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Robust and self-healable nanocomposite physical hydrogel facilitated by the synergy of ternary crosslinking points in a single network†

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Acrylamide (AM) and a small amount of stearyl methacrylate (C18) hydrophobic monomer copolymerize to graft on the surface of vinyl hybrid silica nanoparticles (VSNPs), forming nanobrush gelators, thereby constructing ternarily crosslinked nanocomposite physical hydrogels (TC-NCP gels). The TC-NCP gel is composed of a single network ternarily crosslinked by hydrogen bonds and hydrophobic interactions among the grafting polymer chains as physical cross-linking points and thus the polymer grafted VSNPs as analogous covalent crosslinking points. Under stretching, the physical crosslinking points successively break to gradually dissipate energy and then recombine to homogenize the network. During the stretching process, the polymer chains grafted VSNPs can homogenize the stress distribution as transferring centers. The synergy of the ternary crosslinking points leads the TC-NCP gels to dissipate more energy and redistribute the stress more effectively when compared with hydrogels dually crosslinked by both hydrogen bonds and VSNPs as analogous covalent crosslinking points (without hydrophobic interactions) and by both hydrogen bonds and hydrophobic interactions (without VSNPs). As a result, the TC-NCP gels demonstrate remarkably improved mechanical properties, including tensile strength of 256 kPa, stretch ratio at break of 28.23 and toughness of 1.92 MJ m^{-3} at a water content of 90%. Pure shear test shows that the TC-NCP gel is able to resist notch propagation by micro-crack development from the notch tip to the whole gel network and has a high tearing energy of 1.21×10^4 J m^{-2}. The dynamic nature of the network endows the TC-NCP gels with excellent self-healing ability. The results evidently indicate that constructing a single gel network with hierarchical crosslinking points is a versatile method to fabricate robust hydrogels.

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Introduction

Hydrogels with excellent mechanical properties are crucially important in numerous application fields such as tissue engineering[1] and soft devices.[2–4] However, traditionally prepared hydrogels[5] always have poor mechanical performance, originating from the structural drawbacks, *i.e.* the inhomogeneous distribution of crosslinking points[6] or the lack of mechanism to dissipate the energy in the gel network.[7] To endow hydrogels with excellent mechanical properties, many attempts have been made from the viewpoints of designing a homogeneous gel network or introducing effective structural units for energy dissipation into the gel network.[8–10] As a result, a number of mechanically robust hydrogels have been fabricated such as slide-ring gel,[11] tetra-PEG gel,[12] double network gel,[13–15] organic/inorganic hybrid gel,[5,16] and polyampholyte hydrogel.[17]

In order to simultaneously realize energy dissipation and network homogenization in gels, we have already proposed a fabrication strategy of hierarchical crosslinking (HC) in a single network to prepare super tough and highly stretchable hydrogels.[18–25] Nanocomposite physical hydrogels (NCP gels)[21,22] with super toughness and high stretchability are fabricated using the strategy of dual crosslinking (DC) in a single network. The dual crosslinked NCP (DC-NCP) gels are composed of nanobrush gelators with a structure of polymer chains grafted on vinyl hybrid silica nanoparticles (VSNPs), with dual crosslinking *via* hydrogen bonds among the grafting polymer chains as physical crosslinking points and the polymer chains grafted VSNPs as analogous covalent crosslinking points. Under stretching, the hydrogen bonds as non-covalent bonds break to dissipate the energy and then recombine to homogenize the gel network. During the dynamic break–recombination process of physical crosslinking in the hydrogels, the polymer chains grafted VSNPs homogenize the stress distribution as transferring centers. The synergy of the

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dual crosslinking points endows the DC-NCP gels with superior strength and high stretchability.

Based on the concept of 'dual cross-linked single network gels', it is expected that the non-covalent dynamic bonds such as hydrogen bonds, hydrophobic interactions[26–29] and coordination bonds can be combined in the hydrogels to form HC gels. Therefore, hierarchical crosslinking points in the gels can gradually dissipate energy through successive break–recombination of the non-covalent dynamic bonds. Consequently, super tough gels can be obtained.

In this study, a small amount of C18 as an hydrophobic monomer was used to copolymerize with acrylamide (AM) and then grafted onto the surface of VSNPs to form poly(acrylamide-*co*-C18) (P(AM-*co*-C18)) nanobrush gelators. The grafted polymer chains of the neighbouring gelators can physically interact with each other by two types of non-covalent interactions: hydrogen bonding between the amide groups of PAM blocks and hydrophobic interactions among the hydrophobes of poly-C18 during the formation of the SDS micelles. Therefore, physical crosslinking is accomplished among the gelators by a combination of hydrogen bonds and hydrophobic interactions, and the VSNPs can serve as analogous covalent crosslinking points, thereby forming TC-NCP gels. The mechanical properties and self-healing behavior of the TC-NCP gels were systematically studied with comparison to the DC-NCP gel crosslinked by hydrogen bonds and VSNPs, and the dually crosslinked linear P(AM-*co*-C18) gel (DC-L gel) by hydrogen bonds and hydrophobic interactions among the P(AM-*co*-C18) chains.

Experimental

Materials

Acrylamide (AM), ammonium persulfate (APS) as an initiator and sodium chloride (NaCl) were purchased from Xilong Chemical Co., Ltd. *N*,*N*,*N*′,*N*′-Tetramethylethylene-diamine (TEMED) as an accelerator and vinyl triethoxy silane (VTES) were purchased from Alfa Aesar. Stearyl methacrylate (C18) and sodium dodecyl sulfate (SDS) were purchased from Aladdin.

Hydrogel preparation

DC-NCP gel. An aqueous dispersion of VSNPs with a diameter of 3 nm was prepared according to our previous study.[21] 0.1 mL of an VSNP aqueous dispersion was added to 27 mL of water at 35 °C to obtain a transparent solution. After the addition and dissolution of AM (3 g) for 30 min, 0.015 g of APS as an initiator was added to the solution. The dissolved oxygen in the solution was then removed by three cycles of vacuum evacuation and exchange with nitrogen. Finally, 25 μL of TEMED as an accelerator was added into the prepolymerization solution. The solution was transferred into several plastic syringes with 5 mm internal diameters or a rectangular mold with a thickness of 2 mm and the polymerization was conducted for 1 day at 28 ± 2 °C.

DC-L gel. SDS (0.7 g) was added to 27 mL of 0.3 M NaCl at 35 °C to obtain a transparent solution. Then, C18 and AM were dissolved in the abovementioned solution under stirring for 2 h at 35 °C;[29] the total weight amount of the monomers (C18 and AM) was 3.0 g. After the addition and dissolution of the monomers for 30 min, 0.015 g of APS as an initiator was added to the solution. The dissolved oxygen was then removed by three cycles of vacuum evacuation and exchange with high-purity nitrogen. Finally, 25 μL of TEMED as an accelerator was added to the prepolymerization solution. The DC-L gel was named as DC-L gel-x, where x denotes the weight percentage of C18 with respect to the total weight of the monomers. For example, DC-L gel-5.0% represents that the content of C18 is 5.0 wt% relative to the total weight of the monomers. The solution was transferred into several plastic syringes with 5 mm internal diameters or a rectangular mold with a thickness of 2 mm and the polymerization was conducted for 1 day at 28 ± 2 °C.

TC-NCP gel. SDS (0.7 g) was added to 27 mL of 0.3 M NaCl at 35 °C to obtain a transparent solution. Then, C18 and AM were dissolved in the abovementioned solution under stirring for 2 h at 35 °C;[29] the total weight amount of the monomers (C18 and AM) was 3.0 g. After the addition and dissolution of the monomers for 30 min, 0.015 g of APS as an initiator and 0.1 mL of an VSNP aqueous dispersion were added in the solution. Dissolved oxygen was then removed by three cycles of vacuum evacuation and exchange with high-purity nitrogen. Finally, 25 μL of TEMED as accelerator was added to the prepolymerization solution. The TC-NCP gel was named as TC-NCP gel-x, where x denotes the weight percentage of C18 with respect to the total weight of the monomers. For example, TC-NCP gel-5.0% represents that the content of C18 is 5.0 wt% relative to the total weight of the monomers. The solution was transferred into several plastic syringes with 5 mm internal diameters or a rectangular mold with a thickness of 2 mm and the polymerization was conducted for 1 day at 28 ± 2 °C.

Measurements and characterization

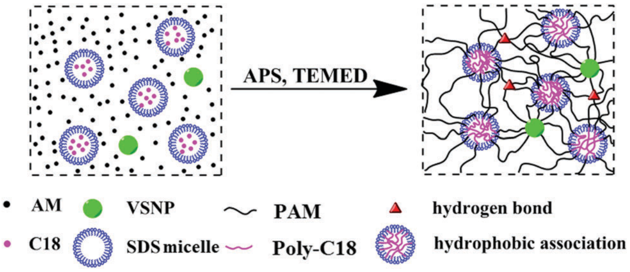
Mechanical measurements. To avoid water loss during the test, the surface of the gel sample was coated with a thin layer of silicone oil. For the tensile and cycle tests, hydrogels of the same size (5 mm $\varnothing \times 60$ mm length) were stretched using an electromechanical testing machine (Zwick-Roell Z005). The following is the measuring conditions: temperature, 25 °C; gauge length, 15 mm and crosshead speed v, 100 mm min^{-1}. The stretch ratio λ under stress was calculated from the ratio of the stretch length $L = L_0 + vt$ and the initial length L_0, where t is the stretch time. The strength was calculated on the basis of the initial crosssection. The tensile modulus was calculated from the increase in stress between $\lambda = 1.05$ and $\lambda = 1.20$. The toughness of the hydrogels is defined as the work done until fracture and was obtained by integrating the area underneath the stress–stretch ratio curve. Cyclic tensile loading–unloading tests were performed on the gel samples upon changing the maximum stretch ratio $\lambda_{\max}$ in a range of 2–21.

The tearing energy was characterized by a pure shear test method.[14] Two gel samples, *i.e.* a notched and an unnotched, were used to measure the tearing energy. The gel samples were in 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 7.5 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 was 100 mm min^{-1}. The force–stretch ratio curves of both the notched and unnotched samples were recorded and the tearing energy was calculated from $T = U(\lambda_c)/(a_0 \times b_0)$, where $U(\lambda_c)$ is the work done by the applied force to the unnotched sample at λ_c, which is the stretch ratio when the notched sample breaks.

Characterization of self-healing. For self-healing characterization, two freshly cut surfaces of the gel were stuck together and pressed with a gentle force only to keep the surface in contact with each other. Afterwards, the rejoined samples were left to self-heal for a certain time (3–72 h) at a certain temperature (25–80 °C) without any external stimulus or pressure in closed plastic syringes to avoid water evaporation. After the treatment, the stress–stretch ratio curves of the healed samples were tested based on the same condition used for the above-mentioned mechanical measurements and then compared with those obtained for the original samples.

Results and discussion

The TC-NCP gels were fabricated *via* grafting copolymerization of AM and C18 on the surfaces of the VSNPs and thereby crosslinked by the hydrogen bonds and hydrophobic interactions among the polymer chains as physical crosslinking points and VSNPs as analogous covalent crosslinking points, as shown in Scheme 1. To reveal the synergy of the hierarchical crosslinking points in a single network, the DC-NCP gel crosslinked by hydrogen bonds and VSNPs and the DC-L gels crosslinked by hydrogen bonds and hydrophobic interactions were also prepared for comparison (see Scheme S1 for their structural representations, ESI†).



Scheme 1 The fabrication process used to prepare the TC-NCP gel. APS as an initiator and TEMED as the accelerator were used to initiate the polymerization.

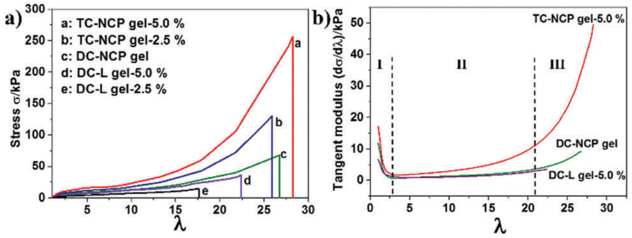


Fig. 1 The (a) stress–stretch ratio (σ–λ) curves and (b) modulus ($d\sigma/d\lambda$) of the gels.

Table 1 Mechanical properties of the DC-L gels, DC-NCP gel, and TC-NCP gels

Sample	Tensile modulus/kPa	λ_b	Tensile strength/kPa	Toughness/ MJ m^{-3}
DC-L gel-2.5%	2.3	17.6	14.7	0.12
DC-L gel-5.0%	3.9	22.4	36.4	0.33
DC-NCP gel	3.6	26.7	70.0	0.63
TC-NCP gel-2.5%	6.4	25.9	124	0.97
TC-NCP gel-5.0%	9.2	28.2	256	1.93

It is obviously shown in Fig. 1a that the TC-NCP gels have greatly improved mechanical performance than the DC-NCP and DC-L gels, clearly illustrating the importance of the coexistence of the ternary crosslinking points in a single network. Variation of the C18 content highlights the key role the hydrophobic interactions have in the outstanding mechanical properties of the TC-NCP gels. Relative to the DC-NCP gels (C18 content is 0), the tensile strength, elastic modulus and toughness of the TC-NCP gels increase remarkably upon increasing the C18 content from 2.5% to 5.0%, as shown in Table 1. This is due to the fact that introducing more C18 can enhance the crosslinking density of the gel, which ensures more stress can be sustained by the gel sample. While the TC-NCP gels and the DC-NCP gel exhibit very similar deformation ability as confirmed by the stretch ratio at break (λ_b) of 25.9–28.2. As previously reported,[21] the λ_b value of the NCP gels was positively correlated with the length of the grafted polymer chains in the gelators. When compared to the DC-NCP gel, the TC-NCP gel only contains less than 5% C18, which may have only a very slight effect on the length of the grafted polymer chains. Therefore, the NCP gels demonstrate a similar deformation capability. When compared to the DC-L gels, VSNPs, as analogous covalent crosslinking points, play an important role in the excellent mechanical performance of the TC-NCP gels. This is based on the fact that VSNPs can sustain and redistribute the applied stress and thus delay crack propagation under stretching, consequently ensuring the TC-NCP gels deform over a large range and withstand increased stress.

To elaborate the non-linear mechanical response of the gel samples during stretching, differential curves relative to the σ–λ curves were plotted as shown in Fig. 1b, as an indication of modulus $d\sigma/d\varepsilon$, which can be divided into three regions. The feature of the three regions results from the changes in the gel network structure in response to the deformation. In the initial stage of the stretching process, the stress was mainly tolerated by the physical crosslinking points, which contribute to most of the tensile modulus. The physical crosslinking points break in region I, which leads to an abrupt decrease in $d\sigma/d\varepsilon$. After the break, the physical crosslinking points can gradually recombine, which contributes to the homogenization of the gel network and toleration of the macroscopic stress,[30] assuring a slight increase in $d\sigma/d\varepsilon$ at region II. It was also found that the $d\sigma/d\varepsilon$ obtained for the TC-NCP gel-5.0% increased more evidently than that found for the DC-NCP gel and DC-L gel-5.0%, implying that the reversible break–recombination of the physical crosslinking points was more efficient in the TC-NCP gel. Upon further elongation ($\lambda > 20$), the chains were stretched to very high extension,[31] as evidenced by a stress hardening in region III. For the DC-L gels, the linear chains can easily slip[32] under large deformation, making the gel sample fracture at the very start of the hardening in region III. For the NCP gels, the polymer chains grafted VSNPs work as analogous crosslinking points to restrict the slippage of the grafted chains and sustain stress even after part of the physical crosslinking points break, as shown by the obvious hardening in region III. The TC-NCP gel exhibits much more remarkable strain hardening than the DC-NCP gel due to the enhanced interactions among the grafted polymer chains. Based on the abovementioned results, it is evident that the mechanical properties of the TC-NCP gels are significantly better due to the synergy of the ternary crosslinking points in the single network.

As previously reported,[21] the reversible physical crosslinking points can effectively dissipate the deformation energy applied to the gel during stretching. Considering the hydrophobic interactions of C18 are incorporated into the TC-NCP gel network, the loading–unloading tests for the gels were conducted to examine the contribution of the hydrophobic interactions of C18 to the energy dissipation. When the TC-NCP gels were subjected to loading–unloading cycles, a pronounced hysteresis was observed with an increasing magnitude as the maximum stretch ratio ($\lambda_{\max}$) was increased, implying the successive energy dissipation by the break of the physical crosslinkings. Comparatively, there was a smaller hysteresis for the DC-NCP gel, as shown in Fig. 2b, elucidating that the incorporated hydrophobic interactions can greatly enhance the energy dissipation of the TC-NCP gels. The DC-L gels also show obvious hysteresis loops, which get bigger upon increasing $\lambda_{\max}$ (Fig. 2c and Fig. S1b, ESI†), whereas the area of the loops are still smaller when compared to the TC-NCP gel-5.0%. Quantification of the dissipated energy was performed by integrating the hysteresis loops at different $\lambda_{\max}$ (Fig. 2d and Fig. S1c, ESI†). It was found that the energy dissipated by the TC-NCP gel-5.0% was higher than the sum of energies dissipated by the DC-NCP gel and the DC-L gel-5.0%. These results indicate that the ternary crosslinking points in the single network work in a synergistic way to toughen the TC-NCP gel; under stretching, the introduced hydrophobic associations ensures the TC-NCP gel network may tolerate an increased stress, resulting in more physical crosslinking points (both hydrogen bonds and the hydrophobic interactions) to gradually break and dissipate more energy and recombine to rearrange the network.

The effective energy dissipation and network homogenization are greatly beneficial for the hydrogels to prevent crack propagation and thus, exhibit high toughness.[7,33,34] Based on the synergy of the HCs, the NCP gel network was able to gradually dissipate energy by the successive breaking of the non-covalent interactions among the polymer chains and then homogenize the network by the subsequent recombination of the non-covalent interactions. Therefore, both the TC-NCP gels and the DC-NCP gels perform excellently in the notch-resistance experiments, as shown in Fig. 3.

The notched TC-NCP gel-5.0% can be stretched up to 22 times its original length (Movie S1, ESI†), which was higher than that found for the notched DC-NCP gel (~13), as shown in Fig. 3a. The obviously improved ability to deform and resist the notch can be attributed to the newly incorporated hydrophobic interactions. The DC-L gel-5.0% shows a lower ability to stop the notch from propagating because its network lacks ways to redistribute the stress. The great enhanced performance of the TC-NCP gel when compared to the DC-NCP and DC-L gels on resisting notch propagation again verifies the crucial role of the synergy of the TCs in a single network for its mechanical properties.

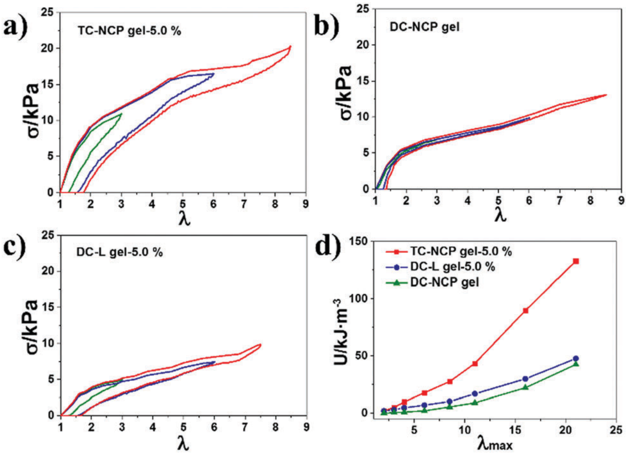


Fig. 2 Loading–unloading experiments performed at different maximum stretch ratios ($\lambda_{\max}$) for (a) the TC-NCP gel-5.0%, (b) the DC-NCP gel and (c) the DC-L gel-5.0%. (d) The dissipated energy (U) of the hydrogels as a function of $\lambda_{\max}$.

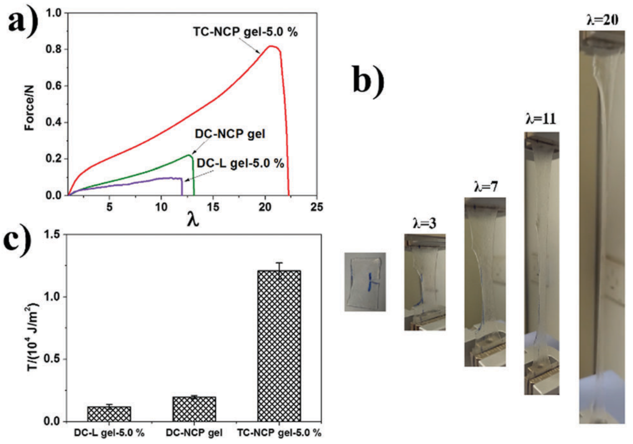


Fig. 3 (a) The force–stretch ratio curves obtained for the notched gel samples, (b) the stretching process of the notched TC-NCP gel-5.0%, and (c) the tearing energy (T) of the gel samples.

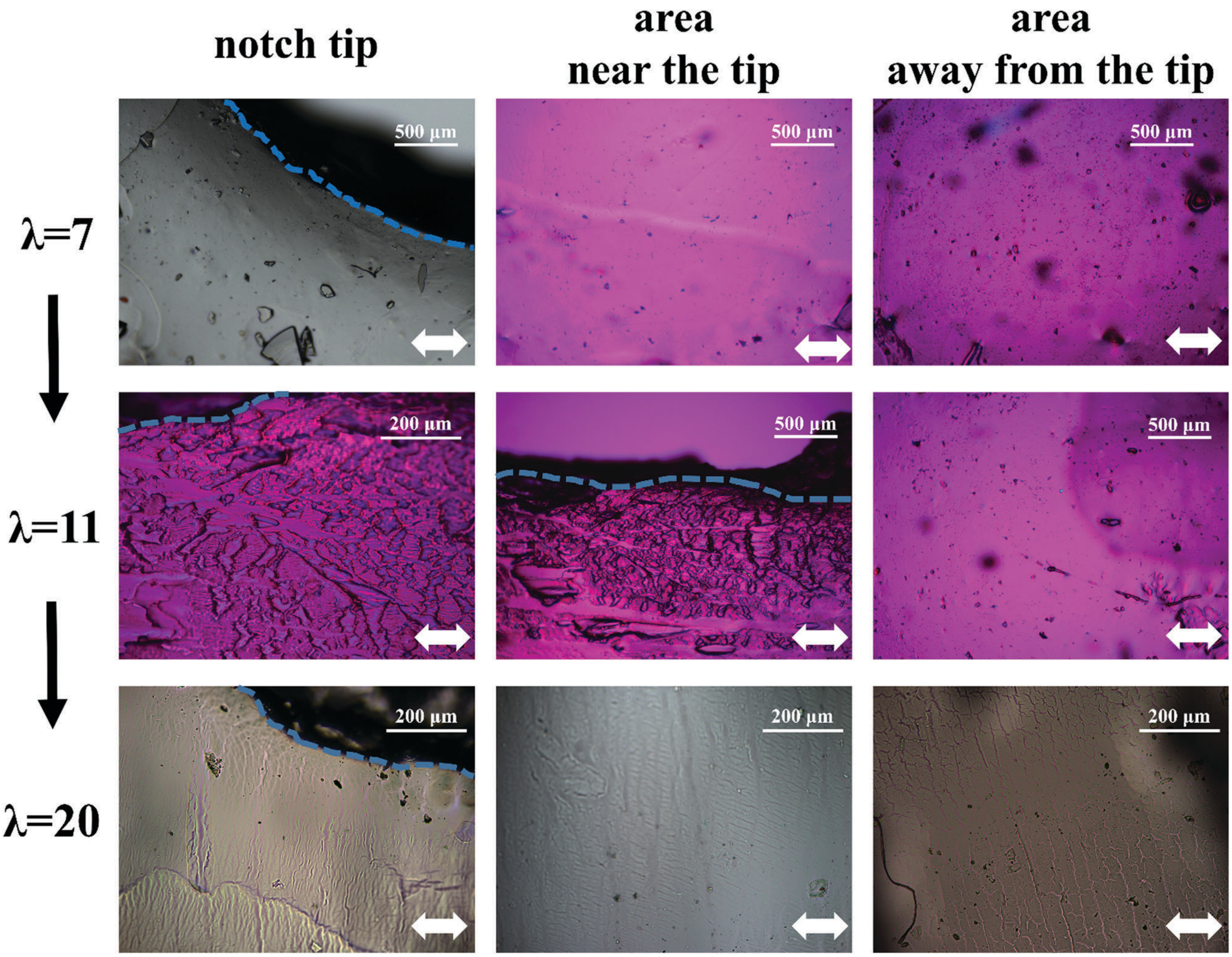


Fig. 4 Polarizing microscopy images of the TC-NCP-5.0% gel sample at different stretch ratio (λ). The dashed lines point out the boundary of the notched gel sample, and the two headed arrows indicate the stretching direction.

A unique micro-crack evolution was observed for the notched TC-NCP gel during stretching. At the early stage of stretching ($\lambda = 7$), the surface of the TC-NCP gel sample is smooth, as shown in Fig. 4a. Then, a large number of micro-cracks were initially observed around the notch tip at $\lambda = 11$, indicating that the gradually increased deformation initiated a stress concentration around the notch tip. The micro-cracks gradually generate from the notch tip to area away from the notch and are finally evenly distributed over the whole surface of the gel sample upon further stretching to $\lambda = 20$. Moreover, the deformation initiated micro-cracks dissipate a lot of energy and hence retard the obvious propagation of the notch following stretching (Fig. 3b). This phenomenon can be explained from the synergistic roles of the TCs in the TC-NCP gel. During the stretching process, the stress sustained by the TC-NCP gel increases monotonically (Fig. 3a). From $\lambda = 0$ to $\lambda = 7$, the stress may stay at a low level. The gel network is capable of tolerating stress easily, as revealed by the smooth surface of the gel sample. Upon increasing λ from 7 to 11, the stress increases further to a higher level. The increased stress may firstly concentrate around the tip of the notch as a defective region,[35] causing micro-crack initiation. Then, stress can be homogeneously redistributed into the whole gel through the polymer chains grafted VSNPs as transfer centers, evidenced by the gradual generation of micro-cracks from the notch tip to the area away from the tip. Along with the stress redistribution process, the physical crosslinking points reversibly break and recombine to dissipate the energy and rearrange the gel network, making a contribution to the excellent notch-resistance performance. Therefore, the stress concentration at the notch tip was mitigated and the notch remains stable without distinct propagation,[33] as shown in Fig. 3b. For this reason, the notched TC-NCP gel sample containing an increased content of C18 was much more tough and stretchable, assuring them to exhibit a remarkably improved tearing energy with a comparative value to that of the articular cartilage (Fig. 3c and Fig. S2b, ESI†).

The physical crosslinkings are thermodynamically reversible in nature, providing the possibility of self-healing of the physical gels.[29] Considering the NCP gels were constructed on basis of non-covalent interactions among the gelators, they should be able to self-heal. The samples of both the DC-NCP gel and the TC-NCP gel-5.0% were firstly cut with knife and the cut surfaces pressed together for 24 h at 60 °C to test their self-healing ability.

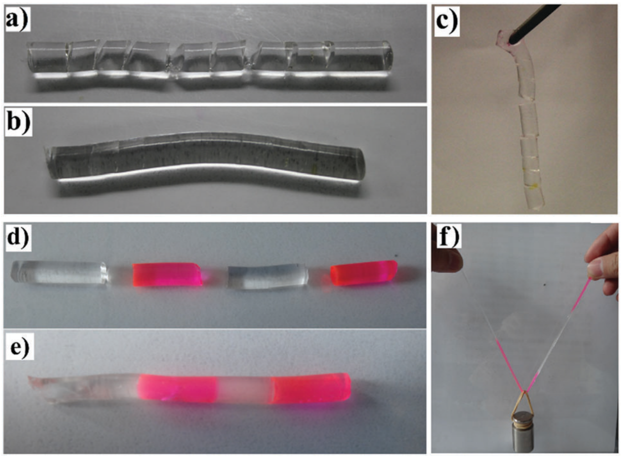


Fig. 5 The self-healing performance of (a–c) the DC-NCP gel and (d–f) the TC-NCP gel-5.0%.

The cut surfaces of the DC-NCP gel were still separated from each other after the treatment as shown in Fig. 5a–c, suggesting that the DC-NCP gel was not able to heal itself. Conversely, the cut pieces of the TC-NCP gel-5.0% with alternative colors can rejoin with each other into a mechanically robust gel, resisting a load of 100 g, as shown in Fig. 5d and e, indicating that the TC-NCP gel is self-healable. The different self-healing behaviors definitely arise from the introduction of long-lived hydrophobic interactions.[36] At a freshly cut surface of the NCP gel, a number of flexible grafted polymer chains must be created mainly by disrupting the physical crosslinking points among them, since the strength of both the hydrogen bonds and hydrophobic interactions were lower than that of the covalent bonds. By adjoining the two cut surfaces, the flexible grafted polymer chains at the two surfaces diffuse into each other by forming hydrogen bonds and hydrophobic interactions. The water molecules at the cut surfaces can form hydrogen bonds with the amide groups of the grafted PAM chains, disturbing the formation of hydrogen bonds between the amide groups significantly. Therefore, the physical crosslinking points among the grafted polymer chains at the cut surfaces have very low density to sustain stress; thus, the DC-NCP gel does not show any obvious self-healing. At the cut surfaces of the TC-NCP gel, the free hydrophobes of C18 are insoluble in water and can associate with each other more rapidly and specifically at the cut surfaces to minimize the interface energy, assuring a high density of crosslinking points between the two cut surfaces. Thus, the self-healing of the TC-NCP gel arises from the reconstruction of the network at the interface due to the mutual diffusion of the long and flexible grafted chains and their subsequent hydrophobic interactions with poly-C18. For this unique mechanism, the TC-NCP gels have the ability of self-healing, whereas the DC-NCP gel does not.

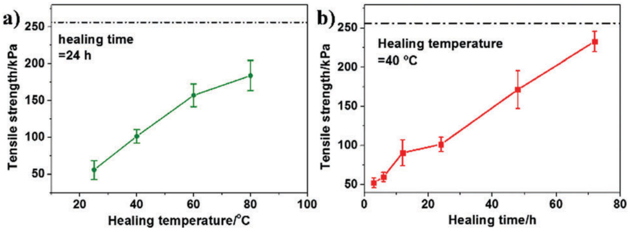


Fig. 6 The tensile strength of the healed TC-NCP gel-5.0% as a function of (a) the healing time and (b) the healing temperature. The dashed line indicates the tensile strength of the original TC-NCP gel-5.0%.

It is evident in Fig. 6 that the self-healing of the TC-NCP gel-5.0% was promoted by increasing the treatment temperature or time (see Fig. S3 for the σ–ε curves of the healed gel samples, ESI†). The gel sample healed for 24 h at 25 °C can sustain a tensile strength of 56 kPa, which is merely about 22% of the tensile strength of the original gel sample. Upon increasing the temperature to 80 °C, the tensile strength of the healed gel sample can recover to about 72% of its original value. This remarkable improvement in self-healing was attributed to the promoting effect of temperature on the diffusion of the grafted polymer chains and the formation of the hydrophobic interactions at the cut interfaces.[36,37] Based on the time–temperature superposition, increasing the healing time can also accelerate the self-healing of the TC-NCP gels as shown in Fig. 6b.

Conclusions

Ternarily crosslinked NCP gel (TC-NCP gel) was easily fabricated *via* the grafting copolymerization of the hydrophobic monomer (C18) and hydrophilic monomer (AM) on the surfaces of VSNPs. The TC-NCP gel was crosslinked by the hydrophobic interactions of C18, hydrogen bonds among the grafted polymer chains as physical crosslinking points and the polymer grafted VSNPs as analogous covalent crosslinking points. According to the mechanical characterization of the tensile stress–strain, cycle loading and fracture toughness, it was verified that the ternary crosslinking points work synergistically to toughen the TC-NCP gels. Therefore, the TC-NCP gel demonstrates markedly improved tensile properties and notch-resistance behavior with a tensile strength of 256 kPa, stretch ratio at break of 28.23, toughness of 1.92 MJ m^{-3} and tearing energy of 1.21×10^4 J m^{-2}. Based on the reversible nature of the hydrophobic interactions of C18, the TC-NCP gels also show excellent self-healing ability. The results evidently reveal that constructing a single gel network with hierarchical crosslinking points is a versatile method to fabricate tough hydrogels.

Acknowledgements

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Notes and references

1 E. S. Place, N. D. Evans and M. M. Stevens, *Nat. Mater.*, 2009, **8**, 457.
2 C. Yao, Z. Liu, C. Yang, W. Wang, X. J. Ju, R. Xie and L. Y. Chu, *Adv. Funct. Mater.*, 2015, **25**, 2980.
3 Y. Huang, M. Zhong, Y. Huang, M. Zhu, Z. Pei, Z. Wang, Q. Xue, X. Xie and C. Zhi, *Nat. Commun.*, 2015, **6**, 10310.
4 E. Zhang, T. Wang, W. Hong, W. Sun, X. Liu and Z. Tong, *J. Mater. Chem. A*, 2014, **2**, 15633.
5 K. Haraguchi and T. Takehisa, *Adv. Mater.*, 2002, **14**, 1120.
6 H. Furukawa, K. Horie, R. Nozaki and M. Okada, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2003, **68**, 031406.
7 H. J. Kong, E. Wong and D. J. Mooney, *Macromolecules*, 2003, **36**, 4582.
8 Y. Tanaka, J. P. Gong and Y. Osada, *Prog. Polym. Sci.*, 2005, **30**, 1.
9 J. P. Gong, *Soft Matter*, 2010, **6**, 2583.
10 S. Naficy, H. R. Brown, J. M. Razal, G. M. Spinks and P. G. Whitten, *Aust. J. Chem.*, 2011, **64**, 1007.
11 Y. Okumura and K. Ito, *Adv. Mater.*, 2001, **13**, 485.
12 T. Sakai, T. Matsunaga, Y. Yamamoto, C. Ito, R. Yoshida, S. Suzuki, N. Sasaki, M. Shibayama and U. I. Chung, *Macromolecules*, 2008, **41**, 5379.
13 J. P. Gong, Y. Katsuyama, T. Kurokawa and Y. Osada, *Adv. Mater.*, 2003, **15**, 1155.
14 J. Y. Sun, X. H. Zhao, W. R. K. Illeperuma, O. Chaudhuri, K. H. Oh, D. J. Mooney, J. J. Vlassak and Z. G. Suo, *Nature*, 2012, **489**, 133.
15 J. J. Wang and X. S. Li, *Chin. J. Polym. Sci.*, 2010, **28**, 849.
16 M. F. Zhu, Y. Liu, B. Sun, W. Zhang, X. L. Liu, H. Yu, Y. Zhang, D. Kuckling and H. J. P. Adler, *Macromol. Rapid Commun.*, 2006, **27**, 1023.
17 T. L. Sun, T. Kurokawa, S. Kuroda, A. Bin Ihsan, T. Akasaki, K. Sato, M. A. Haque, T. Nakajima and J. P. Gong, *Nat. Mater.*, 2013, **12**, 932.
18 J. Yang, C. Gong, F. K. Shi and X. M. Xie, *J. Phys. Chem. B*, 2012, **116**, 12038.
19 J. Yang, F. K. Shi, C. Gong and X. M. Xie, *J. Colloid Interface Sci.*, 2012, **381**, 107.
20 J. Yang, X.-P. Wang and X.-M. Xie, *Soft Matter*, 2012, **8**, 1058.
21 F. K. Shi, X. P. Wang, R. H. Guo, M. Zhong and X. M. Xie, *J. Mater. Chem. B*, 2015, **3**, 1187.
22 M. Zhong, F.-K. Shi, Y.-T. Liu, X.-Y. Liu and X.-M. Xie, *Chin. Chem. Lett.*, 2016, **27**, 312.
23 M. Zhong, Y. T. Liu and X. M. Xie, *J. Mater. Chem. B*, 2015, **3**, 4001.
24 J. Yang, C.-R. Han, J.-F. Duan, M.-G. Ma, X.-M. Zhang, F. Xu, R.-C. Sun and X.-M. Xie, *J. Mater. Chem.*, 2012, **22**, 22467.
25 L. Q. Zhang, L. W. Chen, M. Zhong, F. K. Shi, X. Y. Liu and X. M. Xie, *Chin. J. Polym. Sci.*, 2016, **34**, 1261–1269.
26 C. Bilici and O. Okay, *Macromolecules*, 2013, **46**, 3125.
27 D. Y. Ko, U. P. Shinde, B. Yeon and B. Jeong, *Prog. Polym. Sci.*, 2013, **38**, 672.
28 W. K. Ng, K. C. Tam and R. D. Jenkins, *J. Rheol.*, 2000, **44**, 137.
29 D. C. Tuncaboylu, M. Sari, W. Oppermann and O. Okay, *Macromolecules*, 2011, **44**, 4997.
30 R. Long, K. Mayumi, C. Creton, T. Narita and C.-Y. Hui, *Macromolecules*, 2014, **47**, 7243.
31 T. L. Sun, F. Luo, T. Kurokawa, S. N. Karobi, T. Nakajima and J. P. Gong, *Soft Matter*, 2015, **11**, 9355.
32 T. Baumberger, C. Caroli and D. Martina, *Eur. Phys. J. E: Soft Matter Biol. Phys.*, 2006, **21**, 81.
33 C. Y. Hui, A. Jagota, S. J. Bennison and J. D. Londono, *Proc. R. Soc. London, Ser. A*, 2003, **459**, 1489.
34 Q. Wang, R. Hou, Y. Cheng and J. Fu, *Soft Matter*, 2012, **8**, 6048.
35 F. Luo, T. L. Sun, T. Nakajima, T. Kurokawa, Y. Zhao, A. B. Ihsan, H. L. Guo, X. F. Li and J. P. Gong, *Macromolecules*, 2014, **47**, 6037.
36 U. Gulyuz and O. Okay, *Soft Matter*, 2013, **9**, 10287.
37 K. Haraguchi, K. Uyama and H. Tanimoto, *Macromol. Rapid Commun.*, 2011, **32**, 1253.