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Ultrahigh Tensibility and Stimuli-Response of Polymer-Hectorite Nanocomposite Hydrogels

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Summary: In the field of hydrogels with high mechanical performance, the nanocomposite hydrogel (NC gel) is widely interested due to its unique network structure with extraordinary mechanical, optical, and swelling/deswelling properties. Over the past few years, our group has investigated the fabrication and mechanical properties of a variety of the NC gels with different monomers. The effective network chain density and relaxation were well characterized by dynamic mechanical measurements. From these efforts, we found that the high tensibility of the NC gels came from the low effective network chain density with moderate relaxation. Besides, transparent and ultratensible NC gels with pH response and dual response of pH and temperature have successfully fabricated and characterized. This review will give a brief introduction of our achievements on the understanding of the preparation and properties of NC gels.

Keywords: chain density; nanocomposite hydrogel; pH response; transparency; ultrahigh tensibility

Introduction

Hydrogels, which consist of three-dimensional polymer networks and large amounts of water, have been intensively studied due to their widely potential applications. However, for a long period, the mechanical strength of chemically cross-linked hydrogels is very weak due to their high water content and heterogeneous cross-linker distribution. These fatal defects largely obstruct their application in the human body, such as articular cartilage, semilunar cartilage, tendon and ligament. During this decade, several new hydrogels with high strength, high elongation at break, and high fracture energy have been developed, including topological gels,[1] nanocomposite hydrogels (NC gels) cross-linked with hectorite clay,[2] double-network hydrogels,[3] macromolecular microsphere composite gels,[4] and tera-PEG gels.[5] All these achievements greatly stimulate the studies on the mechanical property and further applications of hydrogels.

Among them, the polymer-hectorite NC gel attracted many attentions due to its facile fabrication and tentative application in cell culture.[6] The NC gels can withstand severe deformations, not only elongation and compression, but also bending, tearing, twisting and even knotting.[7]

The NC gel was firstly reported by Haraguchi et al. in 2002. It was achieved by in situ polymerization of N-isopropylacrylamide (NIPAm) in a hectorite Laponite suspension without any chemical cross-linkers.[2] The exfoliated Laponite platelets served as multifunctional cross-linkers in the gel and the resultant NC gel exhibits extraordinarily good mechanical properties with high transparency, for example, a tensile strength of 10 times higher than that of the chemically cross-linked hydrogel and an elongation of more than 1000%. Then, they reported many results about the influence of Laponite and monomer concentrations on

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the mechanical property of the NC gel.[8–10] Zhu et al. prepared a new NC gel with excellent resilience, low elastic hysteresis and ultrahigh elongation by using polyacrylamide (PAAm) instead of PNIPAm.[11,12] However, most of the reported NC gels were based on the monomers of acrylamide derivatives due to the easy precipitation of Laponite platelets in the presence of ionic monomers. In our lab, we have successfully prepared transparent and ultratensible NC gels with pH response and dual response of pH and temperature by dexterously using the stable window of the Laponite suspension containing ionic monomers.[13–15]

Laponite forms a clear and colorless colloidal suspension in water. For the gel-forming grade Laponite (such as Laponite XLG and Laponite RD), the platelets have strongly negatively charged surface and weakly positively charged rim in aqueous suspension.[16] This Laponite suspension easily becomes a weak gel due to the formation of the "house-of-cards" structure by increasing ionic strength or Laponite concentration.[17–19] Nicolai and Cocard 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 ionic strength.[17] However, the sol-forming grade Laponite (such as Laponite XLS and Laponite RDS), modified from the gel-forming Laponite with tetrasodium pyrophosphate, delays or even prevents the gelation owing to loss of the positive charge at the platelet rim.[20] This delay provides a possible stable window of the Laponite suspension for the in situ copolymerization of acrylamide derivative monomers and ionic monomers.

For better understanding of the origin of this high mechanical performance, Haraguchi, Shibayama and Oppermann systematically studied the polymerization and microstructure of the NC gels. Haraguchi et al. proposed that the initiation occurred near the Laponite surface and suggested a model of Laponite-brush particles at the very early stage of polymerization, which consisted of exfoliated Laponite platelets and grafted polymer chains.[8] Shibayama et al. observed the gelation of the NC gel with dynamic light scattering (DLS) and small-angle neutron scattering (SANS) and found an ergodic-nonergodic transition with larger size of clusters at the gelation threshold than that of chemically cross-linked gel (OR gel). They reported that there was a thin polymer layer surrounding the clay platelet with the thickness of ca. 1 nm due to the interaction between PNIPAm chains and Laponite surface.[21] To investigate the gelation process at different stages, Ferse et al. used a photo-initiator to start and terminate the polymerization by switching on/off the UV light.[22] They concluded that the PNIPAm chains were closely attached to the Laponite surface at the early stage of the polymerization. The microstructure has been also intensively studied with DLS and static light scattering, small-angle X-ray scattering (SAXS), and SANS. For example, Shibayama et al. argued that the PNIPAm chains were anchored to the clay platelets so that there was an excess polymer density close to the surface.[23] SANS results on deformed NC gels revealed that the Laponite platelets were highly aligned with the surface normal parallel to the stretching direction and the PNIPAm chains were elongated parallel to the stretching direction.[24]

Up to now, the origin of ultrahigh tensibility of the NC gel is still unclear. And the development of pH-responsive NC gels with high mechanical performance also didn't make a real breakthrough due to the precipitation of Laponite in the presence of ionic monomers. During the past few years, we have reported some findings in this area by measuring the relaxation modulus of the NC gels, introducing the anionic and cationic monomers to the NC gels.[13–15,25] In this review, we will give a brief retrospection.

Relaxation and Network Chain Density

The NC gels were synthesized through in-situ polymerization of monomers in the aqueous Laponite suspension, which was prepared by dispersing in pure water at desired concentration under stirring for at least 4 h. The monomer, catalyst N,N,N',N'-tetramethylethylenediamine, and the aqueous solution of initiator $K_2S_2O_8$ were subsequently added to the suspension under stirring. The polymerization was allowed to proceed at 30 °C for 72 h. The nomenclature was used as that S and D stood for Laponite-RDS and Laponite-RD, AM, SA, and MA meant the monomer acrylamide, sodium acrylate, and methacrylic acid, respectively. The number in the sample code indicated the clay concentration of 100 × clay/water (w/v) and monomer concentration of 100 × monomer/water (w/v), respectively. For an example, S10AM10 meant a PAAM-Laponite RDS NC gel containing Laponite-RDS of clay-to-water ratio of 10 w/v% and AM of monomer-to-water ratio of 10 w/v%. The conventional PAAM hydrogel cross-linked by N,N'-methylenebisacrylamide (BIS) of 0.8 mol% of the monomer AM concentration was referred to as OR0.8.

During the tensile experiments, we found that the tensile strength increased while the elongation at break decreased at high deformation rate, especially for the samples with high Laponite or monomer concentration. During the stretch, there is a competition between the stretching orientation and relaxation for network chains cross-linked by Laponite platelets. Figure 1 presents examples of PAAm-Laponite RD NC gels. For the gel with lower cross-linker (Laponite) density, the chains can effectively relax, showing almost no deformation rate dependence of the elongation at break. In contrast, for the sample with high cross-linker density (D4AM10), the chains are hard to relax, leading to reduction in the elongation at break with increasing deformation rate.[25]

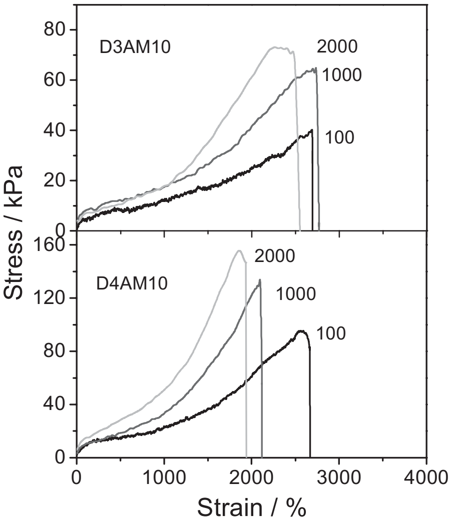

Figure 1.
Stress-strain curves for tensile measurement at indicated crosshead speed for the PAAm (10 w/%)-Laponite RD NC gels with 3 (upper panel) and 4 (lower panel) w/v% of Laponite.

This chain relaxation was also observed during the tensile elongation-recovery experiment as shown in Figure 2 for the same samples. When the sample was stretched to 1600%, below fracture strain, and then recovered at the same speed, a hysteresis in the stress-strain curve appeared.[25] Moreover, the hysteresis represented by the enveloped area was more significant when the Laponite content was high, due to the increase in cross-linking density. The adjustment of the orientation of the network chains and the distribution of physical cross-linkers is the origin of such a strong tensile hysteresis, which is related to the ultrahigh tensibility of the NC gels.

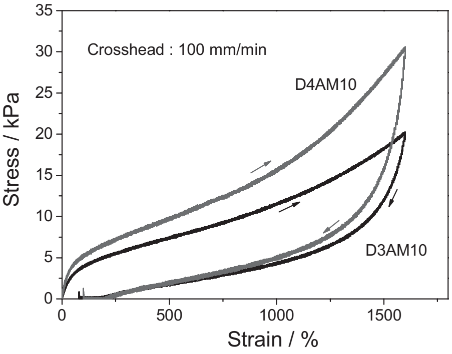

Figure 2.
Hysteresis in stress-strain curve for elongation-recovery circle of the same NC gels as in Figure 1.

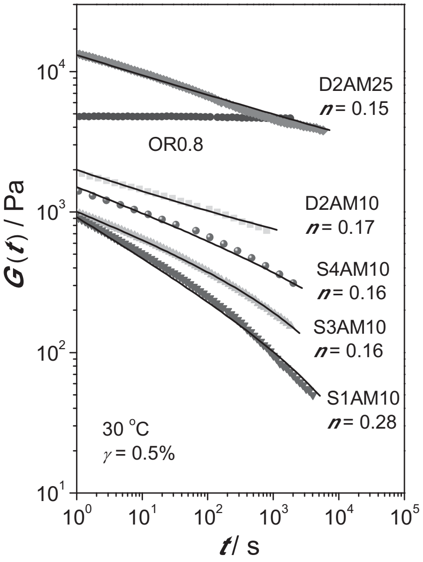

Figure 3.
Relaxation modulus G(t) of the NC gels and OR0.8 gel. The solid lines were fitted by Equation (1) with indicated n.[25]

The relaxation modulus G(t) of the NC gels was measured as a function of observing time (Figure 3). G(t) decreased with time following a downward curve but never went to zero over the test duration, irrespective of concentrations of clay and monomer. On the contrary, no relaxation was observed from the chemically cross-linked OR0.8 gel. This result indicates that the polymer chains cross-linked by Laponite platelets can be partially relaxed during observation, which is consistent with the phenomenon of tensile hysteresis.

The relaxation curve was fitted with the following equation[26,27] and the exponent n was estimated.

$$G(t) = G_e[1 + (t/\lambda_0)^{-n}] \qquad (1)$$

Here, G_e is the equilibrium modulus, λ_0 is a material-dependent time constant.

The relaxation mode for the critical gel is $G(t) = St^{-n}$ with the n value of $0.66 \sim 0.71$.[28] Thirion and Chasset reported the n value in between 0.12 and 0.17 based on equation 1 for natural rubber.[29] For the NC gels, the n value was $0.15 \sim 0.17$, except for the S1AM10 which was still a fluid. The network chain relaxation in the NC gels is similar to that of the lightly cross-linked nature rubber, much slower than that of the critical gel but much faster than that of the chemically cross-linked OR0.8 gel. This moderate relaxation of the NC gels allows the network chains bridging neighboring Laponite platelets to adjust their orientation and distribution, endowing the NC gels high tensibility. Consequently, the NC gel with low n exhibits an evident deformation rate dependence and a strong tensile hysteresis due to its slow relaxation.[25]

Another important factor governing the high deformability of the NC gels is the effective network chain density. The network chain density N of the PAAm-Laponite NC gels was determined from the equilibrium shear modulus G_e based on the rubber elasticity theory at small deformation.[25,30–32]

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

Here, G_e was taken from the plateau modulus in the storage modulus G' vs. angular frequency ω curves. R and T are the gas constant and absolute temperature, respectively.

As a comparison, the network chain density N^* was also calculated from the tensile stress τ and elongation ratio α on the assumption of affine deformation and incompressible volume[9,33]

$$\tau = N^*RT\left[\alpha - (1/\alpha)^2\right] \qquad (3)$$

Here, τ was calculated with the original (undeformed) section area of the as-prepared NC gel and the τ value at elongation of $\alpha = 2$ (strain 100%) was used in calculation.

Figure 4A depicts the estimated values of N and N^* as a function of the Laponite concentration in the NC gels for Laponite RD (D-AM) and RDS (S-AM). The N^* value is much higher than the corresponding N value for the same NC gel due to the departure from the affine deformation assumption and/or contribution from the

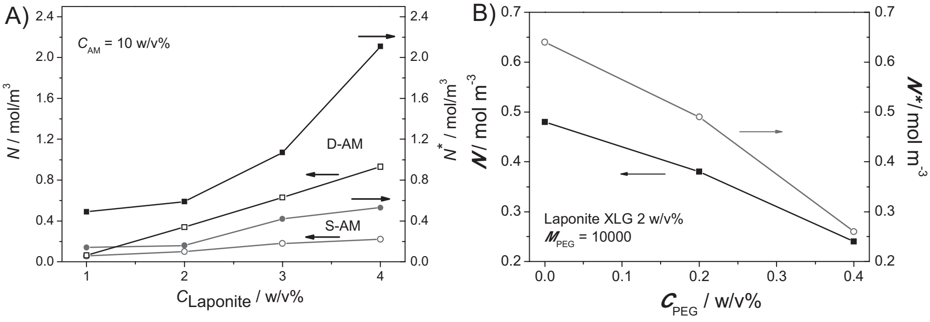

Figure 4.

N and N* values of (A): the PAAm-Laponite NC gels as a function of Laponite concentration; square symbols: with gel-forming clay Laponite RD; circular symbols: with sol-forming clay Laponite RDS and (B) the PNIPAm-Laponite NC gels as a function of added PEG concentration; square symbols: N and circular symbols: N*.

bulk modulus at $\alpha = 2$. Therefore, we rely on the N value for further discussion. For these NC gels, the effective network chain density increased with increasing Laponite concentration, reflecting an increase in the junction number formed by Laponite platelets. The N value of the D-AM gels was higher than that of the corresponding S-AM gels, because of the weak gelation ability of the sol-forming grade clay Laponite RDS.[25]

Adsorption of PEG chains on the Laponite platelets can reduce the binding sites on Laponite surfaces for PNIPAm chain anchoring, thus reduce the effective network chain density in the NC gels. We added PEG with a molecular weight of 10,000 g/mol to the Laponite XLG suspension of 2 w/v%, and then NIPAm monomer of 10 w/v% was in-situ polymerized.[30] Figure 5 illustrates the effect of adsorption of PEG on the tensile strength and elongation at break for these NC gels. According to equation 2 and 3, N and N* were evaluated for the PNIPAm-Laponite NC gels as a function of added PEG concentration and plotted in Figure 4B. N does decreases with increasing PEG in the suspension, indicating that the adsorption of PEG on the Laponite platelets is more preferential than that of PNIPAm.

The N values for the both NC gels (Figure 4 A and B) are in the same order of magnitude about 0.4 mol/m^3. On the other hand, for the chemically cross-linked OR gels, the effective network chain density from the equilibrium shear modulus (about 10 kPa) at 20 °C is about 4.1 mol/m^3 when the cross-linker BIS concentration is 2.77 mol% to the monomer AAm. This is much higher than the N value for the NC gels and endows the chemically cross-linked gel a much lower tensibility. In other words, the low effective network

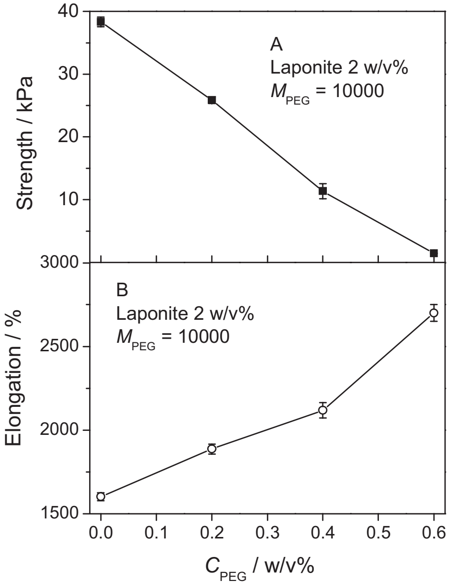

Figure 5.

Tensile strength (A) and elongation at break (B) as a function of added PEG concentration in the PNIPAm-Laponite XLG NC gel with NIPAm of 10 w/v%.[30]

chain density gives the NC gels a high deformability.

Responsive NC Gels

Temperature and pH are most widely used stimulus for the responsive hydrogels. For fabrication of responsive chemical cross-linked hydrogels, the most effective method is to introduce corresponding functional monomers or polymers by copolymerization or interpenetration. Laponite forms a clear and colorless colloidal suspension in water stabilized by the electrostatic repulsive interaction.[34] However, simple addition of ionic components, such as acrylic acid (AA), sodium methacrylate (SMA) or polyelectrolyte to the Laponite suspension will induce the gelation or precipitation. pH and temperature response PNIPAm-Laponite NC gels with a semi-interpenetration network (IPN) structure were reported by Song et al.[27] and Ma et al.[35] Mujumdar et al. prepared the pH-sensitive NC gels by copolymerization of NIPAm and ionizable monomers, such as methacrylic acid (MAA) and SMA.[36] However, these NC gels were not transparent due to the flocculation of Laponite platelets.

In order to introduce ionizable monomers into the NC gels and to maintain their transparency, a stability window of the Laponite suspension during copolymerization is desired. By observing the transmittance and viscosity of Laponite RDS suspensions containing different ionic monomers, we found that the aqueous Laponite RDS suspension containing monomer AAm was stable and transparent within 30 min when the concentration of anionic monomer sodium acrylate (SA) was not beyond 0.15 M in the suspension (Figure 6).

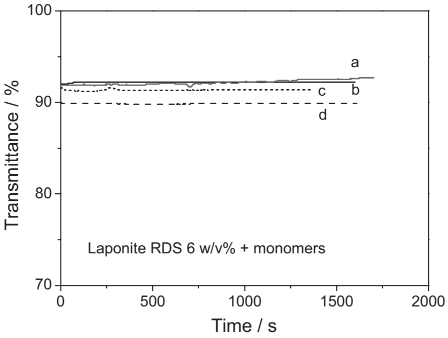

Figure 6.
Transmittance of 6 w/v% Laponite RDS aqueous suspensions with different monomer concentrations: (a) without any monomers, (b) AAm 10 w/v%, (c) (SA + AAm) 10 w/v% with 0.07 M SA, and (d) (SA + AAm) 10 w/v% with 0.15 M SA.[14]

The viscosity change reflects the structure change in the Laponite suspensions. Figure 7A indicates that the viscosity of the Laponite RDS suspension and the suspension containing 10 w/v% AAm is quite low without shear rate dependence, suggesting no physically joints formed in these suspensions. If 0.07 M of anionic monomer SA is added, the suspension viscosity increases because of the aggregates due to the hydrogen bonding and electrostatic interaction. High SA concentration (0.15 M) causes more aggregates in the suspension, exhibiting viscosity decrease with increasing shear rate at 25 °C. Figure 7B shows the viscosity stability of the suspensions. Clearly, we recognize that the Laponite suspensions containing neutral monomers are stable with the ionic monomer SA within 30 min if the SA concentration is not higher than 0.15 M.

In this way, we successfully synthesized PAAm-Laponite NC gels with 11 mol% of SA, named S6SA11 and S6SA11-BIS0.03, the latter contained 0.03 mol% (to all monomers) of cross-linker N,N'-methylenebisacrylamide (BIS). The photos in Figure 8 demonstrate that the NC gel containing SA without BIS is translucent whereas the similar NC gel with a little bit of BIS is very transparent. The introduction of a few amounts of BIS improves the homogeneity of the copolymerized NC gels containing ionic monomers.

The equilibrium swelling volume in pure water increased almost linearly with increasing SA content in the NC gels. The existence of counter ions and electrostatic repulsion between the ionized groups

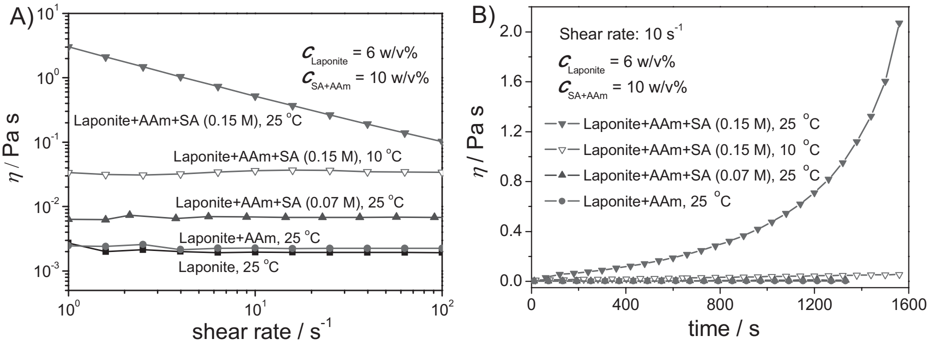

Figure 7.
(A) Shear rate dependence and (B) time dependence of viscosity for the Laponite suspensions just after preparation with indicated AAm and SA concentrations.[14]

enhanced the swelling driving force. When these ionizable NC gels swelled in buffers of different pH, the swelling volume abruptly increased at pH 4 to 5,[14] similar to the swelling of poly(acrylic acid) (PAA) gels.

The pH response of the NC gels containing ionizable SA units was further demonstrated with oscillatory swelling-shrinking behavior (Figure 9). The oscillatory swelling-shrinking behavior of the S6SA11-BIS0.03 gel and OR0.05 gel switched by pH between 7.4 and 3.0 was observed. At pH 7.4, both hydrogels swelled because of ionization of the carboxyl groups, whereas at pH 3.0, they shrunk due to association of the carboxyl groups. The same oscillatory swelling-shrinking behavior for both gels means that the ionic NC gels respond to the pH change as well as the carboxylate hydrogels merely cross-linked with BIS, but the former had ultrahigh tensibility over 2000%.[14]

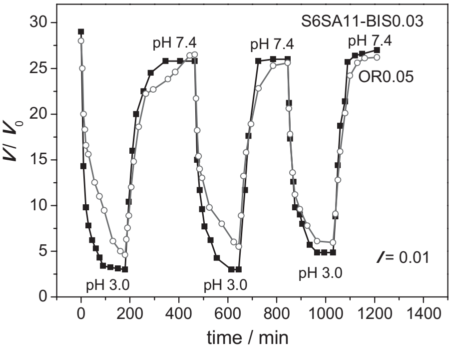

Figure 9.
Oscillatory swelling-shrinking behavior of S6SA11-BIS0.03 gel and BIS cross-linked OR0.05 gel containing 11 mol% of SA upon pH switching between 7.4 and 3.0.[14]

Another anionic monomer SMA was introduced in the PNIPAm-Laponite XLS NC gels through the in situ copolymerization within the stability window. All the ionic NC

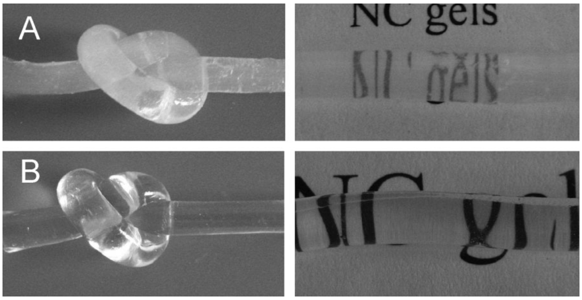

Figure 8.
Appearance of the NC gels: (A) S6SA11 and (B) S6SA11-BIS0.03.[14]

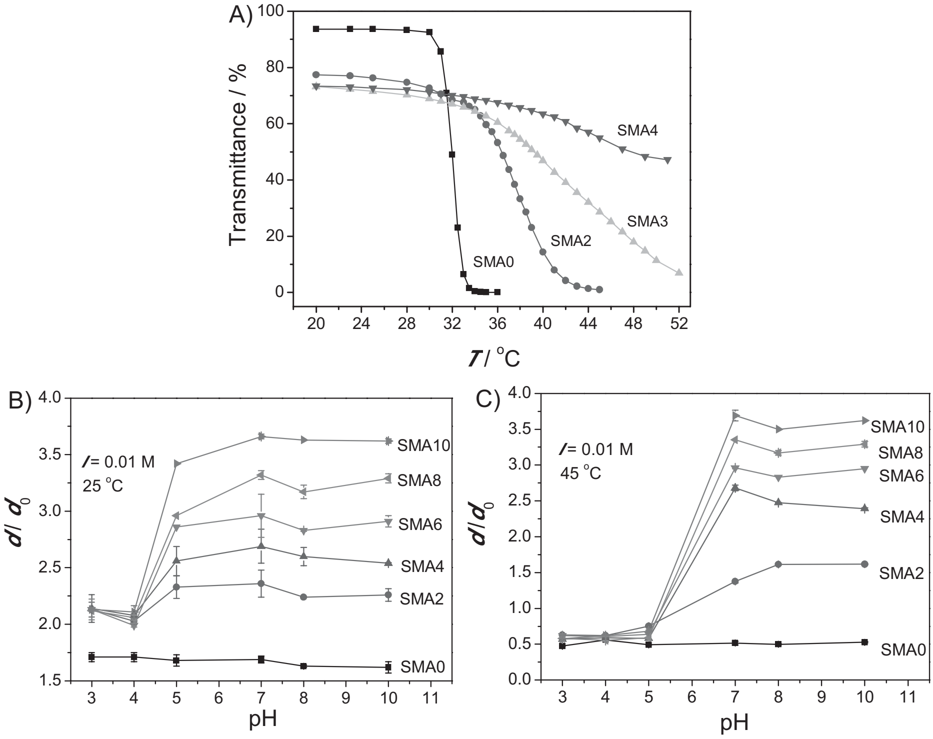

Figure 10.

The temperature dependence of the transmittance for the as-prepared NC gels with different SMA mole percents in the total monomers (A). Swelling ratio expressed by diameter ratio d/d$_0$ of the NC gels in buffers at 25 °C (B) and 45 °C (C).[13]

gels were of high transmittance (~ 80%) and tensibility (the elongation at break is 2500%) at room temperature, manifesting the homogeneous component distribution. Introduction of the monomer SMA into the NC gels also greatly raised the equilibrium swelling volume in pure water. For example, the swelling volume was as high as 1600 times of the original one when 10 mol% SMA was copolymerized.[13] At the same time, the thermo-responsibility of the PNIPAm-Laponite NC gels was retained. Figure 10A depicts the temperature dependence of the transmittance for these anionic NC gels with different SMA concentrations in the as-prepared state. The NC gel containing more SMA units performed a weak temperature response due to the increased hydrophilicity and strong electrostatic repulsion in the gel.

Dual response was found from these PNIPAm-Laponite NC gels with SMA units (Figure 10 B and C). At 25 °C, the swelling ratio increased rapidly with a pH change from 4 to 5 due to the ionization of the carboxyl groups in the NC gels. Then, d/d$_0$ changed slightly, indicating complete ionization of the SMA units. At 45 °C, SMA0 gel without SMA was in shrunk state over the entire pH range because this temperature was higher than the LCST of PNIPAm solution. The other gels containing SMA swelled when pH > 7, even at such a high temperature due to the presence of charged carboxyl groups. For all the gels in low pH buffers (pH < 7), the swelling ratio at 25 °C was always higher than that at 45 °C, suggesting the temperature response of these gels. When the SMA content was low, the temperature response at high pH still existed. Hence, these ionic NC gels have dual response, i.e., swelling and shrinking can be switched by either temperature or pH with precisely controlled SMA content.[13]

Besides the negative chargeable monomers, positively chargeable NC gels were also synthesized by in-situ copolymerization of AAm and 2-(dimethylamino)ethyl methacrylate (DMAEMA) in an aqueous suspension of Laponite XLS within the stability window. When the polymerization was initiated by redox initiator, the DMAEMA amino group served as an accelerator, which resulted in the rapid formation of the NC gel with high heterogeneity. By contrast, when the polymerization was initiated by UV radiation, the reaction proceeded more slowly and the gel formed after 40 min, leading to less heterogeneity in the UV-NC gels. Thus, the UV-NC gels had a higher transparency and better mechanical properties than those of redox initiated ones. The cationic NC gels had high swelling ratio at low pH due to the protonation of the amino groups at the DMAEMA units (Figure 11).[15] When the DMAEMA concentration was higher than 5 mol% in all monomers, the pH-responsive swelling became more distinct. The higher the DMAEMA concentration, the larger was the equilibrium swelling ratio at low pH of $2 \sim 3$. By comparing the swelling ratio of NC gels initiated by redox and UV, the UV-NC gels had a larger swelling ratio than that of redox initiated NC gels.

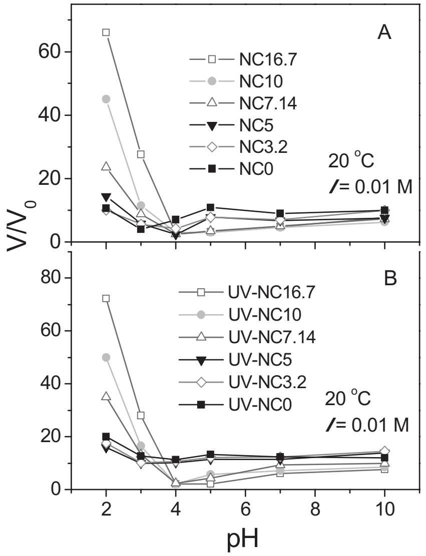

Figure 11.

Equilibrium swelling volume ratio for the AAm and DMAEMA based NC gels in buffers of $I = 0.01\,M$ at 20 °C. (A) Initiated by redox and (B) initiated by UV radiation.[15]

Conclusion

In this short oral presentation at the Polymer Network Group Meeting, we focused on our recent works concerning the mechanical properties and stimuli-response of the NC gels. We have found that the low effective network chain density and moderate relaxation were two of important origins for the NC gels to behave the ultrahigh tensibility. And the stimuli-responsive NC gels were successfully fabricated by copolymerization with ionic monomers within the stability window of the Laponite dispersion. With this knowledge, we are currently attempting to reveal the mystery of the interaction between polymer and Laponite platelets and to optimize the composition of the NC gels for the cell sheet engineering.[37]

The NC gel is a new generation material for a wide variety of applications, especially in the biomedical field for sensors, actuators, devices, and tissues. However, some of the physics and chemistry behind the unique properties of the NC gels are still unknown. And the biological behavior of the NC gel is not sufficiently investigated, such as long-term biocompatibility and controllable biodegradability. At the same time, emerging new techniques strongly supports the understanding of the significant structure-property relations.

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