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Robust Dual Physically Cross-Linked Hydrogels with Unique Self-Reinforcing Behavior and Improved Dye Adsorption Capacity

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Abstract: Dual physically cross-linked (DPC) hydrogels were facilely fabricated by introducing hectorite clay Laponite XLG into hydrophobically associated polyacrylamide (HAPAM) system via one-pot in situ polymerization. The DPC gels exhibited excellent mechanical strength and unique self-reinforcing behavior with the aid of additional cross-linking effect provided by laponite. More impressively, the self-reinforcement of DPC gels could easily be achieved through any of the following three methods: self-healing, remolding or stretching, which was unrealizable for the reported hydrophobic association hydrogels. Compared with HAPAM gels, improved cationic dye adsorption capacity appeared in DPC gels owing to the existence of abundant negative charges on the surface of laponite. Our proposed methodology highlights the possibility of designing a new type of readily self-reinforced physically cross-linked hydrogels, which have great application potential in bioengineering field and the treatment of organic dyes.

Keywords: physically cross-linked, self-reinforcement, mechanical strength, self-healing, dye adsorption.

1. Introduction

Hydrogels, a kind of three-dimensional hydrophilic cross-linked polymers, have attracted great scientific interest over the past several decades. It has been reported that hydrogels can be applied in various fields such as biomimetic actuators [1-4], tissue engineering [5], molecular filters [6, 7] and sensors [8]. Polymer chains of hydrogels are usually cross-linked by covalent or strong physical bonds and swollen in aqueous solution. Unfortunately, the application range of most hydrogels prepared by chemical cross-linking is seriously restricted because of their irreversible cross-linking pattern, low mechanical strength and poor stability. Moreover, the addition of cross-linking agent makes the hydrogel system impure, which is not desirable for biological applications. Therefore, it is very necessary to improve the performance of conventional synthetic hydrogels in order to broaden their application range.

At present, enormous efforts have been devoted to developing tough hydrogels with favorable comprehensive properties, such as double network hydrogels [9-12], sliding-ring hydrogels [13], hydrophobically associated (HA) hydrogels [14], nanocomposite (NC) hydrogels [15], macromolecular microsphere composite hydrogels [16], and dipole–dipole or hydrogen bonding enhanced hydrogels [17, 18]. Among them, HA gels are proved to possess self-healing [19, 20] and reforming [21] capacity without the introduction of extra cross-linking agent. The gelation results from the cross-linking effect supplied by hydrophobically associated micelles [22], whose role is similar to that of cross-linking agents in chemical cross-linked hydrogels. However, because of the single cross-linking pattern, HA gels usually exhibit weaker mechanical strength after loaded. In addition, the conventional amide monomers based HA gels have been considered feeble in dye adsorption on account of their non-ionic monomer composition. Another class of hydrogels physically cross-linked by nanoscopic inorganic materials such as clay is generally called NC gels. For these clay nanocomposite hydrogels, clay are uniformly dispersed and acted as 2-dimensional and multifunctional cross-linkers by adsorbing polymer chains through hydrogen bonding and electrostatic interaction to form a 3-dimensional network. However, NC gels of single cross-linked network usually perform poor mechanical strength [23, 24] and undesirable self-healing efficiency at low clay content [25, 26]. Consequently these inherent drawbacks of HA and NC gels have largely blocked their practical applications. In contrast to single cross-linked hydrogels, DN gels consist of two independently cross-linked networks demonstrate ultrahigh mechanical strength and remarkable toughness [27]. Generally, DN gels exhibit the best mechanical properties when the first network is highly cross-linked and the second only lightly cross-linked [28]. Nevertheless, the majority of DN gels are manufactured by a time consuming two-step approach, during the second step hydrogels with the first network are swelling in precursor solutions of the second network, resulting in an unmanageable total water content of DN gels. Extending this point of view, developing a class of hydrogel with similar network structure to DN gels through one step method seems an appealing alternative. Some approaches have been proposed in an endeavor to obtain this type of hydrogel, namely the dual cross-linked (DC) hydrogel. The existing knowledge of DC hydrogels mainly comes from hybrid physically-chemically cross-linked hydrogels, whose networks are synchronously cross-linked by covalent bonds and physical interactions [29, 30]. On account of the irreversible and permanent cross-linking pattern originated from covalent bonds, the self-healing property of hybrid DC hydrogel is usually suppressed seriously, which, however, prove to be a fantastic feature in applications [31, 32]. For HA and NC gels, though self-healing ability is endowed by reversible cross-linking patterns, the mechanical strength of them after repaired always decreases heavily due to low healing efficiency, resulting in their poor reusability. Reasonably, combining the hydrogel system of HA and NC gels to simultaneously ameliorate the mechanical strength and healing efficiency should be an imperative and instructive attempt.

Self-reinforcement is a desirable property for materials requiring recycle use [33], while it is not readily accessible for hydrogels because of their high water content. Tong et al. observed self-reinforcement from polymer-laponite NC gels by stretching and tearing [34]. The orientation of laponite during elongation was responsible for the self-reinforcement of NC gels. Up to now, no self-reinforcing behavior has been discovered for HA and conventional DC gels, which seriously limited their other applications demanding repeated use such as cartilage, muscle, and adsorbing material for dye wastewater treatment.

In recent years dye contamination has become a serious environmental and social problem due to their environmental toxicity and public health damage. Polymeric hydrogels has been found to be severed as an optimum adsorbing material for dye wastewater treatment in terms of economic feasibility, adsorption-regeneration, simplicity of design, ease of operation and insensitivity to toxic substances [35]. It is known that NC hydrogels can absorb and trap ionic dyes, in which laponite carrying strong negative charges on surface has been demonstrated powerful in dye adsorption because of their high specific surface area, chemical and mechanical stabilities, and a variety of surface and structural properties [36]. However, limited recoverability and self-healing property of NC gels restricted their use for this application. Therefore, it naturally arouses our interest to explore a novel derivation of hydrogels, combining high mechanical strength, self-reinforcing behavior, dye adsorption capacity of HA, NC and DC gels.

The existing literatures lead us to consider that it is supposed not difficult to combine the cross-linking networks of HA and NC gels simultaneously to obtain a type of dual physically cross-linked hydrogels since these two hydrogel systems are quite compatible. As far as we know, although a range of HA hydrogels and NC hydrogels have been reported, in the case of influences controlled by laponite and hydrophobic/hydrophilic monomers on the mechanical properties, there have been little progress in self-reinforcement of NC or HA gels. To the best of our knowledge, no self-reinforced hydrogel has been reported with the combination of HA and NC hydrogel systems so far.

In this work, we report the successful preparation of novel dual physically cross-linked (DPC) gels with unique self-reinforcing behavior and improved dye adsorption capacity by a simple one-pot polymerization method. The self-reinforcement of DPC gels could be achieved through three methods: self-healing, remolding and stretching, which was totally inaccessible for chemically cross-linked or hybrid DC gels. We have explored a strategy to improve the mechanical properties and self-healing efficiency of hydrogels by combining synergistic cross-linking effect provided by hydrophobically associated micelles and laponite nanosheets. The laponite added acts as cooperative cross-linking agent and improves the dye adsorption ability. The results show us an efficient way to synthesize self-reinforced dual physically cross-linked hydrogels for practical application as tough materials in tissue scaffolds and wastewater treatment.

2. Experimental

2.1 Materials

Acrylamide (AM) and potassium persulfate ($K_2S_2O_8$), purchased from Tianjin Bodi Chemical Co., Ltd, were recrystallized from distilled water before use and dried under vacuum at room temperature. Sodium dodecyl benzene sulfonate (SDBS) was provided by Chengdu Kelong Chemical Reagent Factory, Stearyl methylacrylate (SMA) was obtained from J&K Chemical Technology Co., Ltd, both were used without further purification. Synthetic hectorite clay of gel-forming grade Laponite XLG ($Mg_{5.34}Li_{0.66}Si_8O_{20}(OH)_4Na_{0.66}$) was kindly provided by Huizhi Fine Chemical Co., Ltd, and used after dried at 125 °C for 2 h. The dyes, malachite green (MG), methylene blue (MB), methyl orange (MO), basic fuchsin (BF) and crystal violet (CV) were purchased from Haihong Chemical Reagent Factory. All solutions used in experiments were prepared in deionized water.

2.2 Synthesis of DPC gels

DPC gels were synthesized through in situ copolymerization of AM (10 wt%) and SMA (2 mol% relative to AM) in the aqueous suspension of laponite (varied) with SDBS (3 wt%), initiated by KPS (0.5 wt% relative to the total mass of AM and SMA), all the total mass of the initial reaction solution was fixed at 15 g. For example, the experimental procedure used for $DPC_{0.5}$ was as follows: 0.075 g of laponite was first dispersed in deionized water (12.02 g) under stirring for at least 4h until a homogeneous suspension was achieved. Then, the hydrophilic monomer AM (1.50 g) and the surfactant SDBS (0.45 g) were added into the laponite suspension under stirring, 0.14 g of hydrophobic monomer SMA was subsequently put in. The mixture was stirred for another 24 h to make a uniform solution. Finally, the aqueous solution of initiator (KPS 0.0082 g in 0.82 g of water) was added to the former solution. The solution was put into an ampoule and then flame-sealed after being bubbled with N_2 for 10 min to eliminate oxygen, the polymerization was allowed to proceed at 50 °C for 5 h, and then DPC gels samples were obtained.

In this work, DPC gels were designated as DPC_n, where n stood for the mass fraction of laponite (varying from 0.5 to 1.5) relative to the total mass of initial reaction solution. For comparison, HA and NC gels under the same experimental conditions were also prepared. Nomenclature and composition contents of all gels are listed in **Table 1**.

2.3 Characterization

The morphologies of the hydrogels were examined by a Quanta 250 scanning electron microscope (SEM). To prepare the samples, the swollen hydrogels were equilibrated in distilled water at room temperature, and then quickly frozen and freeze-dried. Afterwards, the freeze-dried samples were fractured carefully, gold-coated and subjected to the SEM analysis.

2.4 Mechanical Testing

The measurements of tensile mechanical and hysteresis properties were performed on synthesized hydrogels of the same size (10.0 mm diameter × 60 mm length) using an Instron universal test instrument (Model 5576, Instron Instruments, U.S.A.) with a 1 KN load cell at 25 °C. The tensile strain induced was taken as the change in length relative to the initial length of the specimen. Initial cross-section area was used for calculating tensile stress and elastic modulus, which was calculated from the increase in load detected between elongation of 100% and 200%. For the measurements of hysteresis properties, the sample length between the jaws was 30 mm and the strain was restricted at 1500%. The crosshead speed for the tensile and retraction was fixed at 100 mm/min.

Rheology measurements of DPC, HA gels were conducted with Bohlin Gemini 200 rheometer using a parallel plate of diameter 20 mm at 25 °C. First, the dynamic strain sweep from 0.1% to 10% was carried out at angular frequency of 1 rad/s to determine the linear viscoelasticity region. Then, the frequency sweep was performed over the frequency range of 0.1–100 rad/s at a fixed strain of 1%.

2.5 Dye adsorption research

Desired amounts of dried DPC and HA gels were immersed in 50 mL of 10 mg/L cationic dye solution, respectively. The test temperature was 25 °C. When the equilibrium swelling states of hydrogels were achieved, the dye solution was extracted from the adsorption system for the analysis of dye concentrations by using a UV/vis spectrophotometer (UV-3600) at the maximum absorption wavelength of each dye. The amounts of dye adsorbed on the hydrogel at equilibrium states, Q_e (mg/g), were defined according to Eq. (1):

$$Q_e=(C_0 - C_e) \times V / m \quad (1)$$

where V is the volume of the solution (mL), m is the mass of dried hydrogel (g), C_0 and C_e are the initial and final concentrations of dye solution.

Table 1 nomenclature and composition contents of all gels

samples	laponite[g]	H_2O^a[g]	AM[g]	SMA[g]	SDBS[g]	KPS[g]	H_2O^b[g]
NC_1	0.15	12.59	1.50	0	0	0.0075	0.75
$NC_{1.5}$	0.225	12.515	1.50	0	0	0.0075	0.75
HA	0	12.08	1.50	0.14	0.45	0.0082	0.82
$DPC_{0.5}$	0.075	12.005	1.50	0.14	0.45	0.0082	0.82
DPC_1	0.15	11.93	1.50	0.14	0.45	0.0082	0.82
$DPC_{1.5}$	0.225	11.855	1.50	0.14	0.45	0.0082	0.82

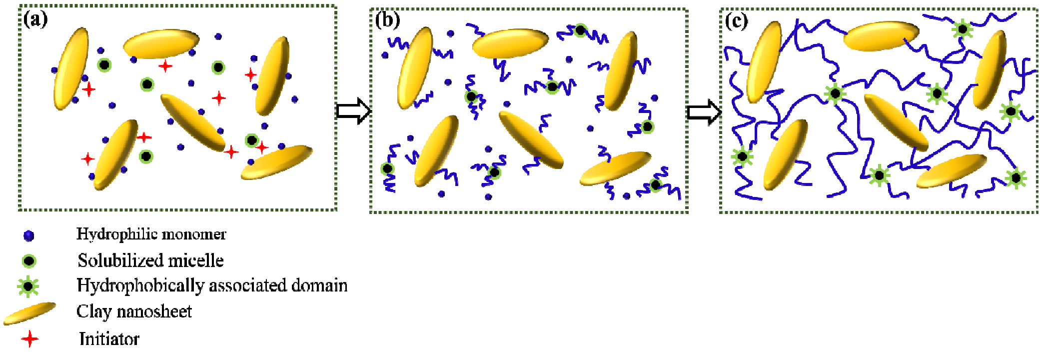
[a] Mass of water used to disperse laponite and dissolve monomers.

[b] Mass of water used to dissolve initiator KPS.

3. Results and Discussion

3.1 Network structure and mechanical properties of DPC gels

In this study, a series of DPC gels containing varying amounts of laponite (0, 0.5, 1.0 and 1.5 wt%) were prepared by one-pot in situ polymerization in the laponite suspension. Compared with conventional chemical hydrogels, no extra cross-linking agent was introduced into the hydrogel system. During the churning process, the hydrophobic monomer SMA was solubilized by SDBS owing to the strong hydrophobic interaction between their hydrophobic side chains, thereby abundant solubilized micelles were formed and stably dispersed in solution [37, 38] (**Scheme 1a**), which cross-linked a portion of PAM chains in the process of polymerization to form partial cross-linking junctions [21, 39]. In the meantime, a number of AM molecules were adsorbed onto laponite due to their intense interaction (**Scheme 1a**). Hence some PAM chains propagated from the surfaces of laponite, resulting in the apprearence of grafted chains, one chain end of which was immobilized on the surfaces of laponite (**Scheme 1b**). As the grafted chains continued to grow until their active sites at the chain ends encountered others on laponite, bimolecular terminations happened and integrated PAM chains generated among each laponite nanosheet [40] (**Scheme 1c**). Thus the laponite sheets were perceived as another part of cross-linking points. Therefore, dual physically cross-linked networks were formed by the combination of these two cross-linking effects, and bulk hydrogel with three-dimensional polymer networks was constructed.



Scheme 1. Formation of DPC gels by in situ micelle polymerization. (a) Stable dispersion of monomers with laponite and initiator in solution. (b) Polymer chains propagated from the surfaces of laponite during polymerization. (c) Hydrogel with dual physically cross-linked network structure was formed.

We compared tensile mechanical properties among HA, NC gels and DPC gels. As shown in **Fig. 1a**, HA gels with single cross-linking network was very ductile and weak (tensile stress of 31.96 KPa). For NC gels with low content of laponite less than 1 wt%, single cross-linking network could not even support their own weight. When it came to 1 wt% (NC_1) or 1.5 wt% ($NC_{1.5}$), though bulk hydrogels were obtained, their mechanical strength was no more than 7 KPa (inset in **Fig. 1a**), which was merely 1/18 that of $DPC_{1.5}$ gel. Therefore, NC gels were eliminated to test for comparison in subsequent measurements since they were too weak to even bear the test conditions. However, when laponite is introduced into the HA network to form DPC gels, additional cross-linking effect tends to enhance mechanical extensibility, strength, and toughness of the gels. It can also be seen in **Fig. 1a** that DPC gels exhibited outstanding mechanical properties compared to either HA or NC gel, and when the concentration of laponite increased from 0.5 to 1.5 wt%, the tensile strength of DPC gels increased obviously. For example, the tensile stress of DPC_1 was 87.19 KPa, which was more than twice the total tensile stress of HA and NC_1 gel. Therefore, we could conclude from these results that dual cross-linking effects provided by both hydrophobically associated domains and laponite played the synergistic effect, allowing DPC gels to survive much higher strength than that of single cross-linked hydrogel. The detailed values of tensile parameters were summarized in **Table 2**.

In **Fig. 1b** we compared the tensile hysteresis curves of DPC and HA gels during a loading-unloading cycle to reveal their energy dissipation capacity, which was another indicator to assess the mechanical property of hydrogels. Hysteresis loops were observed when DPC and HA gels were stretched to 1500% and reverted at the same speed of 100 mm/min. At strain of 1500%, all DPC gels exhibited similar large hysteresis loops, which extended a little with increasing laponite content. While single cross-linked HA gel only showed a very small hysteresis loop. Consistently, $DPC_{0.5}$, DPC_1 and $DPC_{1.5}$ gels had almost equivalent dissipated energies of 147.63, 188.43 and 188.62 KJ/m^3, respectively, which was much higher than that of 43.10 KJ/m^3 for HA gel. One could conclude that energy was dissipated much more efficiently by DPC gels than HA gel during the stretching and reverting, thus resulting in higher mechanical strength and toughness.

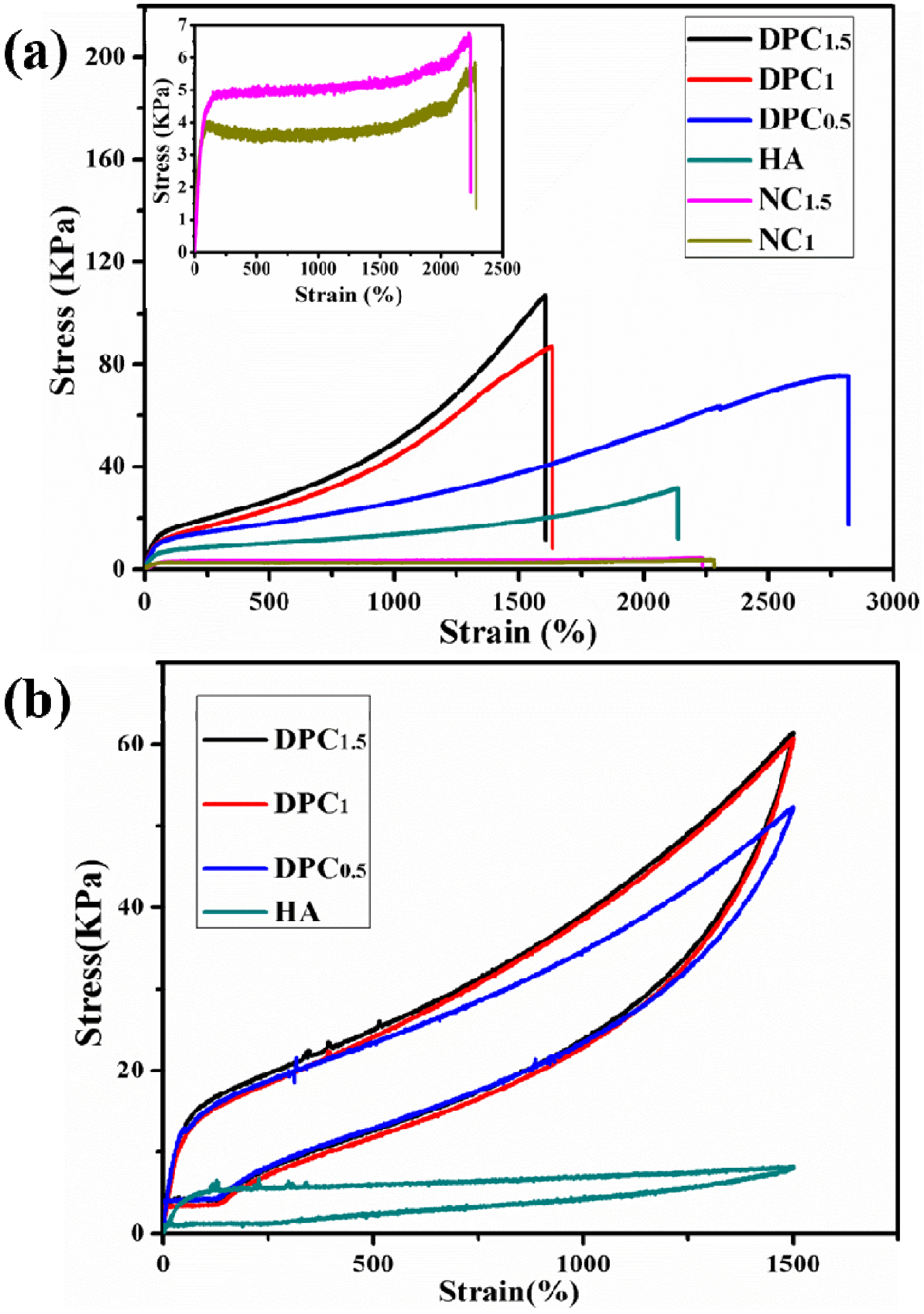


Figure 1. (a) Tensile stress-strain curves of DPC, HA and NC gels with different composition content (inset of stress-strain curves of NC_1 and $NC_{1.5}$ was added for the ease of comparison). (b) Loading–unloading stress–strain curves of DPC and HA gels at the strain of 1500%.

Table 2 Tensile properties of NC, HA and DPC gels

samples	Tensile strength (KPa)	Elongation (%)	Tensile modulus (KPa)	The maximum load (N)
NC_1	5.71	2270	0.12	0.25
$NC_{1.5}$	6.96	2235	0.44	0.39
HA	31.96	2136	0.99	2.19
$DPC_{0.5}$	75.17	2821	1.81	5.32
DPC_1	87.19	1633	2.91	6.33
$DPC_{1.5}$	107.11	1605	3.06	6.96

3.2 Rheology measurements

The shear strain γ dependence of the complex modulus G* was tested at 25 °C and 1 rad/s for HA and $DPC_{0.5}$ to determine the linear viscoelasticity region of the as-prepared hydrogels. It can be seen from **Fig. 2A** that the absolute value of G* turns independent of γ over the range from 1% to 10%. Hence all the viscoelasticity measurements were conducted at γ = 1% to ensure the availability of the linear viscoelasticity and enough sensitivity.

In order to enhance the stability of the pre-polymerization suspension and increase the mechanical properties of conventional single cross-linked HA gels, a reinforcing agent compatible with the polymer in water was required. Laponite was applicable not only for the stabilization of the pre-polymerization suspension but also for the enhancement to the hydrogels, which played the role of cross-linking agent. **Fig. 2B** illustrates the angular frequency ω dependence of the storage modulus G′ and loss modulus G″ for HA and DPC gels with different laponite content. It is obvious that G′ is always much higher than G″ and appeared as a plateau over the observed frequency range for HA and all DPC gels, which indicates that cross-linked networks have been formed in these gels. It is noted that addition of only 0.5 wt% of laponite leads to an evident increase in G′ compared to HA gels. Moreover, higher laponite concentration gives rise to higher G′, which is consistent with the previous tensile tests of the hydrogels. At the frequency of 1 rad/s, the G′ of $DPC_{0.5}$ is 1872 Pa, higher than the 1143 Pa of HA, when the amount of laponite increased to 1.5 wt%, the G′ reached 3726 Pa, which is 226% higher than that of HA gel. These results suggest the excellent physically cross-linking effect provided by laponite appears in DPC hydrogels.

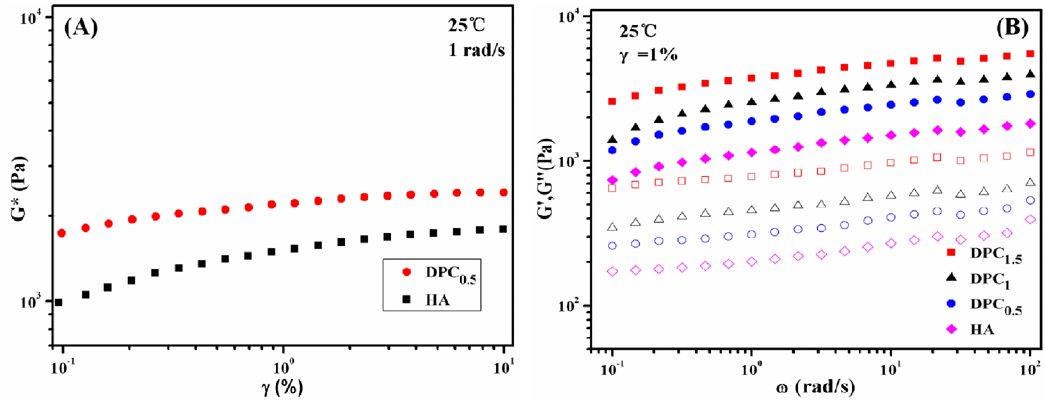


Fig. 2. (A) Shear strain γ dependence of absolute value of the complex modulus G* for the HA and $DPC_{0.5}$ gel at 25 °C and ω = 1 rad/s. (B) Angular frequency ω dependence of storage modulus G′ (solid symbol) and loss modulus G″ (open symbol) at 25 °C for HA and DPC gels.

3.3 Effective network chain density

To further understand the enhancement mechanism of DPC gels, we determined the network chain density from the equilibrium shear modulus based on the rubber elasticity at a small strain of 1% to ensure availability of the assumptions in the theory. The effective network chain density N was calculated according to the formula as in Refs [41, 42].

$$G_e = NRT \qquad (2)$$

Here, G_e was taken from the plateau modulus at G′ vs. ω curves where the plateau appeared and loss modulus G″ was much smaller than G′. R and T are the gas constant and absolute temperature, respectively.

For comparison, the network chain density was also estimated by using the elongation date following the method reported in the literature [43, 44]. For elongation, the effective network chain density N^* is evaluated from the tensile stress τ and elongation ratio γ on the assumption of affine deformation and incompressible volume.

$$\tau = N^*RT\,[\gamma - (1/\gamma)^2] \qquad (3)$$

Here, the τ value at strain of 100% was used in calculation, which was calculated with the original section area of the as-prepared hydrogels. The calculated results of N, N^* for HA and DPC gels were demonstrated in **Fig. 3.** The data obtained from two different methods showed a similar trend for varying laponite concentration. As the laponite content increased, both N and N^* improved distinctly on account of an increase in the cross-linking number formed by laponite. The value of $N^*$from the tensile experiment was much higher than the corresponding value of N from the equilibrium shear modulus for the same HA and DPC gels. This phenomenon could be ascribed to the strain used in the tensile experiment was much larger than that of shear strain $\gamma = 1\%$ used in the shearing measurement, the former seemed inconformable with the affine deformation assumption. Meanwhile, the volume of hydrogels reduced when $\gamma \geq 2\%$ [45], which was another contribution to the phenomenon. Therefore, the value of effective chain density from the linear response to the small shear deformation was more reliable. The elevation tendency of N and N^* with varying laponite concentration indicated again that more cross-linking points were produced in DPC gels by the introduction of laponite.

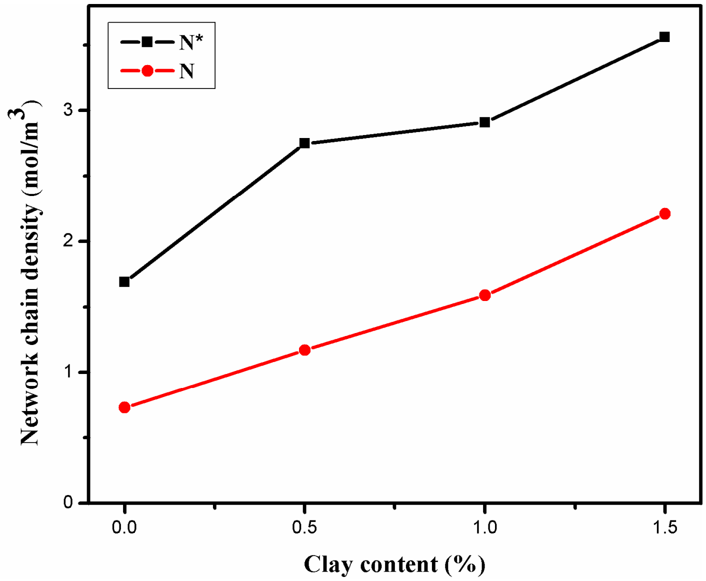


Fig. 3. The effective network chain density of DPC gels (HA gel was expressed as DPC$_0$) with varying laponite content.

3.4 Morphological analysis

The internal microstructures of HA gel and DPC$_{1.5}$ gel were characterized by SEM. As shown in **Fig. 4**, it could be seen that the HA gel presented a heterogeneous network structure with plenty of wrinkles (Fig. 4a1), while DPC$_{1.5}$ showed a much denser homogeneous structure with well-defined pores (Fig. 4b1). Notably, the introduction of laponite showed a dramatic influence on the wall of the pores in the hydrogels. The existence of laponite gave rise to a significant increase in the wall thickness of $DPC_{1.5}$ (Fig. 4a2) in clear comparison to that of HA gel (Fig. 4b2), which indicated that a more compact network structure was generated in $DPC_{1.5}$ gel by the introduction of laponite. Hence when loaded, more effective energy dissipation could be achieved by $DPC_{1.5}$ network, resulting in an improvement of mechanical properties, which was consistent with **Fig. 1**. Moreover, it was easier for dye molecules to be absorbed into DPC gels due to the capillarity caused by smaller and more uniform pores.

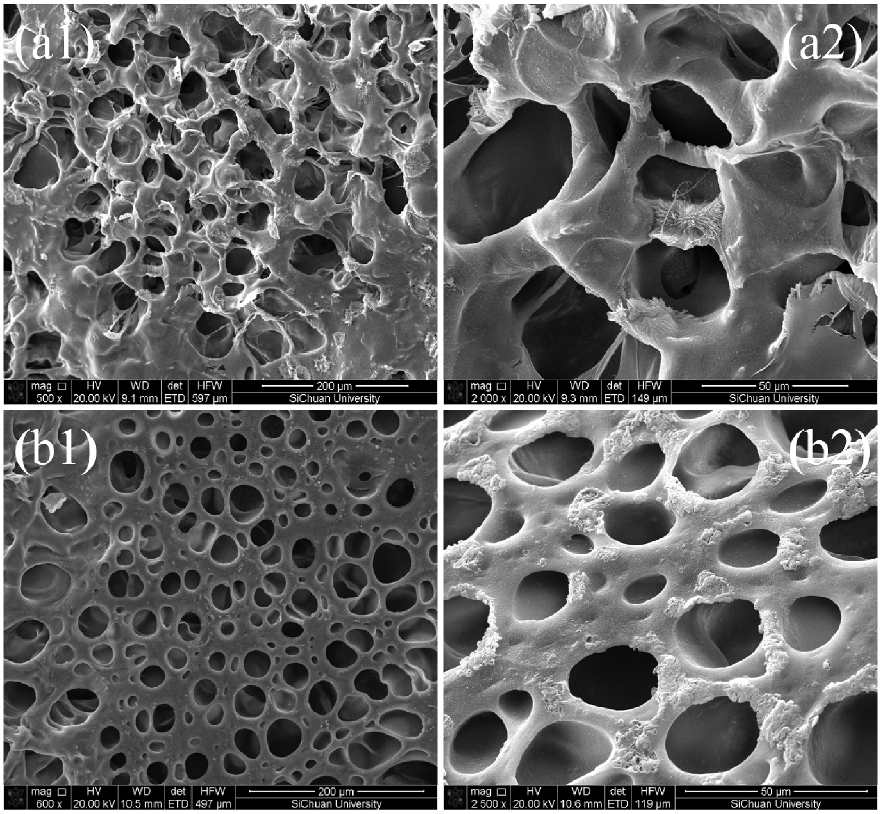


Fig. 4. SEM micrographs of (a1) HA gel, (a2) a local partial enlarged image of (a1), (b1) $DPC_{1.5}$ gel, (b2) a local partial enlarged image of (b1).

3.5 Self-reinforcement of DPC gels achieved by self-healing, remolding and stretching

Dual physically cross-linked network was created in DPC gels by the introduction of laponite without affecting another cross-linking effect, which endowed DPC gels excellent properties such as self-reinforcement and dye adsorption capacity, meanwhile, some excellent properties of HA gels such as self-healing and reforming, were still kept in DPC gels.

Self-healing ability of DPC gels was inherited from HA and NC gels. The self-healing process of $DPC_{0.5}$ gel was shown in **Fig. 5a.** The hydrogel specimen was cut into two separate parts (**Fig. 5a1**), then the two pieces were connected immediately after a small amount of water was sprayed on the cut surfaces (**Fig. 5a2**). The self-healed $DPC_{0.5}$ gel without any sign of a knife-cut was obtained by preserving the cut pieces at room temperature in wet-keeping cabinet for 3 days (**Fig. 5a3**). We further evaluated the self-healing efficiency of $DPC_{0.5}$ gel by tensile measurements, which of HA gel was also investigated as a comparison. As depicted in **Fig. 5b**, both of the self-healed HA gel and $DPC_{0.5}$ gel still possessed high extensibility and could be stretched to a large deformation without breaking. Interestingly, it was noted that the tensile modulus, strength of the self-healed $DPC_{0.5}$ gel exceeded the original specimen (**Fig. 5b1**) in contrast with the sharp decrease in those of HA gel after self-healing (**Fig. 5b2**), suggesting the self-healing efficiency of $DPC_{0.5}$ was superior to that of HA gel apparently and self-reinforcement of DPC gels could be attained by means of self-healing.

It was reported that the conventional HA gels were endowed self-healing ability due to the reversible dissociation process of the physical cross-linking inside the hydrogel network [46, 47]. Unfortunately, the absence of long and flexible polymer chain entanglements after cut usually led to a significant decrease in mechanical strength even after the HA specimen was healed. Thus self-reinforcement was totally unrealizable for HA gels without the aid of cross-linking effect supplied by laponite. The unique polymer-clay dual cross-linked network structure formed in DPC gels by the introduction of laponite played an essential role in improving the strength of DPC gels after healed. Once the DPC gel was obtained after polymerization, numerous dangling polymer chains with only one end anchored to laponite nanosheets and hydrophobically associated domains appeared in the hydrogel network (red lines in **Scheme 2a**), which contributed nothing to the mechanical properties of DPC gels. But when the two cut pieces (**Scheme 2b**) were connected, the mobility of polymer chains at the fresh-cut surfaces was enhanced owning to the lubrication of water, thus most of these dangling chains could be adsorbed onto the adjacent laponite nanosheets through chain diffusion and hydrogen bonding [48, 49], which strengthened the cross-linking effect at the joint section. Meanwhile, additional cross-linking effect supplied by hydrophobic association domains was created again due to the structural reorganization of hydrophobically modified PAM chains [50, 51]. As a consequence, intensive cross-linked network was formed at the self-healing interface by the synergistic effect of dual recross-linking actions (**Scheme 2d**), resulting in a mechanical enhancement of DPC gels. That is, more hydrogen interactions between polymer chains and laponite nanosheets would appear in DPC gels after healed, which would need more energy for the breaking of the hydrogels. Thereby the tensile toughness of DPC$_{0.5}$ after healed was also increased in obviously contrast with HA since the tensile toughness was defined as the area underneath the tensile stress-strain curve (**Fig. S1**).

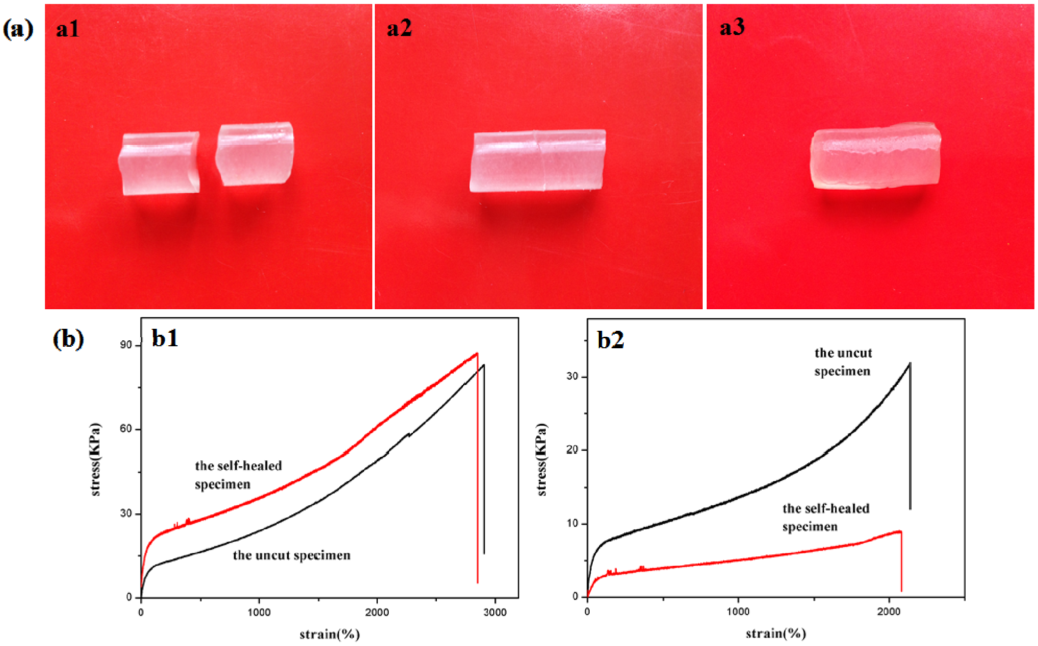


Fig. 5. The self-healing ability of DPC gels and the tensile properties of the self-healed HA and DPC$_{0.5}$ gel. (a1) Two parts came from cutting the DPC$_{0.5}$ gel. (a2) The two pieces were connected. (a3) The DPC$_{0.5}$ gel was healed spontaneously. The stress-strain curves of the self-healed and uncut DPC$_{0.5}$ gels (b1), the self-healed and uncut HA gels (b2).

In addition to self-healing ability, the structural reorganization of hydrophobically modified PAM chains also endowed DPC gels with remolding capacity as well as HA gels [39]. As shown in **Fig. 6a**, the forepart of the original DPC$_{1.5}$ (**Fig. 6a1**) entirely copied the shape of a syringe nozzle after being forced into the syringe with pressing the plunger for 3h at 50 °C (**Fig. 6a2**). The remolded part could still be stretched to a large deformation before breaking (**Fig. 6a3**). Tensile measurements were conducted to evaluate the mechanical strength of $DPC_{1.5}$ after remolding (**Fig. 6b**). It was remarkable that the self-reinforcement emerged in the remolded part by comparison of tensile toughness, which was consistent with the self-healing results (**Fig. S2**).

We suspected that the dangling chains on laponite played a crucial part again in enhancing DPC gels after remolding. When $DPC_{1.5}$ was compressed in syringe, the distance between neighboring laponite nanosheets was shortened (**Scheme 2c**). Moreover, the motility of polymer chains was enhanced thanks to the elevated temperature, offering more opportunities for dangling chains to adhere onto the surfaces of laponite nanosheets. The cross-linking density would inevitably increase as long as the remolding process period was long enough (**Scheme 2d**), resulting a reinforcement in mechanical strength of DPC gels. Both hydrophobically associated domains and laponite nanosheets performed its own cross-linking effect in remolding process. Reversible cross-linking action of hydrophobically associated domains allowed DPC gels to reform into other shapes, at the same time the adsorption of dangling chains onto laponite contributed to the increase in mechanical strength of DPC gels after remolding. Therefore, not only could DPC gels be shape-molded in polymerization process, but also would be remolded by reforming process as thermoplastic resins to obtain stronger mechanical properties, which was totally impossible for hybrid dual cross-linked hydrogels because of the irreversible covalent cross-linked bonds [52]. It was worth nothing that the self-reinforcement process achieved by self-healing and remolding could not be repeated unlimitedly owning to the limited number of dangling chain, which would be discussed in our further work.

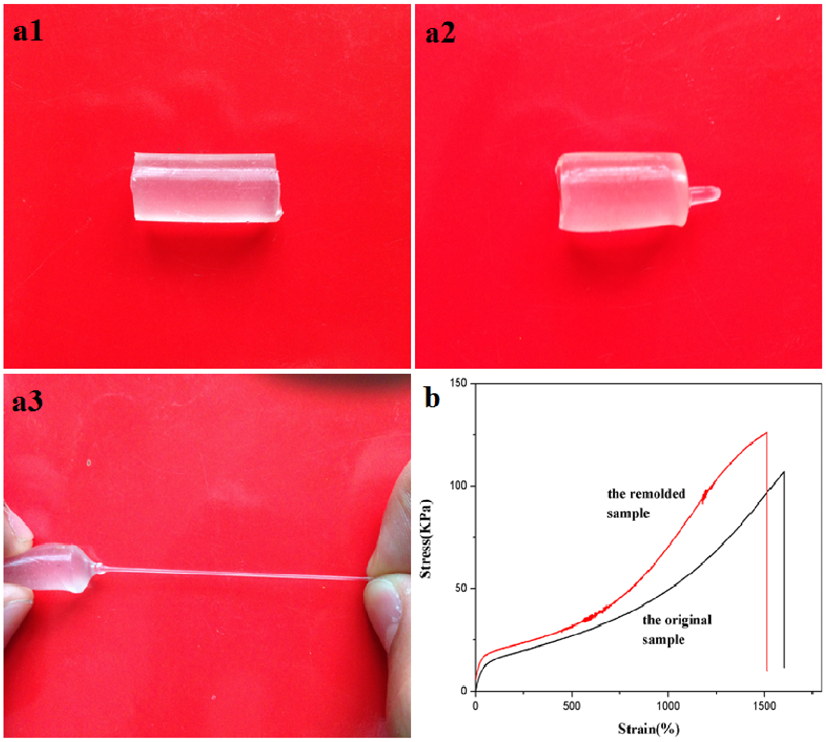
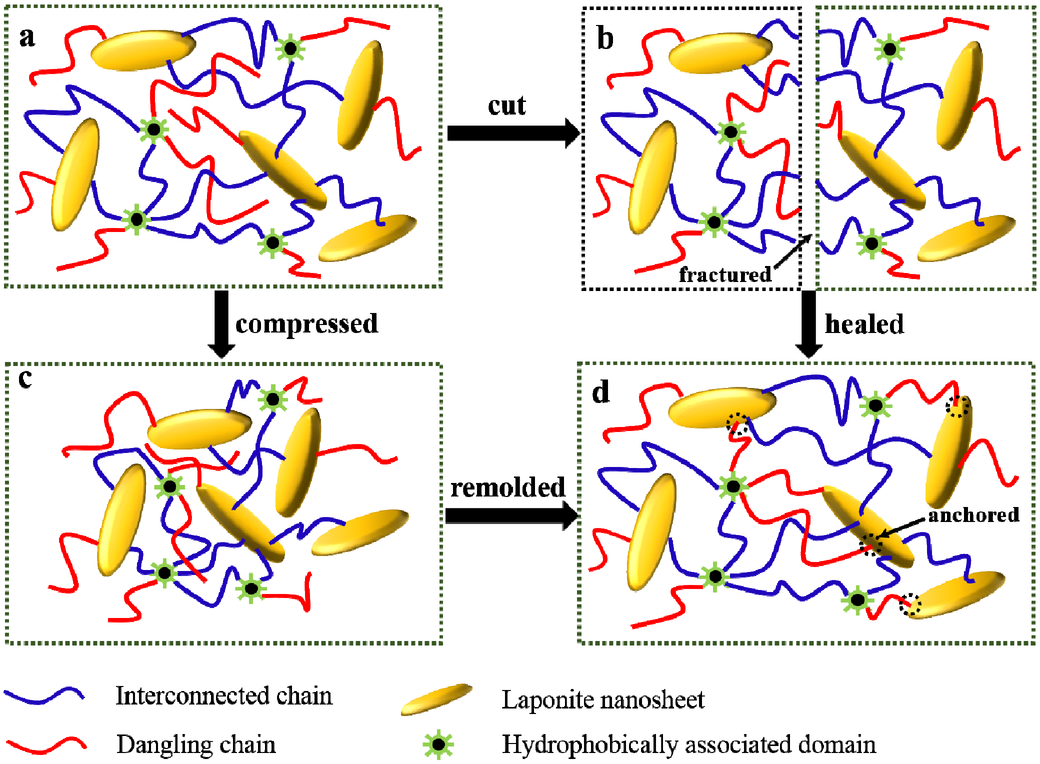


Fig. 6. Remolding exhibition of DPC gels and the tensile property of $DPC_{1.5}$ gel after remolded. (a1) The original sample of $DPC_{1.5}$ gel. (a2) $DPC_{1.5}$ gel copied the shape of a syringe nozzle after remolding. (a3) The remolded part of $DPC_{1.5}$ gel still kept excellent mechanical property. (b) The stress-strain curves of the original and remolded $DPC_{1.5}$ gel.



Scheme 2. Self-reinforcement of DPC gels achieved by self-healing and remolding. (a) The original network of DPC gels. (b) The network of DPC gels after cut. (c) The network of DPC gels during remolding process. (d) The network of DPC gels after healed or remolded.

Intriguingly, by combining the self-healing and remolding abilities, DPC gels could be employed as a sort of self-healing protecting film materials. In this scenario, we were triggered to verify the protective action of DPC gels on easily scratched materials. DPC$_{1.5}$ gel was demonstrated as an example (**Fig. 7a**). By forcibly compressing DPC$_{1.5}$ for 3 h, it completely remolded to be a thin film (**Fig. 7b**). Then we coated a coverslip with DPC$_{1.5}$ as a protecting film (**Fig. 7c**). To imitate the scratch on materials in practical application, a wound was created through knife-cutting (**Fig. 7d**), which, however, did not appear on the surface of coverslip thanks to the protection of $DPC_{1.5}$ film. After closing the notch together and spraying trace amount of water on the cut, the hydrogel film self-healed at room temperature after 3 days, which is found to be inseparable even if the film was stretched (**Fig. 7e**). The self-healed gel could be utilized again as protecting film on the coverslip (**Fig. 7f**). The results obtained here were expected to help widen the practical application of DPC gels due to their fantastic properties by combination of HA and NC hydrogel systems.

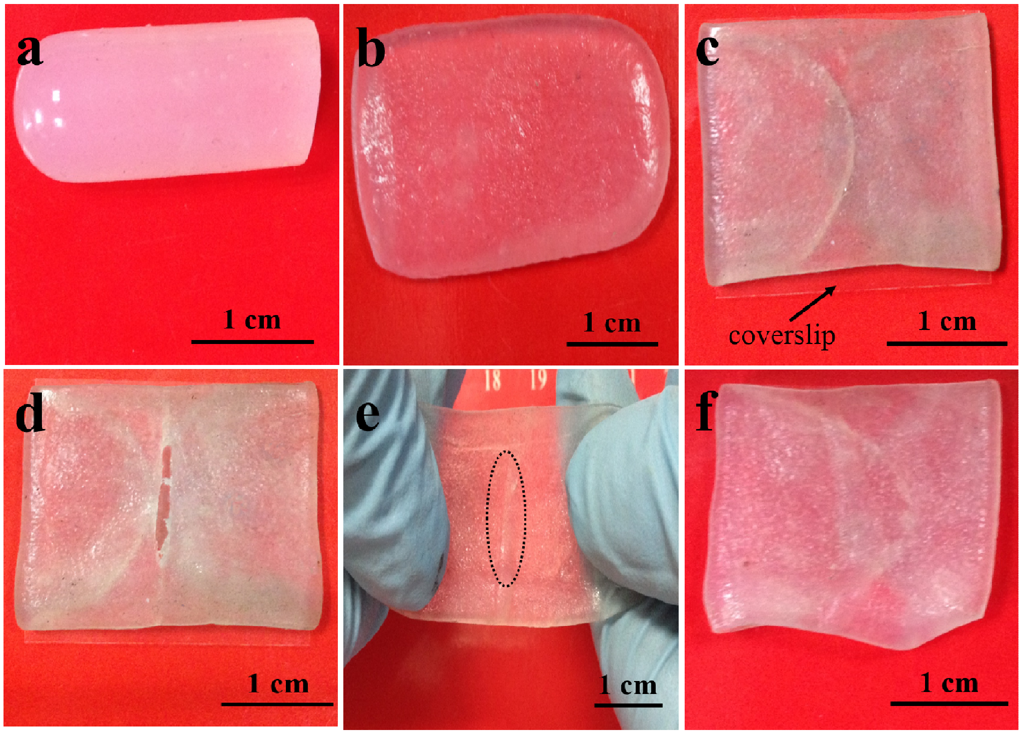


Fig. 7 illustration of DPC gel as protecting film on easily scratched materials. (a) The original sample of $DPC_{1.5}$ gel. (b) Remolded hydrogel film of $DPC_{1.5}$ gel after compression. (c) A coverslip was protected by $DPC_{1.5}$ film. (d) A scratch was created on the surface of protecting film. (e) The gel film self-healed spontaneously. (f) The gel film could be used as protecting film again after self-healed.

Stress softening was discovered in HA gels [39], namely, tensile force of HA gels tended to decrease for consecutive tests since some hydrophobic association micelles was broken in tensile process. However, polymer-laponite NC gels usually showed an enhanced mechanical behavior after stretching to a large deformation due to the orientation of laponite nanosheets in the NC gel during the elongation [15, 48, 53]. The contradictory repeat tensile property between HA gels and NC gels naturally arouses our interest to investigate the repeat tensile property of DPC gels, whose system was a combination of HA and NC gels. **Figure 8** showed the stress−strain curves of DPC gels during the continuous elongations at a fixed strain of 1200% for five times. The stress increased with strain obviously during subsequent tensile after the first stretching. And no fracture appeared during the elongation, suggesting the outstanding tensibility and self-reinforcement property of DPC gels. Thus it could be concluded that the orientation of laponite nanosheets contributed a lot to enhance the mechanical strength and neutralize the reduction caused by the damage of hydrophobically associated micelles.

To sum up of this section, self-reinforcement of DPC gels can be realized by three methods: self-healing, remolding and repeated stretching to a constant strain, which may widen the application of hydrogels in the field of materials requiring recycling use.

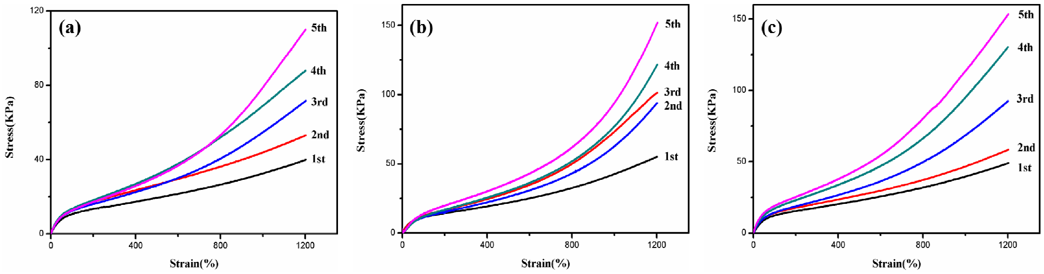


Fig. 8. Stress-strain curves for $DPC_{0.5}$ (a), DPC_1 (b) and $DPC_{1.5}$ (c) gel under repeated stretching to a fixed strain at 1200% for five times.

3.6 Improved dye adsorption capacity of DPC gels

As is known to all, hydrogels often have porous network structure and allow solute diffusion through the hydrogel structure [54]. After introducing laponite bearing abundant negative charges into HA gels, the cationic dye adsorption capacity should be further enhanced.

A series of water soluble cationic dyes (MG, MB, MO, BF and CV) were used for studying the dye adsorption capacity of DPC gels ($DPC_{1.5}$ was shown as an example in **Fig 9**), the dye adsorption performance of DPC gels can be clearly observed by the change in depth of the dye colors. After immersing in each dye solution (10mg/L) (**Fig. 9a**) for 6 h at room temperature, $DPC_{1.5}$ turned its color into the same color of the dye while the dye solution faded obviously (**Fig. 9b**). Then we took all the samples out and immersed them in excess deionized water for 6 h, no leakage was observed and the water always kept clear, indicating a perdurable dye adsorption capacity of DPC gels.

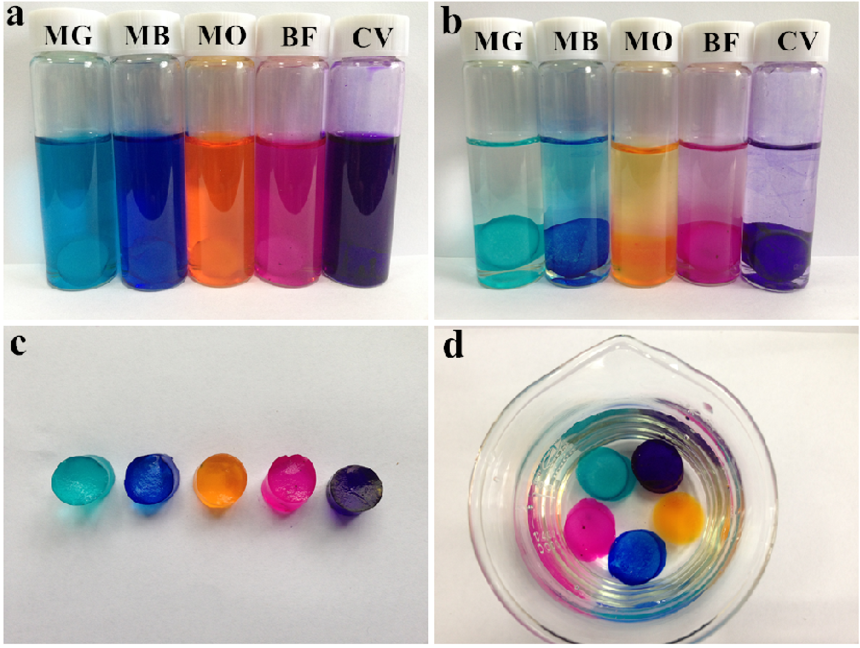


Fig. 9. Photographs of dye solutions (a) before and (b) after adsorption, (c) DPC gels after adsorption of dyes, and (d) DPC gels after immersed in excess deionized water for 3h.

To provide further insight and quantificational evidence for the improved dye adsorption capacity of DPC gels, equilibrium dye adsorption capacities of HA and DPC gels were investigated. The results are listed in **Table 3**. It can be seen from that HA gels have certain abilities to adsorb cationic dyes because of their high swelling ratio, whereas DPC gels possess preferable adsorption capacities compared with HA gels. To compare the dye adsorption capacity more quantificationally, time-dependent adsorption of CV on $DPC_{1.5}$ and HA was conducted as an example (**Fig. S3a**). Apparently, the adsorption rate of CV on $DPC_{1.5}$ was much higher than that on HA, which was reflected by the higher initial slope of the adsorption kinetic curve. Impressively, the equilibrium adsorption amount of CV on $DPC_{1.5}$ outperformed that on HA with an increase of about 740%, indicating that strong driving force for the adsorption of dyes was generated by the introduction of laponite. As for the pseudo-second-order equation, the correlation coefficients of CV on $DPC_{1.5}$ and HA were 0.997 and 0.981, respectively (**Fig. S3b**), suggesting that the adsorption kinetics was well in line with the pseudo-second-order model, which was usually used to forecast the amount of dye adsorbed on hydrogel at a certain time. Since there are a lot of negative charges existed on the surfaces of laponite nanosheets, which are able to interact with cationic dye molecules. Therefore, although the network of DPC gels is more compact, they tend to adsorb more cationic dye molecules instead of water molecules during the swelling process. By this way, DPC gels are endowed superior capacity to adsorb high amount of cationic dye molecules. Thus, with the introduction of laponite, the mechanical tough DPC gels can be widely used in the treatment of dye pollution.

Table 3 The dye adsorption capacities of HA and DPC gels

samples	Q_e(mg/g)/MG	Q_e(mg/g)/MB	Q_e(mg/g)/MO	Q_e(mg/g)/BF	Q_e(mg/g)/CV
HA	19.912	17.398	14.265	36.868	11.737
$DPC_{0.5}$	37.681	45.482	39.362	41.824	31.219
DPC_1	61.273	49.420	42.529	44.221	57.851
$DPC_{1.5}$	68.158	53.368	49.875	66.053	95.736

4. Conclusions

In conclusion, hydrophobically associated PAM hydrogels were introduced with hectorite clay nanosheets Laponite XLG to enhance the mechanical performance and dye adsorption capacity. A series of dual physically cross-linked hydrogels (DPC) were successfully prepared by in situ copolymerization. The laponite nanosheets acted as fresh physical cross-linking points in hydrogel formation, leading to a significant increase in mechanical properties. Meantime, synergistic cross-linking effect appeared due to the unexceptionable compatibility between laponite and the hydrophobically associated system, giving rise to an effortlessly achieved self-reinforcement of DPC gels. The self-reinforcement of DPC gels could be accessed by self-healing, remolding and stretching, which was unrealizable for HA and hybrid dual cross-linked gels. Furthermore, DPC gels exhibited much improved cationic dye adsorption capacities compared with HA gels since large amount of negative charges existed on the surfaces of laponite nanosheets. The novel mechanical strong DPC gels could be expected to widen the applications of HA gels in wastewater treatment and bioengineering.

Acknowledgments

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