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

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A B S T R A C T

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.