Dipole–Dipole and H-Bonding Interactions Significantly Enhance the Multifaceted Mechanical Properties of Thermoresponsive Shape Memory Hydrogels

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High strength hydrogels were previously constructed based on dipole–dipole and hydrogen bonding reinforcement. In spite of the high tensile and compressive strengths achieved, the fracture energy of the hydrogels strengthened with sole noncovalent bondings was rather low due to the lack in energy dissipating mechanism. In this study, combined dipole–dipole and hydrogen bonding interactions reinforced (DHIR) hydrogels are synthesized by one-step copolymerization of three feature monomers, namely acrylonitrile (AN, dipole monomer), acrylamide (AAm, H-bonding monomer), and 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS, anionic monomer) in the presence of PEGDA575, a hydrophilic crosslinker. The electrostatic repulsion from PAMPS allows the gel network to absorb water readily, and meanwhile the synergistic effect of dipole–dipole and H-bonding interactions enable the DHIR hydrogel to withstand up to 8.3 MPa tensile stress, 4.8 MPa compressive stress and 140–716% elongation at break with the fracture energy reaching as high as 5500 J/m^2. In addition, this DHIR hydrogel exhibits reversible mechanical properties after undergoing cyclic loading and unloading. Interestingly, the DHIR hydrogels with appropriate compositions demonstrate temperature-tunable mechanical properties as well as accompanied shape memory effect. The dual noncovalent bonding strengthening mechanism reported here offers a universal strategy for significantly enhancing the comprehensive mechanical properties of hydrogels.

1. Introduction

Polymer gels, a type of intriguing soft and wet materials, have been investigated both theoretically and experimentally in the past decades.[1,2] In particular, hydrogels consisting of water swollen chemically or physically crosslinked polymer networks are being exploited as a wide range of biomedical applications such as cell scaffolds, soft tissue substitutes and bioactuators.[1,3] However, their load-bearing applications are often limited by the poor mechanical performances.[4,5] Conventional hydrogels do not exhibit high mechanical properties because of uneven crosslinking and weak interaction among the chains. Recently, several high mechanical hydrogels have been developed and investigated as potential soft tissue replacements,[6,7] but few of them exhibit a combination of high mechanical properties including stiffness, toughness, tensile and compressive strengths, anti-fatigue as well as mechanical recoverability.[8,9] The well-known slide-ring[10] and tetra-PEG[11] hydrogels are designed to have ideally homogeneous networks to eliminate the intrinsic defects to a maximum extent, eventually leading to the enhanced mechanical properties. Other strategies are advanced to increase the functionalities[12] between two crosslink points to toughen the hydrogels, such as inorganic nanocomposite hydrogels,[13–15] macromolecular microsphere composite hydrogels,[16] graphene[17,18] or its oxide[19] composite hydrogels and micro-[20] or nano-structure[21] hydrogels. All of these gels have high compressive strength and large elongation, but their tensile strength (ranging from 190 kPa to 600 kPa) and modulus are not satisfied enough; furthermore, their high elastic properties show no hysteresis behavior, thus lacking a mechanism for mechanical energy dissipating. As a result, the mechanical properties are observably reduced when the gels contain a defect.[9] In order to solve these problems, a variety of mechanical energy dissipation mechanisms are implemented into the network to toughen the hydrogels. For instance, the PAMPS/PAAm double network (DN) gels can sacrifice the rigid chemical bond of the first network to dissipate energy to achieve MPa magnitude order of tensile and compressive stress but the fatigue resistance is low, and the preparation process is relatively complicated.[22–25] Suo and his co-workers[9] reported synthesis of a hydrogel with high stretchability and astonishing fracture energies of 9,000 J/m^2 by forming interpenetrating polymer networks of covalently crosslinked PAAm and ionically crosslinked zipper-like

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alginate. Another important feature is that the mechanical properties of the gels can mostly be recovered by storing them at a high temperature, but the tensile strengths were lower than 1 MPa. Recently, one-pot preparation of thermo-reversible double-network hydrogels composed of agar and polyacrylamide was reported.[26] This physically linked DN gel simplified the synthetic procedure, and demonstrated 90% recoverable mechanical properties while it was heated up to 100 °C, which is harsh for application in vivo. Except for DN strategy, efforts have been also devoted to seeking new strengthening mechanisms to make mechanically strong single-network hydrogels for the synthesis simplicity, such as hydrophobic interaction,[27] sacrificial lamellar bilayers[28] and ionic crosslink.[29] However, the tensile strengths are far from belonging to high-strength categories. These hydrogels are often endowed with impressive large elongations, though the elastic moduli are much lower than those of load-bearing soft tissues. If we consider replacing the defected cartilages or tendons with synthetic high strength hydrogels, an appropriate elongation is quite enough, whereas one of important considerations is to enhance the ability of a substitute to prevent large deformation in orchestrating multifaceted mechanical properties.

In our previous studies we demonstrated that strong physical crosslinking stemming from diaminotriazine–diaminotriazine (DAT–DAT) hydrogen bondings[30–33] as well as inter-cyano dipole–dipole reinforcement (DDR) could contribute to very strong hydrogels with high moduli and excellent antifatigue performance.[33–35] However, in order to make highly hydrated hydrogels, high concentrations of hydrophilic crosslinkers were indispensable; in some cases, the weight ratio of crosslinker to total monomers even reached 1/2.[35] Although the high degree of chemical crosslinking led to high mechanical properties, the fracture energy was unavoidably sacrificed, rendering the gels highly susceptible to notches.

In this work, we aimed to construct a high strength hydrogel with ultra-toughness. We considered introducing dual physical interactions of dipole–dipole pairings and hydrogen bonding into the networks at a much lower chemical crosslinking density. This system consisted of three main components: A dipole–dipole interacting monomer, acrylonitrile (AN), a hydrogen bonding monomer, acrylamide (AAm) and an anionic monomer, 2-acrylamide-2-methylpropanesulfonic acid (AMPS). We hypothesized that hydrophobic AN-AN dipole pairings would contribute to the increased stiffness, and hydrophilic weaker hydrogen bondings among AAm would be easily fractured to dissipate energy; the electrostatic repulsion of PAMPS was expected to expand the network, thereby enhancing the hydration of the gels. Our previous study has revealed that at an elevated temperature the dipole–dipole interactions were broken, which resulted in thermo-responsive change in modulus of hydrogels.[36] But the temperature was as high as 80 °C, much higher than body temperature. In this study, we would also develop a temperature sensitive high strength shape memory hydrogels with a wider temperature-sensitive window from 15 to 60 °C without occurrence of water loss or uptaking, which is anticipated to extend its potential application as load-bearing soft tissue substitutes and bioactuators.[37]

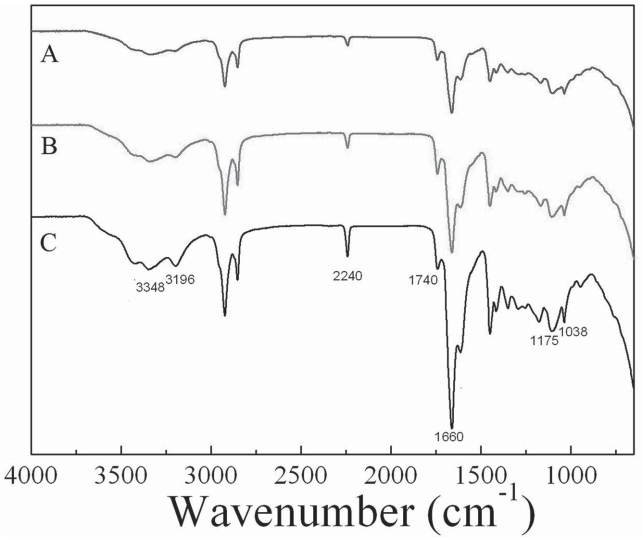


Figure 1. AIR-FTIR spectra of A) DHIR40–5–55–0.0625, B) DHIR60–5–35–0.0625, C) DHIR70–5–25–0.0625 hydrogel samples.

2. Result and Discussion

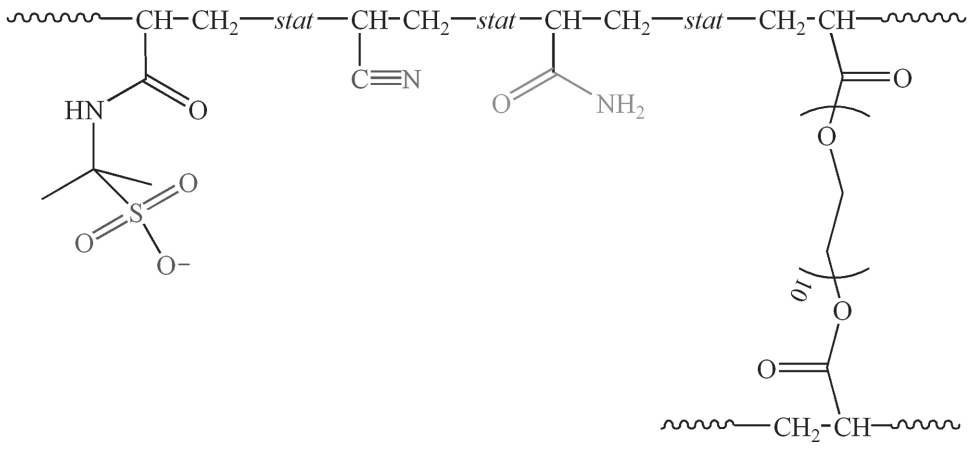
2.1. Characterization of DHIR Hydrogels

Figure 1 displays the AIR-FTIR spectra of the hydrogels. The intense bands appearing at 1740 cm^{-1} in the three spectra are attributed to the stretching vibrations of C = O in PEGDA575 crosslinker. The strong band at 2240 cm^{-1} assigned to C≡N evidences the successful incorporation of polyacrylonitrile in hydrogels.[38] The PAAm component can be confirmed by the appearance of symmetric and anti-symmetric stretching vibration absorption bands of amino at 3348 cm^{-1}, 3196 cm^{-1}, the stretching and bending vibration peaks of carbonyl group on AAm at 1660 cm^{-1} and the bending vibration peak of methylene at 1415 cm^{-1}. The absorption peak of O = S = O at 1175 cm^{-1} and 1038 cm^{-1} suggests the presence of PAMPS in the hydrogel.[36] The schematic diagram of network structure is shown in **Scheme 1**.

2.2. Swelling Characteristics of Hydrogels

Cartilage, a watery substance, contains up of 65 to 80% water, which accounts for the resilience and elasticity of this soft tissue. Polyacrylonitrile (PAN), however, is a hydrophobic resin, so it cannot be directly used as a cartilage substitute. To make the equilibrium water content (EWC) of hydrogels suited for need of cartilage, AN was copolymerized with hydrophilic monomer and crosslinker without hydrolyzing PAN in this study. We found that the hydrogels with 32–98% EWCs could be conveniently synthesized by tuning feed ratios.

The molecular structure of DHIR hydrogel depicted in Scheme 1 clearly shows that the gel includes three main intermolecular forces, that is, attractive dipole–dipole interaction of cyano, hydrogen bonding of AAm as well as electrostatic repulsion of SO_3^-. The attraction from physical interactions and charge repulsion are seemingly contradictive in making



Scheme 1. Molecular structure of DHIR hydrogel.

mechanically strong hydrogels. dipole–dipole interaction is more dependent on the microenvironment of two cyanos, such as distance and configuration of the polymer chains;[38] CN-CN pairings can generate hydrophobic microdomains, and thus is more stable in water. The theoretical calculation of free energies of amide hydrogen bond formation indicates that amide hydrogen bonds are, at best, marginally stable in aqueous phase, while they are very stable in liquid alkane.[39] To inspect the existence of hydrogen bonding among AAm and its influence on the swelling of hydrogels, PEGDA575-crosslinked P(AAm-AMPS), DHIR60–5–35–0.0625 and PEGDA575-crosslinked P(AN-AMPS) hydrogels were immersed in deionized water, PBS and 30 wt% urea solution, a H-bond breaking reagent (**Figure 2**). We find the swelling volume of all the gels remains almost unchanged both in water and PBS, manifesting their "non-swellable" properties.[40] DHIR0–5–95–0.0625 gel in the absence of PAN just slightly increases in swelling volume after being soaked in 30 wt% urea aqueous solution for 1 d, suggesting that even in water and PBS, the majority of hydrogen bondings among AAm may be dissociated due to high degree of hydration and the remaining H-bonds exert a negligible effect on the swelling of hydrogels. Likewise, treatment of DHIR95–5–0–0.0625 hydrogel in the absence of AAm with urea does not vary its volume, indicating urea is unable to influence the dipole interactions. Interestingly, DHIR60–5–35–0.0625 copolymerized with AN and AAm becomes highly swollen in urea solution. This implies that under the protection of hydrophobic microdomains formed by dipole–dipole interaction, H-bonding among AAm can be stabilized and acts as an effective physical crosslinking. The stabilization of H-bonding in hydrophobic micromilieu was also confirmed by the latest work on supramolecular hydrogels.[41] When the DHIR hydrogel was treated with urea, these hydrogen bondings are dissociated to bringing about the expansion of hydrogel network. The result evidences that hydrogen bondings of AAm truly matter in retaining the crosslinking density of network in this DHIR hydrogel.

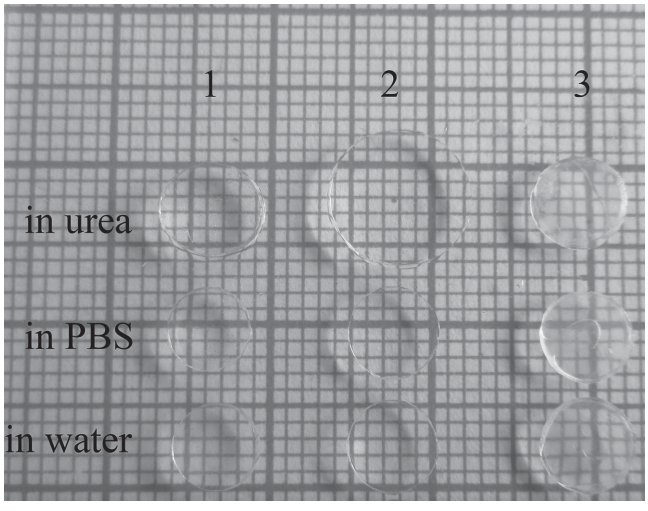


Figure 2. Hydrogel discs of 1) DHIR0–5–95–0.0625, 2) DHIR60–5–35–0.0625, and 3) DHIR95–5–0–0.0625 immersed in 30 wt% urea aqueous solution, PBS and deionized water for 1 day.

In contrast to attractive force of dipole–dipole interaction and hydrogen bonding, the electrostatic repulsion would lead to the expansion of network,[42] generating a negative effect on the dipole–dipole interactions and hydrogen bonding; as a result, the expanded network would weaken the density of physical crosslinking, enabling an appropriate degree of hydration. We established a model to illustrate the synergetic effect of dual physical interactions of dipole–dipole pairing and hydrogen bonding, and the electrostatic repulsion on the properties of hydrogels (**Figure 3**a). The CN–CN dipole pairings and H-bonding are inclined to pull together the network; while negatively charged sulfo groups act to expand the network. We note that our gels were prepared in DMSO. Prior to replacing this organic solvent with water, the gel network was highly swollen due to the strong interaction of DMSO with cynaos and amide moieties, which led to the breakage of CN–CN dipole pairings and AAm–AAm hydrogen bondings. While DMSO in hydrogel was completely replaced with deionized water, the dipole–dipole interaction and AAm-AAm hydrogen bonding would be reconstructed, thereby contributing to the shrinkage of hydrogel somewhat. Nonetheless, the existence of repulsion from SO_3^- and hydrophilic crosslinking aids in maintaining wetting ability of network (Figure 3a).

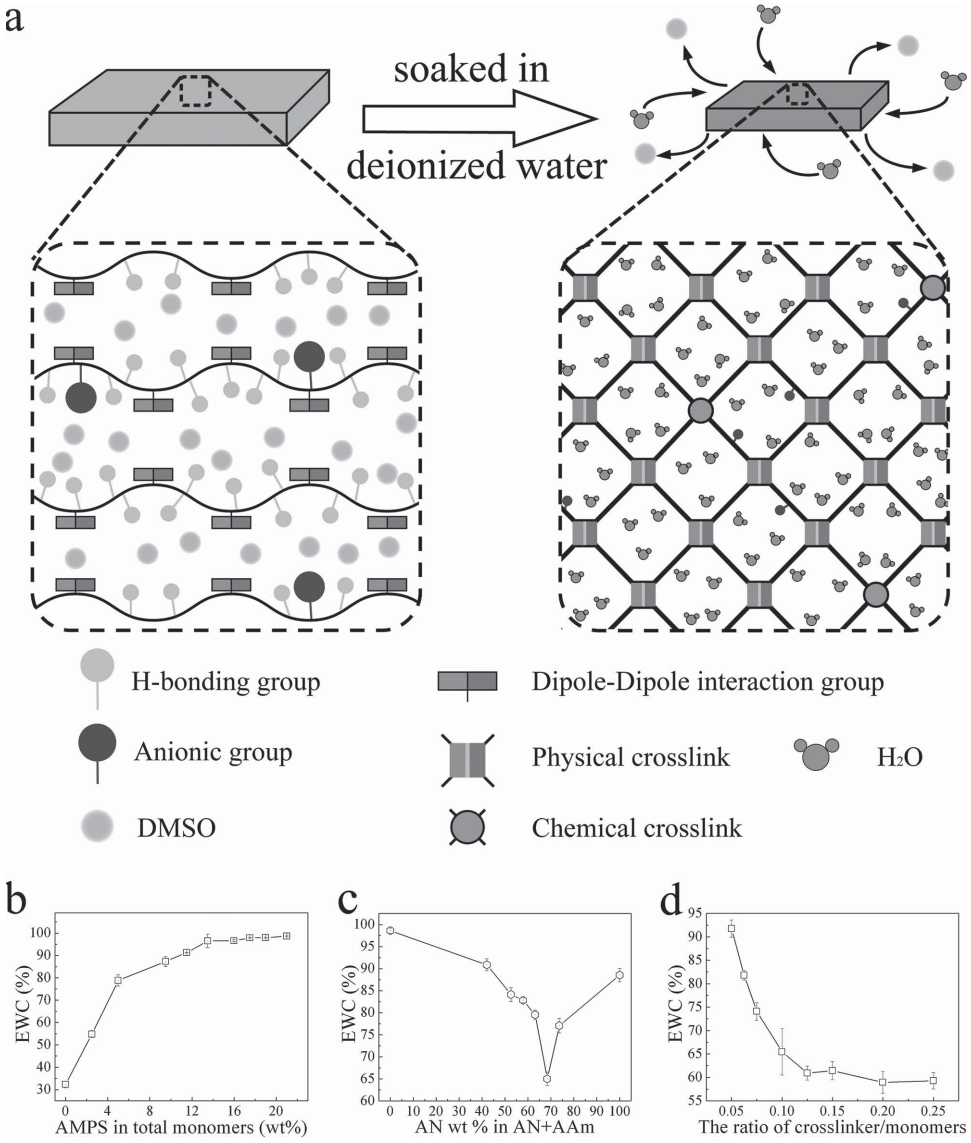


Figure 3. a) Schematic description of the destruction and reconstruction of dual physical crosslinkings in DHIR hydrogel immersing in DMSO and water. Effect of b) AMPS content, c) AN/(AN+AAm), and d) chemical crosslinker content on the EWCs of hydrogels.

Figure 3b shows the effect of AMPS content on the EWCs of the hydrogels. The general feeling is that EWCs of the gels are increased from 30% to 98% upon increasing AMPS content. A close inspection reveals that the EWCs display an increasing trend over 0 wt% to 13.5 wt% AMPS and remain almost unchanged when the concentration is beyond 13.5 wt%. It is not difficult to understand that with an increase in AMPS content, more anionic components are incorporated into the hydrogel, which results in increased repulsion of network, thus allowing more of water to diffuse into the gel. Beyond 13.5 wt% AMPS, the physical attraction and electrostatic repulsion are balanced, and in this case the hydrogel reaches a steady state of swelling state. We also examined the effect of AN content in dipole monomer and H-bonding monomer on the swelling behavior of the hydrogels (Figure 3c). The EWCs do not exhibit a continuous downward trend with the enhancement of AN content. Instead, the swelling degree reaches a minimum value at 68.4 wt% AN content, and then goes up rapidly. This can be interpreted by synergic effect of dual physical interactions. It is possible that physically attractive force from the combined dipole–dipole interaction of AN and H-bond of AAm is intensified with an increment of AN content up to 68.4 wt%. With further increasing AN content, in spite of enhanced dipole–dipole interaction, the contribution from H-bondings of AAm is decreased; thus the net effect of physical attraction is declined. As expected, the EWCs are decreased with enhancing the content of chemical crosslinker due to the increased compactness of network (Figure 3d). Taking into account an appropriate EWC, AN/AAm/AMPS ratio was fixed as 60/5/35 in the following experiment unless otherwise stated.

2.3. Mechanical Properties of the Hydrogels

It has been proven that chemical crosslink contributes to the elasticity of network while physical crosslink tends to

Table 1. Mechanical properties of DHIR60–5–35-d hydrogels with different ratios of crosslinker/monomers.

Ratio of crosslinker/ monomers	Tensile strength [MPa]	Elongation at break [%]	Young's modulus [MPa]	Compressive strength [MPa] at 90%	Fracture energy [J/m^2]
0.0500	5.40 ± 0.07	716.2 ± 18.8	1.83 ± 0.07	5.14 ± 0.35	2005 ± 172
0.0625	8.31 ± 0.44	684.0 ± 57.9	5.61 ± 0.20	4.82 ± 0.45	5496 ± 165
0.0750	7.04 ± 0.52	600.0 ± 25.5	1.96 ± 0.15	4.02 ± 0.77	3654 ± 214
0.1000	4.27 ± 0.21	573.2 ± 31.5	1.52 ± 0.05	2.88 ± 0.30	3076 ± 214
0.1250	3.40 ± 0.13	525.5 ± 16.8	1.10 ± 0.02	2.52 ± 0.56	2789 ± 147
0.1500	3.45 ± 0.41	532.3 ± 10.7	0.87 ± 0.01	2.34 ± 0.23	1845 ± 129
0.2000	1.62 ± 0.03	434.9 ± 7.6	0.64 ± 0.03	1.84 ± 0.11	766 ± 113
0.2500	1.23 ± 0.06	357.4 ± 2.8	0.60 ± 0.01	1.76 ± 0.20	397 ± 25

induce plastic properties.[8,12] In the network where these two crosslinkings co-exist, the elasticity becomes dominated and eventually energy dissipation suffers a lot as the density of chemical crosslink is increased.[9] So it is critical to balance the two crosslinkings to generate a hydrogel with optimal comprehensive properties, that is, high strength, toughness and elasticity. **Table 1** summarizes the mechanical properties of the gels with varied crosslinker content.

From the table, it is clearly seen that x = 0.0625 is the optimum crosslinker content for mechanical properties, and the variation trend of mechanical performance with varied content of crosslinker is in agreement with Suo and his co-workers' work.[9] In our single network hydrogels containing dual physical interactions, the formation of strong dipole–dipole interaction requires relatively short range between cyano group pairs.[38] However, loosely chemical crosslinked network is too sparse to allow cyanos to form an effective interaction. Therefore, at lower crosslinking density, the hydrogels exhibit lower mechanical strengths. While over-crosslinking causes a decline in the chain length between two adjacent crosslink points; hence the resulted rigid polymer networks lead to a decrease of toughness. The decline of fracture energy is the direct evidence, and the decrease of elongation indicates the reduction of chain flexibility. In addition, the inhomogeneity of network generated at higher crosslinking density is also responsible for the decrease of mechanical strengths. In the selected range of crosslinker/monomers ratio as shown in Table 1, the DHIR hydrogels achieved high comprehensive properties with 1.2–8.3 MPa tensile strength, 357%–716% break strain, 0.6–5.6 MPa Young's modulus and 1.76–5.14 MPa compressive strength. It is necessary to point out that over a range of crosslinker/monomers from 0.05 to 0.15, the compressive strengths are lower than the tensile strengths. An explanation is that DHIR hydrogels are relatively softer than polyacrylonitrile-based hydrogel reported previously due to their lower crosslinking density.[35,36] Moreover, our hydrogels were so strong that their compressive strengths exceeded the maximum compression measuring range of our machine (500 N). Therefore, we only recorded the compressive stresses at 90% strain. During this strain of compression, the increased compactness of DHIR hydrogels with lower crosslinking density may not lead to much increased stiffness of polymer network. In this case, the compressive strengths are lower than tensile strengths. While at higher contents of 0.2 and 0.25 crosslinker/monomers, the hydrogels with higher crosslinking density have higher network compactness, and during compression, further increased compactness results in a considerable enhancement in stiffness. Thus, the compressive strengths become higher than tensile strengths under this condition. We noted that only negligible water loss happened during the compression test, and the compressed hydrogels could recover their original shape within 10 min.

The loading-unloading curves and fracture energy of DHIR hydrogels with different compositions are shown in **Figure 4**a–c. The area of hysteresis area reflects the ability of a hydrogel to dissipate the energy per unit volume.[8] For single-network hydrogel, the dissipating energy is mainly dependent on physical crosslink. This energy can be evaluated with the following equation:

$$\Gamma_D = 2V\int_0^h W_D \, dy \tag{1}$$

In the equation, V is the volume fraction of the hydrogel in the process zone,[12] W_D is the mechanical energy dissipated per unit volume of a hydrogel element in the process zone at the undeformed state and is given by the areas of hysteresis loops in stress–strain curves from deforming and undeforming the hydrogel element;[12] h is the width of the process zone around the notch. Figure 4a demonstrates qualitatively that the dissipating energy reaches a maximum value at 0.0625 chemical crosslinker.

In comparison, Table 1, Figure 4b show that the fracture energy is increased dramatically when the ratio of chemical crosslinker increases from 0.05 to 0.0625 and decreases gradually with further increasing content. In our previous studies,[34–36] we demonstrated that dipole–dipole interaction in polyacrylonitrile could strengthen the hydrogel considerably, but owing to high chemical crosslinking density[12] and the absence of friable structure to dissipate energy,[9] the hydrogels were quite sensitive to a notch. Other researchers also reported that H-bonding toughened single network PAAm-based hydrogels could not bear any load when a notch was introduced.[28] As shown in Figure 4c, the fracture energies of H-bonding only and dipole–dipole only reinforced hydrogels are negligible and 484.4 J/m^2, respectively. Comparatively, when we combined hydrophobic dipole–dipole interaction and hydrophilic H-bond to establish a dual physical interaction system, the fracture energy is enhanced significantly at 68.4 wt% AN content, and

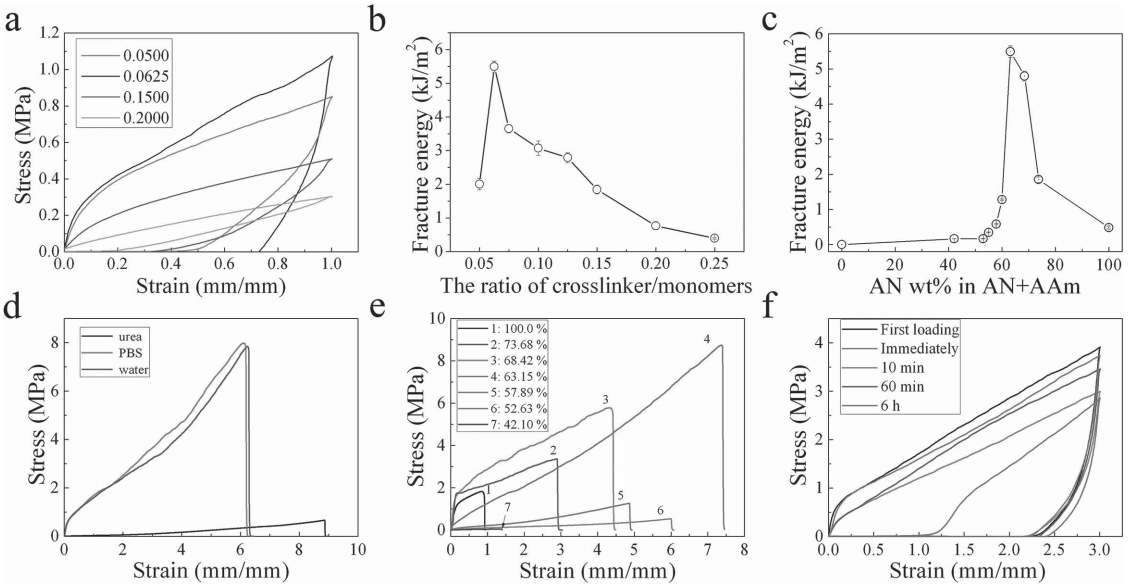


Figure 4. Effect of AN/(AAm+AN) and chemical crosslinker content on the mechanical properties of DHIR hydrogels. a) Hysteresis loops of DHIR60–5–35-x hydrogel with various crosslinker contents(x). b) Fracture energy of DHIR60–5–35-x hydrogels with various crosslinker contents. c) Fracture energy of DHIRa-5-c-0.0625 hydrogels with various AN/(AN+AAm) ratios. d) Tensile stress-strain curves of DHIR60–5–35–0.0625 hydrogel after immersing in 30 wt% urea aqueous solution, PBS and water. e) Tensile stress-strain curves of DHIRa-5-c-0.0625 hydrogels with various AN/(AN+AAm) ratios. f) Mechanical recovery of DHIR60–5–35–0.0625 hydrogel for different waiting times under cyclic tensile tests.

reaches as high as 5495 J/m^2. As shown in the Figure S1 (Supporting Information), the trouser shape DHIR60–5–35–0.0625 hydrogel sample on the electromechanical tester can resist stretching without tearing. Nevertheless, further increasing AN ratio leads to a rapid decrease of the gel in resisting crack. The results imply that an appropriate ratio of AN to AAm is a necessity to construct an efficient energy dissipating mechanism. In DHIR system, rigid dipole–dipole interactions can stabilize and strengthen the network, and under the protection of the hydrophobic aggregated microdomains from dipole–dipole interaction, the flexible hydrophilic H-bonds of AAm is stabilized, serving to toughen the gels by efficiently dissipating energy.[39,40] It is obvious that the synergic interaction does not work in the absence of either, since H-bonds of AAm are liable to be hydrated without the protection of cyano. As shown in Figure 4c, DHIR0–5–95–0.0625 hydrogel is negligible in resisting crack propagation, suggesting the sole H-bonding cannot construct an effective mechanism to dissipate energy. To highlight the key role of hydrogen bonding in maintaining high strength of hydrogels, DHIR60–5–35–0.0625 hydrogel was treated with 30% urea. The gels in PBS and water serve as controls. Clearly, the tensile strengths of the gel samples both in PBS and water are almost identical, close to 8.3 MPa. In urea, due to the breakage of most of hydrogen bonds in network, the fracture stress of the gel decreases dramatically from 8.3 MPa in water and PBS to 0.6 MPa (Figure 4d), and meanwhile, this gel cannot bear any load when a notch was made at one edge. This further corroborates that the sole dipole–dipole interaction in the absence of hydrogen bonds cannot toughen the DHIR hydrogels efficiently. Figure 4e shows the effect of the AN/(AN+AAm) ratio on the tensile strengths. The fracture stress and break elongation of the hydrogel reach the maximum values of 8.3 MPa and 716%, respectively, at 63.15 wt% AN. In this case, the gel can hold 78% EWC. This phenomenon proves that the optimal synergic interaction works at a proper ratio of H-bond and dipole–dipole monomers. It is necessary to point out that the PAMPS is very important to maintain the hydrophilicity of the gels. Without the electrostatic repulsion of these anions, the hydrogel performed like a whitish stiff plastic with a rather low EWC (below 30%).

Figure 4f exhibits the mechanical recovery of DHIR60–5–35–0.0625 hydrogel. The stress-strain curve achieves 80% recovery of hysteresis area after the hydrogel was soaked in water at 25 °C for only 10 min and the complete recovery was observed after 6 h. The DN hydrogels were shown to be slower in accomplishing this recovery (nearly 24 h).[9,26] The capacity of our hydrogels to recover mechanical properties suggests good fatigue resistance.[8,12] Figure S3 (Supporting Information) clearly demonstrates that the fractured hydrogel pieces are able to perfectly recover to the original shape and size without any residual strain.

Figure 5 illustrates the mechanism underlying the energy dissipation of DHIR hydrogel network during the cycling test. The chemical crosslinking can prevent the permanent deformation of hydrogels; the CN–CN dipole pairings and AAm–AAm H-bondings act as dynamic crosslinking points whose dissociation and association are reversible during loading and unloading. The breakage of physical crosslinkings can dissipate the mechanical energy efficiently to toughen the hydrogel, and reconstruction of the dissociated noncovalent crosslinkings contributes to the recovery of network after the load is released.

2.4. Thermoresponsive Mechanical Properties

Thermo-responsive hydrogels which are capable of changing volume or mechanical properties in response to temperature

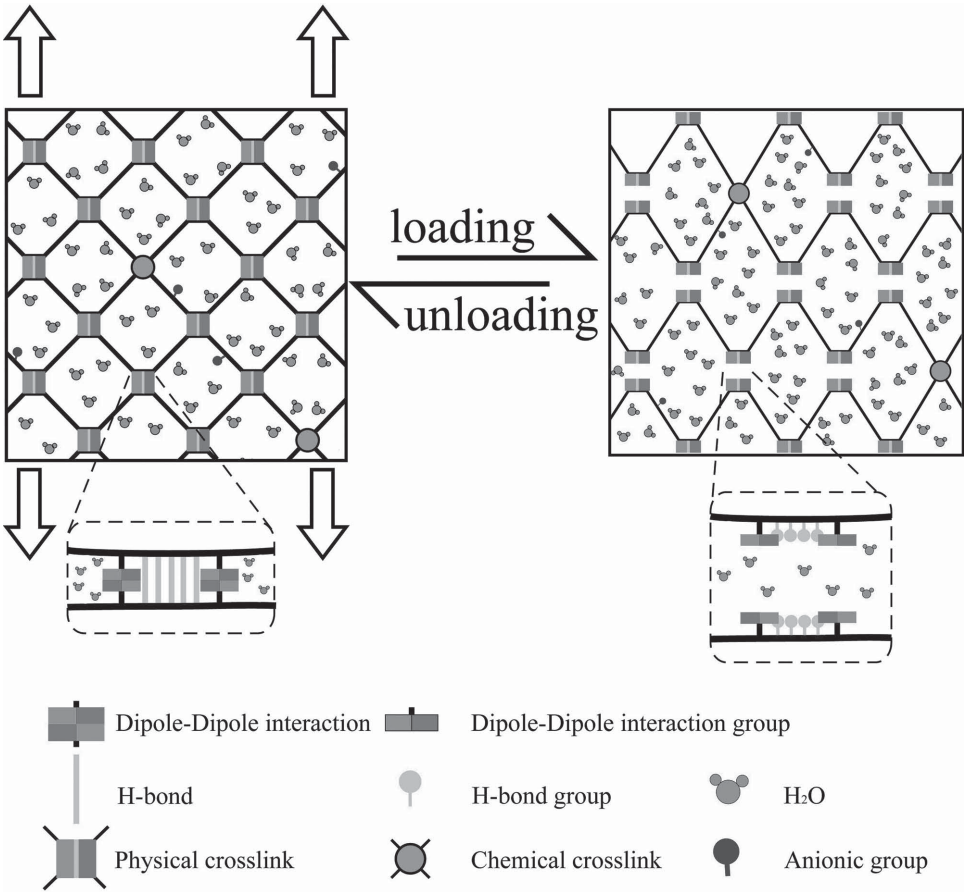


Figure 5. Mechanism underlying the energy dissipation of DHIR hydrogel network during the cycling test.

stimulus have been widely used in various biomedical applications.[1,43] We have demonstrated previously that PAN-based hydrogel treated in selected regions at 85 °C, exhibited diversified shape changing and memory behavior in response to zinc ion,[36] but the high temperature limits its applications as biomaterials. Furthermore, CN-CN pairing in dipole–dipole reinforced (DDR) hydrogel[36] can be only dissociated slowly by elevating environment temperature. In this work, we introduced the hydrogen bonding into the DDR hydrogel. Because of the reduction in the total physical crosslink intensity, DHIR hydrogels demonstrated a temperature sensitive behavior over a wide and lower temperature window (**Figure 6**).

In this study, we first tried to measure the thermal behavior of the DHRI hydrogels by differential scanning calorimetry, but observed no transition peak from 10 °C to 80 °C, suggesting that chemical crosslinking restrains the endothermic behavior of disruption of dipole–dipole pairings as well as AAm-AAm hydrogen bondings. Then we performed dynamic mechanical analysis (DMA) to record the variation in G′ (elastic moduli) and G″ (loss moduli) of the hydrogels over a temperature range from 10 to 60 °C. At 10 °C, G′ values of three representative hydrogels, DHIR70–5–25–0.0625, DHIR60–5–35–0.0625 and DHIR40–5–55–0.0625, are 21 MPa, 16.7 MPa and 3.1 MPa, respectively. Upon increasing temperature, all the three gels exhibit a reduction trend in elastic moduli. The gels are stiff at 10 °C and become softened along with the increase of temperature. With a decrease in AN content, the softening temperatures shift to a relatively low value. From 10–35 °C, the elastic moduli of DHIR70–5–25–0.0625 and DHIR40–5–55–0.0625 are decreased to 1/3 and 3/5 the original value, respectively. In comparison, G′ value of DHIR60–5–35–0.0625 drops precipitously by 1/325. Therefore, a pronounced modulation of thermo-responsive mechanical properties can only be realized by controlling an appropriate composition ratio at which synergistic effect of dipole–dipole interaction and H-bonding is maximized. The loss modulus is the vital factor to characterize internal friction, reflecting viscous flow. For hydrogel, viscous property was primarily attributed to weak and reversible physical interaction rather than strong bond.[8,9,12] In Figure 6b, G″ values of DHIR60–5–35–0.0625 and DHIR40–5–55–0.0625 hydrogels exhibit the similar trend as the G′; while DHIR70–5–25–0.0625 shows a little different variation in loss modulus with temperature, and the G″ values are relatively lower than the former two. This further verifies that too much strong dipole–dipole interaction is adverse to the formation of effective mechanical energy dissipating mechanism. It is noted that G″ shows a peak around 35 °C, which corresponds to the maximum mechanical energy dissipation.

One interesting phenomenon is that the DHIR hydrogels exhibit temperature sensitive memory behavior (**Figure 7**). It is well known that much work has been reported on shape memory polymers;[44] while shape memory hydrogels,[45] one

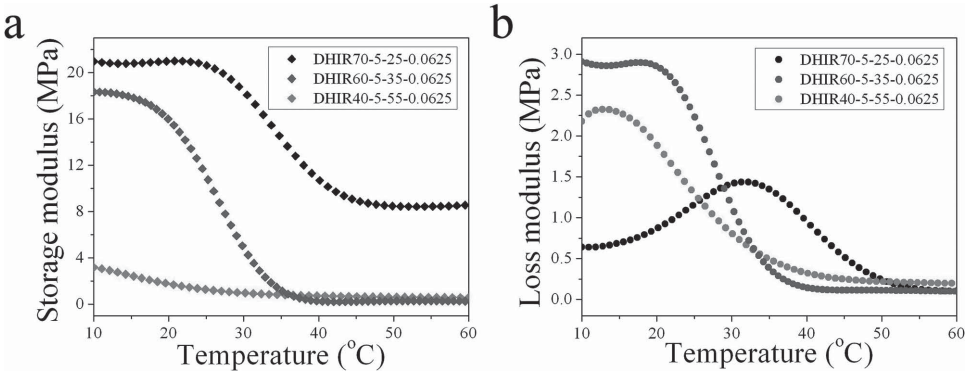


Figure 6. Variation in a) storage moduli and b) loss moduli of DHIR hydrogels as a function of temperature.

type of stimuli-responsive soft and wet materials, in particular high strength shape memory hydrogels are just beginning to attract academic interest.[46]

In our experiment, to realize the shape memory effect, we heated up one straight gel strip to 60 °C, and deformed it to a spiral by hand. Then the spiral shaped hydrogel was placed into 35 °C water for 5 min to fix the temporary shape. After that, the spiral was straightened to a strip at 35 °C, and immersed into 15 °C water for 5 min. The straight strip shape was well preserved. Subsequently, the strip was transferred into 35 °C water. Immediately, the gel transformed into a spiral which was stable at this temperature (Figure 7 and movie in Supporting Information). Again, the spiral was dropped into 60 °C water; the hydrogel lost its temporary shape, and recovered to its original straight shape within 5 min. It is worthwhile to note that the water contents of DHIR hydrogels remained almost unchanged during temperature change.

The thermoresponsive shape memory of DHIR hydrogel can be explained by temperature-modulated change in reversible physical crosslinking. In DHIR hydrogel, chemical crosslinking from polyethylene glycol diacrylate contributes to the elasticity of network, and physical crosslinking from dipole–dipole and hydrogen bonding interactions serve to lock temporary shape at a temperature below the transition temperature, above which, physical crosslinking was much weakened, thereby leading to the unlocking of temporary shape; as a result, the gel returned from deformed state to original shape. Temperature-induced locking and unlocking of physically crosslinked network was directly reflected by the variation in the elastic modulus, as shown in Figure 6a. Upon heating up to 60 °C, the modulus of DHIR60–5–35–0.0625 hydrogel decreases sharply to 210 kPa, due to breakage of most physical crosslinking. In this case, the gel can be deformed readily. While temperature is decreased to 35 °C, the modulus rebounds to 1 MPa because of partial reformation of dipole–dipole pairing and hydrogen bonding of AAm, which can serve as crosslinking points to fix the temporary shape. Further cooling down to 15 °C, along with the reconstruction of most physical crosslinkages, the modulus of gel is increased significantly to its original value, 16 MPa, which is high enough for fix straight shape. As the temperature is increased from 15 °C to 35 °C, the disturbance of dipole–dipole interaction would have a negative effect on the total physical crosslinking, so, the hydrogel network cannot withstand the shrinking stress in extended state at this moment. Therefore, the straight strip turns to the intermediate state, that is, a spiral instantly. With further elevating temperature to 60 °C, most of physical fixing points are dissociated, and the gel becomes so soft that it cannot retain the temporary shape, eventually converting into the permanent state, straight strip, within 5 min.

Figure 7. Actual observation of the shape memory effect of DHIR60–5–35–0.0625 hydrogel. The gel was dyed with diluted Rodamine B to acquire a clear observation.

Next, we evaluated the thermoresponsive shape memory effects of DHIR hydrogels by cyclic shape-memory experiments at different temperatures under angle-controlled conditions.[34] The shape fixity ratio (R_f) of a representative DHIR60–5–35–0.0625 hydrogel was determined at 15 °C, and its shape recovery ratio (R_r) was measured at 35 °C. The R_f and R_r values are 100% and 99%, respectively, indicating the dipole–dipole and H-bonding interactions are able to well maintain temporary shape and heating-induced breakup of physical crosslinking can lead to a complete recovery of permanent shape. Herein, the cycle of shape memory was repeated four times (Figure S2, Supporting Information). As shown in the figure, the shape recovery is very quick with recovery time being less than 19 s; moreover, perfect reproducible shape memory effects can be achieved.

3. Conclusion

In summary, we demonstrated that incorporating dipole–dipole and hydrogen bonding interactions in one single polymer network could significantly enhance the multifaceted mechanical properties of hydrogels including high tensile and compressive stresses, excellent toughness, elasticity, recoverability of mechanical behavior, temperature-tunable mechanical strength as well as accompanied shape memory effect, aided by presence of polyanion and hydrophilic crosslinker. The dual non-covalent bonding reinforcement mechanism reported here offers a universal and simple strategy for designing and fabricating high performance hydrogels suited for replacement of load-bearing soft tissues

4. Experiment Section

Materials: Acrylonitrile (AN, 97%, Kewei Company, Tianjin University, Tianjin, China), 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS, 98%, Alfa Aeser), polyethylene glycol diacrylate (PEGDA575, Mn = 575, Aldrich), acrylamide (AAm, 98%, Alfa Aeser) and 2-hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone (IRGACURE-2959, 98%, Aldrich) were used as received. All other chemicals and solvents are analytical grade.

Preparation of DHIR Hydrogels: An appropriate mass or volume of AN, AAm, AMPS and PEGDA575 was first dissolved in DMSO according to the specified formulations. Then 3 wt% a photoinitiator IRGACURE 2959 (relative to total mass of monomers and crosslinker) was added into the solution and stirred thoroughly under nitrogen atmosphere till it was completely dissolved. Subsequently, the mixture was cast into disc molds (diameter 12.6 mm, thickness 0.5 mm) or tubular molds (inner diameter 10 mm, length 12 mm) and the polymerization was carried out for 1 h in a crosslink oven (XL-1000 UV Crosslinker, Spectronics Corporation, NY, USA). The obtained hydrogels were immersed thoroughly in deionized water which was refreshed every 12 h for 5 days to remove the unreacted monomers and DMSO. A series of hydrogels were prepared by varying feed ratios (see Supporting Information, Table S1). The resulting hydrogels were named as DHIRa-b-c-x, where a, b, c respectively represent the percentage composition of AN, AMPS and AAm in the total monomer, and *x* is the mass ratio of crosslinker to total monomers. It is noted that all the initial solid content was fixed at 21%.

Characterization of Hydrogels: Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy (PerkinElmer spectrum 100, USA) was used to confirm the formation of the gels.

Determination of Equilibrium Water Content (EWC): The EWCs of the hydrogels were measured at room temperature using a gravimetric method. The cylinder samples of hydrogel fully swollen in deionized water were taken out and weighed on a microbalance after removing the surface water with wet filter paper. Then the hydrogel was dried in a vacuum oven at 50 °C until reaching a constant weight. The equilibrium water content (EWC) was defined as:

$$\mathrm{EWC} = \frac{m_{\mathrm{wet}} - m_{\mathrm{dry}}}{m_{\mathrm{wet}}} \times 100\% \quad (2)$$

where m_{wet} is the wet weight and m_{dry} is dry weight of each sample. The average values and errors were calculated from at least five independent data for each specimen.

Measurement of Mechanical Properties: For mechanical test, all the hydrogel samples were fully swollen in deionzed water at room temperature. The mechanical properties of hydrogels were tested on WDW-05 electromechanical tester (Time Group Inc, China) at room temperature (25 °C) in air environment. At least five specimens were tested for each property. It is noted that immediately before testing, water was sprayed on the surface of hydrogel samples mounted on the tester to prevent inner water evaporation; the nominal strains and stresses of the hydrogels were determined in this study. For tensile test, the hydrogel discs were cut into dumbbell specimens in accordance to GBT 528–20094 (width: 2 mm; gauge length: 10 mm, thickness: 0.5 mm) by a gel cutter (Xuan Yu Inc, China). The applied strain rate was fixed at 0.0833/s for tensile test and 0.1666/s for loading-unloading test. For compression tests, the hydrogel discs were cut into cylinders (10 mm in diameter and 8 mm in height) and measured on the same tester with an applied strain rate of 0.0166/s. The iron plates were lubricated with silicone grease to prevent friction during loading. For tearing test, the hydrogel discs were cut into trouser shape specimens in the standard of 1/2 size of GBT 529–2008 A (width: 7.5 mm, length: 50 mm, notch length: 20 mm, thickness: 0.5 mm). The applied strain rate was set at 0.0833/s. The fracture energy was calculated as:

$$\Gamma = \frac{F_{\mathrm{ave}}}{d} \quad (3)$$

where F_{ave} is the average force during the tear and d is the thickness of trouser samples.

Dynamic Mechanical Analysis (DMA): The elastic moduli of the samples (cylinders, 10 mm in diameter and 8 mm in height) were tested on a NETZSCH Dynamic Mechanical Analyzer, working in a compression mode at 1 Hz over a temperature range of 10–60 °C and the load was fixed at 0.6 N. The experiment was carried out in nitrogen atmosphere with a heating rate of 3 °C/min.

Observation of Shape-Memory Effect of DHIR Hydrogel: The hydrogel sheet in equilibrium swelling state was cut into a rectangular strip with a dimension 95 mm × 5 mm × 0.5 mm. Subsequently the strip was heated up to 60 °C and twined on a glass rod (diameter 4 mm) to form a spiral-like shape. Then the spiral shaped hydrogel was placed into 35 °C water for 1 min to fix the temporary shape. After that, the spiral was strengthened to a straight strip at 35 °C and immersed into 15 °C water for 1 min. The straight strip shape was well preserved. Finally, the strip was transferred in sequence into 35 °C and 60 °C water to observe shape recovery.

Supporting Information

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

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