Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Self-Healable, Tough and Highly Stretchable Ionic Nanocomposite Physical Hydrogels

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

We present a facile strategy to synthesize self-healable tough and highly stretchable hydrogels. Our design rationale for the creation of ionic cross-linked hydrogels is to graft acrylic acid monomer from the surface of vinyl hybrid silica nanoparticles (VSNPs) for the growth of poly(acrylic) acid (PAA), thus the obtained VSNP-PAA nanobrush can be used as gelator. Physical cross-linking through hydrogen bonding and ferric ion-mediated ionic interactions between PAA polymer chains of the gelators yielded ionic nanocomposite physical hydrogels with excellent and balanced mechanical properties (tensile strength 860 kPa, elongation at break ~2300%), and the ability to self-repair (tensile strength ~560 kPa, elongation at break ~1800%). The toughness and stretchability arise from the reversible cross-linking interactions between the polymer chains that help dissipate energy through stress (deformation) triggered dynamic processes. These unique properties will enable greater application of these hydrogels materials, especially in tissue engineering.

1. Introduction

Hydrogels are chemically or physically cross-linked three dimensional polymer networks that absorb and retain a large amount of water.[1] Chemical cross-linking arises from covalent bond formation, while physical cross-linking results from a combination of intermolecular interactions such as hydrogen bonding, van der Waals forces, ionic interactions, chain entanglements, crystallization and other non-covalent interactions.[2-4] Owing to their excellent biocompatibility and stimuli-responsive abilities, hydrogels can be applied in a diverse range of applications, including cosmetics, actuators, tissue engineering and drug delivery.[5-10] However, the scope of these hydrogel applications is constrained because traditional chemically cross-linked hydrogels possess low mechanical strength, poor toughness, and limited extensibility and recoverability. These shortcomings arise due to the inhomogeneity of the gel network and lack of effective energy dissipation under deformation.[11-14] To address this, a number of mechanically robust hydrogels have been developed using new polymerization methods and novel microstructures, including slide–ring hydrogels,[11] Tetra–PEG hydrogels,[12, 13] double–network hydrogels (DN hydrogels),[14] nanocomposite hydrogels,[15, 16] hydrophobic modified hydrogels,[17] ionically cross-linked hydrogels,[18, 19] macromolecular microsphere composite (MMC) hydrogels [20] and dipole–dipole and hydrogen bonding reinforced hydrogels.[21] These hydrogels have extraordinary mechanical properties, such as high deformability and toughness, when compare to traditional hydrogels. The slide–ring[11] and Tetra–PEG hydrogels[12, 13] have ideally homogeneous network structures and can be stretched more than ten times their initial length. In DN-hydrogels, for example, the internal fracture of the densely cross-linked network dissipates energy under large deformation, while the loosely cross-linked network retains the configuration after deformation, contributing to their tough and elastic nature.[22, 23] However , the covalent bonds serve as "sacrificial bonds", and once the brittle network is broken the covalent bond cannot be recovered.[22] To overcome this, dynamic physical cross-linking, *e.g.*, ionic bonding or hydrogen bonding, instead of rigid covalent cross-linking in the first network, thereby constructing novel DN hydrogels.[24-32] Sun and coworkers reported a notch–insensitive hybrid DN-hydrogel, in which the covalent bonds were combined with ionic bonds, thus allowing the mechanical properties of the hybrid DN-hydrogels to be recovered after internal rupture.[27] The toughness was attributed to the synergistic effect of crack bridging by the network of covalent crosslinks and hysteresis through unzipping the network of ionic crosslinks.[27] Despite the hybrid DN-hydrogels having a high stretchability and toughness, they possessed relatively low fracture strength of ca. 156 kPa. When the Ca^{2+} was replaced by other multivalent ions (*e.g.,* Ba^{2+}, Al^{3+}, Fe^{3+}), the hybrid DN hydrogels undergo a yielding phenomenon that improved the mechanical properties.[28] Recently, a review by Zhao provided guidance on the general principles that would enable the preparation of tough hydrogels with multiple mechanisms for dissipating mechanical energy and maintaining high elasticity.[33]

Nanocomposite (NC) hydrogels, consisting of both inorganic and organic components, are now one of the most widely explored soft material types. It is generally accepted that NC hydrogels can effectively integrate the unique properties of the organic and inorganic components to achieve an obvious synergistic effect.[34] For example, nano-clay composite hydrogels were first reported by Haraguchi, and prepared by *in situ* free radical polymerization of monomers from an initiator absorbed onto sheet–like nano-clay through ionic interactions.[15, 16, 35] Nanocomposites based on silica nanoparticles have attracted great attention because of their relatively low production costs, uniform structure, easily controllable size and the abundance of functionalizable groups on the surface,[36] and their use to reinforce hydrogels is well documented.[37] We recently reported on the use of vinyl-functionalized silica nanoparticles to prepared hydrogels,[38-41] finding that the length of the grafted polymer chains and the content and diameter of the nanoparticles influenced the gel's properties. Physical interactions among the grafted polymer chains form the basis of the hydrogel networks and the nanoparticles act as 'analogous covalent cross-linking points'. The distribution of cross-linking points and the flexibility of polymer chains can thus be easily manipulated by changing the nanoparticle content, providing a great diversity of ways in which to tune the mechanical properties of polymer hydrogels.

In this work, we report a facile one-pot method for the preparation of tough and highly stretchable physical hydrogels using vinyl-hybrid silica nanoparticles (VSNP) as multivalent covalent cross-linking agents and ferric ions as ionic cross-linkers. Without any added organic cross-linkers, tough and stretchable nanocomposite ionic cross-linked VSNP/PAA physical hydrogels (Ionic-NCP gels) were obtained.

2. Materials and Methods

2.1 Materials

Triethoxyvinylsilane was purchased from Acros (Acros 174610250, 97%) and used as supplied. Acrylic acid (AA) was purchased from Beijing Chemical Reagent Factory, purified by distillation under reduced pressure and stored in a refrigerator before use. Ammonium persulfate (APS), *N,N'*-methylenebisacrylamide (Bis) and $Fe(NO_3)_3•9H_2O$ were purchased from Beijing Chemical Reagent Co. Ltd., and other chemicals were used as received.

Vinyl-hybrid silica nanoparticles (VSNP) VSNP was prepared as described in our previous work.[41] Typically, a mixture of 3.8 g triethoxyvinylsilane and 30 g deionized water were mixed and magnetically stirred at room temperature. After 12 h the silica suspension was obtained. The diameter of the silica suspension was determined to be approximately 3 nm by a transmission electron microscope measurement.

2.2 Synthesis of hydrogel

Ionic-NCP gel preparation: Briefly, acrylic acid monomer (AA) and a suspension of VSNPs (0.50 wt% relative to AA) were added to deionized water and stirred for 2 hours. Next, the ionic crosslinker, $Fe(NO_3)_3•9H_2O$ (0.50 mol% of AA) was added into the mixture and stirred for several hours, obtaining a reddish brown homogeneous solution. After cooling in an ice bath, the ammonium persulfate initiator (0.05 wt% of AA) was added and the solution was bubbled with nitrogen in order to remove the dissolved oxygen—this was necessary to avoid instantaneous polymerization. The uniform suspension was then transferred into several plastic syringes (5 mm internal diameter) and the polymerization performed at 30 °C under a nitrogen atmosphere for 30 h.

NCP gel preparation: The NCP gel (H_2O = 80 wt%, VSNP = 0.50 wt%) was prepared as follows: 6.00 g (83.3 mmol) AA and 23.75 g deionized water were gradually added into a 100 mL flask, and mixed by stirring at room temperature. A 0.267 mL VSNP suspension (11.25 wt%) was then redispersed in the above solution by stirring at room temperature. After 2 h, 12 mg ammonium persulfate (APS) was added into the mixture and stirring for adding few minutes. After degassing by bubbling with N_2 for 30 minutes, the uniform suspension was transferred into several plastic syringes of 5 mm internal diameter. The polymerization was performed at 40 °C for 30 h in a water bath under a N_2 atmosphere. And the chemically cross-linked PAA gel was prepared using the same procedure as the NCP gel added Bis (0.05 wt% relative to AA) instead of the VSNP.

2.3 Self-healing experiment

The cylindrical Ionic-NCP gels (VSNP = 0.50 wt%, Fe^{3+}= 0.50 mol%, H_2O = 80 wt%) samples were cut using a knife, and then the two freshly cut surfaces were placed together (without adding any chemicals) within the plastic syringes (the same size of the as-prepared gel sample). To avoid water evaporation, the plastic syringes were wrapped with polyethylene films, and then stored in sealed polyethylene bag at the prescribed temperatures (4−70 °C) or times (0.5−48 h). After the allotted time, the healed hydrogels were subjected to mechanical measurements at ambient temperature to study the self-healing properties of the Ionic-NCP gels.

2.4 Characterizations

Uniaxial tensile measurements: For mechanical properties measurement, cylindrical Ionic-NCP hydrogel samples (5 mm diameter × 60 mm length) were tested using a Shimadzu AGS-X test machine at ambient temperature under the following conditions: cross–head speed = 100 mm min^{-1}, sample length between jaws = 15 mm. The tensile strength (from the initial cross–section of 19.62 mm^2) and percentage elongation at break were recorded. The initial slope of the elongation at break between 0 and 40% of the stress–strain curve was used to calculate the initial elastic modulus. The fracture energy of the hydrogels was defined as the work done until fracture and was obtained by integrating the area underneath the stress–strain curve.

Loading–Unloading Measurements: Energy dissipation studies were performed by conducting loading–unloading measurement on samples (dimensions above), using a ZwickProLine Z005 table-top instrument at ambient temperature and crosshead speed 100 mm min^{-1}.

3. Results and Discussion

Our design rationale for the creation of ionic cross-linked hydrogels is to graft acrylic acid monomer from the surface of vinyl hybrid silica nanoparticles (VSNPs) for the growth of poly(acrylic) acid (PAA), thus the obtained VSNP-PAA nanobrush can be used as gelator (**Fig. 1a**). Physical cross-linking will be accomplished using a combination of hydrogen bonding and ferric ion-mediated ionic interactions between the polymer chains of the nanobrushes (**Fig. 1b**).The VSNPs will serve as multivalent covalent cross-linking points once the physical cross-links have been established, thereby reinforcing the network structure under any applied stress (**Fig. 1a**). Uniform and multivalent VSNPs were prepared as described in our previous work[41] with diameters of 3 nm by a universal sol-gel method (**Fig. S1**†, ESI). The ionic cross-linked and VSNP-reinforced physical PAA nanocomposite hydrogels (Ionic-NCP gels) were then prepared by one-pot *in situ* polymerization. All reaction parameters (component ratios)were optimized to maximize the mechanical properties of the resulting Ionic-NCP gels (vide infra). Unless stated otherwise, the composition of the Ionic-NCP gels discussed hereafter is 0.50 mol% Fe^{3+}, 0.50 wt% VSNP, and 80 wt% H_2O.

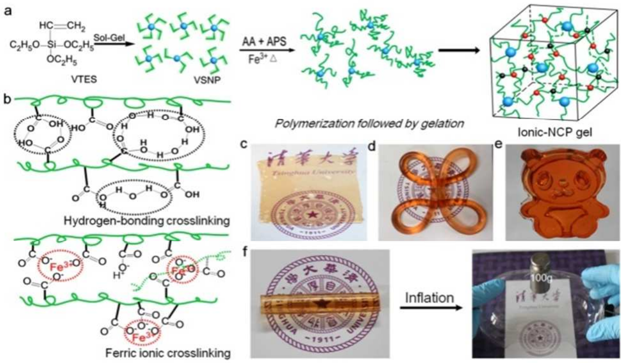

Fig. 1 Preparation of Ionic-NCP gels, illustration of their network structure and demonstration of their pliability. The Ionic-NCP gels were prepared by first synthesizing the vinyl hybrid silica nanoparticles (VSNPs) from vinyl-triethoxysilane (VTES), followed by the aqueous polymerization of acrylic acid (AA) on the VSNPs' surface in the presence of ferric (Fe^{3+}) ions (a). Illustration of the physical crosslinks formed by hydrogen bonding and Fe^{3+} ionic interactions (b). The formed Ionic-NCP gels could be cast or molded into a variety of forms, including films/membranes (c), flexible cylinders (d), a Chinese Panda (e), and tubes that can be inflated into balloons (f).

The Ionic-NCP gels created by this method are expected to have a network structure that is constructed through a combination of ferric ion-mediated reversible physical cross-linking, intra- and inter-polymer chain hydrogen bonding, physical entanglement of the polymer chains and multivalent covalent cross-linking through the VSNPs (**Fig. 1a** and **b**). This combination of cross-linking interactions gave rise to Ionic-NCP gels that exhibit extraordinary shape modulation characteristics and mechanical properties (**Fig. 1c–f**). For instance, the Ionic-NCP gels can form films/membranes (**Fig. 1c**), flexible cylinders (**Fig.1d**), molded shapes such as a Chinese Panda (**Fig.1e**) and tubes (**Fig. 1f**). The exceptional mechanical properties can be effectively demonstrated by the inflation of the tubular forms into balloons that can easily support a 100 g weight with no obvious effect on the structural integrity (**Fig. 1f**). Furthermore, their highly stretchable and recoverable nature can be seen through repeated inflation and deflation cycles (**Video 1**†, ESI). During these dynamic deformations, the rough surface of the tube can be seen to become progressively smoother with increasing cycle number. Even when highly stretched, the Ionic-NCP gel of the balloon can undergo further compressions (**Video 2**†, ESI), with the balloon quickly recovering its shape once the applied stress was removed. This behavior strongly emphasizes the excellent adaptability and recovery properties that the Ionic-NCP gels possess, being both tough and highly stretchable.

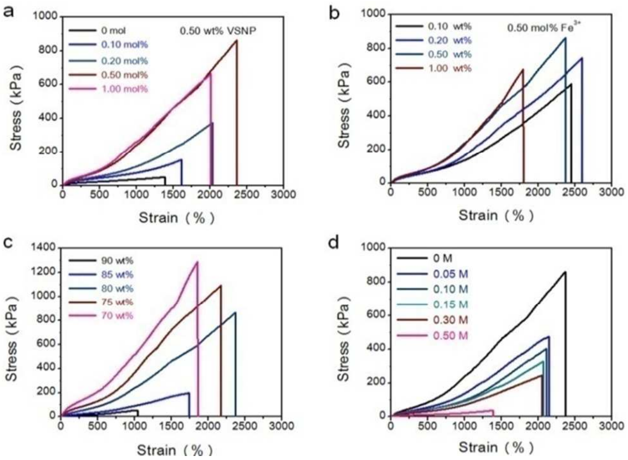

Fig. 2 Mechanical property characterization of the Ionic-NCP gels. Dependence of the tensile strength and maximum elongation on Fe^{3+} mol% (a), VSNP wt% (b), water content (c) and NaCl concentration (d).

Quantification of the Ionic-NCP gel's mechanical properties was performed by subjecting cylindrical samples (5 mm diameter × 60 mm length) to an applied uniaxial stress (at a constant rate of 100 mm min^{-1}) until fracture occurred. The tensile strength (from an initial cross-section of 19.62 mm^2) and percentage elongation at break were recorded. The prepared Ionic-NCP gels were found to have excellent mechanical properties (**Fig. 2a**), with the tensile strength and elongation at fracture being approximately 860 kPa and 2300% of the initial length, respectively. These values are similar to the most extensively studied tough DN-hydrogels (sub-MPa to several MPa tensile strength),[14, 22] nanocomposite hydrogels (0.1 MPa to 1 MPa),[15, 16] and the tough physical hydrogels.[19] In contrast, the hydrogel formed in the absence of ferric ions (with hydrogen bonding cross-links only) was found to be much weaker, with a tensile strength less than 50 kPa at fracture and an extension of fourteen times the initial length (**Fig. 2a**), illustrating the importance of the ionic cross-linking. And it's testified that the significant improvement of the mechanical performance by introduction of ferric ion-mediated ionic interactions in the PAA hydrogels, which compared with our previous work.[41]

Variation of the ferric ion concentration highlights the key role that they play in the outstanding mechanical properties of the Ionic-NCP gels. An improvement in the tensile strength, elastic modulus, elongation at break and fracture energy of the gels increase remarkably with the gradual increase of Fe^{3+} content from 0~0.5 mol%. And then a decline of mechanical properties was observed for the gels with higher Fe^{3+} content than 0.5 mol%. (Fig. 2a and Table S1†, ESI). At a moderate content of ferric ions, its increase could facilitate the polymerization of PAA and increase the crosslinking density of the gel, which ensures more stress to be sustained by the gel sample. However, with a further increase of the ferric ions content, it may retard the radical polymerization and reduce the molecular weight of PAA and degrade the mechanical properties of the gel.[42-44] Therefore, the mechanical properties of the gels exhibit a trend of first increase and then decrease with the ferric content increase. Given that the VSNPs are expected to act as multivalent covalent cross-linking points, it would be anticipated that they too would be a key player in the emergent mechanical properties of the Ionic-NCP gels. To confirm this, we prepared hydrogels with various VSNP concentrations (**Fig. 2b** and **Table S2**†, ESI), finding that as the VSNP content increased an enhancement in all mechanical properties was observed. Above 0.50 wt% VSNP, however, all of the mechanical properties, with the exception of the elastic modulus, were reduced. This phenomenon perhaps results from the interplay between macromolecular weight of the PAA and the amount of silica particles. Under deformation, the VSNPs absorb and redistribute (relax) the applied stress and thus delay crack propagation via the numerous flexible PAA chains grafted to their surface. The network of dynamic physical cross-links then allows this dispersed energy to be dissipated through disruption of the intermolecular interactions that can later reform. Increasing the amount of VSNPs will reduce the overall macromolecular weight of the polymer given that there are a greater number of initiation points for polymer growth for a fixed AA monomer concentration. Consequently, the average polymer length will be reduced as the VSNP content is increased, in turn reducing the PAA chain flexibility. In contrast, the fewer VSNPs there are, the less cross-linking points there will be and the less applied stress that can be absorbed and redistributed.

The polymer concentration was also found to be important, as variation in the water content was found to significantly influence the elastic modulus, tensile strength and fracture energy of the Ionic-NCP gels (**Fig. 2c** and **Table S3**†, ESI). All Ionic-NCP gels of varying water content were found to have good deformation characteristics, stretching to approximately twenty times their initial length, with the exception of a water content higher than 90 wt% which managed only a ten-fold elongation. For a water content below 80 wt%, the tensile strength and fracture energy were approximately 1.0 MPa and 10 MJ m^{-3}, respectively, though this was at a cost of reduced elongation—indicative of a less elastic material. As shown in the **Fig.** 2c, the tensile strength of the Ionic-NCP gels decreases with increasing water content. It results from the lower polymer concentration in per unit cross-sectional area with increasing water content. And it is also shown that the elongation at break increases in the beginning and then decreases. This phenomenon can be ascribed to the interactions between the grafted PAA chains and Fe^{3+} ions. The movement of the PAA chain becomes easy, and the PAA chains are sufficiently extended when increasing the water content. Moreover, the polymer concentration for per unit cross-sectional area decreases, resulting in the higher applied stress on each of the grafted PAA chains. Meanwhile, the break–recombination of the reversible ionic and H-bonding crosslinking during deformation should be slow at lower polymer concentration. Consequently, it is not efficiently to bear the applied stress. Therefore, it exhibit a relative low strain at higher water content (*e.g.*, 90 wt%). Besides, macromolecular weight should be influenced by the monomer and ferric ions concentrations during the *in situ* polymerization. Therefore, the Ionic-NCP gel with a moderate water content exhibits a balanced mechanical performance. Furthermore, we found that the addition of increasing amounts of NaCl during polymerization significantly degrades the mechanical performance of the Ionic-NCP gels (**Fig. 2d**). When the concentration of NaCl is 0.5 M, the mechanical properties of the Ionic-NCP gel becomes very weak, and these vale are similar as the NCP gel (free of Fe^{3+} ions VSNP/PAA hydrogel). This presumably results due to disruption of the ionic interactions between the Fe^{3+} ions and polymer carboxylate ions. Similar effects have been seen for polyampholyte hydrogels.[19] It also indicated that the ionic interaction play an important role in the excellent mechanical performance of the gels.

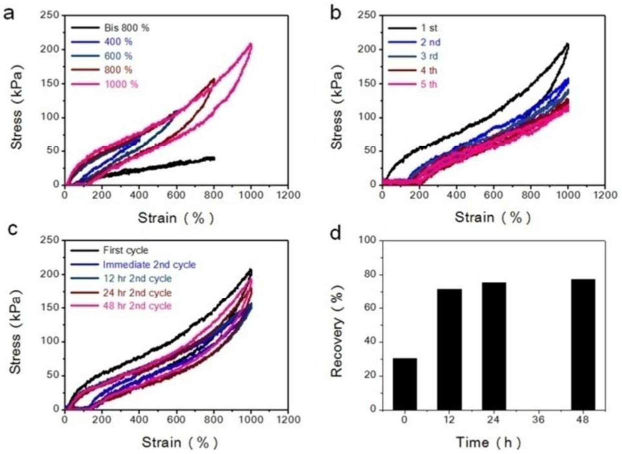

Fig. 3 Loading-unloading experiments performed at different maximum strains (a), performed repeatedly without rest (b) and repeated after a certain recovery period (c), recovery efficiency as a function of times at 40 °C (d).

As noted earlier, the incorporation of physical cross-links such as ionic and hydrogen-bonding interactions is an effective means of dissipating any deformation energy that is applied to the system.[27, 28] This energy dissipation can be studied by applying and releasing strain (loading–unloading), either in isolated or repeated cycles. Viscoelastic systems that can disperse the applied energy, such as physical hydrogels, will typically exhibit different load and unload stress-strain curves (hysteresis), with the area between the two curves equal to the energy dissipated per unit volume. When the Ionic-NCP hydrogels were subjected to a loading-unloading cycle a pronounced hysteresis was observed, with the magnitude increasing as the maximum strain was raised (**Fig. 3a**). In contrast, there was negligible hysteresis seen for hydrogels that had been chemically cross-linked using *N*,*N'*-methylenebisacrylamide (BIS), displaying the more elastic behavior typical of this system type. These results imply that the network of the Ionic-NCP gels is rearranging and effectively dissipating the applied energy during deformation.

Under repeated loading–unloading cycles, the hysteresis becomes much smaller if the next cycle is conducted immediately after the previous, such that little recovery time is allowed. In fact, with increasing number of loading–unloading measurement cycles the loops become less and less pronounced (**Fig. 3b**). This can be attributed to the rupture of a significant portion of the physical cross-links within the network that took place in the initial cycle, such that the amount of energy that can be dissipated per cycle is reduced as the number of applied cycle increases. The mechanical behavior thus becomes more akin to that of an elastic material, suggesting that the bulk of the energy is now being redistributed by the covalent cross-linking provided by the VSNPs, rather than through the physical cross-links. Similar to most ionic cross-linked hydrogels, however, the ionic crosslinking is recoverable if given sufficient time.[18, 19, 27] To examine the time-dependent recovery properties of the Ionic-NCP hydrogels, an initial loading-unloading cycle was first performed on a sample that was then stored at 40 °C in a sealed polyethylene bag to prevent evaporation of the water. After a prescribed time, loading–unloading measurements of the sample were taken at ambient temperature. We found that a recovery time of at least 12 h was required prior to the second cycle in order to recover greater than 70% of the prior mechanical properties, with the extent of recovery remaining almost unchanged thereafter (**Fig. 3c**, and **3d**). The absence of a full recovery is likely due to the permanent deformation that occurred as a result of the initial load–unload cycle, such that the cross-linking density is lowered by the increased volume of the hydrogel.

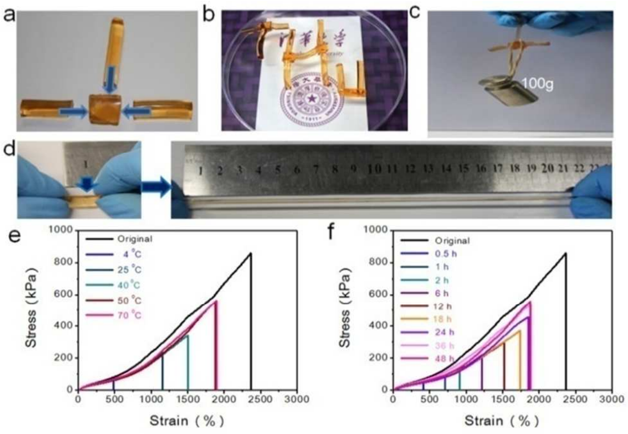

Fig. 4 Self-healing properties of Ionic-NCP gels. Images of severed cylinder samples of different sizes that were connected and healed as indicated (a), free-standing healed samples after incubation at 50 °C for 48 h (b), and the healed hydrogel suspending a 100 g weight (c), Stretching of the healed Ionic-NCP gel to more than eighteen times for its initial length (d), mechanical properties of the healed Ionic-NCP gels as a function of temperature presented for 48 h (e), and incubation time at 50 °C (f).

A further advantage to physical cross-links (no-covalent interactions), *e.g.*, hydrogen bonding, hydrophobic effects, host-guest recognition, electrostatic, metal-ligand interactions and their recoverable nature is that they provide the means for self-repair.[8, 17, 19, 42, 45, 46] As documented by Wei the ionic bonding between Fe^{3+} and carboxylic acid endow the property of self-healing.[42] We found that these Ionic-NCP gels exhibit excellent self-healing properties (**Fig. 4**). Without adding any chemicals, by simply placing two hydrogel portions together allowing enough time for physical interactions to reestablish the network at the interface, the healed hydrogel could be stretched to approximately fifteen times its initial length and possessed good tensile strength (**Fig. 4d–f**). The effectiveness of the healing process was dependent upon the temperature (**Fig. 4e**) and recovery time (**Fig. 4f**), with higher temperatures and longer incubation times being ideal (**Fig. S 2a**† and **b**†, ESI). Ionic-NCP gels that were healed at 50 °C for 48 h, for instance, exhibited an elongation up to 1800% (**Fig. 4d–f** and **Video 3**†, ESI) and a highest tensile strength up to 560 kPa (**Fig. 4 d–f**). Good self-healing was evident even at a low temperature of 4 °C (**Fig. 4e**). The self-healing of the Ionic-NCP gels results from diffusion of Fe^{3+} ions and the grafting PAA polymer chains on the surface of VSNPs on the cut-off surfaces of the damaged specimen. The mutual diffusion of PAA polymer chains and the movable Fe^{3+} ions at the interface of two damaged gel samples and their subsequent interactions with each other contribute to the reconstruction of a unique network.

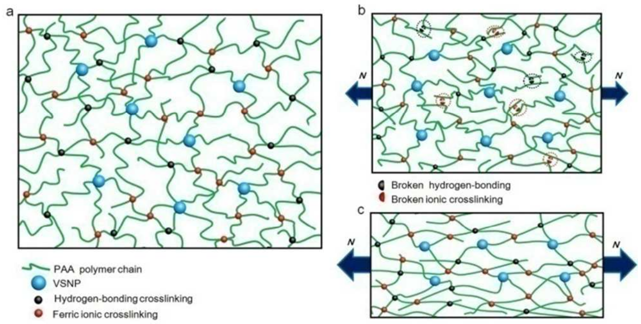

Fig. 5 The origin of the mechanical properties. At rest, the Ionic-NCP gel consists of relaxed polymer chains that adopt random coil conformations, and are linked through physical crosslinks made up of hydrogen bonding and ionic interactions (a). The VSNPs consequently act as analogous covalent crosslinks. Upon deformation, the polymer chains become extended and distribute and relax the applied energy throughout the network via the VSNPs and other polymer chains. As the stress increases, physical crosslinks begin to break, effectively dispersing the energy (b). These ruptured crosslinks can be reformed due to their reversible nature, lending the Ionic-NCP gel a dynamic nature that leads to more homogenization of the network (c).

As stated previously, the Ionic-NCP gels are constructed through a combination of ferric ion-mediated and hydrogen bonding reversible physical cross-linking and multivalent covalent cross-linking through the VSNPs (**Fig. 5**). Ionic cross-linking is facilitated by the ferric ions with the intra- and inter-PAA polymer chains. In the network reported here, since one end of polymer chains is covalently attached to the silica nanoparticles' surface, the VSNPs act as "analogous crosslinking points" once the hydrogen bonding or ionic crosslinking is established between the polymer chains. In the relaxed state (**Fig. 5a**) (no stress loaded), the grafted polymer chains assume a random coiled conformation and the primary crosslinking mechanisms are through hydrogen bonding and ionic interactions and polymer chain entanglement. Upon stretching, the energy is dispersed through the network by the uncoiling of the polymer chains and the aid of the VSNPs. Once it becomes more difficult to unravel the chains, either due to entanglement with other chains or they are at their fullest possible extension, then the energy is dissipated through rupture of the physical crosslinks

(**Fig. 5b**). These physical interactions can of course reform, resulting in the more homogenization of the network structure (**Fig. 5c**). By dispersing the applied stress throughout the network via the polymer chains and anchoring VSNPs, the propagation of cracks is delayed and gives rise to the excellent mechanical properties observed. During this dynamic deformation process, the applied stress is transformed into fracture energy, which can subsequently be turned into applied work by means of the dynamic absorption–relaxation processes associated with the breaking and rebuilding of the physical crosslinks. Cracks will develop in the material once the majority of physical crosslinks in a particular area have been broken, such that the VSNPs will no longer act as effective covalent crosslinks. At this point, the interactions are no longer sufficient to maintain the network integrity and the hydrogel will rupture.

The tough and stretchable nature of these Ionic-NCP gels is thus clearly attributable to the reversible physical cross-links between polymer chains that allow the applied energy to be dissipated. While the stress triggered dynamic rearrangement of the network maintains the configuration as a whole, it gradually homogenizes the network structure. This can be clearly seen in the repeated inflation and deflation of the tubular hydrogels (**Video 1**†, ESI), as the apparent surface defects become smoother after each repetition on the surface, indicating that rearrangement of the network structure to a more homogeneous state is occurring.

4. Conclusion

We have successfully demonstrated a facile one-pot in situ polymerization strategy to prepare self-healable tough and highly stretchable hydrogels. The mechanical properties can be easily tuned by modulation of the component concentrations (VSNPs, Fe^{3+}, monomer, and water). These novel ionic nanocomposite physical hydrogels exhibit exceptional mechanical strength as the introduction of VSNP and ferric ions provides the means to effectively disperse any applied stresses. Furthermore, the dynamic nature of the physical crosslinking endows these Ionic-NCP gels with excellent self-healing properties, with the healed gels able to be stretched more than eighteen times their initial length and possessing a fracture tensile strength higher than 560 kPa. This combination of excellent mechanical properties, facile preparation, efficient recoverability, and self-healing properties that these hydrogels possess holds the promise for their utility in a diverse range, such as tissue engineering and soft robotics.

Acknowledgements

This research was financially supported by the National Nature Science Foundation of China (NSFC) (No.21474058), State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University (Project No.LK1404) and Tsinghua University Scientific Research Project (No.2014Z22069).

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†Electronic Supplementary Information (ESI) available: See DOI: 10.1039/b000000x/

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