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Network chain density and relaxation of *in situ* synthesized polyacrylamide/hectorite clay nanocomposite hydrogels with ultrahigh tensibility

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ABSTRACT

Nanocomposite hydrogels (NC gel) D-AM and S-AM were synthesized through *in situ* polymerization of acrylamide (AM) with hectorite clays of Laponite RD and RDS, respectively. The tensile performance of the NC gel was observed at different crosshead speeds and all of the NC gels exhibited an extremely high tensibility, e.g., the elongation at break even higher than 4000%, except for two samples with the lowest Laponite content of 1 w/v%. Strong tensile hysteresis was observed in the elongation–reversion curve, indicating a slow relaxation in the NC gels. Dynamic moduli G' and G'' within linear viscoelasticity illustrated that the network structure was formed in these gels with the junction of Laponite platelets. The Laponite RD showed stronger gelation capability than the tetrasodium pyrophosphate modified Laponite RDS. The relaxation modulus $G(t)$ for the NC gels was found to be similar to the slow rubber relaxation with the critical exponent n of about 0.16, much lower than 0.66–0.71 for the critical gel at the sol–gel transition. In comparison, the chemically cross-linked hydrogel showed almost no relaxation during the same time interval. The effective network chain density of the NC gel was determined from equilibrium shear modulus, which was evidently lower than that of the chemically cross-linked hydrogels. The present results reveal that the high deformability of these NC gels comes from their low effective network chain density with moderate relaxation.

1. Introduction

Polymer gels have been widely studied as unique smart materials for several decades. However, two fatal defects restrict their applications: low response rate and weak mechanical strength. Recently, Haraguchi and Takehisa reported a novel polymer–clay nanocomposite hydrogel (NC gel), which was fabricated by *in situ* polymerization of *N*-isopropylacrylamide (NIPAm) in aqueous suspension of hectorite clay Laponite [1]. The Laponite acted as the cross-linker in the NC gel and the NC gel exhibited extraordinarily high tensibility with high transparency, such as high ultimate strength (10 times larger than that of the chemically cross-linked hydrogel (OR gel)), high elongation (about 1300%, 50 times larger than that of the OR gel) [1]. They intensively investigated the transparency and mechanical performance and found partially reversible deformation, abnormal necking from the NC gels containing the clay even up to 25 mol% [2–9]. The layered porous structure was observed from dried NC gel [10] and abnormally hydrophobic surface was obtained on this NC gel [11]. This unique NC gel was found useful in cell cultivation for the easy separation from the cell sheet [12]. Highly deformable NC gel was also realized with polyacrylamide (PAM) synthesized in the hectorite clay suspension, showing elongation up to 2800% [13].

The origin of the high strength and deformability becomes an interesting mystery, which has recently motivated many investigations focusing on the NC gel structure. The gel heterogeneity was found to become dominant by increasing the clay concentration but the chain dynamics of the NC gel was similar to that in the conventional OR gel [14]. In deformed NC gels, the clay platelets, embedded in the PNIPA network and screening the concentration fluctuation, were highly aligned with their surface normals parallel to the stretching direction and the PNIPA chains were elongated parallel to the stretching direction, showing the "plane cross-linking" effect [15,16]. Two correlation lengths were discovered from the NC gel: the larger one around 200–250 nm was related to the kinetic rearrangement of the clay particles and the smaller one was similar to that in the OR gel [17]. By adopting the nonergodic method, the thermal fluctuation of the clay platelets in the NC gel was found to be largely suppressed upon network formation [18].

The most important structure factor governing the high deformability of the NC gel is the effective network chain density. Haraguchi et al. evaluated the network chain density N^* and molecular weight M_c of the cross-linked chain thread according to

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Table 1
Mechanical properties and structure parameters of the NC gels with different Laponite contents[a]

Hydrogel	Tensile strength (kPa)	Elongation (%)	G_e[b] (Pa)	N[c] (mol/m^3)	τ ($\alpha = 2$) (kPa)	N^*[d] (mol/m^3)
D1AM10	4.44	1310	158	0.063	2.17	0.49
D2AM10	7.43	4210	854	0.34	2.62	0.59
D3AM10	46.1	2690	1580	0.63	4.71	1.07
D4AM10	110	2650	2360	0.93	9.29	2.11
S1AM10	4.47	1320	144	0.057	0.62	0.14
S2AM10	3.97	4900	245	0.10	0.69	0.16
S3AM10	19.7	4590	457	0.18	1.84	0.42
S4AM10	28.1	3850	549	0.22	2.34	0.53
S10AM10	107	4070	–	–	–	–

[a] The tensile strength and elongation obtained at the crosshead speed of 100 mm/min.
[b] The equilibrium shear modulus determined from rheology measurements.
[c] The effective network chain density determined from equilibrium shear modulus.
[d] The effective network chain density determined from tensile detection.

the tensile stress at the elongation ratio of 2 [2,3]. Determination of N^* was under the assumptions of affine deformation and volume incompressibility (i.e., Poisson's ratio = 0.5) during the tensile measurement. On the other hand, the functionality of a clay platelet, unlike a chemical cross-linker, may change with reactive conditions. Therefore, the network chain density is desired to be determined within the framework of rubber elasticity under small deformation.

In the present work, two kinds of the NC gel with ultrahigh elongation (>4000%) were prepared and their effective network chain density was determined with dynamic shearing deformation at small strain within the linear viscoelasticity region. Furthermore, the chain relaxation in the NC gel during elongation at high tensibility was investigated at different deformation rates and discussed with the help of relaxation exponent *n*.

2. Experimental

2.1. Materials

Acrylamide (AM) and potassium peroxydisulfate ($K_2S_2O_8$) were analysis grade reagents and purified by recrystallization from deionized water and dried under vacuum at room temperature. Synthetic hectorite clays Laponite RD and Laponite RDS (Rockwood Ltd.) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED, Sinopharm Group Chemical Reagent Co. Ltd.) were used as-received. Milli-Q ultrapure water was used in all the experiments and argon gas was bubbled into the purified water for more than 1 h prior to use.

2.2. Synthesis of nanocomposite hydrogels

The PAM–Laponite nanocomposite (NC) gel was synthesized through *in situ* free radical polymerization of AM in the aqueous suspension of Laponite. The Laponite suspension was prepared by dispersing in pure water at desired concentration under stirring for at least 4 h. The monomer AM, catalyst (TEMED), and the aqueous solution of initiator $K_2S_2O_8$ (20 mg/mL) were subsequently added to the Laponite suspension under stirring. In all cases, the mole ratio of monomer:initiator:catalyst was kept at 100:0.263:0.453. The monomer concentration was varied from 1 to 25 w/v% and the Laponite concentration was changed from 1 to 10 w/v%. The free radical polymerization was allowed to proceed in a water bath at 30 °C for 72 h. The NC gel was formed in two shapes of glass vessels: a column of 25 mm diameter × 1.5 mm thickness for rheology measurement and a rod of 6.0 mm diameter × 80 mm length for tensile measurement.

In this paper, the NC gel was referred to as S-AM gel coded with SmAMn and D-AM gel coded with DmAMn, where S and D stand for Laponite RDS and Laponite RD, respectively, and *m* and *n* stand for 100 × clay/water (w/v) and 100 × monomer/water (w/v), respectively. For example, S10AM10 means a PAM–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 PAM hydrogel cross-linked by *N*,*N*′-methylenebisacrylamide (BIS) of 0.8 mol% of the monomer AM concentration, referred to as OR0.8, was prepared for reference.

2.3. Mechanical measurements

Tensile strength was measured on the as-synthesized NC gel of 6.0 mm diameter × 80 mm length with a Zwick Roell testing system at 30 °C. The sample length between the jaws was 20 mm and the tensile experiment was carried out at crosshead speed of 100, 1000, and 2000 mm/min, respectively. The tensile strain induced was taken as the change in length relative to the initial length of the specimen. The tensile strength was estimated on the area of the initial cross-section. The hysteresis was measured on the as-synthesized NC gel under the same conditions, except that

Table 2
Mechanical properties and structural parameters of the NC gels with different monomer contents[a]

Hydrogel	Tensile strength (kPa)	Elongation (%)	G_e[b] (Pa)	N[c] (mol/m^3)	τ ($\alpha = 2$) (kPa)	N^*[d] (mol/m^3)
D2AM10	7.43	4210	854	0.34	2.62	0.59
D2AM15	9.65	3770	907	0.36	3.59	0.81
D2AM20	35.1	2700	1490	0.59	8.57	1.94
D2AM22	94.3	3220	3840	1.52	18.0	4.09
D2AM25	117	3410	5760	2.28	34.1	7.73
S2AM10	3.97	4900	245	0.10	0.69	0.16
S2AM15	5.65	4290	308	0.12	1.43	0.32
S2AM20	30.7	3240	723	0.29	7.70	1.75
S2AM22	58.0	2990	3790	1.50	15.8	3.58
S2AM25	88.4	4730	4540	1.80	22.2	5.03

[a] The tensile strength and elongation obtained at the crosshead speed of 100 mm/min.
[b] The equilibrium shear modulus determined from rheology measurements.
[c] The effective network chain density determined from equilibrium shear modulus.
[d] The effective network chain density determined from tensile detection.

the strain was restricted at 1600%. The crosshead speed for the tensile and retraction was fixed at 100 mm/min.

Dynamic moduli were measured on the as-synthesized NC gel to evaluate the network chain density with a strain controlled rheometer ARES-RFS (TA) using parallel plates of diameter of 25 mm. The gel sample stuck the fixture well without slippage. Silicone oil was laid on the edge of the fixture plates to prevent solvent evaporation. First, the dynamic strain sweep was carried out at angular frequency of 1 rad/s to determine the linear visco-elasticity region. Then, the frequency sweep was performed over the frequency range from 0.001 to 100 rad/s. The stress relaxation measurement was performed at a constant shear strain of 0.5%. All rheology measurements were carried out at 30 ± 0.1 °C controlled by a Peltier plate.

3. Results and discussion

3.1. *Ultrahigh tensibility of nanocomposite hydrogels*

At first, we measured the tensile strength and elongation at break of the D-AM (A) and S-AM (B) gels to confirm their ultrahigh tensibility and Tables 1 and 2 summarize the results for the NC gels with different compositions. For the NC gels containing clay of 1 w/v% or less, the strength was too low to bear high elongation. When the Laponite RD content was higher than 4 w/v%, high viscosity of the aqueous suspension became a hindrance to prepare homogeneous gels. Therefore, we did not prepare D-AM gels with Laponite RD higher than 4 w/v%. All samples in Tables 1 and 2, except D1AM10 and S1AM10, exhibit extremely high tensibility,

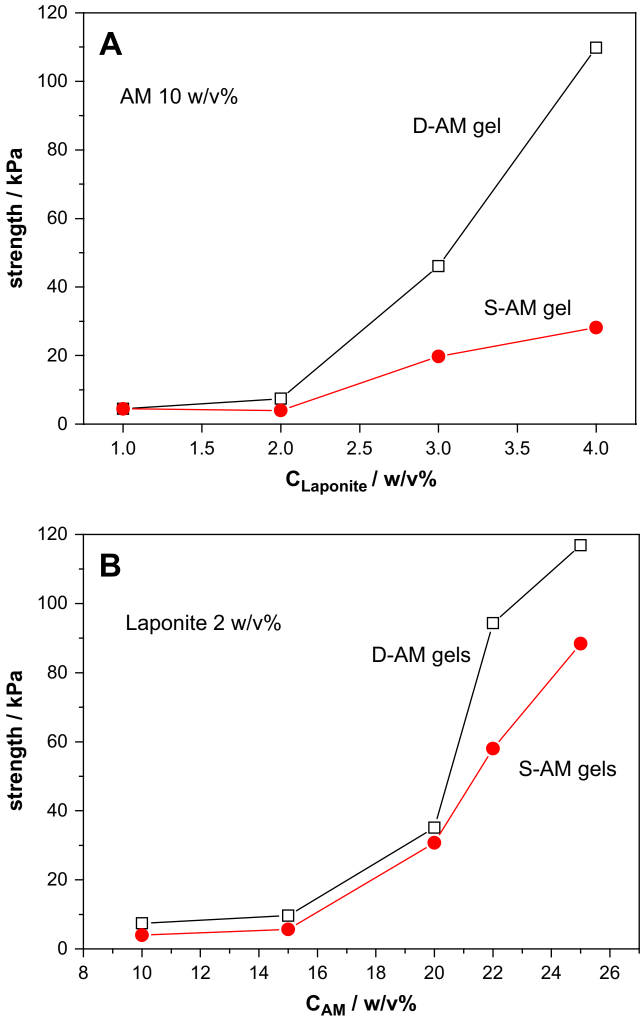

Fig. 1. Change of tensile strength at break as a function of Laponite content at a constant AM content of 10 w/v% (A) and as a function of monomer content at a constant clay content of 2 w/v% (B) for the NC gels: D-AM gels (open squares) and S-AM gels (solid circles).

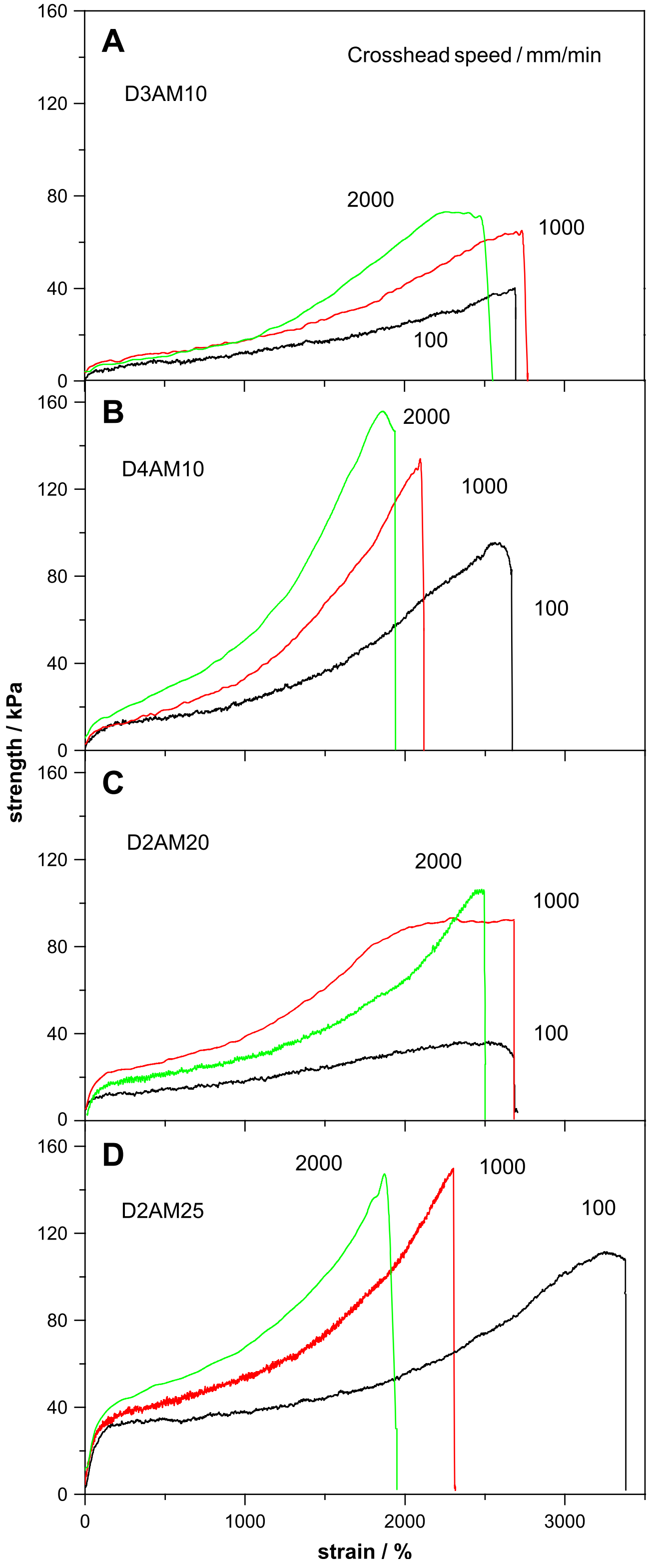

Fig. 2. Stress–strain curves for elongation of the NC gels with the indicated composition at indicated crosshead speed.

even higher than 4000%, which is the highest value reported up to now [13].

Fig. 1 depicts the tensile strength as a function of Laponite and monomer concentrations for the NC gels. One can see from Fig. 1A that the tensile strength of the D-AM gels increases dramatically with increasing Laponite concentration C_{Laponite} when it is higher than 2 w/v%. For example, the strength is only 7.43 kPa for D2AM10 and increases to 110 kPa for D4AM10. In contrast, the tensile strength for the S-AM gels increases gradually with raising Laponite concentration, becoming much lower than that of the D-AM gel at the same Laponite concentration. For comparison, the strength of D4AM10 with 4 w/v% of Laponite RD is 110 kPa, approaching to the value of 107 kPa for the S10AM10 gel containing 10 w/v% (Table 1) of Laponite RDS. This is due to the different charge states for the Laponite RD and RDS platelet surfaces, which will be discussed later.

Fig. 1B illustrates the AM concentration C_{AM} dependence of the tensile strength for the NC gels with the same clay content of 2 w/v%. The strength increases with increasing C_{AM} in the observed C_{AM} range. When $C_{\mathrm{AM}} \leq 20$ w/v%, the tensile strength for these NC gels is similar, almost independent of the clay category. When $C_{\mathrm{AM}} > 20$ w/v%, the D-AM gels start to exhibit higher tensile strength than the S-AM gels due to the higher gelation capability of the Laponite RD than Laponite RDS.

The Laponite RD platelet has strongly negatively charged surfaces and a weakly positively charged rim in aqueous dispersion [19–22]. While, the Laponite RDS platelet, similar to Laponite RD in structure, is modified by tetrasodium pyrophosphate ($Na_4P_2O_7$), consequently having negative charges at both surfaces and edges [23]. Therefore, the Laponite RD is easy to form the “house-of-cards” structure when dispersed in aqueous medium due to the coexistence of electrostatic repulsion and attraction among the clay platelets [24–26]. The aqueous suspension of Laponite RD without polymer can form a gel when its concentration exceeds 3 w/v% [27]. The Laponite RD platelets form effective cross-linking junctions in some *in situ* polymerized hybrid hydrogels [17]. As known from Table 1, strong gels of the Laponite RD appear when $C_{\mathrm{Laponite}} > 2$ w/v% for our *in situ* polymerized NC gels. But, much higher AM concentration is required for constructing strong hydrogels if $C_{\mathrm{Laponite}} = 2$ w/v% (Table 2). At the same time, the surface modification of clay platelets with pyrophosphate (Laponite RDS) changes the interaction between the PAM and clay platelets, consequently changing the gel strength.

Fig. 2 illustrates the stress–strain curves of elongation for the D-AM gels at crosshead speed of 100, 1000, and 2000 mm/min, corresponding to the maximum strain rate of about 0.08, 0.83, and 1.67 s^{-1}. When either the Laponite content or monomer concentration is high (e.g., D4AM10 and D2AM25), the gel becomes harder with increasing the crosshead speed, showing a decreased tensibility and increased tensile strength. While, for the gels of D3AM10 and D2AM20 with lower Laponite or monomer content, the tensibility is almost independent of the crosshead speed and the strength is much lower than that of the D4AM10 and D2AM25. This is the competition result of the stretching orientation and relaxation for

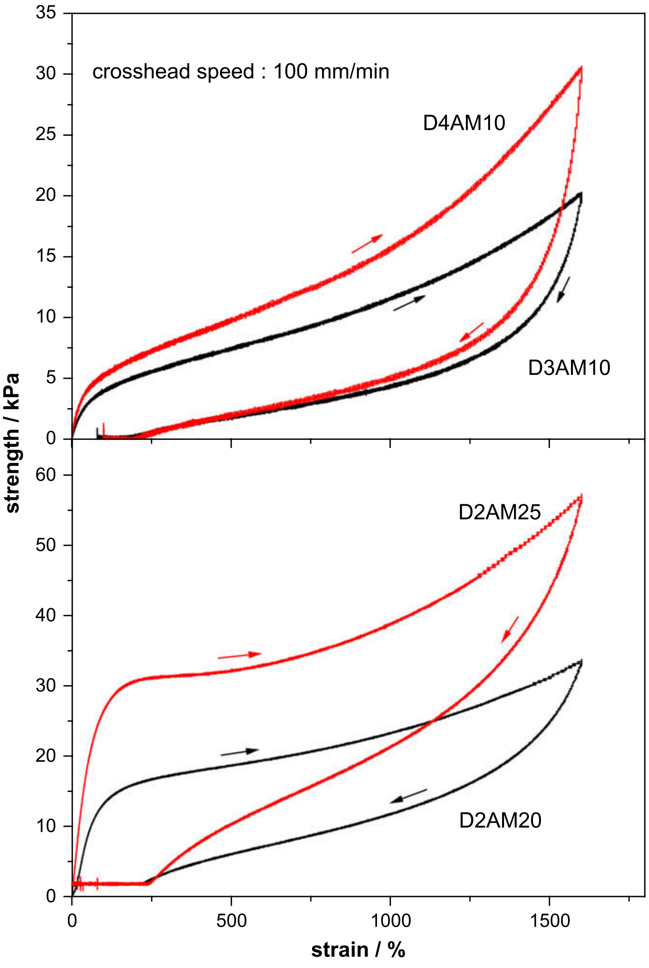

Fig. 3. Stress–strain curves for elongation–recovery of the indicated NC gels.

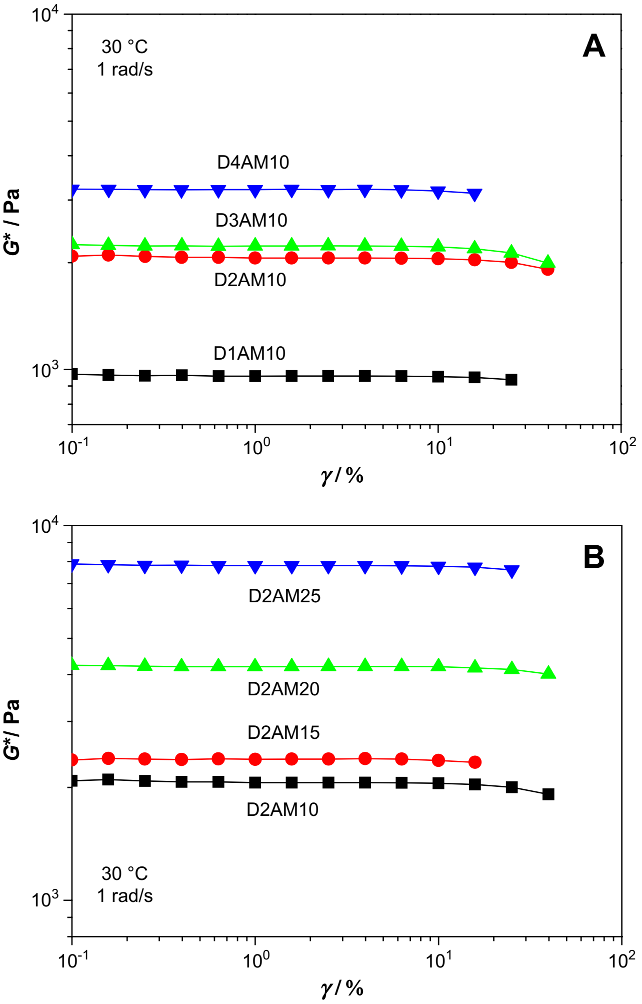

Fig. 4. Shear strain γ dependence of absolute value of the complex modulus G^* for the indicated D-AM gels at 30 °C and $\omega = 1$ rad/s.

the network chains cross-linked with Laponite platelets. According to the NC gel structure model proposed by Shibayama et al., the molecular chains bridging neighboring clay platelets are very long with lots of effective cross-links [15]. For the gels D3AM10 and D2AM20, the chain is longer due to lower cross-link density N (shown in Tables 1 and 2, will be discussed later), so that the chain can relax the stretching stress and avoid break. On the other hand, the chain is shorter for the gels D4AM10 and D2AM25 with higher cross-link density N. When the deformation is faster than the chain relaxation, the sample will break at lower elongation ratio.

When the NC gels were stretched to 1600% well below the macroscopic rupture strain and reverted at the same speed, a hysteresis in the stress–strain curve was observed. Fig. 3 shows that the tensile hysteresis is strong for the D-AM gels. Moreover, the hysteresis represented by the enveloped area is more significant when either the Laponite content or monomer concentration is high (e.g., D4AM10 or D2AM25). This is due to their higher cross-link density, in consistent with that found from Fig. 2. The ultrahigh tensibility of our NC gels reflects the adjustment of the orientation of the network strands and the distribution of physical cross-links, which seems to be the origin of such a strong tensile hysteresis.

3.2. *Viscoelasticity of nanocomposite hydrogels*

In order to determine the linear viscoelasticity region, the shear strain γ dependence of the complex modulus G^* was tested at 30 °C

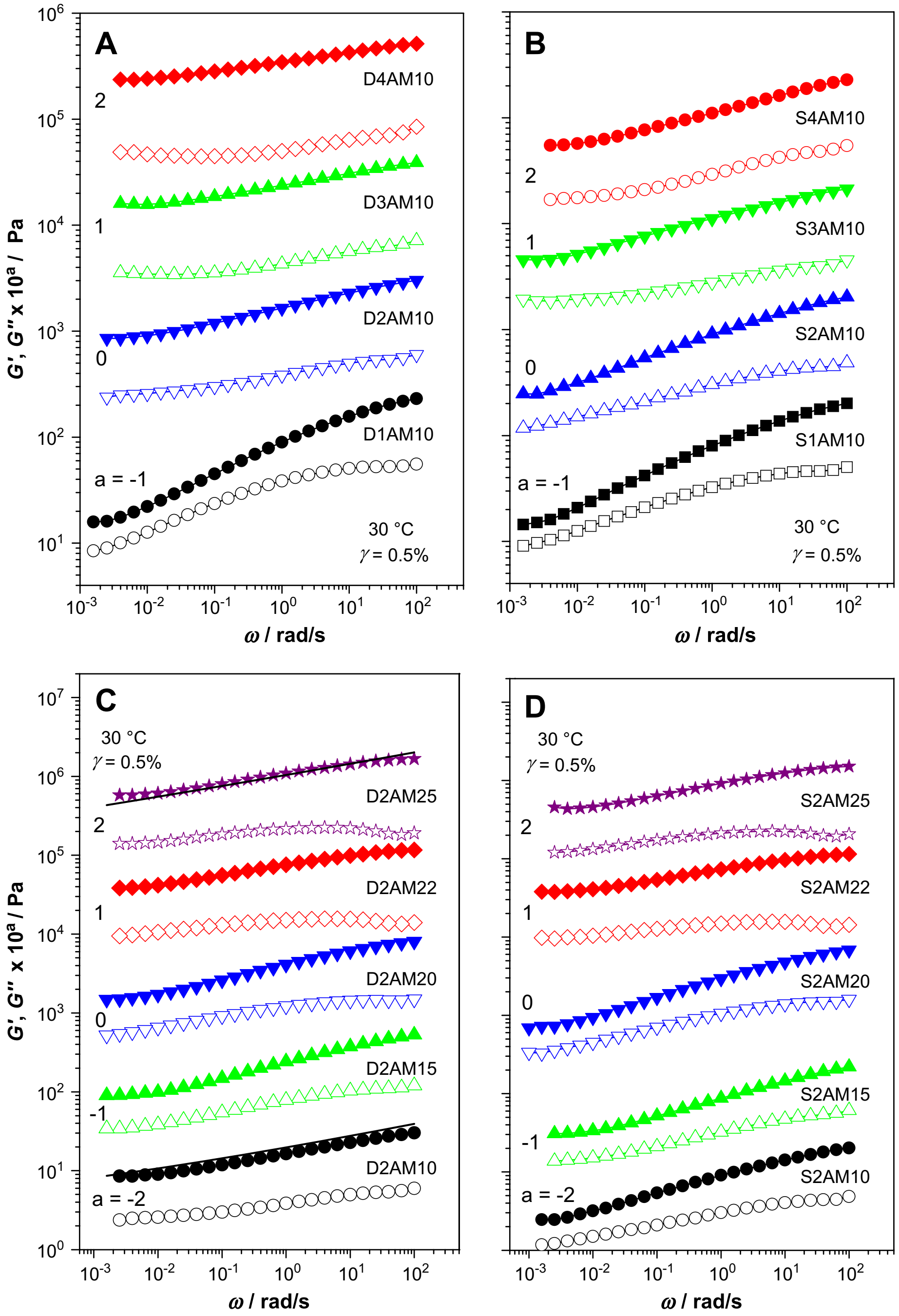

Fig. 5. Angular frequency ω dependence of storage modulus G' (solid symbol) and loss modulus G'' (open symbol) at 30 °C for the NC gels of D-AM (A), S-AM (B) with different clay contents and D-AM (C), S-AM (D) with different monomer AM contents. Data have been vertically shifted by a factor of 10^a with given a to avoid overlapping. Solid curves in (C) are calculated from the relaxation modulus $G(t)$ using Eq. (2).

and 1 rad/s for the NC gels. Fig. 4 demonstrates the results for the D-AM gels with various concentrations of clay (A) and monomer (B). The absolute value of G^* increases with raising clay and monomer concentrations, in consistent with the change of tensile strength in Tables 1 and 2. The absolute value of G^* is independent of γ over the range from 0.1 to 10% for all the samples. Therefore, all the viscoelasticity measurements were carried out at $\gamma = 0.5\%$ to ensure availability of the linear viscoelasticity and enough sensitivity.

Fig. 5 depicts angular frequency ω dependence of the storage modulus G' and loss modulus G'' for the NC gels with different clay and monomer concentrations. G' is always higher than G'' over the observed frequency range and importantly G' appears as a plateau in low frequency range for all the NC gels. This indicates that cross-linked networks have been already formed in these gels.

Fig. 5A and B illustrates the dynamic moduli varying with clay content at constant AM concentration of 10 w/v% for the D-AM gels (A) and S-AM gels (B), respectively. Increasing clay concentration leads to an increase in G' and G'', resulting in a more obvious plateau. Furthermore, G' of the D-AM gel is higher than that of the S-AM gel with the same composition, suggesting that the network of the D-AM gels is more perfect with higher elasticity than that of the S-AM gels. When the clay concentration is 1 w/v%, the G' value is very small and the plateau in the G' vs. ω curve appears at very low frequency. This indicates that only a weak network is formed in the gels D1AM10 and S1AM10, producing very low tensile strength and elongation.

Fig. 5C and D represents that the dynamic moduli at a constant clay concentration of 2 w/v% increase with increasing monomer concentration, especially when $C_{AM} \geq 15$ w/v%. However, the plateau region appears at almost the same frequency region for these gels with the same clay concentration. And the curves of G' vs. ω are almost parallel for these gels with the same clay concentration but different AM concentrations. The above facts imply again that the Laponite platelet does act as the cross-link in these NC gels.

Fig. 6 displays the relaxation modulus $G(t)$ of the NC gels as a function of observing time compared with that of the BIS cross-linked gel OR0.8. $G(t)$ decreases with time following a downward curve but never goes to zero over the test duration, irrespective of concentrations of clay and monomer. On the contrary, the relaxation was not observed from the OR0.8 gel. This means that the polymer chains cross-linked by Laponite platelets can be partially relaxed during the observing time. The $G(t)$ data here are in consistent with G' in Fig. 5 for the same NC gel. For example, G' for the D2AM25 is about 5.6 kPa at 2×10^{-3} rad/s, while its $G(t)$ is 5.3 and 3.8 kPa at 500 and 6000 s, respectively, reasonably reflecting the relaxation.

We fit the relaxation curve with the following equation [28,29] and estimated the exponent n.

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

Here, G_e is the equilibrium modulus, λ_0 is a material-dependent time constant. In order to check the availability of this equation, the storage modulus $G'(\omega)$ was derivated through the Fourier transform of Eq. (1) as

$$G'(\omega) = G_e + G_e\lambda_0^n\omega^n\Gamma(1-n)\cos\left(\frac{n\pi}{2}\right) \tag{2}$$

where $\Gamma(m)$ is the gamma function of m. For the D2M25 and D2AM10 gels, the calculated $G'(\omega)$ in Fig. 5C almost quantitatively predicts the observed $G'(\omega)$.

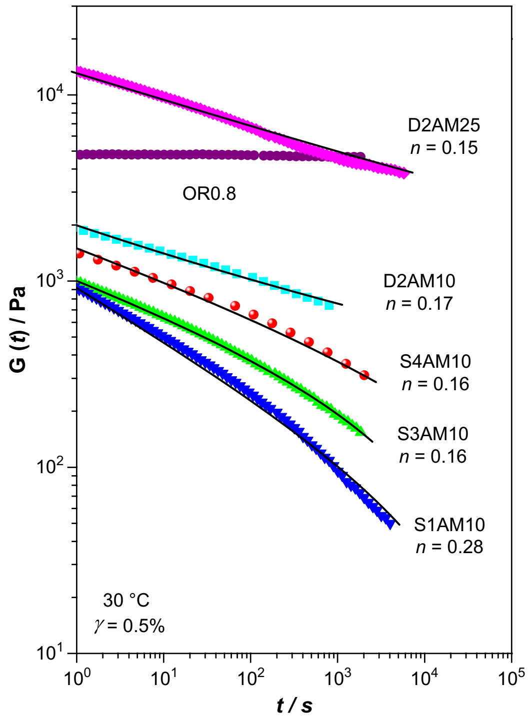

Fig. 6. Relaxation modulus $G(t)$ of the NC gels compared with the BIS cross-linked OR0.8 gel. The solid lines: fit by Eq. (1) with indicated n.

For the NC gels shown in Fig. 6, the n value is 0.15–0.17, except for the S1AM10. For the S1AM10 gel with the lowest Laponite concentration, the cross-link is so weak that the relaxation is somewhat fast. This relaxation mode is similar to $G(t) = St^{-n}$ for the critical gel [29] but the n value is much smaller than that of 0.66–0.71 for the critical gel. Thirion and Chasset estimated the n value in between 0.12 and 0.17 based on Eq. (1) for natural rubber [28]. The above facts denote that the network chain relaxation in the NC gels is similar to that of the cross-linked nature rubber, much slower than that of the critical gel at the sol–gel transition but much faster than that of the completely cross-linked OR0.8 gel. This moderate relaxation allows the network chains bridging neighboring Laponite platelets to adjust their orientation and distribution, endowing the NC gels high tensibility. Therefore, the D2AM25 gel with a low n exhibits an evident stretching speed dependence in Fig. 2D and a strong tensile hysteresis in Fig. 3 due to its slow relaxation process.

3.3. Effective network chain density

In order to understand the ultrahigh tensibility of the NC gel, we determined the network chain density from the equilibrium shear modulus based on the rubber elasticity at small deformation of 0.5% strain to ensure availability of the assumptions in the theory. The effective network chain density N in hydrogels is related to the equilibrium shear modulus G_e as in Refs. [17,30,31].

$$G_e = NRT \tag{3}$$

Here, G_e was taken from the plateau modulus at G' vs. ω curves where the plateau appeared and loss modulus G'' was much smaller than G'. R and T are the gas constant and absolute temperature, respectively. The estimated N values are listed in Tables 1 and 2 together with the G_e values.

For comparison, we also estimated the network chain density based on the elongation data following the way reported in the literature [2,3]. For elongation, the effective network chain density N^* is evaluated from the tensile stress τ and elongation ratio α on the assumption of affine deformation and incompressible volume [2,3,30].

$$\tau = N^* RT\left[\alpha - (1/\alpha)^2\right] \tag{4}$$

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. The estimated N^* values are also listed in Tables 1 and 2.

We demonstrate the effective network chain density N and N^* for the as-prepared NC gels in Fig. 7. The data obtained from two methods show a similar trend for varying with the concentration of either clay or monomer. The effective network chain density increases with increasing clay concentration due to an increase in the junction number formed by Laponite platelets (Fig. 7A). Both N and N^* are higher for the D-AM gels than those for the corresponding S-AM gels, leading to a low tensibility for the D-AM gels, because of the higher cross-link functionality of the Laponite RD than the Laponite RDS.

However, the N^* value from the tensile experiment is much higher than the corresponding N value from the equilibrium shear modulus for the same NC gel. There are two possible reasons for this deviation: The strain of 100% ($\alpha = 2$) used in the tensile experiment is much larger than that of $\gamma = 0.5\%$ used in the shearing measurement, the former seems to cause a departure from the affine deformation assumption. Another reason is the contribution from volume compression when $\alpha \geq 2$ [15]. Therefore, the N value from the linear response to the small shear deformation is more reliable.

It is surprising that the effective network chain density increases also with the monomer concentration (Fig. 7B), instead of expected decrease. This means an increase in the cross-linking functionality of the Laponite platelets. In other words, the number of network chains connected by one Laponite platelet increased. Therefore, increasing monomer concentration at constant Laponite content results in that more network chains are formed within per unit volume cross-linked by the Laponite platelets.

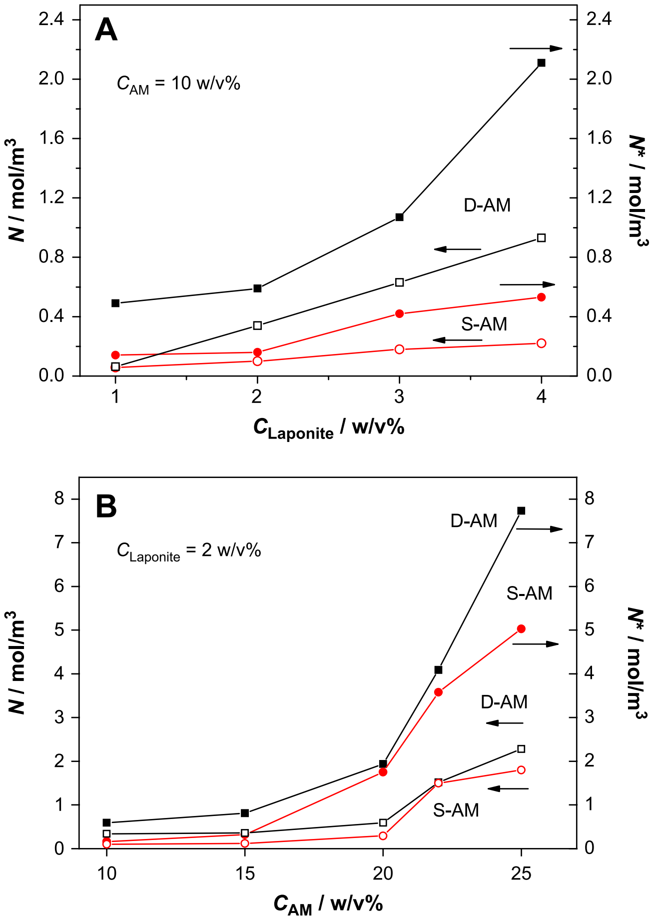

Fig. 7. The effective network chain density N^* determined from tensile stress (solid symbols) and N from equilibrium modulus (open symbols) varying with Laponite concentration $C_{Laponite}$ at constant AM concentration C_{AM} of 10 w/v% (A) and with C_{AM} at constant $C_{Laponite}$ of 2 w/v% (B) for the D-AM gels (squares) and S-AM gels (circles).

For the OR gel, we estimated its effective network chain density from the literature data of equilibrium shear modulus. When the BIS concentration is 2.77 mol% of the monomer AM, the effective network chain density from the equilibrium shear modulus of about 10 kPa at 20 °C is about 4.10 mol/m^3 [32]. This is much higher than the N values for the D-AM and S-AM gels and endows the BIS cross-linked gel a much lower tensibility.

Haraguchi et al. [2] estimated the effective network density N^* based on the tensile deformation for the PNIPAm–Laponite XLG gel NC3 as 0.88 mol/m^3, which was higher than 0.59 mol/m^3 for the D2AM10 gel having similar composition. Okay and Oppermann [31] estimated the effective network density N from the final elastic modulus G'_∞ as about 10 mol/m^3 for the dry NC gel with 4 w/v% of Laponite RDS and 5 w/v% of AM, which was equal to about 0.5 mol/m^3 for the as-prepared gel (The polymer volume fraction was calculated from the initial monomer concentration [33].) This value is comparable with the present data determined from the S-AM gels having similar composition.

4. Conclusions

Nanocomposite hydrogels D-AM and S-AM were synthesized through *in situ* polymerization of AM with Laponite RD and RDS, respectively. All of them, except D1AM10 and S1AM10 with the lowest Laponite content, exhibited an extremely high tensibility (e.g., the elongation at break even higher than 4000%). Dynamic moduli within linear viscoelasticity illustrated that the network structure was formed in these gels with the junction of the Laponite platelets. The Laponite RD had stronger gelation capacity than the tetrasodium pyrophosphate modified Laponite RDS. The relaxation modulus $G(t)$ for these gels was found to be similar to the slow rubber relaxation with the critical exponent n of about 0.16, much lower than 0.66–0.71 for the critical gel at the sol–gel transition. In comparison, the chemically cross-linked gel showed almost no relaxation during the same time interval. The effective network chain density of these gels determined from equilibrium shear modulus was evidently lower than that of the chemically cross-linked hydrogels. The present results reveal that the high deformability of these NC gels comes from their low effective network chain density with moderate relaxation.

Acknowledgements

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