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Mechanical Properties and Phase Transition of High Clay Content Clay/Poly(N-isopropylacrylamide) Nanocomposite Hydrogel

Yang Liu,[1] *Meifang Zhu,**[1] *Xiaoli Liu,*[1] *Y.M. Jiang,*[1] *Y. Ma,*[1] *Z.Y. Qin,*[1]
Dirk Kuckling,[2] *Hans-Jürgen P. Adler*[2]

Summary: A series of high clay content Clay-S/PNIPAAm nanocomposite hydrogels (S-N gels) has been successfully prepared by in situ polymerization. Their mechanical properties and phase transition behavior has been systematically investigated. It was found that S-N gels show high tensile strength, high elongation at break, fast stress relaxation, high hysteresis, and poor resilience, which may be ascribed to the hydrophilicity and flexibility of PNIPAAm chains. It was also concluded that the macroscopic phase transition behavior of S-N gels depend on the ratio of Segments II (thermosensitive segments) to Segments I (non-thermosensitive segments).

Keywords: clay; gels; hydrogels; nanocomposites

Introduction

In the past several decades, poly(N-isopropylacrylamide) (PNIPAAm), as a regular thermosensitive hydrogel, has attracted many scientific interests due to its unique thermosensitivity. This hydrogel has been successfully used in many fields, like the characterization of protein,[1] drug delivery system,[2] and microcomponent[3] etc. Since 1980's, PNIPAAm hydrogel has been systematically investigated.[4–11] However, most researcher focus on improving its thermo-responsive rate using different methods,[12] like using, thin layers or small particles,[13–16] cold-treatment,[17] introducing macro- or nanoporous structures,[18,19] grafting polymers,[20–22] hydrophobic crosslinkers,[23] with hydrophilic silica as nano-sized water reservoirs[24] or preparing gels in organic/water mixture media[25] etc. The thermosensitivity of PNIPAAm gel has been improved considerably using the above methods; however, its inherent weak mechanical properties strongly restrict its application.

Haraguchi et al. prepared a kind of nanocomposite PNIPAm hydrogels using hectorite as crosslinker replacing traditional organic crosslinkers, which show excellent fracture strength and tensile elongation.[26] It was found that the mechanical properties of the nanocomposite hydrogels became better with increasing hectorite content of hydrogels.[27–29] However, high hectorite content aqueous dispersions are hard to prepare, even using special mixers, due to the high viscosity of clay aqueous dispersion. To increase the hectorite content in the PNIPAAm gels become the key for increasing the fracture strength of these gels further.

Recently, we successfully prepared high clay content nanocomposite Clay-S/PNIPAAm hydrogels (S-N gels) by choosing a kind of hectorite modified by tetrasodium pyrophosphate (i.e. ionic dispersant).[30] This kind of clay can easily be dispersed in water and can form a low viscous aqueous

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[1] State Key Lab for Modification of Chemical Fiber and Polymer Materials, College of Material Science and Engineering, Donghua University, 1882 West Yan-an Road, Shanghai 200051, China.
Fax: 86-21-67792199
E-mail: zhumf@dhu.edu.cn

[2] Institute of Macromolecular Chemistry and Textile Chemistry, Dresden University of Technology, Mommsenstr. 13, D-01069 Dresden, Germany

dispersion at high content under 10 wt%. S-N gels show extremely high tensile strength, such as 1 MPa at clay content: 15/100 (clay/water weight ratio).

In this paper, we further investigate the mechanical properties and phase transition of S-N gels, based on our previous work.[30] We believe the high clay content nanocomposite hydrogels with surprising mechanical properties and interesting phase transition behavior will have wide potential applications, such as man-made parenchyma and microchannel components etc.

Experimental Part

Materials

N-isopropylacrylamide (NIPAAm) (99%, Acros Co., Belgium), synthetic hectorite-Laponite XLG (Clay-G) (Rockwood Co., U.S., $Mg_{5.34}Li_{0.66}Si_8O_{20}(OH)_4Na_{0.66}$) and Laponite XLS (Clay-S) (Rockwood Co., U.S., 92.32 wt% $Mg_{5.34}Li_{0.66}Si_8O_{20}(OH)_4Na_{0.66}$, 7.68 wt% $Na_4P_2O_7$), *N*,*N*′-methylenebisacrylamide (NMBA), potassium persulfate (KPS), *N*,*N*,*N*′,*N*′-tetramethyldiamine (TEMED) (Shanghai Chemical Reagent, Analytic Reagent). All reagents were used as received. All solutions used in experiments were prepared in deionized water.

Synthesis of Nanocomposite Hydrogels

The synthetic procedure is the same as that reported previously.[30] In this paper, nanocomposite hydrogels are expressed as G*x*N*y*, or S*x*N*y* gel, where G, S, and N stand for Clay-G, Clay-S, and PNIPAAm respectively, and *x* and *y* stand for 100 × clay/water (w/w) and 100 × monomer/water (w/w), respectively. For example, S10N10 stands for PNIPAAm gels containing Clay-S with clay/water weight ratio: 10/100 and PNIPAAm with polymer/water ratio: 10/100; SxN10 stands for PNIPAAm gels containing different Clay-S and PNIPAAm with polymer/water ratio: 10/100.

Measurements of Tensile Properties

Tensile strength measurements were performed on hydrogels of the same size (5 mm diameter × 80 mm length) using a Dejie DXLL-20000. The following conditions were as follows: temperature 25 °C; a sample size of 5 mm in diameter and 80 mm length; gauge length of 30 mm; crosshead speed of 100 mm/min.

Measurement of Stress Relaxation and Elastic Hysteresis

Stress relaxation measurements were performed on hydrogels under the conditions, which were almost the same as tensile strength measurements, except for fixed strains: 700%; relaxation time in all measurements: 10 min.

Elastic hysteresis measurements were performed on hydrogels of the same size (5 mm diameter × 60 mm length) using a Shimadzhu AGS-500ND. The conditions were almost the same as tensile strength measurements, except for maximum strains: 700%; the same tensile rate and retraction rate: 100 mm/min; three cycles for every measurement.

The hysteresis is determined by evaluating the area between the extension and retraction curves and a hysteresis ratio, h_r, can be defined by evaluating the ratio of hysteresis to the integrated area of the extension curve.[31]

Elastic recovery is defined by the ratio of the strain corresponding to firstly reaching zero stress during retraction to the fixed maximum strain (700%).

Measurements of Deswelling Behavior

Hydrogels were transfered from water at 20 °C to water at 50 °C. For each measurement, the hydrogels were removed from the water and weighted after excess water removed from the surface by wet filter papers. All starting gels were as-prepared hydrogels (prepared at 5 °C) with the original water/polymer ratio (w/w) and sample size (5 mm diameter × 30 mm length).

Measurements of Transparency

Transparency of the gels which were synthesized in the quartz cell (10mm × 10mm × 40mm) were measured using the UV/VIS spectrophotometer (UV 1901, Puxi Co. China). The temperature of the quatz cell was regulated electrically. Transparency at 600 nm was recorded after 30 min at every temperature.

Characterization of DSC

Differential scanning calorimeter (DSC) measurements were performed using a Mettler-Toledo DSC-822 apparatus in a nitrogen gas atmosphere for as-prepared gels, with heating from 25 to 45 °C at a heating rate of 1 °C/min.

Results and Discussion

Mechanical and Tensile Properties of S-N Gels

Figure 1 shows tensile properties of S-N gels. As shown in Figure 1a, the stress and strain of S2N10 are very close to that of G2N10; moreover they almost show the same stress-strain curve. This result indicates that Clay-S has the same ability to improve mechanical properties of PNIPAAm hydrogels as Clay-G, and the mechanical properties of S2N10 gel are not affected by ionic dispersant. Also, it was observed that the tensile properties of nanocomposite PNIPAAm gels considerably depend on clay content. For example, the stress increases from 70 kPa of S2N10 to 1 MPa of S15N10.

The elongation at break of S*x*N10 is very high, and almost independent on clay content, fluctuating between 1300% and 1450%. The excellent mechanical properties are due to two reasons. One is that the uniform dispersion of clay platelets in S-N gels leads to the narrow distribution of molecular weight between crosslink points, effectively avoiding the stress concentration, and improving the tensile strength; the other reason is that the molecular weight between crosslink points in S-N gels is high, generally larger than 10000 g/mol,[27,32] increasing the elongation at break. Figure 1b shows tensile properties of S15N*y* gel. As shown in Figure 1b, the tensile properties of S15N*y* greatly depend on the polymer content. The tensile strength increases with increasing polymer content, for example, the tensile strength increases from 172 kPa of S15N3.75 to 1 MPa of S15N10. In addition, the elongation at break of all S15N*y* gels is higher than 1000%, indicating that all samples form a complete network structure.

Stress Relaxation and Elastic Hysteresis of S-N gels

Figure 2 shows stress relaxation and elastic hysteresis loops of S-N gels. As shown in Figure 2a, stress of all S-N gels is lost very quickly with increasing time, and the stress loss for different S-N gels is almost independent on clay content (i.e., stress loss for every S-N gel is about 50% and 75% in 30s and 10min, respectively.). This result indicates the inherent properties of polymer chains play a dominant role in stress relaxation. Figure 2b shows elastic hysteresis

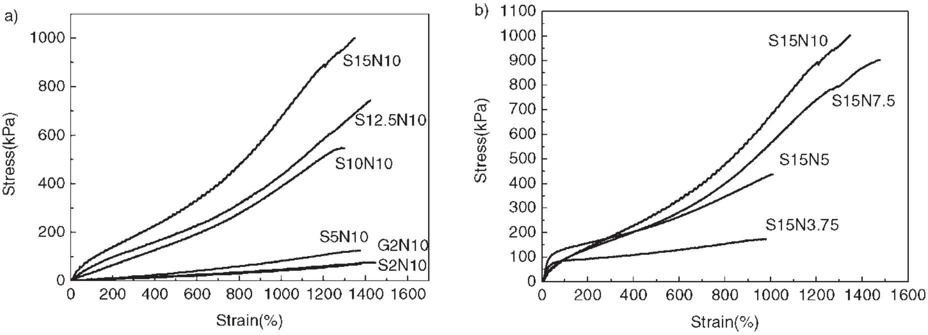

Figure 1.
Tensile properties of S-N gels. (a. S*x*N10 gels, b. S15N*y* gels).

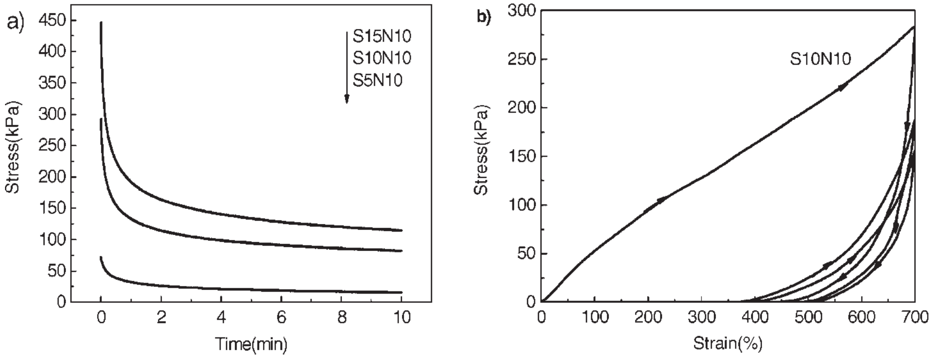

Figure 2.
Stress relaxation and elastic hysteresis loops of S-N gels. (a. Stress relaxation of S-N gels, elongation for S-N gels: 700%; b. Elastic hysteresis loops of S10N10 gel).

loops of S10N10 gel. As shown in Figure 2b, hysteresis of S10N10 gel is quite large, h_r in the first cycle, the second cycle and the third cycle are 87%, 50% and 50% respectively, and its elastic recovery is poor, only 32% in the first cycle. Compared with PAAm nanocomposite hydrogels reported in our previous paper,[33] S-N gels show larger stress loss, higher h_r, and poorer elastic recovery. This is due to the different size and hydrophilicity of their side groups. The bigger the side group, the larger the internal friction force. Moreover, the stronger the hydrophilicity of side group, the more complete the hydration of polymer chains. Water will be a better lubricant for higher hydrophilic polymeric network, and reduce internal friction force among molecules considerably. Compared with the side group of polyacrylamide, $-CONH_2$, the side group of PNIPAAm, $-CONHCH(CH_3)_2$, show bigger size and weaker hydrophilicity, thus there is a larger internal friction force in S-N gels, which leads to large stress loss, high hysteresis, and poor elastic recovery.

Phase Transition of S-N gels

Figure 3 shows deswelling behavior of S-N gels. As shown in Figure 3a, the deswelling kinetics of S2N10 gel is the same as that of traditional PNIPAAm gels, i.e. the water retention (W_t/W_0) decreases with increasing deswelling time. However, S10N10 and S15N10 gels hardly show deswelling behavior, quite different from that of traditional chemical crosslinked PNIPAAm gels. Their swelling ratio does not decrease with increasing time, which means the disappearance of deswelling behavior.

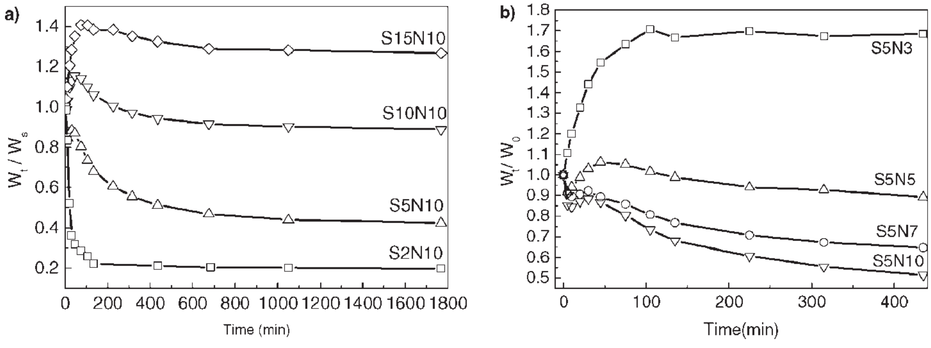

Figure 3.
Deswelling behavior of S-N gels.(a.SxN10 gels, b. S5Ny gels).

According to these results, when the clay content in S*x*N10 gels is high (larger than 10), the thermosensivity of PNIPAAm chains completely disappear due to the effects of clay platelets. Because clay platelets are hydrophilic, those PNIPAAm chains connecting or near the clay platelets are hydrophilized by clay platelets. Thus the conformational transition of those PNIPAAm chains from hydrophilic coil to hydrophobic globule is restricted. At low clay content S*x*N10 gels, the clay platelets are less, most PNIPAAm chains are hardly restricted by the clay platelets, remaining their conformational transition ability. Therefore, S2N10, S5N10 gels still show deswelling behavior at temperature above the LCST of PNIPAAm (32 °C).

As shown in Figure 3b, the deswelling rate of S5N*y* decrease with increasing polymer content, and their deswelling behavior disappears when polymer content is higher than 5, as the S5N3 curve in Figure 3b. As we know, it is up to the competition result between swelling trend and phase transition trend whether S-N gels show deswelling behavior. As to S5N*y* gels, the clay content is fixed, and the phase transition trend of S5N*y* gels become weaker and weaker with decreasing polymer content. As long as the polymer content is low, like S5N3 and S5N5, the deswelling behavior of S5N*y* gels completely disappears, showing only swelling behavior. Therefore, based on Figures 3a and 3b, the existence of deswelling behavior of S-N gels depends on the weight ratio of clay to polymer; in the case of S*x*N10 and S5N*y*, deswelling behavior completely disappears when the weight ratio of clay to polymer is higher than 1.

Transparency of S-N Gels at Different Temperature

Figure 4 shows transparency of S-N gels at different temperature. As shown in Figure 4a, the transparency thermosensitivity of S*x*N10 gels is greatly affected by clay content; the temperature dependence of transparency become less obvious with increasing clay content. As long as the clay content is high enough, like 15, the transparency of S*x*N10 gel is almost constant, independent on temperature. For instance, the transparency of S2N10 and S5N10 gels shows a sharp drop around 32 °C, the LCST of PNIPAAm, while transparency of S10N10 and S15N10 changes little during the whole temperature scope. The above results indicate that the conformational transition of PNIPAAm chains in high clay content S-N gels are thoroughly restricted, and the macroscopic thermosensitivity disappears, which agree with the results in Figure 3.

As shown in Figure 4b, the scope of transparency changes of S5N*y* gels decreases with increasing polymer content. This is also due to the hydrophilicity effects of clay platelets on PNIPAAm chains. However, when temperature is below 32 °C (the LCST of PNIPAAm), the optical

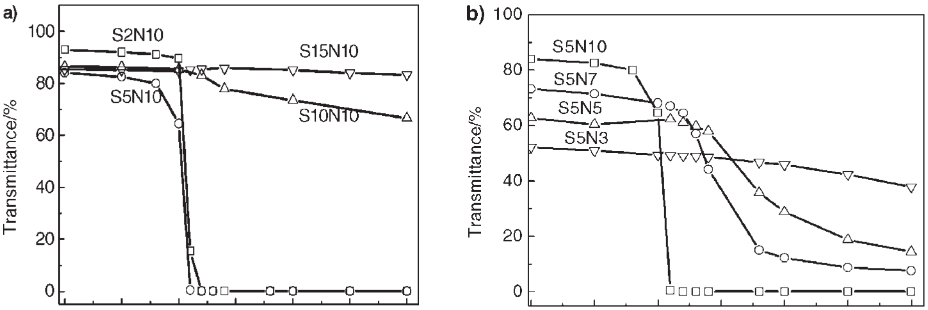

Figure 4.
Transparency of S-N gels at different temperature. (a. S*x*N10 gels; b. S5N*y* gels).

transparency decreases with decreasing polymer content. For example, at 20 °C, the transparency of S5N10 and S5N3 is 84%, 52%, respectively. This may be due to the fact that the inhomogeneity of S5N*y* gels becomes more remarkable with decreasing polymer content.

Heat Effects of the Phase Transition of S-N gels

The heat effects of the phase transition of S-N gels were investigated using differential scanning calorimeter (DSC). As shown in Figure 5, the heat effects of phase transition of S-N gels become weaker with increasing clay platelets or increasing polymer content. When the clay content of S*x*N10 is higher than that of S10N10 or the polymer content of S5Ny is larger than that of S5N5, i.e. the weight ratio of clay to polymer is above 1, the heating effects of phase transition disappear. This is in agreement with those results of deswelling behavior and transparency changes of S-N gels. The reason is the restriction of clay platelets on the conformational transition of PNIPAAm too. However, the three results of some S-N gels do not perfectly agree. For instance, the deswelling behavior and the endothermal peak of S5N5 almost disappear, while its transparency still declines apparently with increasing temperature. Although the essential reason for deswelling behavior, transparency changes, and heating effects is the same: the conformational transition of PNIPAAm chains, this is just the necessary condition, not the sufficient condition. As to S-N gels, the hydrophilization of clay platelets on PNIPAAm chains is a kind of short-range interaction, whose effective distance is about several nanometers around the clay platelets. The distance between two neighbour clay platelets is about 30-60 nm,[32] beyond the effective distance of hydrophilization, and the molecular weight of PNIPAAm between two neighbour clay platelets is about 20000–40000 g/mol.[27,32] Therefore, these segments of PNIPAAm chains between clay platelets can transfer their conformation, which is confirmed by the deswelling behavior, transparency changes, and endothermal peak of S5N10. Accordingly, the segments of PNIPAAm chains in S-N gels can be divided into two sorts: one are those near clay platelets, hydrophilized by clay platelets, called Segments I, the others are those far away from clay platelets, beyond the hydrophilization effective distance, sustaining the ability to transfer their conformation, called Segments II. Thus, the ratio of Segments I to Segments II determines whether the deswelling behavior, transparency changes, and endothermal peak appears or not. In this paper, samples are as-prepared gels, whose water content is 80–93% (S15N10 and S5N3). The weight of samples for DSC is about 10 mg (solid content: 0.7–2 mg, S5N2.5 and S15N10; PNIPAAm content: 0.2–0.9 mg, S5N2.5 and S2N10), and the conformational transition of PNIPAAm is

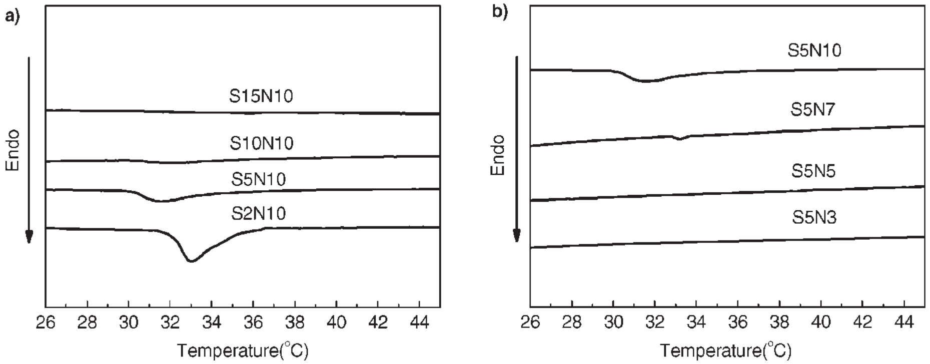

Figure 5.
DSC curves of S-N gels. (a. S*x*N10 gels; b. S5N*y* gels).

a secondary transition. Therefore, as the weight ratio of clay to polymer increases, the ratio of Segments I to Segments II increases, and the number of Segments II is so less that the heat effects of conformation transition of Segments II can not be observed by DSC. The transparency change directly results from the aggregates of Segments II having transferred conformation. When the size of these aggregates is large enough to reflect visible light, the transparency will decline sharply. Although the ratio of Segments II is not high in S5N5, the number of Segments II is enough to form large aggregate area, reflecting light and decreasing transparency. Deswelling behavior is due to the shrinking force from the conformation transition of the Segments II. As to S5N5, the aggregate area is large enough to affect the transparency, but the shrinking force is not enough to make the macroscopic gel collapse because of the low ratio of Segments II.

Conclusions

A series of high clay content Clay-S/PNIPAAm nanocomposite hydrogels (S-N gels) havebeen successfully prepared by in situ polymerization. Their mechanical properties and phase transition behavior were systematically investigated. It was found that S-N gels show high tensile strength (up to 1 MPa), high elongation at break (above 1000%), fast stress relaxation (stress loss: 50% in 30 s), high hysteresis (hysteresis ratio:87% in 1st cycle), and poor resilience (elastic recovery: 32%), which result from the hydrophilicity and flexibility of PNIPAAm chains. The phase transition behavior of S-N gels depend on the ratio of Segments II (thermosensitive segments) to Segments I (non-thermosensitive segments). When the weight ratio of clay to polymer is above 1, the macroscopic phase transition behaviors of S-N gels completely disappear.

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