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Toughening Mechanism of Nanocomposite Physical Hydrogels Fabricated by a Single Gel Network with Dual Crosslinking — The Roles of the Dual Crosslinking Points*

Fu-kuan Shi, Ming Zhong, Li-qin Zhang, Xiao-ying Liu and Xu-ming Xie**
Key Laboratory of Advanced Materials (MOE), Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

Abstract A facile method to fabricate tough and highly stretchable polyacrylamide (PAM) nanocomposite physical hydrogel (NCP gel) was proposed. The hydrogels are dually crosslinked single network with the PAM grafted vinyl hybrid silica nanoparticles (VSNPs) as the analogous covalent crosslinking points and the reversible hydrogen bonds among the PAM chains as the physical crosslinking points. In order to further elucidate the toughening mechanism of the PAM NCP gel, especially to understand the role of the dual crosslinking points, the PAM hybrid hydrogels (H gels) and a series of poly(acrylamide-*co*-dimethylacrylamide) (P(AM-*co*-DMAA)) NCP gels were designed and fabricated. Their mechanical properties were compared with those of the PAM NCP gels. The PAM H gels are prepared by simply mixing the PAM chains with bare silica nanoparticles (SNPs). Relative to the poor mechanical properties of the PAM H gel, the PAM NCP gel is remarkably tough and stretchable and also generates large number of micro-cracks to stop notch propagation, indicating the important role of PAM grafted VSNPs in toughening the NCP gel. In the P(AM-*co*-DMAA) NCP gels, the P(AM-*co*-DMAA) chains are grafted on VSNPs and the polydimethylacrylamide (PDMAA) only forms very weak hydrogen bonds between themselves. It is found that mechanical properties of the PAM NCP gel, such as the tensile strength and the elongation at break, are enhanced significantly, but those of the P(AM-*co*-DMAA) NCP gels decreased rapidly with decreasing AM content. This result reveals the role of the hydrogen bonds among the grafted polymer chains as the physical crosslinking points in toughening the NCP gel.

Keywords Dual crosslinking single network; Nanocomposite physical hydrogel; Toughening mechanism

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INTRODUCTION

Hydrogels are crosslinked networks of hydrophilic polymer in which a large volume of water is absorbed. As soft and wet materials, hydrogels have attracted broad attention as bear-loading tissues[1, 2], artificial muscle[3, 4], articular cartilage[5–7], and soft devices[8, 9], owing to their similarity in elastic moduli and high water content[10]. Most of the hydrogels are a single network crosslinked by one type of interactions, choosing from covalent bond[11], coordination bond[12], hydrogen bond[13], hydrophobic association[14], host-guest interaction[15], *etc*. However, they are usually weak and brittle. For example, the covalently crosslinked hydrogels[11] are extremely

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** Corresponding author: Xu-ming Xie (谢续明), E-mail: xxm-dce@mail.tsinghua.edu.cn
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brittle with the tensile strength lower than 10 kPa. And most of the physically crosslinked hydrogels *via* hydrogen bonds[13], hydrophobic association[14] or host-guest interaction[15] are also weak with the tensile strength lower than 40 kPa. The poor mechanical properties of hydrogels are due to the structure drawbacks of the inhomogeneous distribution of crosslinking points[16, 17] or the lack of energy dissipation mechanism[18]. To overcome the mechanical limitations and broaden the potential applications of hydrogels, many researchers attempted to fabricate tough hydrogels with a homogeneous distribution of chemical crosslinking points[16, 19–22] or introduce effective energy dissipation mechanism[18, 23–26] in the gel networks. Almost all the hydrogels mentioned above are chemical gels with pretty complicated molecular design and preparation processes. While only a few tough hydrogels[27–29] are produced totally *via* physically crosslinked networks by some specific compositions.

We previously proposed an approach of utilizing the synergy of hierarchical crosslinking points in a single gel network to toughen hydrogels by the combination of network homogenization and energy dissipation[30–41]. According to this concept, several types of NCP gels with enhanced toughness and high stretchability[30–39] are fabricated by a facile and one-pot process. For the PAM NCP gel[32], it is composed of VSNP/PAM nanobrush gelators, which are formed *via* the grafting polymerization of acrylamide (AM) on the surface of VSNPs. The obtained PAM NCP gel is dually crosslinked by hydrogen bonds as the physical crosslinking points among the PAM chains and PAM chains grafted VSNPs as the analogous covalent crosslinking points. The synergy of the dual crosslinking points in the single gel network ensures the PAM NCP gel to maintain excellent mechanical properties, including high stretchability and tensile strength. To further elucidate the synergy of the dual crosslinking points in toughening the PAM NCP gels clearly, the PAM hybrid gels (H gel) and a series of the P(AM-*co*-DMAA) NCP gels are designed and fabricated. The PAM H gels are composed of the PAM chains that is simply mixed with the bare silica nanoparticles (SNPs), and the P(AM-*co*-DMAA) NCP gels are composed of the P(AM-*co*-DMAA) chains grafted on VSNPs similar to the PAM NCP gels. Usually polydimethylacrylamide (PDMAA) only forms weak hydrogen bonds between themselves. Their mechanical properties are systematically compared with those of the PAM NCP gel to investigate the roles of the PAM grafted VSNPs and the hydrogen bonds among the PAM chains in the NCP gel networks, respectively.

It should be noticed that the structures between the PAM H gel and the PAM NCP gel are different. The former is prepared by simply blending the PAM chains with SNPs, while the latter is obtained *via* covalently grafting PAM chains on the surfaces of VSNPs. The role of the PAM grafted VSNPs could be evaluated by comparing the PAM NCP gel with the PAM H gel. In addition, changing the ratio of AM and DMAA in the P(AM-*co*-DMAA) NCP gels could tune the density and strength of hydrogen bonds among the grafted P(AM-*co*-DMAA) chains, thus the role of the hydrogen bonds among the grafted polymer chains in the NCP gel could be evaluated. This work provides a better understanding of the relationship between the network structure and the tensile properties of the NCP gels, which may open a way to develop a new generation of NCP gels with desirable properties.

EXPERIMENTAL

Materials

Acrylamide (AM) and ammonium persulfate (APS) were purchased from Xilong Chemical Co., Ltd. Silica nanoparticle (SNP) in a water suspension (Ludox SM colloidal silica 30 wt% suspension) was purchased from Sigma Aldrich. Dimethylacrylamide (DMAA) and vinyltriethoxysilane (VTES) were purchased from Alfa Asear.

Preparation of the Hydrogels

SNP was used to fabricate the PAM H gels. The mass ratio of [water]:[monomer]:[APS]:[SNP] was 30:9:0.045:0.4. AM (9 g), APS (0.045 g) and SNP (0.036 g) were added into water (30 mL). The mixture was stirred to form a transparent and homogeneous solution. And then the solution was added into a tube. After three degassing cycles, the tube was sealed under N_2. The free-radical polymerization was allowed to proceed in a

water bath at (28 ± 2) °C for 20 h.

For the fabrication of the P(AM-*co*-DMAA) NCP gels: a fixed mass ratio of [water]:[monomer]:[APS]:[VSNP] was 30:9:0.045:0.4 and the mass ratio R between AM and the total mass of DMAA and AM was varied from 0 to 100%. VSNP with a diameter of 3 nm was used in the fabrication process. The detailed fabrication method for VSNP and the gel samples are according to the description in the previous report[32]. When R = 0% or 100%, DMAA or AM was used as sole monomer to fabricate NCP gel, which is represented by PDMAA NCP gel or PAM NCP gel.

Except for specific clarification, all the gels contain the same amount of water (77%); VSNPs in the NCP gel and SNPs in the PAM H gel are 0.4% with respect to the weight of monomers.

Characterization and Measurements

To avoid water loss during the test, the surface of the gel sample is coated with a thin layer of silicone oil. Tensile mechanical measurements were performed on the hydrogels with the same size (5 mm Φ × 60 mm length) using a universal material testing machine (Zwick-Roell Z005, Zwick-Roell, Ulm, Germany). The testing conditions were as follows: temperature of 25 °C; gauge length of 15 mm; crosshead speed of 100 mm/min. The strain under stress is calculated on the basis of the change in length relative to the initial length of the sample. The stress was calculated on the basis of the initial cross section area. The initial tensile modulus was calculated from the initial slope of the stress-strain curves of gel samples. Cyclic tensile loading-unloading tests were performed on the fresh samples with a certain maximum strain. After the first cycle test, the sample was stored at room temperature for different time intervals. Then second tensile loading-unloading tests were conducted on the samples for comparison with the first cyclic tension data. A pure shear test was also used to characterize the toughness[28]. Two different samples, *i.e.* a notched and an unnotched, were used to measure the tearing energy. The gel samples were cut into a rectangular shape with a width of 25 mm (a_0), length of 40 mm, and thickness of 2 mm (b_0). An initial notch of 5 mm in width was cut using a razor blade for the notched gel sample. The test piece was clamped on two sides, and the distance between the two clamps was fixed at 15 mm (L_0). The cross speed is 100 mm/min. The force-displacement curves of both the notched and the unnotched samples were recorded, and the tearing energy was calculated from $T = \mathrm{U}(L_c)/(a_0 \times b_0)$, where $\mathrm{U}(L_c)$ is the work done by the applied force to the unnotched sample at the critical stretching distance L_c, and L_c is the displacement when the notched sample breaks.

RESULTS AND DISCUSSION

The Role of the PAM Grafted VSNPs in Toughening the PAM NCP Gels

VSNPs are multifunctional silica nanoparticles with a large number of vinyl groups on the surface[32]. The vinyl groups of VSNPs could react with AM, which ensures the PAM chains to be grafted on the surface of VSNPs, as schematically shown in Fig. 1(a). However, SNPs are bare silica nanoparticles with only hydroxyl groups on their surfaces (see Fig. S1 in supporting information, SI). There is only weak interaction between them and the PAM chains[42, 43]. For the preparation of PAM H gel, SNPs are simply mixed with the PAM chains, as shown in Fig. 1(b). It is clear that the only difference in the network structures for the two gels is whether the nanoparticles are covalently bonded with the PAM chains. By comparing their mechanical properties, it could be revealed that the PAM grafted VSNPs function as the analogous covalent crosslinking points in toughening the PAM NCP gel.

As shown in Figs. 2(a) and 2(b), the PAM NCP gel is tough and highly stretchable, which could be knotted and then stretched to about 25 times of the original sample length. Also, the stretched gel sample is highly resilient and its knot could be untied without damage (Fig. 2c). On the contrary, the PAM H gel is weak and soft. It could only be stretched to 10 times of the original sample length (Figs. 2d and 2e) and showed an obvious plastic deformation as evidence of yielding (Fig. 2f). Therefore, compared with the PAM H gel, the superior performance of the PAM NCP gels qualitatively illustrates that the PAM grafted VSNPs play an important role in toughening the PAM NCP gel.

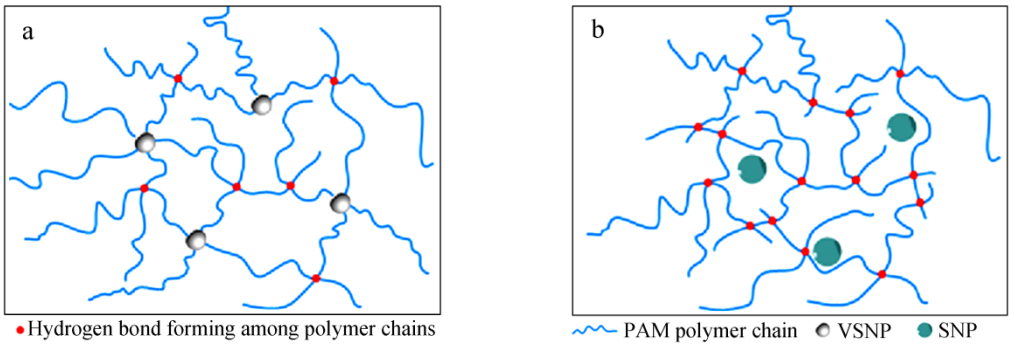

Fig. 1 Schematic illustration of the network structures of (a) the PAM NCP gel and (b) the PAM H gel

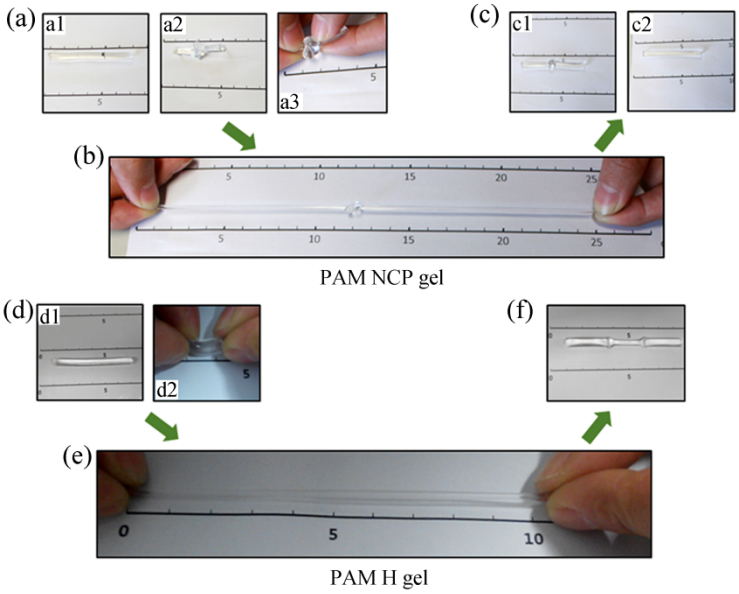

Fig. 2 Mechanical performance of the PAM NCP gel (a–c) and the PAM H gel (d–f): (a) knotting, (b) stretching the PAM NCP gel to 25 times of the original length, (c) unknotting after the stretching of the PAM NCP gel, (d) the original sample of the PAM H gel, (e) stretching to 10 times of the original length and (f) plastic deformation of the PAM H gel after the stretching

The results of tensile test for both the PAM NCP gel and the PAM H gel are shown in Fig. 3(a). At a strain smaller than 150%, the PAM H gel shows almost the same stress-strain behavior as that of the PAM NCP gel. This is due to the effect of hydrogen bonds among the PAM chains. For both the PAM H gel and the PAM NCP gel, the hydrogen bonds form among the PAM chains and act as the physical crosslinking points, which is the main contributor to withstand the stress at a lower strain[32]. The stress-strain behavior of the two gel samples is similar at the initial tensile process. When the strain is higher than 150%, the stress tolerated by the PAM NCP gel increases monotonically until the sample breaks, indicating that the PAM grafted VSNPs function as the analogous covalent crosslinking points in the NCP gel to maintain the gel networks even when part of the hydrogen bonds start to break under the condition of tension. However, there is only weak interaction between SNPs and PAM chains in the PAM H gel[42, 43] (see also Fig. S2 in SI), so that the stress of the PAM H gel decreases with increasing the elongation after yielding based on the break of hydrogen bonds among the PAM chains during stretching (the strain is higher than 150%). Therefore, the PAM NCP is of a remarkable high tensile strength of 313 kPa, which is almost ten times of that of the PAM H gel (35 kPa). Evidently, the PAM NCP gel is also highly stretchable with the elongation at break of 3205%, which is about three times higher than

that of the PAM H gel (990%). This is due to the fact that the PAM grafted VSNPs can maintain the networks to deform in a large range even after part of the hydrogen bonds among the PAM chains are broken. However, the PAM H gel is crosslinked only by the hydrogen bonds among the PAM chains, which are easily disrupted by the tensile stress. It indicates that the PAM NCP gel is much more stretchable than the PAM H gel.

A cyclic tensile test of the PAM NCP gel and the PAM H gel at a maximum strain of 500% were further performed to evaluate the role of VSNPs in toughening the PAM NCP gel. The loading-unloading curves are shown in Fig. 3(b). Both the PAM NCP gel and the PAM H gel show a big hysteresis loop in the first loading-unloading cycle. The area surrounded by the loop indicates the energy dissipated through the break of hydrogen bonds among the PAM chains. The stress of the PAM NCP gel monotonously increases under stretching, but the PAM H gel exhibits an obvious strain-softening phenomenon after yielding. It is obvious that the PAM NCP gel displays a higher resilience and a smaller residual deformation. These differences also attribute to the crucial effect of the PAM grafted VSNPs points for sustaining stress even after part of hydrogen bonds among the PAM chains are broken in the PAM NCP gel. On the other hand, the PAM H gel is only crosslinked by hydrogen bonds among the PAM chains. Along with the hydrogen bonds broken under stretching, the PAM chains are easy to slip in a large range, which causes a plastic deformation and strain-softening phenomena of the PAM H gel in the first loading process. Furthermore, the immediate second loading-unloading cycles for the two gel samples were performed. The results are shown in Fig. 3(b). In the second loading, the softened PAM H gel sample showed a monotonously increased stress with the increase of strain[44] because the PAM chains might be oriented after the chains slippage and the hydrogen bonds recombination during the first loading-unloading cycle. According to the experimental results, it is clearly verified that the PAM grafted VSNPs affords the PAM NCP gel with great toughness and high stretchability by acting as the analogous covalent crosslinking points.

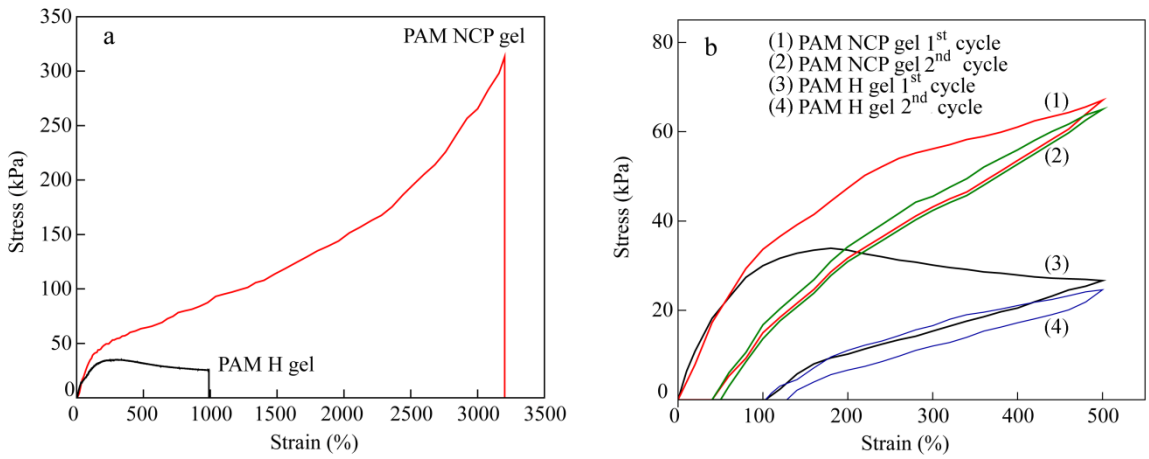

Fig. 3 (a) Stress-strain curves of the PAM NCP gel and the PAM H gel and (b) the first and the immediate second loading-unloading cycles of the PAM NCP gel and the PAM H gel with a maximum strain of 500%

Furthermore, we cut a notch in both the PAM NCP gel and the PAM H gel samples and then stretched them to rupture by means of the universal material testing machine. Figure 4(a) demonstrates the whole tensile process of the notched PAM NCP gel sample. From the unloaded and fractured PAM NCP gel sample as shown in Figs. 4(a4) and 4(a5), no obvious propagation is observed at the notch until the sample ruptures (see Video S1 in SI). And a large micro-crack zone is clearly visible around the notch (Fig. S3 in SI). The notched PAM NCP gel sample could be stretched to about 17 times of the original length before rupture. Its tearing energy calculated is about 20788 J/m^2, comparable with that of cartilage and muscles[45] (see Fig. S4 in SI). However, the notch of PAM H gel sample rapidly propagates (see Video S2 in SI) and ruptures early at the small strain of 180 % as shown in Fig. 4(b). And the tearing energy of PAM H gel is only about 593 J/m^2, about two magnitudes lower than that of the PAM NCP gel. The different performance in fracture behavior indicates that the stress is easily

redistributed homogeneously in the networks of the PAM NCP gel, but still concentrated in the networks of the PAM H gel.

The varied fracture behavior of the two gels can be explained in terms of the response of their networks to the stress. When the notched gel sample is tolerated by stress, usually the stress is easy to concentrate at the tip of the notch. The fracture of physical gels is usually processed *via* the breaking of crosslinking points and the following frictional sliding[46]. For the PAM NCP gel, the PAM chains are grafted on the surface of VSNPs. It can be speculated that the VSNPs act as the centers to transfer the stress tolerated by PAM chains at the tip of the notch to the other PAM chains away from the notch[47], with also the reversible break and recombination of the physical crosslinking points to dissipate the energy and homogenize the networks[48], as testified by micro-cracks in a large area (Fig. S3). And the VSNPs also can terminate the deformation initiated micro-cracks to further develop into a catastrophic fracture[49]. Thus the PAM NCP gel is highly resistant to the notch and thus exhibits a great toughness. On the contrary, the PAM chains are simply mixed with SNPs for the PAM H gel. The stress tolerated by the PAM chains at the tip of the notch cannot be redistributed but still concentrate there and the physical crosslinking points rapidly break, as convinced by the fast propagation of the notch for the PAM H gel upon deformation. Consequently, the PAM NCP gel exhibits large fracture toughness due to the synergy of the dual crosslinking points[32, 33]. This effective notch-resistance mechanism of the PAM NCP gel may be similar to the rubbery polymer with enhanced toughness achieved by the polymer grafted nano-silica[50].

We may conclude the toughening mechanism of PAM NCP as below: when the PAM NCP gel is subjected to a tension force, the PAM grafted VSNPs function as both the analogous covalent crosslinking points to sustain stress, and the transfer centers to make the applied stress be rapidly and uniformly distributed in the whole networks.

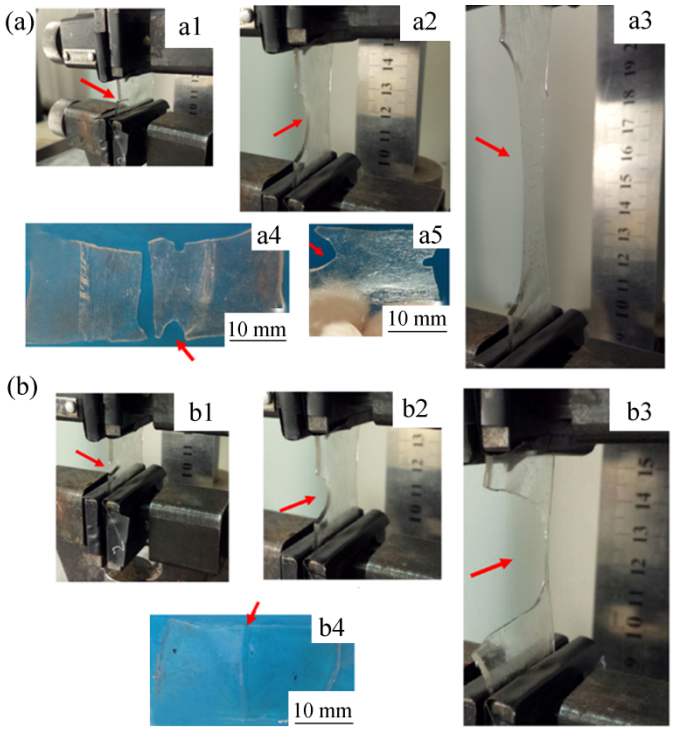

Fig. 4 Optical photographs of (a) the loading process (a1, a2, and a3) and the fractured PAM NCP gel with a notch (a4 and a5), and (b) the loading process (b1, b2, b3) and the fractured PAM H gel sample with a notch (b4)
The notch in the gel samples are pointed out by red arrows.

The Role of Hydrogen Bonds among the PAM Chains in Toughening the PAM NCP Gels

According to the structure model of the PAM NCP gel as shown in Fig. 1(a), hydrogen bonds among the grafted PAM chains act as the physical crosslinking points in the networks[32]. To elucidate their role in toughening the PAM NCP gels, we choose two different monomers, *i.e.* AM and DMAA, to fabricate the P(AM-*co*-DMAA) NCP gels. For PAM chains, there are many primary amide groups ($-CONH_2$). As shown in Fig. 5(a), two primary amide groups can form a stable cyclic dimer structure with two intermolecular hydrogen bonds[51], or a stable tetragonal structure with four intermolecular hydrogen bonds[52, 53] assisted by a water molecule as a bridge. For the PDMAA chains, the main chain is the same as that of PAM, except for that they have tertiary amide ($-CON(CH_3)_2$), which can only form two relatively weak intermolecular hydrogen bonds with the assistance of water molecule as a bridge[52, 53], as shown in Fig. 5(b). Therefore, changing the ratio of AM and DMAA in P(AM-*co*-DMAA) means varying the density and strength of the hydrogen bonds among the P(AM-*co*-DMAA) chains. By comparison of the mechanical properties of the P(AM-*co*-DMAA) NCP gels and the PAM NCP gel, the role of hydrogen bonds as the physical crosslinking points among the grafted polymer chains can be elucidated.

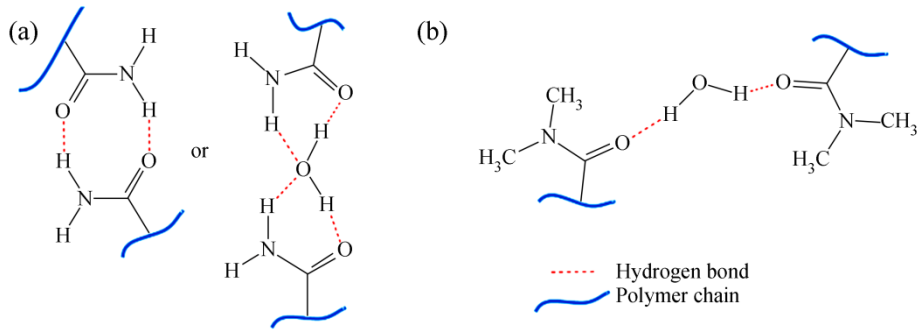

Fig. 5 Schematics of the hydrogen bonds formed among (a) the PAM chains and (b) the PDMAA chains

A series of P(AM-*co*-DMAA) NCP gels with different copolymerization mass ratio *R* of AM/(AM + DMAA) were fabricated, and their stress-strain curves are shown in Fig. 6(a). With increasing *R* from 0% to 100%, the performance of P(AM-*co*-DMAA) NCP gels gradually turned from soft and weak to tough and highly stretchable, which is a reflection of the important role of hydrogen bonds among the grafted polymer chains in toughening the NCP gels. With the varying of *R*, the tensile strength of P(AM-*co*-DMAA) NCP gels increases from 18 kPa to 313 kPa, as shown in Fig. 6(b). This is attributed to the fact that the PAM chains can form more strong hydrogen bonds than PDMAA. The rise of *R* in the P(AM-*co*-DMAA) NCP gels leads to a remarkable increase in both strength and density of the hydrogen bonds among the grafted polymer chains. These stronger hydrogen bonds act as the physical crosslinking points to assure that the NCP gel networks not only deform in a larger range but also withstand considerably more stress at a fixed strain. Comprehensively, the tensile strength of the PAM NCP gel (*R* = 100%) is even one order of magnitude higher than that of the PDMAA NCP gel (*R* = 0%). The stronger hydrogen bonds can effectively depress the slippage of the grafted polymer chains from each other. So the P(AM-*co*-DMAA) NCP gel with a higher PAM mass ratio can deform in a larger range and hence exhibits a higher value of elongation at break as shown in Fig. 6(c). The hydrogen bonds as the physical crosslinking points have a positive correlation with the value of the tensile modulus as mentioned in our previous paper[32]. Thus the raise of *R* leads to a great increase of tensile modulus of the P(AM-*co*-DMAA) NCP gels as shown in Fig. 6(d). Therefore, it is clearly illustrated that the hydrogen bonds play the role of physical crosslinking points to sustain stress in the NCP gels.

To investigate the effect of the hydrogen bonds on the energy dissipation, the loading-unloading experiments of P(AM-*co*-DMAA) NCP gels are performed and the results are shown in Fig. 7. It can be seen that with tuning *R*, the hysteresis loops become larger and larger as shown in Fig. 7(a). The dissipated energy during

loading-unloading, *i.e.* the area surrounded by the hysteresis loop, also increases with the increase of *R* as shown in Fig. 7(b), indicating that the increase of *R* leads to the increase of both density and strength of hydrogen bonds among the grafted polymer chains. During the loading process, these hydrogen bonds among the grafted polymer chains in NCP gel dynamically break to dissipate energy. After the break, they could recombine gradually due to the nature of noncovalent interaction[54]. Because the hydrogen bonds among the grafted polymer chains in the P(DMAA-*co*-AM) NCP gel with a higher *R* is more conductive to dissipate energy, the hysteresis loop and dissipated energy of P(DMAA-*co*-AM) NCP gel become larger, implying that the reversible break and recombination of hydrogen bonds are the main cause for the energy dissipation.

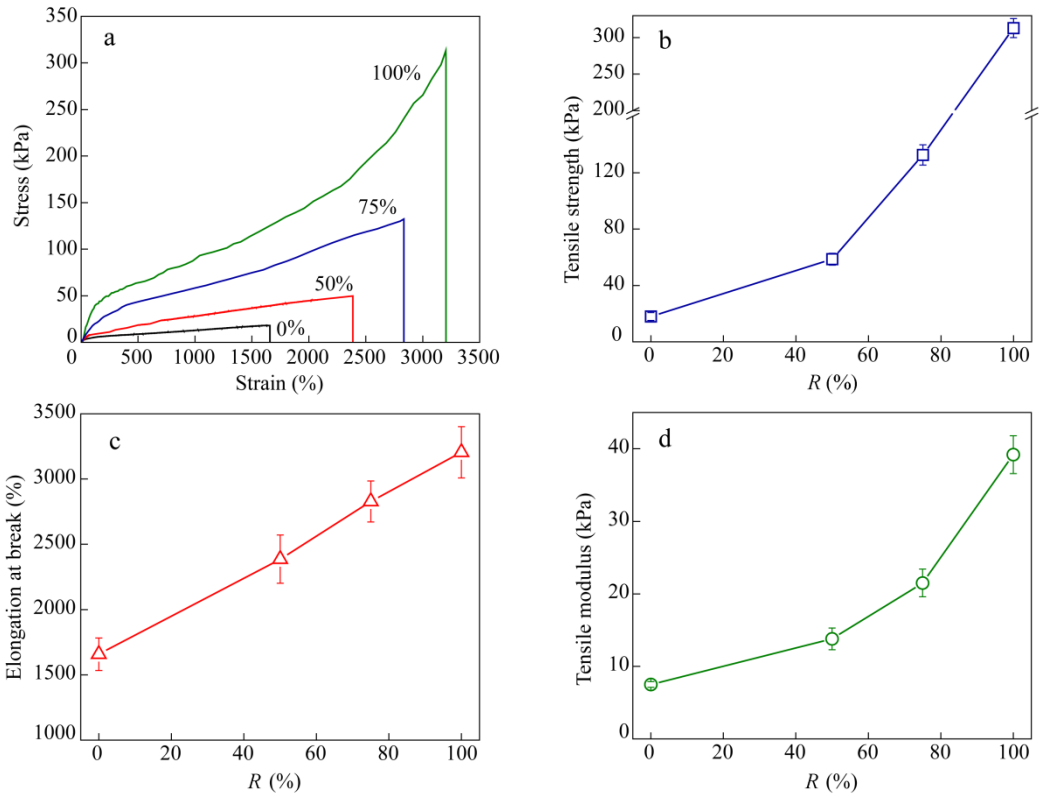

Fig. 6 Mechanical properties of the P(AM-*co*-DMAA) NCP gels: (a) stress-strain curves, (b) tensile strength, (c) elongation at break and (d) tensile modulus as a function of copolymerization mass ratio *R*

The second loading-unloading tests were conducted on both the PAM NCP gel (*R* = 100%) and the PDMAA NCP gel (*R* = 0%) stored for a prescribed time at room temperature after the first loading-unloading cycle. The results are shown in Figs. 7(c) and 7(d). The second loading curves of both the PAM NCP gel and the PDMAA NCP gel could recover to the first loading curve with the storing time increased from 1 min to 60 min. It evidently indicates that the PAM NCP gel can recover more rapidly and notably than the PDMAA NCP gel. This can also be explained in terms of the recombination of hydrogen bonds. It is reported that the association energy of the hydrogen bonds among the PAM chains is relatively higher than that among the PDMAA chains[51, 52]. Comparatively, the hydrogen bonds in the PAM NCP gel recombine more rapidly after the break under the first loading process, which ensures that the second loading curve recovers rapidly and notably to the first loading curve. This result shows that the hydrogen bond among the grafted PAM chains is more favorable to dissipate energy and homogenize the NCP gel networks[32] through the break and recombination process. And it also inspires that the mechanical properties of the NCP gels could be further improved by the incorporation of other stronger noncovalent interactions among the grafted polymer chains.

Therefore, the striking difference among the mechanical behaviors of the P(AM-*co*-DMAA) NCP gels with different *R* verifies the role of hydrogen bonds as the physical crosslinking points in toughening the NCP gels: the hydrogen bonds can sustain stress and dynamically break to effectively dissipate energy and recombine to homogenize the NCP gel networks under stretching.

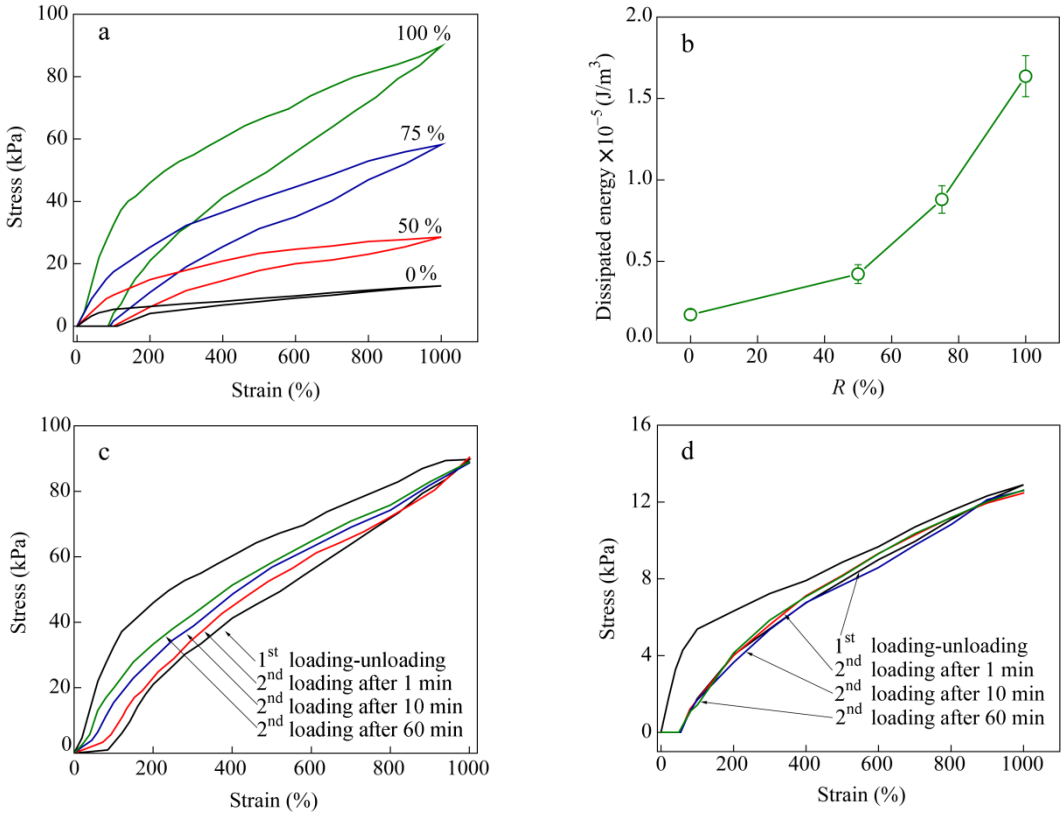

Fig. 7 (a) First loading-unloading cycles and (b) dissipated energy of the P(AM-*co*-DMAA) NCP gel with different copolymerization mass ratio *R*; first loading-unloading cycle and second loading curves after stored for prescribed time intervals of (c) the PAM NCP gel (*R* = 100%) and (d) the PDMAA NCP gel (*R* = 0) with 1000% strain

CONCLUSIONS

Comparing the mechanical properties of the PAM NCP gel with those of both the PAM H gel and the P(AM-*co*-DMAA) NCP gel, we elucidate the roles of dual crosslinking points in toughening the PAM NCP gel. The PAM grafted VSNPs can be applied as the analogous covalent crosslinking points to sustain stress and as the transfer centers for the stress homogenization in the NCP gels, leading to the fact that the mechanical properties of the NCP gels are much better than those of the PAM H gel because the PAM chains are covalently grafted on VSNPs in the PAM NCP gel. Further, comparing the mechanical properties of PAM NCP gel with those of a series of the P(AM-*co*-DMAA) NCP gels, it is found that hydrogen bonds among the grafted PAM and PDMAA chains act as the physical crosslinking points to maintain stress and dynamically break and recombine to effectively dissipate energy and homogenize the NCP gel networks. The stronger the hydrogen bonding is, the more the dissipated energy and the higher the mechanical properties are under stretching. Our study provides a facile and versatile method to fabricate new generations of tough and highly stretchable hydrogels through constructing hierarchical crosslinking points in a single network.

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