



# Swelling and mechanical behavior of poly(*N*-isopropylacrylamide)/Na-montmorillonite layered silicates composite gels

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## Abstract

Clay–polymer hydrogel composites have been synthesized based on poly(*N*-isopropylacrylamide) (PNIPAM) gels containing 0.25–4 wt% of the expandable smectic clay Na-montmorillonite layered silicates (Na-MLS). The morphology of the composite gels has been studied using a polarized optical microscope. The size of Na-MLS aggregates increases with Na-MLS concentration. The swelling ratio of the Na-MLS/PNIPAM composite in water is increased at the low Na-MLS concentration but decreases as the concentration increases. Correspondingly, the shear modulus of the gel is found to exhibit a distinct minimum against clay concentration. For Na-MLS concentrations ranging from 2.0 to 3.2 wt%, the composite gels have larger swelling ratio and stronger mechanical strength than those for a pure PNIPAM. The presence of Na-MLS does not affect the value of the lower critical solution temperature (LCST) of the PNIPAM. However, the gel volume change at the LCST is first increased and then decreased upon the increase of the Na-MLS. No pH induced phase transition is observed for the Na-MLS/PNIPAM composites. The experimental results can be explained by considering that Na-MLS is physically entrapped inside rather than chemically bonded into the gel.

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## 1. Introduction

Gels are crosslinked polymer networks swollen in a liquid medium. The liquid inside the gel allows diffusion of some solute molecules, while the polymer network serves as a matrix to hold the liquid together. Poly(*N*-isopropylacrylamide) (PNIPAM) gel is a temperature sensitive gel exhibiting the volume phase transition at approximately 34 °C [1,2]. Below this volume phase transition temperature,  $T_c$ , the gel swells and it shrinks as the temperature is raised. On the other hand, un-crosslinked PNIPAM polymer chains in water exhibit low critical solution temperature behavior. The temperature sensitivity of the PNIPAM gel has attracted considerable attention in recent years due to both fundamental and technological interest [3–10]. The PNIPAM and its derivatives have potential applications for controlled drug delivery, chemical separation, sensors and actuators.

Swelling and mechanical properties of PNIPAM gels

have been investigated intensively [2,11,12]. It has been found that increasing crosslinker concentration can enhance PNIPAM mechanical strength [13]. However, a large amount of crosslinkers could result in the shift of the volume transition temperature and in the reduction of swelling capability [14,15]. It is well known that the properties of gels can be significantly enhanced by incorporation of inorganic ordered systems, in particular clays, into the gels [16–19]. As a model system, sodium montmorillonite layered silicates (Na-MLS) are widely used as an additive for plastics to improve their physical properties. The chemical structure of the Na-MLS has been reported [20].

It has been found that incorporating clay into poly-(acrylamide) gel enhanced the gels elastic modulus while exhibiting no significant improvement in its swelling ability [17]. PNIPAM/Na-MLS composite materials have been made with high Na-MLS concentrations (above 3.5 wt%) and their swelling behavior as a function of temperature has been studied [18]. However, the potential of low content Na-MLS (less than 3.5 wt%) on the swelling ratio, the volume phase transition temperature and shear modulus of

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the PNIPAM gel has not been investigated so far. In this article, we present the results of the swelling and elastic properties of a series of PNIPAM composites with Na-MLS concentrations ranging from 0.25 to 4.0 wt%.

## 2. Experimental

### 2.1. Sample preparation

The gels were prepared by free radical copolymerization of monomers in aqueous suspensions of Na-MLS (Southern Clay Products, Texas). A series of gel disks and filaments were made, respectively, for shear modulus and swelling ratio measurements. 0.2 g Na-MLS was first suspended in 20 ml water thoroughly under ultrasonic irradiation. Then, 1.56 g *N*-isopropylacrylamide (NIPAM), 26.6 mg methylene-bis-acrylamide (BIS) as crosslinker, and 48  $\mu$ l tetramethyl-ethylene-diamine as an accelerator were dissolved in 20 ml Na-MLS water suspension at 21 °C. The solution was bubbled with nitrogen gas for 30 min to remove dissolved oxygen. The polymerization was initiated by adding 8 mg ammonium persulfate (APS). Three micro-liter glass capillaries with an inner diameter of 0.269 mm were inserted into the solution. The solution climbed along the capillary tubing due to the high surface tension. After 24 h, the micro capillaries were drawn out carefully from gelled PNIPAM. The PNIPAM filaments were obtained by carefully breaking the capillaries in de-ionized water. To make the transparent PNIPAM gel filaments more easily identifiable, they were dyed with brilliant blue. This sticks to the filament surface without changing the gel properties. The gel disks were made in the glass test vials having a diameter of 2.54 cm. The synthetic chemical compositions were the same as described above. The vial was then broken carefully and a thin copper thread was used to cut the gel into a series of 1 mm-thick disks. The gel disks were kept in distilled water for the shear modulus measurement. The same procedure was used to prepare pure PNIPAM gel and other Na-MLS/PNIPAM gel composites with Na-MLS concentration ranging from 0.25 to 4.0 wt%. The composition and properties of Na-MLS/PNIPAM composites are

listed in Table 1. For swelling ratio measurements, the use of filaments can substantially reduce the waiting period.

### 2.2. Shear modulus measurements

A Paar Physica UDS200 rheometer with a 25 mm parallel plate were used for shear modulus measurements. Torque amplitude sweeps were first conducted in order to determine the linear elastic region. The torque amplitude ranged from 0 to 1 mN m and frequency was kept at 1 Hz for all the measurements. The sample was placed very carefully into the rheometer to prevent the disruption of the gel structure. Measurements were commenced after a waiting time of 10 min. Following this procedure, we were able to obtain reproducible results. The relative compression of the samples was in the range from 1.0 to ca. 0.5. Values of the elastic modulus  $G$  were calculated from the formula:  $\tau = G\gamma$ , where  $\tau$  is shear stress and  $\gamma$  is the shear strain of a sample.  $G$  was calculated from the slope of the linear region of the stress–strain plot.

## 3. Results and discussion

The level of homogenous distribution of the Na-MLS platelets within the PNIPAM matrix is first determined using polarized optical microscopy. The presence of water limits our use of X-ray diffraction (XRD) and Transmission electron microscopy (TEM). When the montmorillonite is mixed with water, two dispersions have been commonly identified: the exfoliated (when the basal interlayer of the montmorillonite is completely disrupted) and intercalated (when the interlayer basal spacing increases relative to the original montmorillonite). In our earlier paper [21], we have demonstrated that even when Na-MLS is exfoliated, the individual clay platelets form aggregates where the face of one platelet has a face–face interaction with others at its edge. This leads to the increase of clay domain size with concentration. XRD and TEM measurement have confirmed that exfoliated dispersions show signs of aggregation similar to clay + water suspensions [22]. In aggregation, two or more particles clump together, touching only at certain

Table 1

Composition and characterization results for Na-MLS/PNIPAM samples, in which NIPA, BIS, APS and water amounts were 1.56 g, 0.0266 g, 0.048 ml and 20 g for all the samples preparation

Sample	Na-MLS (g)	Na-MLS percentage in the sample (wt%)	$\Delta I/I_0$ (A.U.)	$d/d_0$ (A.U.)	Shear modulus (Pa)
1	–	–	0.535	1.122	1882
2	0.05	0.25	–	1.194	1067
3	0.1	0.5	0.563	1.208	865
4	0.2	1.0	0.564	1.187	1198
5	0.3	1.5	0.622	–	1565
6	0.4	2.0	0.494	1.171	2097
7	0.5	2.5	0.43	1.151	2699
8	0.6	3.0	0.351	1.127	3304
9	0.8	4.0	–	1.098	4316

points. The aggregated clays retain their identity but move kinetically as a single unit [23].

Here, optical microscopy images for different concentration of Na-MLS/PNIPAM composites show the same phenomenon in Fig. 1. With increasing clay concentration, the average platelet size varied from 1 to 5  $\mu\text{m}$  gradually as the concentration of Na-MLS increased from 0.5 to 2.0 wt%, and an average agglomerate separation of 10, 4 and 3  $\mu\text{m}$  was observed for 0.5, 1.5, 2.0 wt% Na-nanocomposites, respectively. It revealed that Na-MLS tends to form larger aggregates in a PNIPAM gel matrix when its concentration above 1.5 wt%. In the low Na-MLS concentration ranging from 0 to 1.5 wt%, the small Na-MLS aggregates are well dispersed inside PNIPAM matrix as suggested by the evenly distributed small black dots in Fig. 1(b) and (c). When the Na-MLS concentration reached 2 wt%, larger aggregates were formed as indicated by the increased concentration and dimensions of the black dots in Fig. 1(d). This morphology will be related to the swelling and mechanical properties of the gels. Increased turbidity of samples having more than 2% clay prevented optical analysis of the samples with higher clay concentrations.

Fig. 2 shows the equilibrium swelling ratio  $d/d_0$  and shear modulus of gel composites as a function of Na-MLS concentration at 21 °C, where  $d$  and  $d_0$  are, respectively, the diameter of the filaments in water at room temperature and the inner diameter of the capillary tubing. The value of  $d/d_0$  increased sharply from 1.12 of pure PNIPAM to the highest value 1.2 of 0.5 wt% Na-MLS incorporated composite. In this low Na-MLS concentration range, Na-MLS are easily ionized and evenly distributed in the PNIPAM gel. This

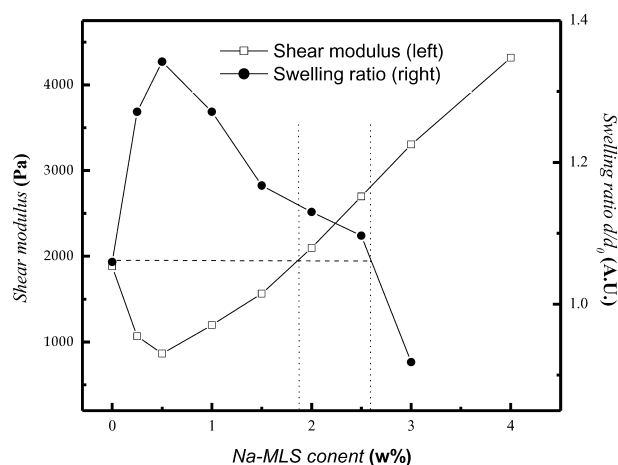


Fig. 2. Swelling ratio ( $d/d_0$ ) for the PNIPAM gel and its composites at 23 °C, where  $d$  is the equilibrium gel filament diameter and  $d_0$  is the capillary diameter. The shear moduli of Na-MLS/PNIPAM composites are also shown in the figure, measured at 23 °C.

enhances the hydrophilicity of PNIPAM gel and makes it swell more. However, in the higher Na-MLS concentrations above 1.0 wt%, the  $d/d_0$  decreases linearly with the increasing of Na-MLS concentration. This is partly due to the strong binding of sodium cations to the negatively charged MLS associates. These counter-ions are not free and cannot contribute to the osmotic pressure, resulting in the shrinkage of the gel.

Let us now discuss the mechanical properties of the gel composites. The dependence of the shear modulus  $G$  on the Na-MLS concentration is also shown in Fig. 2. Adding Na-MLS in the region of small concentrations leads to a

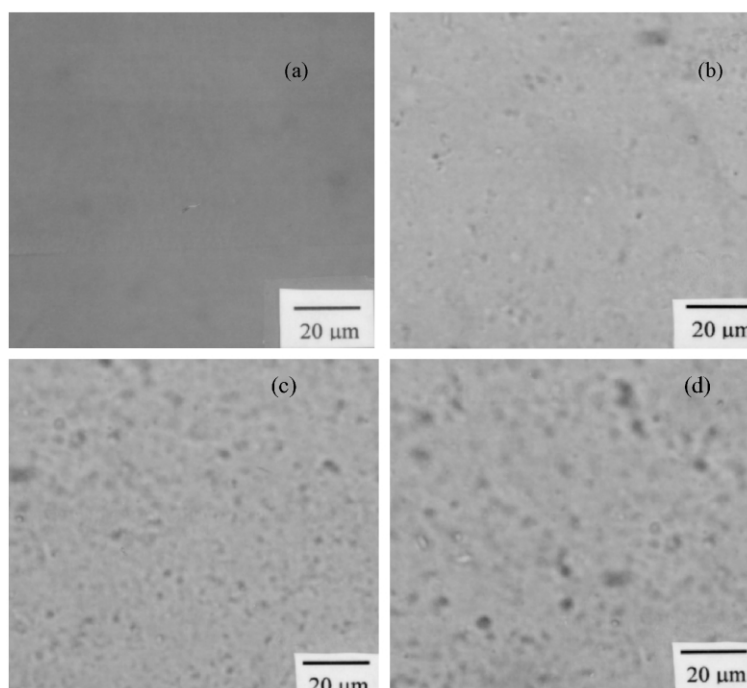


Fig. 1. Optical images of composite gels by Axioplan polarizing optical microscope. (a) Pure PNIPAM, (b) 0.5 wt%, (c) 1.5 wt%, and (d) 2.0 wt% Na-MLS/PNIPAM composite gels.

decrease of the  $G$  values from 1880 Pa of the pure PNIPAM to the minimum 865 Pa of 0.5 wt% Na-MLS composite. Further increase of Na-MLS concentration from 0.5 to 4.0 wt% is accompanied by the increase of the shear modulus from 865 to 4320 Pa. Clearly, below 0.5 wt%, the Na-MLS are well separated and their hydrophilicity plays a major role. Above 0.5 wt%, the Na-MLS is associated to strengthen the gel network, resulting in the increase of the shear modulus. Specially, we have identified a narrow Na-MLS concentration ranging from 2.0 to 3.2 wt%. In this range, the gels have a larger swelling ratio and higher shear modulus than those for a pure PNIPAM. This is a significant result because an increase in swelling ratio is usually accompanied by a decrease in shear modulus for non-composite gels [13].

The temperature induced-volume phase transitions were determined for all Na-MLS/PNIPAM composites in water. The Na-MLS/PNIPAM filaments in water were heated gradually from 21 to 39 °C using a home made temperature controller with an accuracy of 0.5 °C. The lengths of the filaments were measured at each temperature after it reaches the equilibrium value about 2 h. Volume variation of the gel filament is represented by the change of  $l/l_0$ , where  $l_0$  is the length of filament when it is formed in the capillary tubing, and the  $l$  is temperature dependent length. Typical temperature induced volume phase transition curves of pure PNIPAM gel filament and its composites, with up to 4.0 wt% of Na-MLS, are shown in Fig. 3. By comparing these curves it is apparent that the  $T_c$  ( $\sim 34$  °C) of the neutral PNIPAM gel in water is unaffected by the presence of Na-MLS in the concentration ranging from 0 to 4.0%. It is well known that increasing the crosslinker concentration could substantially increase the gel mechanical strength, however, it could also bring the  $T_c$  to a slight higher temperature [24]. The plausible explanation is that the charged MLS start to

sterically obstruct and electrically repulse one another. The strong collapse force of the PNIPAM gel is consequently being weakened.

The changes of the filament length  $\Delta l/l_0$  for the PNIPAM gel and its composites are compared and shown in Fig. 4, where  $\Delta l$  is the filament length difference below and above the  $T_c$  ( $\sim 34$  °C) and  $l_0$  is the equilibrium filament length at 22 °C. This parameter is defined to numerically represent the extent of gel volume change induced by the temperature at the  $T_c$ . It is interesting to observe that the volume change of the PNIPAM is increased first by Na-MLS additives in the range of 0–1.5 wt%, and then decreased linearly as more Na-MLS are incorporated. The extent of gel volume change at the  $T_c$  is the balance of competition between two contradictory driving forces: one is increased hydrophilicity arising from the well-dispersed Na-MLS, and the other is the strong self-association tendency from increasing amount of Na-MLS. This phenomenon is well explained by the morphology of the Na-MLS shown in Fig. 1. At low additive concentration below 1.5 wt%, the contribution from well-separated small Na-MLS aggregates is dominant as shown in Fig. 1(b) and (c). It therefore, leads to the enhanced volume change. As Na-MLS concentration increased above 1.5 wt%, however, the self-associate force of MLS is overwhelmed and causes a reduction in the volume change.

It has been reported that the copolymer gels comprising *N*-isopropylacrylamide (NIPA) and sodium acrylate (SA) are sensitive to a pH change [25]. The Na-MLS/PNIPAM composites, however, exhibit no much sensitivity to pH conditions. The swelling ration  $d/d_0$  was kept almost constant as the pH environment changed from 2 to 10 at 21 °C as shown in Fig. 5. This suggests that Na-MLS is physically entrapped rather than chemically bonded into the gel network.

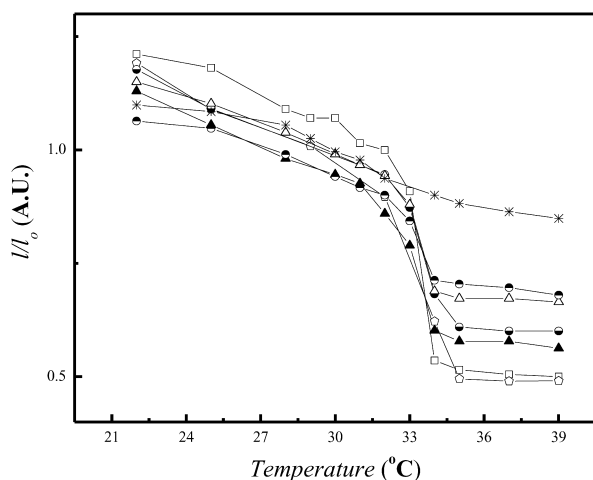


Fig. 3. Temperature dependence phase transition of the PNIPAM gel and its composite with up to 4.0 wt% of Na-MLS in water, in which  $\blacktriangle$  stands for pure PNIPAM;  $\square$  for PNIPAM + 0.5% Na-MLS;  $\circ$  for PNIPAM + 1% Na-MLS;  $\bullet$  for PNIPAM + 2% Na-MLS;  $\triangle$  for PNIPAM + 2.5% Na-MLS;  $\odot$  for PNIPAM + 3% Na-MLS;  $\times$  for PNIPAM + 4% Na-MLS.

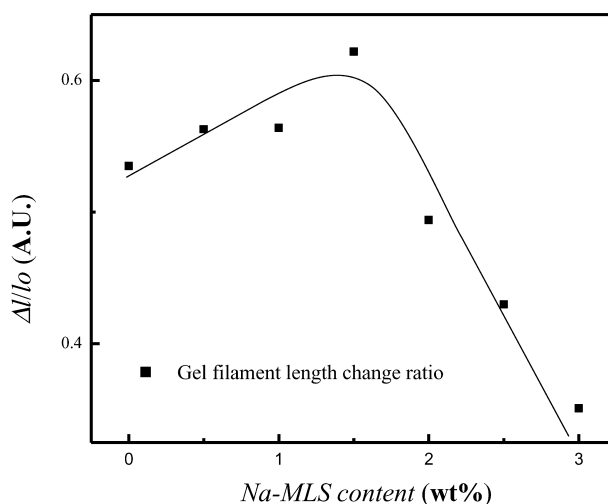


Fig. 4. The relative size change ( $\Delta l/l_0$ ) over the volume phase transition temperature for the PNIPAM gel and its composites, where  $\Delta l$  and  $l_0$  are the filament length difference between 22 and 37 °C and equilibrium filaments length at 22 °C, respectively.

#### 4. Conclusion

Clay-polymer hydrogel composites have been synthesized based on poly(*N*-isopropylacrylamide) (PNIPAM) gels containing 0.25–4 wt% of the expandable smectic clay Na-montmorillonite layered silicates (Na-MLS). Their structure and property relationship has been investigated combining measurements of morphology, shear modulus, and swelling ratio as a function of temperature and Na-MLS concentration. Specifically, a polarized optical microscopy study has revealed that Na-MLS form aggregates in the PNIPAM gel and the size of aggregates increases with Na-MLS concentration. Incorporation of Na-MLS clay into a neutral PNIPAM network improves the gel mechanical properties, while not detrimentally affecting volume phase transition temperature. The shear modulus of the gel composite first decreases and then increases with the increasing Na-MLS concentration, exhibiting a distinct minimum. In Na-MLS additive concentrations ranging from 2.0 to 3.2 wt%, both swelling ratio and shear modulus of the composite gels have been improved comparing with the pure PNIPAM gel. The difference in gel volume below and above  $T_c$  can be enhanced by adding small amount of Na-MLS (<1.5 wt%). The composite gel does not response to the pH change, indicating that Na-MLS is physically entrapped inside the gel matrix.

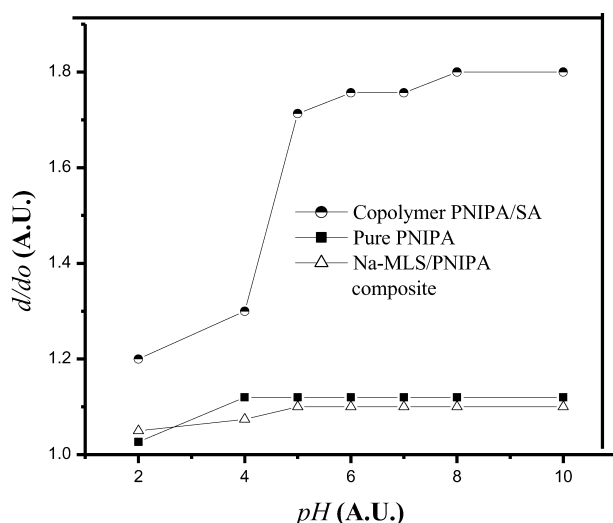


Fig. 5. pH Sensitivity of NIPA-SA copolymer [25], pure PNIPAM and Na-MLS/PNIPAM composite gels. The weight ratios of NIPA to SA in NIPA-SA copolymer and PNIPAM to Na-MLS in Na-MLS/PNIPAM composite are 1/0.048 and 1/0.385, respectively.

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