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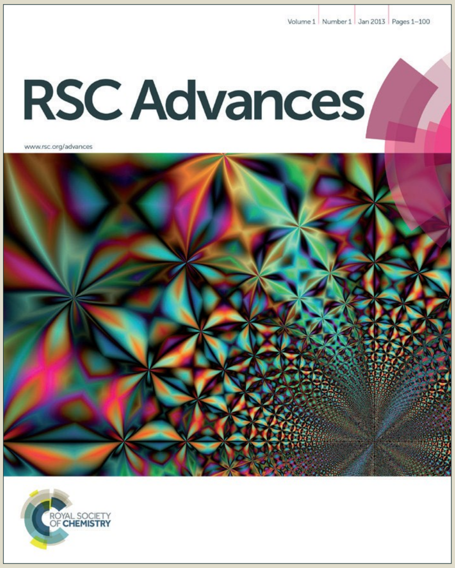

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ARTICLE

A facile approach to prepare strong poly(acrylic acid)/Laponite ionic nanocomposite hydrogel at high clay concentration

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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A facile strategy was developed to prepare mechanically strong Laponite-based ionic nanocomposite (NC) hydrogels at high clay concentration. Based on the thixotropy of acrylic acid (AA)/Laponite dispersion, a series of ionic poly(acrylic acid) (PAA)/Laponite NC hydrogels were successfully prepared without the addition of additional dispersing monomers. Fourier transform infrared spectroscopy (FTIR) and thermogravimetric (TG) analysis demonstrated the composition and thermostability of the NC hydrogels, respectively. Network of the hydrogels were examined by scanning electron microscopy (SEM). And the dispersion of Laponite nanoplatelets in this ionic hydrogels were investigated by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The hydrogels exhibited viscoelastic solid-like properties as revealed by dynamic mechanical analysis (DMA) within linear viscoelasticity region, and demonstrated that the network structure were formed with the junction of ionic monomer AA and Laponite platelets. The hydrogels showed improved mechanical properties (i.e. tensile strength: 308 kPa, elongation at break: 1110%), which were due to more effective cross-link points provided by the high content of Laponite and the entanglements among PAA chains. This approach is synthetically simple and dramatically increases the choice of strong hydrogels for applications.

1 Introduction

Over the last few years, the utility of inorganic nanoscale particles as filler to enhance the polymer performance has been established. Of particular interest is nanocomposite technology consisting of a unique organic (polymer)/inorganic (clay) network structure because they often exhibit remarkably improved mechanical properties as compared with those of virgin polymer or conventional composites (micro/macro-composites).[1-11] These concurrent property improvements are well beyond what can be generally achieved through the preparation of micro/macro-composites. It is well known that the clay content plays an important role in the mechanical property of the nanocomposite (NC) hydrogels. An increase in Laponite content usually enhances gel strength.[2, 3, 5, 10, 12] Laponite, carrying strong negative charges on the surface and weak positive charges on the rim, can form a clear and colorless colloidal dispersion in water, which is stabilized by the repulsive electrostatic interaction.[10, 13-16] However, it is hard to prepare high concentration of Laponite aqueous dispersions, even using special mixers, due to the high viscosity caused by the electrostatic attraction among surfaces and edges of different clay discs. Thus, the Laponite concentration during the preparation of NC hydrogel reported was usually below 10 wt% (against water). To combat the problem, Zhu et al used $Na_4P_2O_7$-modified Laponite to prepare successfully poly(*N*-isopropylacrylamide)/clay NC hydrogel under a clay concentration of 15 wt% since the edge of clay discs were negatively charged after modification and thus prohibited the formation of ‘House of Cards’.[10] Occasionally, a special fractional step method was reported to get clay dispersion of 20 wt% (25 mol%, against water) and fabricated series of poly(*N*-isopropylacrylamide)/Laponite NC hydrogels. However, complex mixing process and temperature control was needed before polymerization.[17]

Typically, the NC hydrogels were composed of nonionic monomers crosslinked by Laponite due to special colloid properties of Laponite.[8, 10, 12, 14, 18-22] There was limited success in preparation of ionic NC hydrogels. Aggregation and gelation occurred when ionic monomers were added to the clay dispersion, therefore resulting in poor optical and mechanical properties of ionic NC hydrogels. Numerous attempts to overcome the problem have been reported thus far, in which two main strategies were developed: (1) use nonionic monomers to pre-adsorbed onto surface of Laponite before further polymerization of ionic monomers;[13, 23-28] (2) choose specific ionic monomers to realize good dispersion of Laponite.[29-31]

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In our previous work, transparent ionic NC hydrogels cross-linked by Laponite XLG was successfully synthesized via the in-situ free radical polymerization of AA with assistance of 2-acrylamido-2-methylpropanesulphonic acid (AMPS)[29] and sodium dodecyl sulfate (SDS),[32] and its ultimate tensile strength can reach 189 kPa and 162 kPa, respectively. The addition of AMPS or SDS can successfully avoid the aggregation of Laponite in the ionic monomer AA. During the research process above, we found that Laponite/AA aqueous dispersion under high clay concentration had a remarkable thixotropy. The monomers tightly stuck onto clay discs without precipitation because of the high viscosity of the dispersion. However, under constant stirring, the mixtures appeared a shear thinning behavior. It made it possible to obtain a uniform reaction system by simply mixing all reagents under stirring. Then homogeneous mixture carried out polymerization without stirring to get an ionic PAA/Laponite NC hydrogel. Being intrigued with this phenomenon, we developed a facile one-pot process to prepare ionic NC hydrogels at high clay concentration in the presence of ionic monomers without additional dispersing monomers. To the best of our knowledge, this is the first report that strong ionic PAA/Laponite hydrogel was prepared by direct addition of AA into Laponite dispersion followed by in-situ polymerization. The NC hydrogels exhibited an improved mechanical property and would have potential applications in biomedical and tissue engineering.

2 Experimental

2.1 Materials

Laponite XLG ($Mg_{5.34}Li_{0.66}Si_8O_{20}(OH)_4Na_{0.66}$, Rockwood, USA), acrylic acid (AA, Tianjin Fuchen Chemical Reagents Factory, China), *N,N*'-methylenebisacrylamide (BIS, Tianjin Guangfu Institute of Fine Chemicals, China), potassium persulfate (KPS, Beijing Beihua Fine Chemicals Co., Ltd., China), sodium hydroxide (NaOH, Shanghai Kechang Fine Chemicals Company, China), and tetrasodium pyrophosphate ($Na_4P_2O_7$, Shanghai Kechang Fine Chemicals Company, China) were used as received. Deionized water was used in all experiments.

2.2 Synthesis of the hydrogels

Typically, 1.12 g Laponite was dispersed in 8 mL of deionized water under stirring for 20 min to make 14 wt% Laponite dispersion (against H_2O). Then, a desired amount of $Na_4P_2O_7$ was added into the dispersion to reduce the viscosity. The mass ratio of $Na_4P_2O_7$ to Laponite was kept at 0.0768:1,[10] which was followed by the addition of 6.0 mL of AA neutralized by 30 wt% of NaOH solution to get a neutralization degree of 40 mol% in an ice bath before. The mixture was ultrasonicated for 5 min, and afterward stirred for 20 min followed by addition of 8.7 wt% KPS (relative to the weight of AA). Polymerization was performed in airtight glass tubes in a water bath at 50°C for 72 hours. After polymerization, the as-prepared hydrogels were removed, cut into disks, and then soaked in a large amount of deionized water for 1 week. The water was exchanged every 2 days for the removal of monomers and oligomers which were not actually incorporated into the hydrogels. After at least 1 week, the hydrogels PAA/Laponite were dried in an oven at 80°C until a constant weight was obtained.

As a control, organically crosslinking gels were prepared according to the procedure above except 0.04 wt% BIS (relative to the weight of AA) was used instead of $Na_4P_2O_7$ and Laponite.

2.3 Characterization

Rheology measurements were carried out on a stress-controlled rheometer Discovery HR-1 using parallel platelets of diameter of 25 mm at 25°C. A thin layer of silicon oil was laid on the rim of the fixture to prevent water evaporation and CO_2 dissolution. The viscosity of the dispersion was measured with a shear rate of 50 s^{-1}. Before every measurement of thixotropy, all the AA/Laponite dispersions were preliminarily aged for 1 hour, followed by a 300 seconds steady pre-shear at 10 s^{-1} to achieve a reproducible initial state. Then, the steady flow measurements of the AA/Laponite dispersions were carried out in the range of shear rates from 10^{-3} s^{-1} to 3000 s^{-1} to determine the shear viscosity and shear stress.

Fourier transform infrared (FTIR) spectra were obtained using a Bruker Eqinox 55 spectrometer with milled dried NC gels by the conventional KBr disk method in the range of 400-4000 cm^{-1} with 2 cm^{-1} of spectral resolution. X-ray diffraction (XRD) patterns were performed using a Bruker D8 Advance X-ray diffractometer (40 kV, 100 mA) equipped with Cu Kα X-ray (λ=0.154 nm) scanning in a step of 1°/min from 2° to 15°. Transmission electron micrograph (TEM) was conducted with Hitachi H-600 transmission electron microscope with an accelerating voltage of 100 kV. Ultrathin films were prepared for TEM observation by cutting dried gels embedded in epoxy resin using an ultramicrotome. Scanning electron microscopy (SEM) images of samples were obtained using LEO-1430VP at an accelerating voltage of 20 kV. The hydrogels were allowed to reach equilibrium in deionized water overnight prior to freeze-drying (FD-1C-50) for 48 hours. Then, the hydrogels were coated with gold prior to SEM analysis. Thermogravimetric (TG) analyses were carried out using a TG/DTA STA-449F3 (NETZSCH) instrument, heating samples from 30 to 800°C at a heating rate of 10°C min^{-1} in an air flow. The clay content in the NC dried gels was evaluated from the residual weight at 800°C. All the hydrogels for TG test were neutralized by 36 wt% HCl for 24 hours first, then filtered, and finally washed with deionized water until no Cl^{-} in filtrate was found. The residue was dried in an oven at 80°C until a constant weight was obtained before test.

Dynamic mechanical analysis (DMA) were measured on the as-synthesized NC gel samples to estimate the viscoelasticity of PAA/Laponite NC hydrogels with a dynamic mechanical analyzer (DMA Q800, TA Instruments) with the tension fixture. The gel sample stuck the fixture well without slippage. Silicone oil was laid on the edge of the fixture platelets to prevent solvent evaporation. First, the dynamic strain sweep was carried out at constant frequency of 1 Hz to determine the linear viscoelasticity region. Then, the frequency sweep was performed over the frequency range of 0.01 to 100 Hz. The dynamic frequency sweep was measured at a constant strain of 0.1%. All Dynamic mechanical tests were carried out at 30°C.

Tensile measurements were performed on as-prepared gels with the same size (5.5 mm diameter×60 mm length) with a static mechanical tester (H5KT, Tinius Olsen, USA) at 25°C. The sample length between the jaws was 20 mm and the crosshead speed was 100 mm/min. The tensile strain was taken as the length change related to the original length and the tensile strength was estimated on the cross section of the original sample. All samples were performed in triplicate, and average values were reported.

3 Results and discussion

3.1 Interaction between Clay and AA

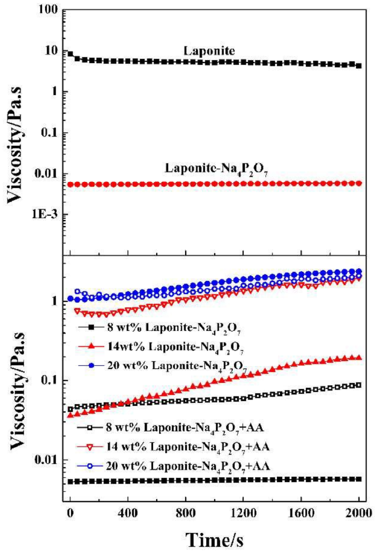


Fig. 1 Time dependence of viscosity for: a-Laponite and $Na_4P_2O_7$-modified Laponite dispersion (the Laponite concentration is 8 wt%), b-AA/$Na_4P_2O_7$-modified Laponite dispersions with different Laponite concentration. All the samples were measured just after preparation.

When the Laponite XLG was dispersed in water at a clay concentration higher than 2 wt% for a definite time (different time for different concentration), the clay discs would form a ‘House of Cards’ structure, due to the electrostatic attraction among surfaces and edges of different discs, and whereupon the mixture became very viscous.[10, 13-16, 33] This made it hard to mix with monomers or other reagents by normal mixing methods, which was the reason for most of the NC hydrogels was prepared at low clay concentration. Besides, direct addition of even small amount of ionic monomers into Laponite dispersion induced gelation and the clay dispersion became subsided and opaque quickly due to the decrease of the Debye distance for the electrostatic repulsion.[13, 23-26, 29, 32-34] So it has been challenging to synthesize ionic NC hydrogels at high Laponite concentration.

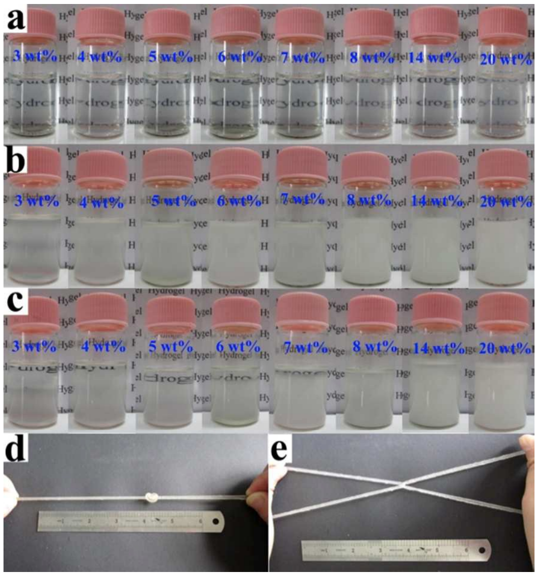


Fig. 2 Optical images of: a-different Laponite content (from 3 wt% to 20 wt%) are dispersed homogeneously by addition $Na_2P_2O_7$, b-upon addition of AA to the $Na_4P_2O_7$-modified Laponite dispersion, c-the AA/ $Na_4P_2O_7$-modified Laponite mixtures stand for 12 hours, d-knotted, and e-elongation of cross bended PAA/Laponite hydrogel.

The Laponite XLG had a certain fluidity when the Laponite was modified by $Na_4P_2O_7$ even though at high clay concentration (above 8 wt%), which allowed it possible to obtain a uniform dispersion of Laponite and monomers by mixing (Fig. 1a). The viscosity increased with increasing concentration of Laponite because of the electrostatic interaction among surfaces and edges of different Laponite platelets. The addition of AA induced the instability of the dispersion, and showed slight increase in viscosity with measurement time (Fig. 1b). The transparent Laponite dispersion (Fig. 2a) showed a steep decrease in transmittance and became opaque, while the viscosity increased steeply simultaneously (Fig. 2b). These facts suggested that aggregates formed in the dispersion because of the decreased electrostatic repulsion among the Laponite platelets caused by increased ionic strength. The mixtures will separate into two layers after standing for several hours when the Laponite concentration was less than 8 wt% in AA/Laponite system (Fig. 2c). However, further to increase Laponite concentration to 8 wt% or more, the dispersion remained stable without stratification and settlement after standing in 50°C water bath more than 12 hours. More importantly, the dispersion exhibited quite good flowability under stirring (Fig. 3). This made it possible to mix all reactants to obtain uniform precursor system. As a result, homogeneous ionic NC hydrogel can be produced via in-situ copolymerization of AA in the $Na_4P_2O_7$-modified Laponite dispersion without the help of other dispersing reagents (Fig. 2d-e).

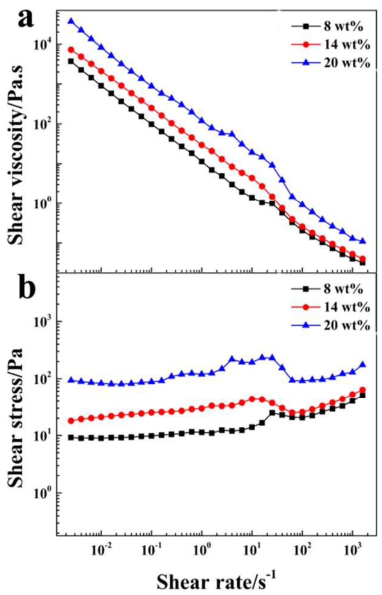


Fig. 3 Shear viscosity and shear stress vs. shear rate for the dispersion of AA/$Na_4P_2O_7$-modified Laponite at different Laponite concentrations (from 8 wt% to 20 wt%).

3.2 Formation of the network structure

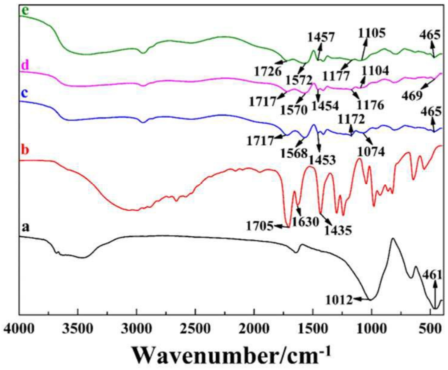


Fig. 4 FT-IR spectra of a-clay, b-AA, and PAA/Laponite NC hydrogels at different Laponite concentrations c-8 wt%, d-14 wt% and e-20 wt%, respectively (The degree of neutralization is 40 mol%).

FT-IR studies were conducted to investigate the gel formation between PAA and Laponite platelets (Fig. 4). The absorption bands of Laponite at 1012 and 461 cm^{-1}, which could be ascribe to Si-O stretching (in-plane) and Si-O bending modes, respectively (Fig. 4a).[35, 36] Compared with the FTIR spectrum of Laponite (Fig. 4a), the absorption bands of Laponite at 1172-1177 cm^{-1}, 1074-1105 cm^{-1} and 465-469 cm^{-1} were obviously observed in the spectrum of PAA/Laponite hydrogel, suggesting that Laponite incorporating in the hydrogel. Besides, small additional peaks appeared between 600 and 800 cm^{-1}, which confirmed the presence of metal-oxide stretching vibration in the PAA/Laponite NC hydrogels (due to clay).[37, 38] In Fig. 4c-e, a series of new absorption bands at 1717-1726 cm^{-1} (C=O stretching of –COOH group), 1568-1572 cm^{-1} and 1453-1457 cm^{-1} (asymmetric and symmetric stretching –COO$^-$ groups) appeared in the spectra of PAA/Laponite hydrogel (Fig. 4c-e), indicating the existence of PAA chains. We had not found any absorption peak of unsaturated C=C bonds at 1630 cm^{-1}, which gave an eloquent proof that AA was successfully polymerized. Furthermore, the absorption bands of –COOH groups and –COO$^-$ group generated obvious blue shift effect (from 1717 to 1726 cm^{-1} for –COOH group and from 1568 to 1572 cm^{-1} for –COO$^-$ group, respectively) with the increase of Laponite concentrations from 8 wt% to 20 wt% (Fig. 4c-e), which suggested that the cross-linked network formed. These results indicated that the carboxylic groups of PAA were dissociated into COO$^-$ groups which were complex with Laponite through electrostatic interaction during the polymerization procedure.

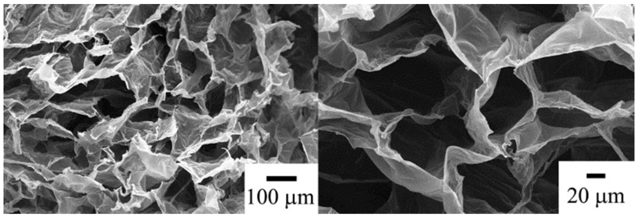


Fig. 5 SEM photos for freeze-dried PAA/Laponite NC hydrogels at 14 wt% Laponite and 40 mol% degree of neutralization (a-original magnification×300, b-original magnification×1,000).

The microstructure of freeze-dried hydrogel was analyzed via SEM (Fig. 5). We noticed that the hydrogels presented large interconnected pores with pore size of 20-120 μm while the pore walls were in several micrometers. Furthermore, the pores tended to be connected to each other and formed some open channels, which could remarkably facilitate the migration of water in and out of the NC gels when the gels swelled in the water.

Fig. 6 was XRD patterns of PAA/Laponite NC hydrogel to observe the distribution of Laponite. Pure Laponite exhibited a diffraction peak about at 2θ=4.88^o-6.89^o, corresponding to a basal spacing between Laponite platelets.[28] In the case of the ionic NC hydrogel with different concentration of Laponite (from 8 wt% to 20 wt%), no distinct diffraction peak were observed in the range of 2θ from 2^o to 8^o. This meant that there was no regular stacking of Laponite in dried NC gel. And the peaks near 10^o were according to the existence of polyacrylate in the ionic NC hydrogels.[39, 40]

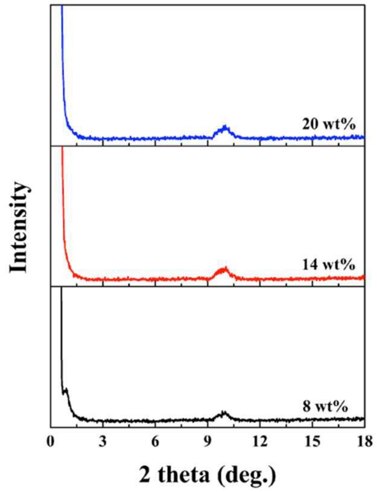


Fig. 6 XRD patterns for Laponite and PAA/Laponite ionic NC hydrogels at different Laponite concentrations (The degree of neutralization is 40 mol%).

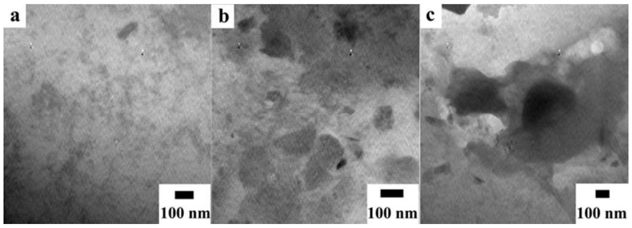
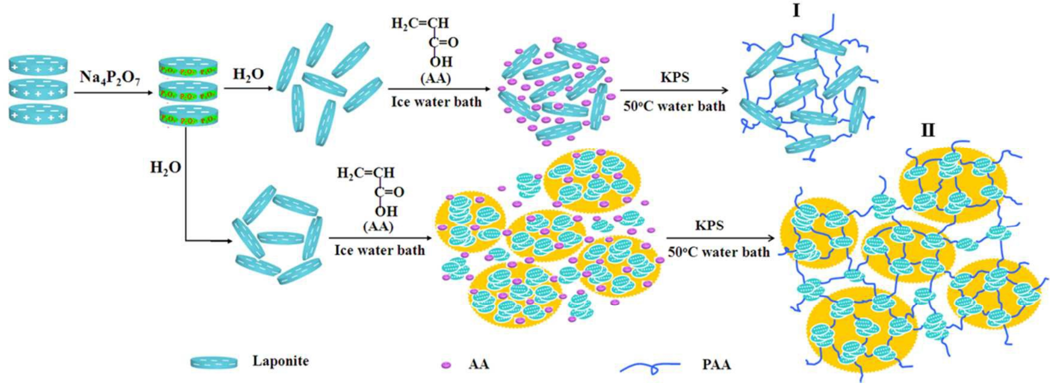


Fig. 7 TEM of PAA/Laponite NC hydrogels at different Laponite concentrations a-8 wt%, b-14 wt% and c-20 wt%, respectively (The degree of neutralization is 40 mol%).

The dispersion of clay platelets in the hydrogels were further investigated by TEM measurements (Fig. 7). It showed that, even in the dried gel, Laponite was substantially exfoliated and dispersed uniformly by the polymer matrix when clay contents was low (Fig. 7a), while part of the clay nanosheets existed as small aggregates when Laponite contents was higher than 8 wt% (Fig. 7b and Fig. 7c), and this phenomenon was more obvious in 20 wt% of Laponite concentration. The exfoliated clay platelets or small aggregates were coexistence in PAA/Laponite hydrogel. According to the mechanism for the NC hydrogels suggested by Haraguchi,[18] the clay particles tended to cleave into single disklike unites with 30 nm in diameter and 1 nm thick when dispersed in water,[41, 42] then acted as a multifunctional crosslinker to interact with nonionic polymers by polar or coordination interaction. However, in our work, there were two mechanism coexisted for formation of the ionic NC hydrogel because of two dispersing states of Laponite in the polymer matrixes: mono-nanosheets and small aggregates (Scheme 1). The exfoliated clay platelets or small aggregates and monomer AA were dispersed homogeneously in the initial reaction system. The initiator KPS was closely associated on the clay surfaces because of the strong ionic interactions between KPS and clay. As a result, the free-radical reaction occurred on the clay surfaces, and thus the PAA chains were attached to the clay platelets forming a network structure by polar or electrostatic interaction. In contrast, the crosslinking of Laponite in mechanism II was not as effective as the one in mechanism I due to partial aggregation of Laponite.



Scheme 1. Propose mechanism for the ionic PAA/Laponite NC hydrogel.

3.3 Thermogravimetric analysis

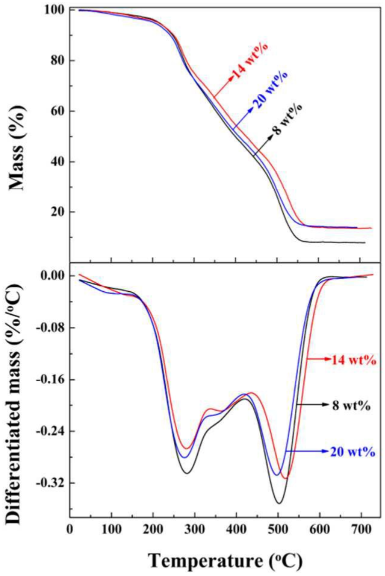


Fig. 8 Thermogravimetric analyses and their differential curves of the PAA/Laponite ionic NC hydrogels at different Laponite concentrations (The degree of neutralization is 40 mol%). All the gels have been treated by HCl before test.

The thermal stability of PAA/Laponite hydrogels was investigated using thermogravimetric analysis (TGA). The TG curves of the samples prepared under different concentration of Laponite (from 8 wt% to 20 wt%) were shown in Fig. 8. The TGA traces indicated that there were three major steps during decomposition of the hydrogel. The differentiated TGA traces (DTGA) displayed two large and one small peak above 200°C for all hydrogels. The peak at around 280°C (279°C for 8 wt% Laponite, 281°C for 14 wt% Laponite, and 276°C for 20 wt% Laponite, respectively) and a small peak at 360°C (355°C for 8 wt% Laponite, 365°C for 14 wt% Laponite, and 352°C for 20 wt% Laponite, respectively) were coupled to decomposition step one and two which were attributed to the evaporation of water and decomposition of some functional groups, such as carboxyl groups in the polymer chains accordingly. The other peaks at around 500°C (503°C for 8 wt% Laponite, 517°C for 14 wt% Laponite and 494°C for 20 wt% Laponite, respectively), came from decomposition of the polymeric network. The final residual char yield was 7.88 wt%, 13.60 wt% and 13.89 wt%, respectively. It would be concluded from all the above results that the NC gels containing 13.60 wt% clay possessed higher thermal stability than that of 7.88 wt%, which indicated that the thermal stability of the PAA/Laponite hydrogel was enhanced by the incorporation of only small amount of clay nanolayers. It implied that most of the clay platelets in the NC hydrogels acted as crosslinkers and the polymer chains were attached on their surface. However, the gels prepared under 20 wt% of Laponite concentration contained only 13.89 wt% clay content, which did not perform better thermal stability than the one under 14 wt% of Laponite concentration as we predicted. This was probably because that the clay discs at high concentration were inclined to stack together and formed small aggregates. As a result, the small aggregates cannot show as effective crosslinking as exfoliated ones. During the washing after polymerization some soluble inorganics was eluted away, resulting in the lower than expected char yields. Generally, there was no significant difference found in the thermal stability of the hydrogels. It indicated that effective crosslinking and dispersing state of Laponite acted an important role in thermal properties of NC hydrogels.

3.4 Mechanical properties

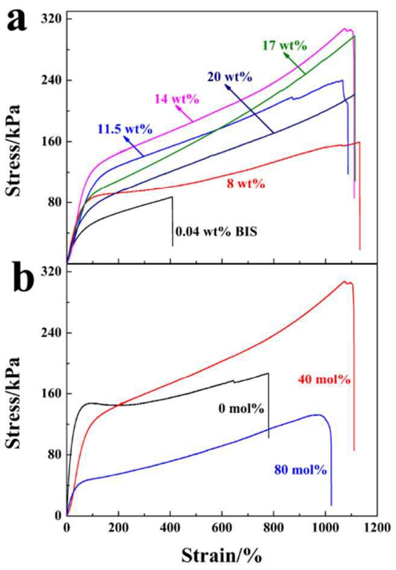


Fig. 9 Stress-strain curves: a-the NC gels at different Laponite concentrations and organic crosslinking hydrogel with 0.04 wt% BIS (the degree of neutralization is 40 mol%); b-NC hydrogels at 14 wt% Laponite concentration with different degree of neutralization: 0 mol% (without neutralization), 40 mol% and 80 mol%.

Stress-strain curves of the hydrogels were showed in Fig. 9 (mechanical factors were given in Table 1 accordingly). The maximum strength reached 308 kPa with elongation at break of 1110% for the NC gels at Laponite concentration of 14 wt% (Fig. 9a). It was much higher than the chemically crosslinking hydrogel, which exhibited poor mechanical properties and broke at a low stress of 87 kPa with a relative low strain of 408% (0.04 wt% BIS content) (Fig. 9a). The tensile strength was also much higher than the NC gels poly(AMPS-*co*-AA)/Laponite (189 kPa) prepared by our group recently.[29] In this NC gels systems, Laponite acted as a multi-functional cross-linker to fabricate a unique polymer/clay network structure.[1, 43] Generally, increase of Laponite content in the hydrogel would lead to an increase of the crosslinking density. As a result, the tensile strength was enhanced. However, further to increase Laponite concentration to 20 wt%, a decrease in tensile stress of the hydrogel was observed instead. According to the TEM morphology (Fig. 7), some clay discs stacked-together and formed small aggregates in higher Laponite concentration, which reduced the efficiency of crosslinking and caused the decreased tensile strength.

In contrast, the hydrogel prepared at 14 wt% Laponite concentration showed a highest tensile strength but in a low elastic modulus.

Table 1 The mechanical factors of PAA/Laponite NC hydrogel with different Laponite concentration (The degree of neutralization is 40 mol%).

Clay concentration (wt%)	Fracture stress (kPa)	Fracture strain (%)	Elastic modulus (kPa)	Dissipated energy (M J m^{-3})
8	159.23	1131.20	157.51	1.29
11.5	240.37	1089.00	131.25	1.81
14	308.00	1110.00	75.70	2.19
17	297.56	1114.10	127.00	1.94
20	219.82	1109.90	131.48	1.54

Degree of neutralization of AA made an effect not only on the dispersion of Laponite, but also on the mechanical property of hydrogel. Fig. 9b showed stress-strain curves of the hydrogel prepared at 14 wt% Laponite. The tensile strength increased from 186 kPa to 308 kPa when the degree of neutralization increased to 40 mol%, and then fall rapidly to 132 kPa with further increase neutralization degree to 80 mol%. At a low neutralization degree, polymer chains were curly since there existed more -COOH groups, which was not conducive to hydrogel strength. Along with the increasing degree of neutralization, -COOH groups in polymer chains was deprotonized and polymer chains were expanded and entangled in some degree, which made a big contribution to high gel strength. A further increase in neutralization degree (larger than 40 mol%) made the electrostatic interaction of charged groups on elastic free energy decreased, thus the tensile strength decreased.[44] Generally, the ionic PAA/Laponite NC hydrogels exhibited a robust mechanical behavior under large deformation.

3.5 Dynamic mechanical analysis

DMA is a nondestructive method used to characterize the viscoelastic properties of materials. To further study the effect of Laponite on mechanical performance of PAA/Laponite hydrogel, dynamic viscoelasticity of the hydrogels were examined by a dynamic mechanical analyzer. To determine the linear viscoelasticity region, a strain sweep from 0.1% to 100% strain was then conducted at a frequency of 1.0 Hz and 30°C on the fully formed NC hydrogels. After strain sweeps, a strain of 0.1% was selected for subsequent frequency sweeps to ensure availability of the linear viscoelasticity and enough sensitivity.[45]

Dynamic frequency sweep tests were performed in the linear viscoelastic range to determine the frequency dependence of storage modulus (G') and loss modulus (G").[46] The storage modulus G′ describes the stiffness or elastic character of a material and the loss modulus G" describes its viscous properties. In this section, G′, G" and tan δ (loss factor) of the NC hydrogels with different concentrations of Laponite were presented in Fig. 10 as a function of testing frequency, the frequency sweep using the appropriate strain 0.1% (as determined in the preceding section) allowed us to choose a frequency to ensure that the sweeps reflected the formation of the hydrogel network. G' was higher than G" over the frequency range analyzed when frequency swept from 0.01 to 100 Hz at 30°C (Fig. 10). The G' and G" of all the hydrogels was slightly dependent on the frequency. This was attributed to the relationships between the chain segments movement and the change of frequency. When the frequency was low, the PAA macromolecular chains can keep up with change of frequency, and the hysteresis effect was very low.

As the frequency further increased, the chain segments were stretched and orientated. Therefore, G' increased with the increasing frequency. In the NC gels, cross-links were formed by non-covalent bonds such as electrostatic interaction and hydrogen bonding. As the frequency proceeded, there was a regional monotonic increase in modulus. Simultaneously, G′ was gradually getting closer to G", suggesting the entanglement of polymer chains and indicating the existence of the crosslinked networks have been already formed in these hydrogels.[43, 47] It can be observed that G' of the gels at clay concentration of 8 wt% and 20 wt% exceeded 5×10^{6} Pa, while G' of the other one remained slightly below this value, indicating that the different existence form of clay could impact on the dynamic viscoelasticity of the NC gels. However, the G' of the

NC gels with 14 wt% clay concentration (2.5×10^6 Pa) was about 300 times more than the G' of the biocompatible adhesives PAA/Laponite NC gels in Shen's work, in which the clay concentration were in the range of 1-2 wt%.[5]

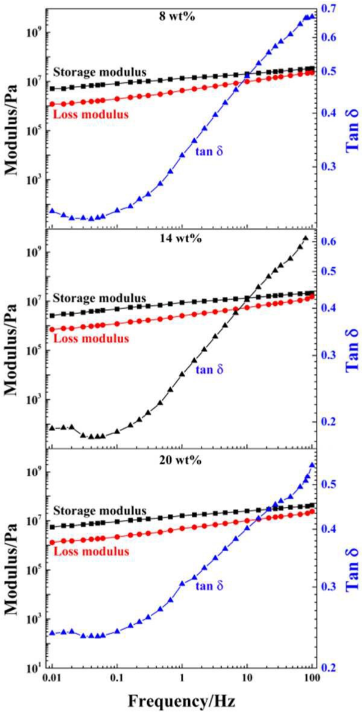


Fig. 10 Frequency dependence of storage modulus, loss modulus and tan δ for the NC hydrogels at different Laponite concentrations measured at strain of 0.1% (The degree of neutralization is 40 mol%).

The tan δ of these NC gels with different clay concentrations varied with respect to the frequency applied. At first, a decreasing trend was observed until 0.04 Hz, and then an increasing trend, due to the enhanced influence of the viscous part. Over the whole frequency range tan δ grow rapidly when the frequency was greater than 0.04 Hz, along with a slightly steeper increase of G" with the frequency than that of G'. The hydrogels at 8 wt% and 20 wt% clay concentrations were slightly more elastic than the samples at 14 wt%, which was consistent with elastic modulus. It was most probably due to the different morphologies and PAA average molecular weight of the prepared hydrogels, which have an effect on the energy dissipating mechanism during the deformation process of the NC hydrogels.

4 Conclusions

We have successfully demonstrated a facile one-pot strategy to prepare a series of strong nanocomposite hydrogel at high clay concentration. These PAA/Laponite NC hydrogels revealed desirable mechanical properties with the Laponite as the cross-linker and reinforcing agent. FTIR and SEM analysis suggested that the cross-linked network composed of PAA and Laponite was formed. And combined with the results of XRD, TEM, TG and mechanical property analysis, we can draw a conclusion that in the gel matrix Laponite existed in two forms: mono-nanosheets and small aggregates, which led to some abnormal behaviors in the thermostability and mechanical property. However, this method made it possible to obtain a uniform ionic NC hydrogel with high clay content only in the presence of ionic monomers by a facile one-pot process. DMA within linear viscoelasticity confirmed that the network structure was formed with the junction of the ionic monomer AA and Laponite platelets. In summary, this combination of improved mechanical properties and facile preparation promised these hydrogels broad potential applications, such as biomedical, tissue engineering in future.

Acknowledgments

Financial supports for this work were provided from International Science and Technology Cooperation Project (20146008) and the Excellent Doctor Innovation Program of Xinjiang University (No. XJUBSCX-2014011).

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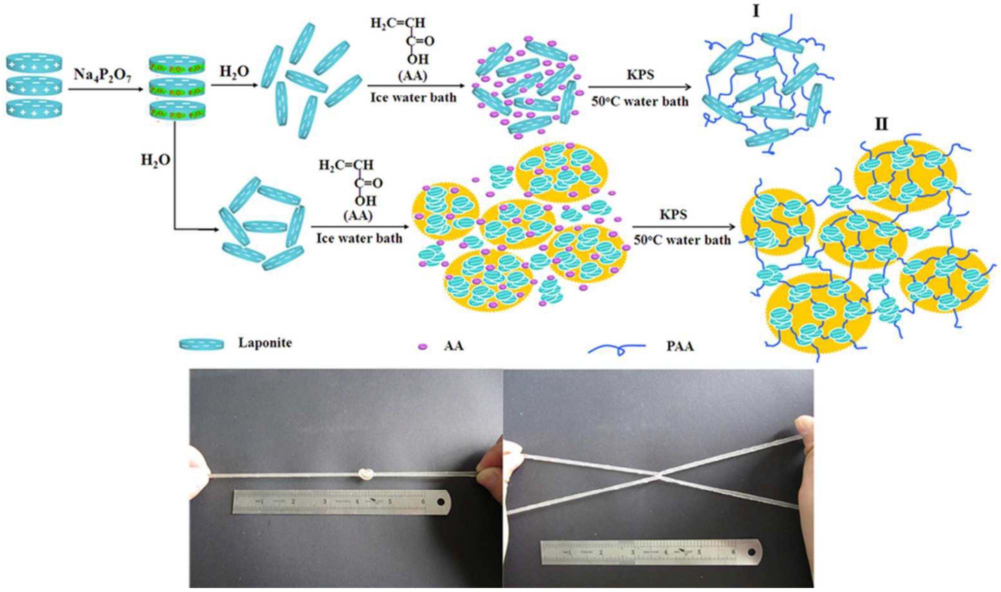

A facile strategy was developed to prepare mechanically strong Laponite-based ionic nanocomposite (NC) hydrogels at high clay concentration. Based on the thixotropy of acrylic acid (AA)/Laponite dispersion, a series of ionic poly(acrylic acid) (PAA)/Laponite NC hydrogels were successfully prepared without the addition of additional dispersing monomers. The hydrogels showed improved mechanical properties.
80x47mm (300 x 300 DPI)