_{hys} of 86 kJ m^{-3} for HPAAm gel (Table S4, Supporting Information). These results support that upon deformation both Agar/HPAAm and Agar/PAAm DN gels dissipate energy more efficiently than HPAAm gel, thus leading to high mechanical strength and toughness. After the first loading–unloading cycle, the second loading cycle was applied immediately to the same gel specimens. It can be seen in Figure 4b that all three types of gels exhibited very small hysteresis loops, indicating that the first-loading-induced network fracture cannot recover immediately without the resting, resulting in very limited energy dissipation in the second loading. The small plateau region in the loading/unloading curves was mainly caused by residual strain effect (Figure 4a,b). This residual strain effect can be effectively eliminated after 2 min resting time (Figure 3c). Quantitatively,

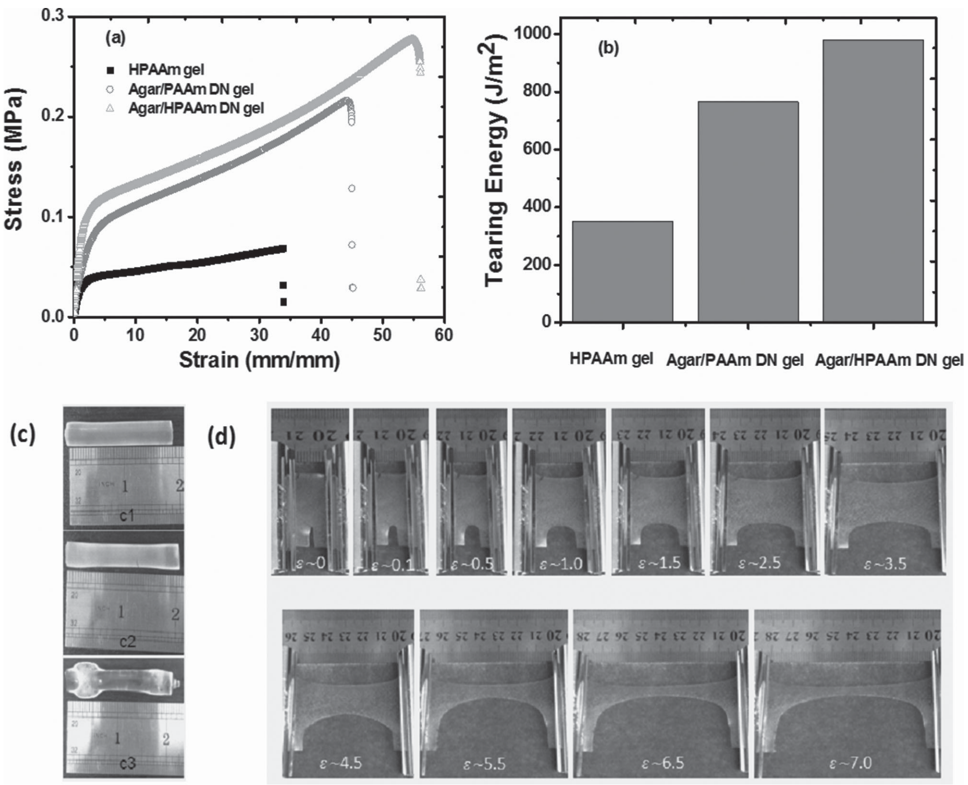

Figure 3. a) Tensile stress–strain curves of HPAAm gel, Agar/PAAm DN gel, and Agar/HPAAm DN gel. b) Tearing energies of HPAAm gel, Agar/PAAm DN gel, and Agar/HPAAm DN gel at a 50 mm min^{-1}. c) Visual inspection of the recovery of Agar/HPAAm DN gel before tensile tests (c1) and after tensile tests for 2 min (c2), as well as of HPAAm gel after tensile test for 1 h (c3). d) Crack resistance by stretching a notched Agar/HPAAm DN gel.

Agar/HPAAm DN gel, Agar/PAAm DN gel, and HPAAm SN gel lost their 84%, 90%, and 60% of toughness (i.e., the corresponding $U_{\mathrm{hys},s}/U_{\mathrm{hys},f}$ values of 16%, 10%, and 40%, Table S4, Supporting Information) and their 78%, 67%, and 62% of elastic modulus (i.e., the corresponding E values of 106 kPa/22 kPa, 63 kPa/21 kPa, and 37 kPa/14 kPa, Figure 4c and Table S4, Supporting Information), respectively. These results indicate that regardless of different network chemistry, structures, and interactions, the first loading soften and weaken all the three gels, but softening behaviors concomitantly with large energy dissipation become even more prominent for both Agar/HPAAm DN gel and Agar/PAAm DN gels.

2.4. Self-Recovery and Fatigue Resistance of Agar/HPAAm DN Gel

Considering that both networks in Agar/HPAAm DN gel are physically linked via reversible noncovalent interactions, we further conducted the loading–unloading tests to examine the self-recovery properties of Agar/HPAAm DN gels at room temperature without any external stimuli. Two recovery rates (%) are defined: a ratio of elastic modulus (E, represents a stiffness recovery) and a ratio of energy loss (U_{hys}, represents a toughness recovery) at different resting times to that of the first loading cycle at a maximum $\lambda_{\max}$ of 10. **Figure 5**a showed that both recovery rates of Agar/HPAAm DN gels increased as time. The hysteresis loop after 10 min recovery is much larger than that of without recovery (Figure S1, Supporting Information). Specifically, Agar/HPAAm gels achieved a rapid recovery of ≈50% of stiffness (53 kPa) and ≈40% of toughness (197 kJ m^{-3}) after 2 min, and a maximal recovery of ≈66% of stiffness (70 kPa) and ≈52% of toughness (262 kJ m^{-3}) after 120 min. The stiffness recovery is comparable to that of hybrid Agar/PAAm DN gel (≈63 kPa), but is almost 2 times larger than that of HPAAm SN gel (≈37 kPa) (Tables S4 and S5, Supporting Information). The internal damage of networks can be much better recovered with the increase of resting time before reloading. The rapid self-recovery property of Agar/HPAAm DN gel may also indicate good fatigue resistance of the gel at the same conditions. In Figure 5b and Figure S2, Supporting Information, after the first loading, dissipated energies remained almost unchanged at ≈225 kJ m^{-3} for successive five loading–unloading cycles with 10 min resting between each cycle. This value (≈225 kJ m^{-3}) was ≈3 times larger than the dissipated energy of the immediate second loading without recovery (80 kJ m^{-3}), and also even larger than that of HPAAm SN gel in the first loading (86 kJ m^{-3}).

Interestingly, we found that Agar/HPAAm DN gels behaved like a rubber ball (**Figure 6**a). A ball made of Agar/HPAAm DN gel (≈3 cm in diameter) can bounce back to the half of height where the ball was dropped (Movie S2, Supporting Information). More impressively, a scaled-up Agar/HPAAm DN gel disk (12 cm in diameter) can bear car crash back-and-forth for 40 times, while still retaining its integrity without any observable breakage (Figure 6b and Movie S3, Supporting Information). In contrast to our hybrid Agar/PAAm DN

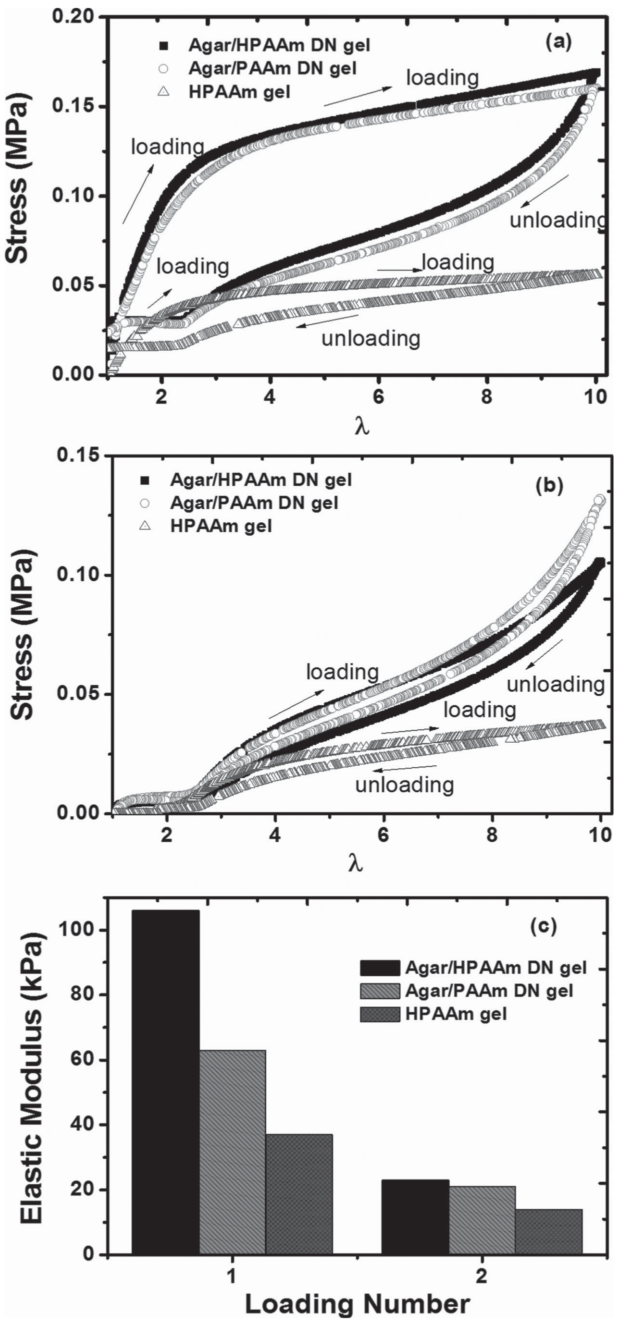

Figure 4. a) The first and b) the second, immediate cyclic loading–unloading stress–strain curves of Agar/HPAAm DN gel, Agar/PAAm DN gel, and HPAAm gel at $\lambda = 10$. c) Comparison of elastic modulus of Agar/HPAAm DN gel, Agar/PAAm DN gel, and HPAAm gel between the first and the second immediate loadings.

gels that show no recovery at temperatures below agar T_m of ≈90 °C, Agar/HPAAm DN gels show not only highly mechanical strengthens and toughness, but also rapid self-recovery and superior fatigue resistance at room temperature. The results support our new design strategy that introduction of a ductile gel with strong physical interactions as the second network enables to help dissipate energy, thus promoting improve mechanical strength and fatigue resistance.

2.5. Self-Healing of Agar/HPAAm DN Gel

Different from self-recovery tests using the intact gels, we further challenged our Agar/HPAAm DN gel for its self-healing property. The Agar/HPAAm DN gel was cut into two or multiple pieces completely, and the cut pieces were physically put together at room temperature for 24 h. **Figure 7**a showed that one healed gel with alternative colors can withstand the load of their own weights and bending, while another healed gel was mechanically stable to resist the breaking to withstand a rather large stretching of ≈200%. The same tensile tests were performed on the original and healed gel samples to quantitatively evaluate their mechanical properties and to relate to their self-healing properties. Figure 7b showed that the healed Agar/HPAAm DN gel achieved σ_f of 0.109 MPa and ε_f of ≈170%, while the healed HPAAm SN gel showed much lower σ_f of 0.033 MPa and ε_f of ≈125%. Healing efficiencies ($\sigma_f/\sigma_{f,0}$) of Agar/HPAAm and HPAAm gels were 40% and 50%, respectively (Figure 7c). The effects of healing reagent (H_2O, tetrahydrofuran (THF), or SDS/NaCl solution), heating treatment (10–30 min heating at 95 °C), and healing times (48 and 72 h) on the healing efficiency of Agar/HPAAm DN gel were also investigated (data not shown). Overall, healing efficiency did not exceed 40%. Our results further demonstrate that use of the second, physically linked ductile network introduces a new self-healing property to DN gels.

2.6. Toughening Mechanisms of DN Gels

Current knowledge of DN gels from synthesis methods to toughening mechanisms mainly derives from chemically cross-linked DN gels. Only a few hybrid physically–chemically linked DN gels were developed recently, all of which have the first networks being physically linked via ionic association, hydrogen bonds, and/or hydrophobic interactions. Different from these chemically linked or hybrid-linked DN gels, here we developed a new type of DN gels with both networks being fully physically linked. Considering different network structures and underlying association forces among the three types of gels (i.e., physically linked Agar/HPAAm, chemically linked PAMPS/PAAm, and hybrid-linked Agar/PAAm DN gels), it is more important to compare and reveal some similarities and differences for possible toughening, fatigue resistance, and self-healing mechanisms among these DN gels.

For the chemically linked PAMPS/PAAm DN gels,[23,36,38] the toughening mechanism is mainly based on the "sacrificial bonds" concept. Briefly, upon deformation, the first network of the gels made of strong polyelectrolytes permanently ruptures into small clusters, and these broken clusters likely serve as sacrificial bonds to protect the second chemically linked network and to increase its resistance against crack propagation by forming a large damage zone. Meanwhile, permanent damage of the first network also causes the irreversible energy dissipation in the hysteresis measurement.

For hybrid Agar/PAAm DN gels, different tensile behaviors (e.g., much lower yielding stress/strain, no stable necking platform, and simultaneous necking) were found, suggesting

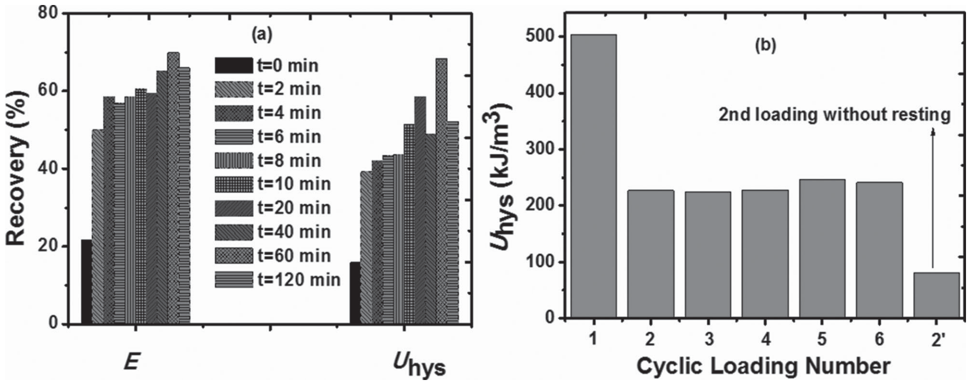

Figure 5. a) Stiffness and toughness recoveries of Agar/HPAAm DN gel at different resting times when comparing elastic modulus and dissipated energies to those of the initial first loading. b) Dissipated energies of Agar/HPAAm DN gel for the same gel specimen in six successive loading with 10 min recovery between two tests at $\lambda = 10$.

a new "chain-pulling-out" fracture mechanism.[39] During the deformation process, the first agar network does not fracture into small clusters, instead the agar chains progressively pull out from the aggregated agar helical bundles. Such "chain-pulling-out" and disassociation behaviors of agars neither break the first network nor change agar helical conformation, thus the agar network retains its continuous phase. This continuous fracture process causes hybrid Agar/PAAm DN gels to show velocity-dependent fracture behaviors and toughness, which is fundamentally different from the nearly velocity-independent mechanical properties in chemically linked PAMPS/PAAm DN gel. In addition, agar helical bundles can reform more efficiently during a time-interval after the loading or under temperature stimuli, leading to the self-recovery of internal damage.

For both chemically linked PAMPS/PAAm and hybrid-linked Agar/PAAm DN gels, large hysteresis and high toughness origins from the fracture of the first network, regardless of physically or chemically linked, resulting in effective energy dissipation. Meanwhile, the PAAm chains in the second network cannot bear large stress due to their soft nature. After the elastically effective chains of the first network are fractured at small strains, the stress will be transferred back to the elastically ineffective chains in the first network from the PAAm network at larger strains, resulting in further breaks of those ineffective chains in the first network. Thus, on subsequent loadings, the fracture energy of the gels is much reduced.

The Agar/HPAAm DN gel exhibited similar yielding, large hysteresis, and softening behavior to conventional chemically linked PAMPS/PAAm DN gels, suggesting that the fracture of the first network, regardless of physically or chemically bonded network, is a general way to effectively dissipate energy upon deformation. However, different from the network structures of hybrid-linked Agar/PAAm and chemically linked PAMPS/PAAm DN gels, Agar/HPAAm DN gels with both networks being physically linked showed that when Agar/HPAAm DN gel was stretched, both networks participated in energy dissipation via chain dissociations (**Figure 8**), resulting in a large hysteresis of DN gels. Thus, Agar/HPAAm DN gels exhibited slightly higher mechanical strength and toughness than hybrid Agar/PAAm gel (Figure 3a,b). Since the second network is designed and formed with reversible, noncovalent bonds via strong hydrophobic interactions between SDS micelles and alkyl groups of SMA side chains, the temporarily dissociated noncovalent bonds in the second HPAAm network can be rapidly reconstructed at room temperature without any external stimuli, leading to the fast self-recovery of hydrogel's stiffness (≈60%) and toughness (40%–50%) from the softening even after several minutes (Figure 5a and Table S5, Supporting Information). But, a full recovery of mechanical properties cannot be realized at room temperature, because the broken agar network is unable to automatically recover via the reformation of agar helical bundles at room temperature. In sharp contrast to the former hybrid Agar/PAAm gels whose recovery solely origins from the first agar network under elevated temperatures, the self-recovery of Agar/HPAAm DN gel at room temperature without any

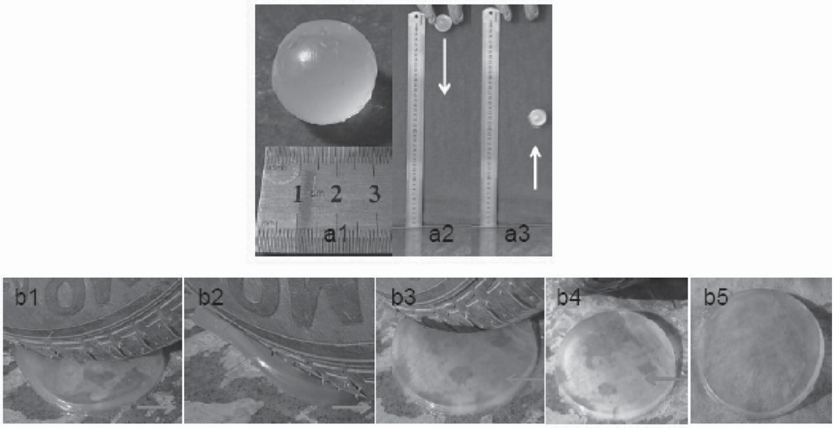

Figure 6. a1) A ball made of Agar/HPAAm DN gel with a 3 cm diameter; the ball is freely dropped (a2) and bounced back to the half-height where it was dropped (a3); b1–b4) a Agar/HPAAm DN gel disk (12 cm in diameter and 1 cm in thickness) was crashed by a car for 40 times and the gel was recovered immediately after 40-time car crash (b5). The red arrow indicates a car crash direction.

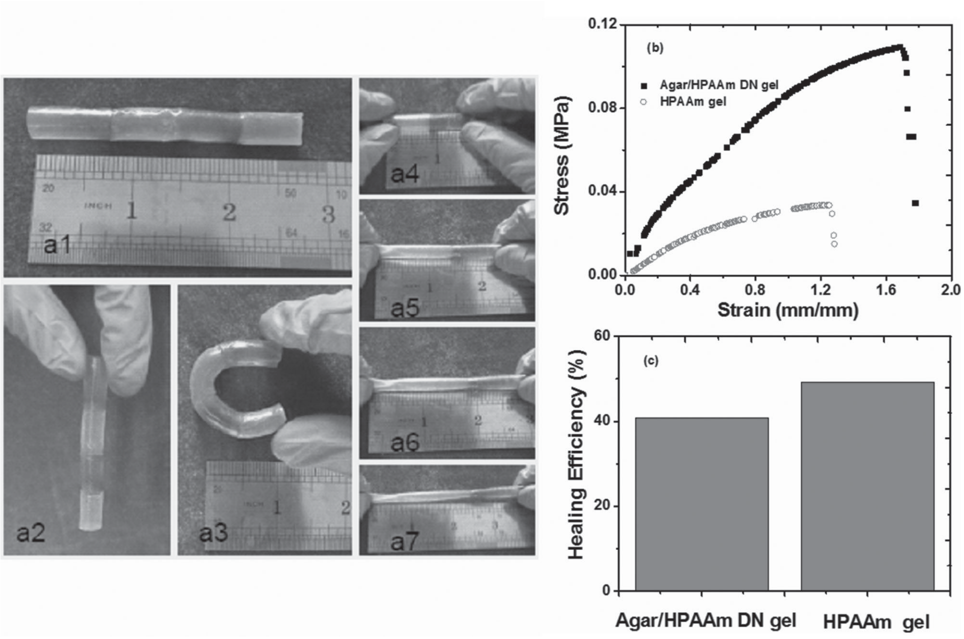

Figure 7. a) Self-healing properties of Agar/HPAAm DN gel at room temperature for 24 h. The healed gel (a1) can bear its weight (a2), can be bended without break (a3), and can be stretched up to ≈200% in length (a4–a7). b) Tensile stress–strain curves of healed Agar/HPAAm DN gel and healed HPAAm SN gel. c) Healing efficiency of Agar/HPAAm DN gel and HPAAm SN gel.

external stimuli origins from the second HPAAm network via reversible hydrophobic interactions. Due to the rapid self-recovery of Agar/HPAAm DN gel at room temperature, Agar/HPAAm DN gel possessed remarkable fatigue resistance upon successive cyclic loading. Agar/HPAAm DN gel exhibited the higher elastic modulus and dissipated energies after the first loading in a short recovery time than HPAAm gel at the first loading (Tables S4 and S5, Supporting Information). This indicates that during the (re)loading process, the second HPAAm network helps to bear stress as the first agar network is fractured. Consequently, the stress acting on the second network will not transfer back to the agar network, leading to that (i) only elastically effective chains in the agar network are fractured and (ii) the remaining agar network can still retain some elastic modulus. Thus, as the second HPAAm network was reconstructed upon unloading/resting, the elastic modulus of Agar/HPAAm DN gel (53–70 kPa) was higher than that of HPAAm gel (37 kPa) (Tables S4 and S5, Supporting Information), demonstrating its excellent fatigue resistance with larger dissipated energies.

The self-healing property of Agar/HPAAm DN gel also comes from the second HPAAm network. As the cut gel pieces were in contact with each other, the HPAAM chains at the two outermost layers tended to be reassembled with SDS

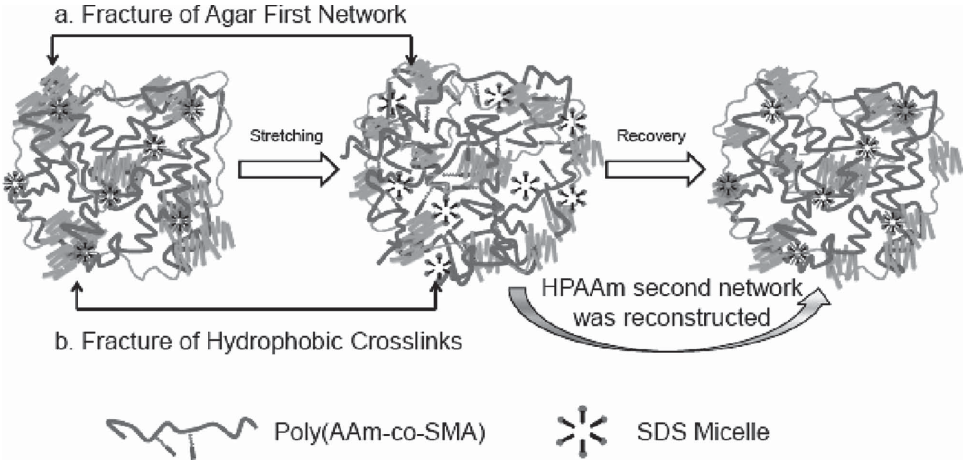

Figure 8. Schematic of the fracture and self-recovery mechanisms of Agar/HPAAm DN gels.

micelles at the interface via hydrophobic interactions. The healing efficiency of the gels was ≈40% under a wide range of conditions tested, largely relying on the diffusion ability of hydrophobic components across a rupture interface. Taken together, our new design strategy is demonstrated to use a ductile and tough (not ductile and soft) gel as the second network for fabrication of a new type of fully physically linked DN gels with high strength, toughness, fatigue resistance, and self-healing properties.

3. Conclusions

In this work, we developed a new design strategy to fabricate a new type of fully physically linked Agar/HPAAm DN gel, consisting of the hydrogen-bond crosslinked agar gel as the first network and the hydrophobically crosslinked HPAAm gel as the second network. Use of ductile, nonsoft HPAAm gel as the second network can not only effectively dissipate energy and thus greatly enhance the mechanical properties, but also introduce superior self-recovery and self-healing properties via reversible network reconstruction. At the optimal formulation, Agar/HPAAm gels showed high mechanical strength and toughness, comparable to conventional chemically linked DN gels and superior to hybrid-linked DN gels. More importantly, due to its unique physically, reversible network structures, the gels can sufficiently and quickly reconstruct the gel network structures, leading to rapid self-recovery and self-healing from softening and damages without any external stimuli at room temperature. Additionally, a unique combination of the one-pot synthesis method and the gel system enables to produce any free-shapeable complex-shape gels. Our design strategy may open a new gel platform for development of soft-and-tough materials with many integrated mechanical properties, particularly by tuning the second network structures and properties.

4. Experimental Section

Materials: All chemicals and solvents purchased were of the highest available purity, and unless otherwise stated they were used as received. Agar (gel strength of >800 g cm^{-2} and melting point of 85–90 °C) was purchased from Sigma-Aldrich Inc., 2-hydroxy-4′-(2-hydoxyethoxy)-2-methylpropiophenone (Irgacure 2959) and acrylamide (AAm, 98%) were purchased from TCI Shanghai Inc. Stearyl methacrylate (SMA), sodium dodecyl sulfate (SDS), and sodium chloride were purchased from Aladdin (Shanghai) Inc.

Preparation of Agar/HPAAm DN Gels: Agar/HPAAm DN gels were synthesized by a one-pot method as reported in our previous work with modification.[35] The composition of DN gels was referred to as A_x-H_y-Am_z, where A, H, and Am represent agar, hydrophobic monomer (SMA), and AAm, respectively, x is the concentration of agar (mg mL^{-1}), y is the molar ratio of SMA to AAm, and z was the total monomer concentration of SMA and AAm (% w/v). 7% SDS/ 0.5 M NaCl aqueous solution was used as solvent as reported by Okey's group.[40] For example, A_{20}-$H_{1.0}$-Am_{30} meant agar was 20 mg mL^{-1}, SMA was 1.0 mol% of AAm, and the total monomer was 30% w/v in feed. Briefly, for synthesis A_{20}-$H_{1.0}$-Am_{30}, agar (200 mg), AAm (2.8636 g), SMA (0.1364 g, 1 mol% of AAm), Irgacure 2959 (0.0913 g, 1 mol% of total monomer), and 7% SDS/0.5 M NaCl aqueous solution (10 mL) were added into a reactor, and the reactor was sealed under N_2 protection after three degassing cycles and then gradually heated up to 95 °C in an oil bath for about 10–20 min to dissolve all the reactants in the SDS/NaCl solution. The resulting solution was transparent, low viscosity, and could be easily injected into a plastic mold (D = 8.5 mm), and followed by cooling the solution at 4 °C for 30 min to form an agar gel first network. The photopolymerization reaction was carried out to form an Agar/HPAAm DN gel under UV light (λ = 365 nm wavelength, intensity of 8 W) for 1 h. The HPAAm gels were synthesized with the same process of Agar/HPAAm DN gels expect for no agar added. Agar/PAAm DN gels were also prepared as reported previously but 7% SDS/0.5 M NaCl aqueous solution was used as solvent instead of water, and MBA was used as chemical cross-linker of PAAm network (0.03 mol% of AAm). After polymerization, all the gels were stored at 4 °C for mechanical tests. Before mechanical tests, the gel specimens were stayed at room temperature about 30 min.

Mechanical Tests: Tearing testing was performed using commercial test machine with a 100 N load cell. The gel samples were cut into a trousers shape (40 mm in length, 10 mm in width, and 10 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 at 50 mm min^{-1}. The tearing energy (T) is defined as the work required to tear a unit area, as estimated by[41]

$$T = \frac{2F_{\text{ave}}}{w} \quad (1)$$

where F_{ave} is the average force of peak values during steady-state tear, and w is the width of the specimen. Uniaxial tensile tests of as-prepared gels (diameter = 8.5 mm and length = 60 mm) were carried out using a universal tensile tester equipped with a 100 N load cell with a crosshead speed of 100 mm min^{-1}. For hysteresis measurement, gel specimens were first stretched to a maximum extension ratio $\lambda = 10$ and then unloaded. The elastic modulus (E) was calculated in the initial linear range from the stress–strain curves. The dissipated energy (U_{hys}) was estimated by area below the stress–strain curves or between the loading–unloading curves. For self-healing tests, gel specimens were first cut into two pieces, and then contacted for healing 24 h at room temperature. After healing, the tensile test was conducted at the same crosshead speed of 100 mm min^{-1}.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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