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Synthesis and dual response of ionic nanocomposite hydrogels with ultrahigh tensibility and transparence

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ABSTRACT

Ionic nanocomposite hydrogels cross-linked by hectorite Laponite XLS with high tensile strength and ultrahigh tensibility were successfully synthesized for the first time via *in situ* copolymerization of *N*-isopropylacrylamide (NIPAm) and sodium methacrylate (SMA). The pH and temperature response, transparency, and mechanical properties of the ionic hydrogels were investigated. The results showed that the addition of only 2 mol% of SMA endowed the nanocomposite hydrogels with pH response, while the temperature response remained in the whole pH range. All the as-prepared hydrogels, even with 10 mol% of SMA, demonstrated transparency higher than 75%. The tensile strength evidently decreased from 60 kPa to 45 kPa when the SMA content was higher than 6 mol%. The elongation at break increased with increasing SMA content and 2800% was achieved for the sample containing 10 mol% of SMA. The effective network chain density was estimated from the tensile stress at elongation of 200% and the equilibrium storage modulus. The low chain density was the intrinsic origin of the ultrahigh tensibility for these ionic NC gels. This work provides a new way to prepare dual responsive hydrogels with ultrahigh tensibility and high transparency.

1. Introduction

Since Tanaka et al. found the volume phase transition of the partially hydrolyzed polyacrylamide gel in water/acetone mixture [1], hydrogels have been intensively studied as smart materials. Applications of responsive hydrogels have been attempted in many fields including biomedicine engineering [2–7]. However, poor mechanical properties of the hydrogels obstruct their usages in many fields, such as non-degradable drug carrier, tissue engineering scaffold, etc.

Recently, Haraguchi et al. reported a novel nanocomposite hydrogel (NC gel) with high mechanical properties, which was prepared by *in situ* polymerization of *N*-isopropylacrylamide (NIPAm) in hectorite Laponite XLG suspension [8]. Laponite platelets were recognized as well-defined discs with thickness of ca 1 nm and diameter of ca 30 nm, carrying negative charge on the surface and positive charge on the edge [9,10]. The Laponite platelets served as multifunctional cross-linkers in the NC gel, which endowed the gel with high ultimate tensile strength (about 70 kPa), high tensibility at break (about 1300%), and high transparence. So far, people focused on the forming mechanism [11,12], composition optimization [13–15], and structure [16–23] of the NC gel. Zhu et al. also prepared the NC gel using acrylamide (AAm) monomer instead of NIPAm [24,25]. However, all the NC gels reported up to now are based on the monomers of acrylamide derivatives and no other response than temperature has been reported.

For fabricating responsive hydrogels, functional monomers should be introduced into the network, such as NIPAm for temperature response, acrylic acid (AA) for pH response. Dual temperature and pH response hydrogel was achieved by copolymerization of NIPAm and AA cross-linked by *N*,*N*′-methylenebisacrylamide (BIS) [26,27]. However, this hydrogel was very weak and brittle with low transparence, unsatisfying the requirement of actual applications. Therefore, the essential improvement of the dual responsive hydrogels to high mechanical property and transparence is desired for several decades.

The NC gel with Laponite brings forth a new way to strong and responsive hydrogels. Simple addition of ionic monomers of AA or sodium methacrylate (SMA) to the Laponite suspension, however, induced gelation or precipitation [28,29]. Laponite can form a clear and colorless colloidal suspension in water stabilized by the electrostatic repulsive interaction. Laponite suspension changed to a weak gel due to the formation of the house-of-cards structure by

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increasing the ionic strength or Laponite concentration [30–32]. Nicolai and Cocard [31] found that gelation occurred in a gel-forming grade Laponite suspension of 1 w/v% when the ionic strength was 5 mM. The gelation process became very fast with increasing the ionic strength [30]. The sol-forming grade Laponite modified from the gel-forming Laponite with inorganic polyphosphate, can delay or even prevent the gelation owing to loss of the positive charges at the platelet edge [33].

A semi-interpenetrating network (IPN) of the NC gel containing linear carboxymethyl chitosan (CMCS) was designed for the temperature and pH response [34]. But the ultimate tensile strength of the semi-IPN NC gel was 38 kPa, about 1/2 of the original NC gel reported by Haraguchi et al. [8] with the similar elongation of about 1300%. Additionally, the semi-IPN NC gel was opaque because of the incompatibility of CMCS and PNIPAm [34].

In this article, we described the preparation and properties of a novel pH and temperature responsive transparent nanocomposite hydrogel containing ionic segment of SMA cross-linked by a hectorite clay of Laponite XLS.

2. Experimental

2.1. Materials

N-Isopropylacrylamide (NIPAm, Acros, 1% stabilizer) was recrystallized from hexane/toluene mixture. Sodium methacrylate (SMA) was obtained from neutralization of distilled methacrylate acid (MAA) with 2 M of NaOH aqueous solution. Potassium peroxydisulfate ($K_2S_2O_8$) was analysis grade reagent and recrystallized from deionized water. Synthetic clay Laponite XLS (Rockwood Ltd., 92.32 wt% $Mg_{5.34}Li_{0.66}Si_8O_{20}(OH)_4Na_{0.66}$ and 7.68 wt% $Na_4P_2O_7$) was used after dried at 100 °C for 2 h. *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (TMEDA, Sinopharm Group Chemical Reagent Co., Ltd.) was used as-received. Pure water was produced by deionization and filtration with a Millipore purification apparatus (resistivity >18.2 MΩ cm) and bubbled with argon gas for more than 1 h prior to use.

2.2. Synthesis and swelling of NC gels

The nanocomposite hydrogel (NC gel) was prepared by *in situ* copolymerization of SMA and NIPAm in the Laponite suspension. The procedure was similar to that reported by Haraguchi et al. [8] and the most difference was addition of ionic monomer SMA. At first, Laponite XLS was dispersed in pure water under stirring for 2–3 h to make a uniform suspension. Then, the monomer NIPAm was added and stirred in an ice water bath for another 1–2 h. Finally, desired amounts of SMA solution of 0.5 M (pH ≈ 6), initiator KPS solution of 20 mg/mL, and reducer TMEDA were added to the system under stirring. The polymerization was carried out in a capillary (diameter $d_0 = 1$ mm) or a glass tube (diameter $d_0 = 4$ mm) at 20 °C for 24 h. In all cases, the mole ratio of total monomers (NIPAm + SMA) to initiator to reducer was kept at 100:0.370:0.638. The total monomer concentration was fixed at 1 mol/L and the Laponite concentration was fixed at 2 w/v%. The NC gel was referred to as SMA*m*, where *m* represented the mole percent of SMA in the total monomers.

After polymerization, the NC gel was taken out from the capillary and soaked in a large amount of pure water with daily refreshment at 25 °C for at least 10 days to remove impurities and to reach the swelling equilibrium. The swelling experiment was also carried out in buffer solutions of different pH at ionic strength $I = 0.01$ M at 25 °C and 45 °C, respectively. The buffers were prepared as follows: pH 3 from phthalic acid and KH phthalate; pH 4 and pH 5 from glacial acetic acid and sodium acetate; pH 7 and pH 8 from KH_2PO_4 and Na_2HPO_4; pH 10 from NaOH and NaCl. The diameter d of the gel sample was measured by a microscope with a calibrated scale. The swelling ratio V/V_0, defined as the swollen volume at the equilibrium related to that of as prepared gel, was calculated from gel diameter ratio d/d_0 as $V/V_0 = (d/d_0)^3$ under isotropic swelling assumption, where d_0 was the diameter of the as prepared gel.

2.3. Transmittance and ζ-potential

Transparency of the copolymerization suspension and the NC gel was monitored at wavelength $\lambda = 600$ nm with a UV/Vis spectrophotometer (U-3010, Hitachi). The reaction suspension was contained in a quartz cell (10 mm × 10 mm × 40 mm) with a cap. The NC gel was equilibrated at desired temperature for 10 min before data collection.

ζ-Potential of the Laponite XLS in aqueous suspension of 2 w/v% (pH ≈ 8.5) was measured with a Zetasizer Nano-ZS90 (Malvern). The suspension was filtered through a Millipore filter of 0.45 μm pore size into the cell. The ζ-potential value was the average of at least three successive measurements.

2.4. Mechanical measurements

Tensile strength was measured on the as-prepared NC gel of 4.0 mm diameter × 60 mm length with a Zwick Roell testing system 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. The hysteresis was measured on the as-prepared NC gel under the same conditions, except that the strain was restricted below 800%.

Rheology measurements were carried out on the as prepared NC gel with a strain controlled rheometer ARES-RFS using the parallel plate of diameter of 25 mm. Silicone oil was laid on the edge of the fixture plates to prevent water evaporation. The frequency sweep test was performed over the range of 0.01–100 rad/s at strain of 1% within the linear viscoelasticity region determined by the dynamic strain sweep at 3.14 rad/s. All rheology measurements were performed at 20 ± 0.1 °C controlled by a Peltier plate.

3. Results and discussion

3.1. Stabilization and copolymerization of ionic NC gels

Direct addition of small amount of SMA into a 2 w/v% of Laponite suspension induced gelation within 12 h due to the decrease in the Debye distance for the electrostatic repulsion. In the present case, the sol-forming grade Laponite XLS was stabilized with adsorbed neutral monomer NIPAm, which allowed it possible to be mixed directly with ionic monomer SMA without gelation and precipitation. This stabilization effect for the suspension was checked with zeta-potential. The zeta-potential was −55.2 mV, −32.8 mV and −28.0 mV for the Laponite XLS aqueous suspension of 2 w/v%, the same suspension with 1 M NIPAm, and the same suspension containing 0.9 M of NIPAm and 0.1 M of SMA, respectively. The decrease in absolute value of the zeta-potential after adding NIPAm was due to the effective adsorption of NIPAm monomers on the Laponite platelets [11]. The adsorption of NIPAm partially reduced the surface charge of the Laponite platelets like adsorbing PEG [35]. All the present suspensions with remained charges were still stable for more than 12 h, long enough for the *in situ* copolymerization.

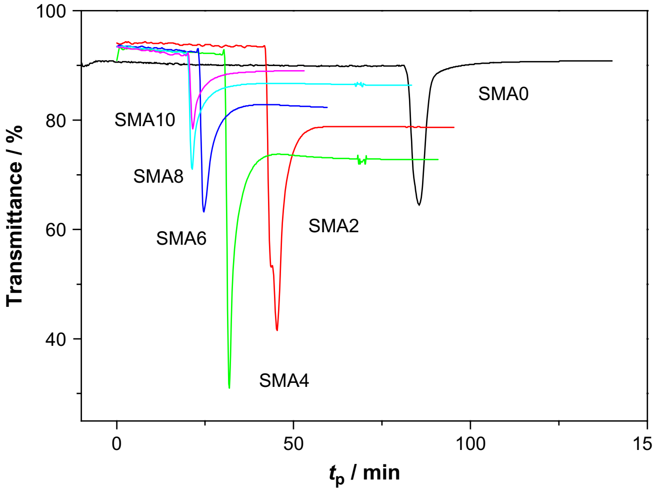

Fig. 1. Transmittance of the copolymerization suspensions for the indicated ionic NC gels varying with reaction time t_p.

Transmittance of the suspension during polymerization is depicted in Fig. 1. At the beginning of polymerization, all the suspensions exhibit high transparence above 90%. There is an abrupt drop in transmittance for all the suspensions appearing at about tens of minutes after starting the reaction. After reaching the minimum, the transmittance returns to a high level quickly. This phenomenon is similar to that reported by Haraguchi et al. [11] and Miyazaki et al. [12]. Haraguchi et al. ascribed the transparency decrease to the formation of the clay/polymer brush particles at the early stage of polymerization, which caused light scattering because of the local density fluctuation and aggregation of such particles [11]. Miyazaki et al. accounted for this characteristic drop in transmittance as the formation of huge clusters of microgels prior to the gelation [12].

By careful observation, the transmittance minimum appears earlier with increasing SMA content in the polymerization suspension, probably due to the higher reactivity of SMA monomer than that of NIPAm monomer [27]. According to the literature arguments [11,12], the addition of SMA may accelerate the formation of the polymer–Laponite brush particles and the aggregation of these particles, leading to the early appearance of the transmittance minimum. At the same time, the deepest minimum value appears at the SMA concentration of 4 mol%, reflecting the most aggregation at this composition. It seems that when more SMA is added, the chain propagating from the Laponite platelet carries more negative charges and depresses the aggregation causing the minimum shoaled. Finally, all the NC gels are transparent and homogeneous as shown in Fig. 2.

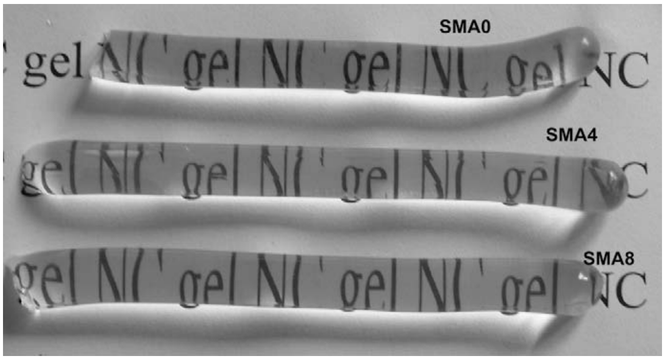

Fig. 2. Photos of the ionic NC gels of SMA0, SMA4, and SMA8.

3.2. Thermo and pH response of ionic NC gels

Thermal response of the NC gels containing ionic SMA monomers was detected by the temperature dependence of the transmittance as illustrated in Fig. 3. All the samples are transparent at room temperature (Fig. 2). Without SMA, the NC gel becomes a normal Laponite–PNIPAm gel and exhibits a distinct change in transmittance at ca 32 °C, corresponding to the phase separation in aqueous PNIPAm solutions and in PNIPAm hydrogels [36,37]. With 2 mol% of SMA, the transmittance transition temperature of SMA2 increases from 32 °C to 37 °C and the transition is not as sharp as that of SMA0. Further increase in the SMA content results in a gradual transmittance decrease for SMA3 and SMA4. At low temperature, the NC gel is hydrophilic and swollen; while at temperature above the LCST of the PNIPAm solution, the NC gel shrinks due to the hydrophobic aggregation, which leads to decrease of the gel transmittance. However, the addition of the ionic monomer SMA enhances the hydrophilicity of the PNIPAm chains and increases the osmotic pressure of the ionic NC gel. Consequently, the shrink of the NC gel requires more energy to overcome the electrostatic repulsion, causing disappearance of the transmittance transition. On the other hand, this disappearance of the transition implies the joint of the ionic monomer SMA into the network of the NC gel, because the copolymerization with ionic monomers causes the PNIPAm gel to lose the volume phase transition [26,27,38,39].

Copolymerizing SMA into the NC gels enhances hydrophilicity of the network chains and raises the equilibrium swelling ratio in pure water. The equilibrium swelling ratio of the NC gels, expressed by d/d_0 and listed in Table 1, increases with the SMA content. This phenomenon provides another evidence of successful introduction of the ionic SMA into the NC gel together with NIPAm. For all the gel samples, no distortion in the cylindrical shape was observed during the swelling process. Owing to the addition of SMA, the existence of counter ions and electrostatic repulsion between ionic SMA groups increase the osmotic pressure and equilibrium swelling volume of the ionic NC gels. The swelling volume is even as high as 1600 times of the original one ($d/d_0 = 11.8$).

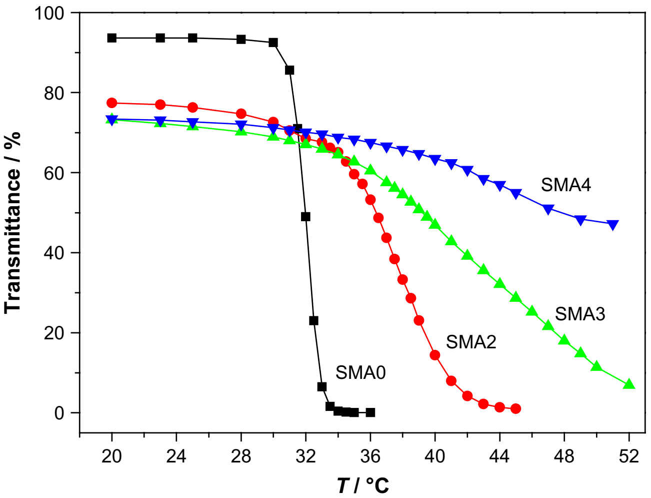

Fig. 3. Temperature dependence of transmittance of the NC gels with different contents of ionic monomer SMA.

Table 1
Swelling ratio and mechanical properties of ionic nanocomposite hydrogels.

Sample	Swelling ratio (d/d_0)	Strength (kPa)	Elongation (%)	E^a (kPa)	τ^b ($\alpha = 2$) (kPa)	N^{*c} (mol/m^3)	G_e^d (Pa)	N^e (mol/m^3)
SMA0	1.91	64.2 ± 1.5	1679 ± 70	3.68	3.04	0.70	654	0.27
SMA2	4.98	61.5 ± 2.1	1847 ± 15	3.63	3.01	0.69	708	0.29
SMA4	7.33	58.0 ± 1.4	2002 ± 50	3.70	3.12	0.72	610	0.25
SMA6	10.03	59.8 ± 1.1	2074 ± 47	3.74	3.05	0.70	714	0.29
SMA8	10.50	45.9 ± 2.0	2530 ± 100	3.56	2.90	0.67	714	0.29
SMA10	11.83	37.5 ± 1.2	2874 ± 30	3.62	2.94	0.68	712	0.29

[a] Young's modulus obtained from initial slope of the stress–strain curve.
[b] Stress at elongation of 100%.
[c] The effective network chain density determined from τ with Eq. (1).
[d] The equilibrium shear modulus determined from rheology measurements.
[e] The effective network chain density determined from G_e with Eq. (2).

Fig. 4 depicts the equilibrium swelling ratio d/d_0 with error bar for the ionic NC gels as a function of pH at 25 °C (A) and 45 °C (B). At 25 °C, the swelling ratio increases rapidly with pH at pH of 4–5 due to the ionization of the carboxyl groups in the NC gels. Then, d/d_0 changes slightly, indicating complete ionization of the SMA units. But d/d_0 is lower than that in pure water because the ion strength of the buffers is 0.01 M.

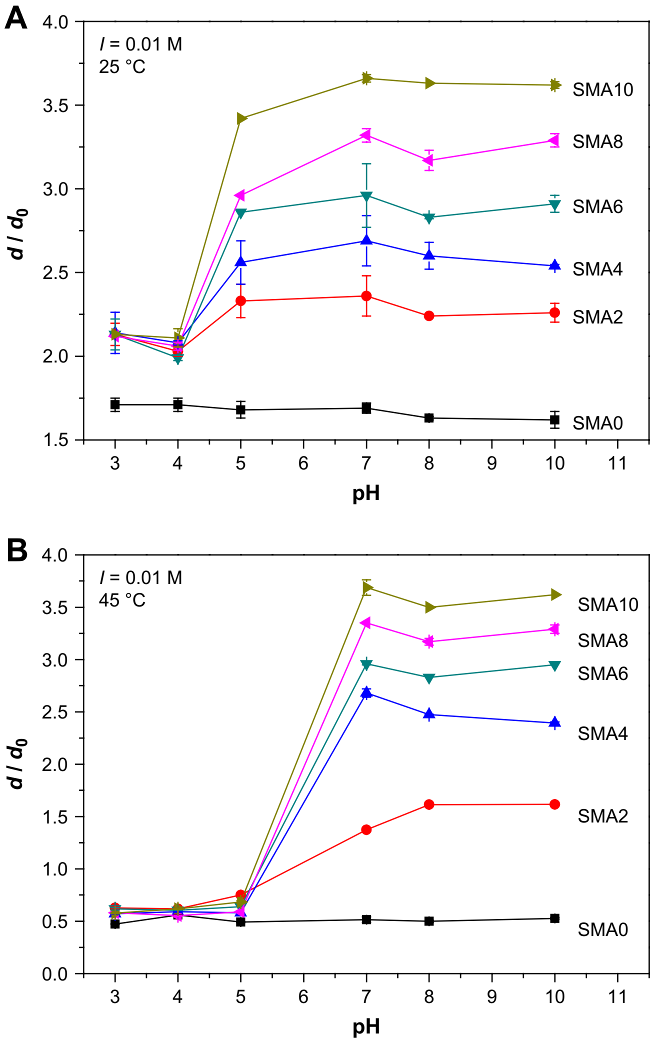

Fig. 4. Equilibrium swelling ratio d/d_0 of the NC gels containing ionic monomer SMA in buffer solutions at 25 °C (A) and 45 °C (B).

In order to reveal the dual response to pH and temperature of the ionic NC gels with different SMA contents, we observed the change of the equilibrium swelling ratio with pH at 45 °C (Fig. 4B). At 45 °C, SMA0 gel without SMA is in shrunk state over the entire pH range because this temperature is higher than the LCST of the PNIPAm gel. The other NC gels containing SMA units swell when pH > 7, even at such a higher temperature due to the presence of charged carboxyl groups.

At pH 7.0, the swelling ratio of SMA2 at 25 °C is about 13.1, much higher than 2.6 at 45 °C, suggesting the temperature response of this ionic NC gel. For the sample SMA4, however, the swelling ratio at 25 °C is similar to that at 45 °C, losing the temperature response due to the strong electrostatic repulsion. Hence, we can conclude that the ionic NC gels have dual response, i.e., swelling and shrinking can be switched by either temperature or pH with precisely controlling the SMA content as long as the charge density is not too high.

3.3. *Mechanical properties of ionic NC gels*

We measured tensile strength and elongation at break on the samples with different SMA contents to examine whether the unique high tensibility of the NC gel remained in the ionic NC gels. The appearance of the NC gel during elongation is illustrated in Fig. 5. The NC gel is deformed uniformly under tensile force without necking (Fig. 5B) due to its low chain density (see Table 1 and to be discussed later) and amorphous structure. The fracture usually occurred at a point close to one jaw collet. The gel sample recovers a large proportion of the elongation when broken (Fig. 5C) induced by the elastic energy stored in the network.

Fig. 6A demonstrates the stress–strain curves for some NC gels as examples with the inset showing the initial part the S–S curves, which are similar with each other and start to separate at the strain of ca 150%. Young's modulus E was determined from the initial part of the S–S curves and listed in Table 1 with the ultimate tensile strength and elongation at break. One can see that E is almost constant for all the NC gels while the addition of ionic SMA segments decreases the tensile strength and increases the elongation. When the SMA content is higher than 6 mol%, these changes become more obvious. It is unexpected that the elongation at break for the NC gel SMA10 is even higher than 2800%. The exact reason for the extremely high tensibility of the ionic NC gels is still unclear until now. We consider that the addition of the ionic SMA monomers will form a random copolymer with NIPAm jointed by Laponite platelets, which may reduce the twist of the chain threads during polymerization process due to electrostatic repulsion. This makes the chains in the NC gel easily be elongated to a high level. The NC gel samples became dried due to the water evaporation when elongated at rate lower than 100 mm/min and no reproducible data were obtained. Recently, we reported that the tensibility was almost independent of the crosshead speed for the NC gel of AAM and gel-forming grade Laponite RD at low concentrations [40]. The concentrations of Laponite of sol-forming grade and the total monomers in the present NC gels are low and the network chains are long due to the low cross-link density. Therefore, the chain can relax the stretching stress and avoid break until a high level. Zhu et al. reported that the tensile strength of PNIPAm/Laponite XLS NC gels increased greatly with the increase of Laponite content, while little change was found in the elongation at break [13,15].

When the NC gels were stretched to 800%, well below the macroscopic rupture strain, and reverted at the same rate of 100 mm/min, a hysteresis in the stress–strain curve was observed

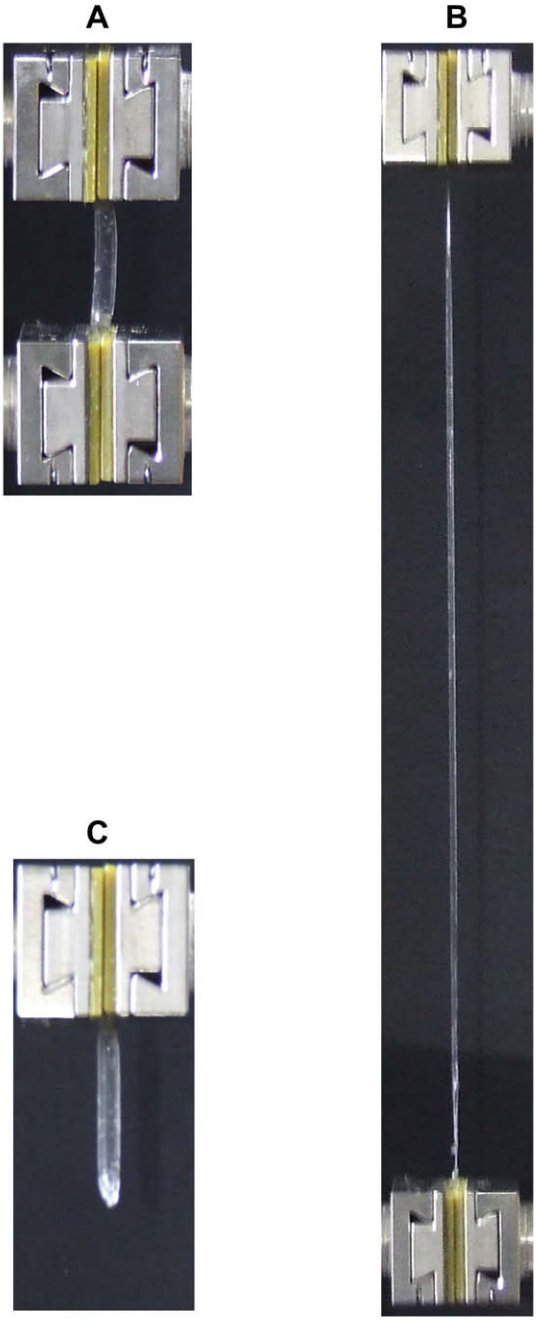

Fig. 5. Appearance of the NC gel during the elongation, A: before elongation; B: in elongation; C: after break.

(Fig. 6B). This means that the elongated NC gels cannot recover the original length when released to low stress because the network chains at low cross-linking density creeps under the stress.

The network chain density N^* based on the elongation data was estimated following the equation [40]:

$$\tau = N^* RT\left[\alpha - (1/\alpha)^2\right] \qquad (1)$$

Here, τ is the stress at elongation of $\alpha = 2$ (stain 100%), R and T are the gas constant and absolute temperature, respectively. The estimated N^* values are summarized in Table 1, which are almost constant owing to the same content of Laponite in all the gel samples.

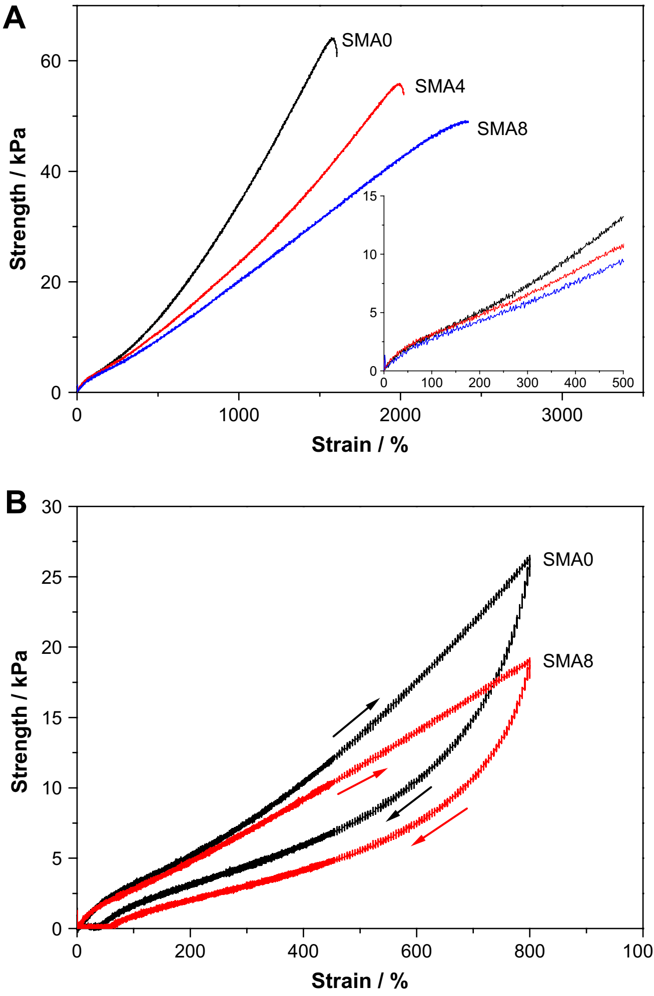

Fig. 6. A: Stress–strain curves for elongation at 100 mm/min of the NC gel SMA0, SMA4, and SMA8; the inset shows the initial part of the stress-strain curve. B: Stress–strain curves for elongation-recovery of the NC gel SMA0 and SMA8 at 100 mm/min.

The storage modulus G' and loss modulus G'' were measured within the linear viscoelasticity region as a function of angular frequency ω to evaluate the effective chain density of these ionic NC gels. G' for all the samples is about one order of magnitude higher than G'' with a slightly declined plateau over the entire frequency range observed, indicating the existence of a weakly cross-linked network in each sample. Actually, G' values for all the samples are almost the same (Table 1), suggesting no significant difference in the effective chain density for these ionic NC gels. This result is similarly attributed to the same concentration of Laponite XLS used in these NC gels as the cross-linker.

The effective network chain density N in NC gels can be also evaluated from the equilibrium modulus G_e [40]:

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

Here, G_e was taken as the plateau modulus at G' vs. ω curves. The estimated N values listed in Table 1 are almost the same for all the samples. However, both the E and N^* values are higher than the corresponding $3G_e$ and N values for the same NC gel. We have pointed out two possible reasons for this deviation, i.e., departure from the affine deformation and the volume compression even during the initial elongation [40]. The low chain density of N is the intrinsic origin of the ultrahigh tensibility for the ionic NC gels.

4. Conclusion

The ionic monomer SMA has been successfully copolymerized into the nanocomposite hydrogel as p(NIPAm-*co*-SMA)/Laponite XLS for the first time by delicately equilibrating the electrostatic repulsion and van der Wals attraction in the aqueous Laponite suspension. The ionic NC gels demonstrated the pH and temperature sensitivities as a novel dual responsive material with ultrahigh tensibility and transparence. With an increase of SMA concentration in the gel, the tensile strength decreased and the elongation at break increased. The introduction of ionic SMA segments into the PNIPAm chains may reduce the twist of chain threads between the Laponite platelets in favor of large deformation.

Acknowledgements

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