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Polymer 47 (2006) 1–5
polymer
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Polymer Communication

High clay content nanocomposite hydrogels with surprising mechanical strength and interesting deswelling kinetics

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Received 6 September 2005; received in revised form 28 October 2005; accepted 13 November 2005
Available online 28 November 2005

Abstract

A series of high hectorite content nanocomposite Poly (*N*-isopropylacrylamide), (PNIPAAm), hydrogels have been successfully synthesized by choosing a special kind of hectorite (Laponite XLS) modified by tetrasodium pyrophosphate. It was found that these hydrogels show surprising mechanical properties (i.e. tensile strength: 1 MPa, elongation at break: 1400%) and complicated deswelling behavior, which are due to the high clay content of the hydrogels and ionic dispersant contained in Laponite XLS, respectively.

Keywords: Hydrogels; Poly(*N*-isopropylacrylamide); Hectorite

1. Introduction

In past several decades, polymer hydrogels have attached many scientific interests for their unique properties such as good osmotic property, elasticity. They have been used in a variety of applications [1], such as separation membranes, biosensors, artificial muscles, chemical valves [2,3], superabsorbents [4,5], and drug delivery devices. Poly(*N*-isopropylacrylamide) gel (PNIPAAm), as well-known temperature sensitive hydrogels, have been investigated systematically since 1980's [6–13]. Many researchers focus on improving its response rate in different ways [14], like using, thin layers or small particles [15–17], cold-treatment [18], introducing macro- or nanoporous structures [19,20], grafting polymers, hydrophobic crosslinkers [21], with hydrophilic silica as nano-sized water reservoirs [22] or preparing gels in organic/water mixture media [23] etc. Although fast responsive rate is important in many applications. A problem for some applications of PNIPAAm gels or other hydrogels is their weakly mechanical properties.

Recently, Haraguchi et al. prepared a kind of nanocomposite PNIPA hydrogels using hectorite as crosslinker replacing traditional organic crosslinkers, which show excellent fracture strength and tensile elongation [24]. It was found that the mechanical properties of the nanocomposite hydrogels became better with increasing hectorite content of hydrogels [25–27]. However, high hectorite content aqueous dispersions are hard to prepare, even using special mixers, due to the high viscosity of clay aqueous dispersion. Thus, the highest hectorite content of nanocomposite hydrogels reported [25] was about 6.8 wt% with respect to water content, and the tensile strength of the PNIPAAm nanocomposite hydrogel was about 270–300 kPa for the water/polymer ratio 10/1 (w/w). So how to increase the hectorite content in the PNIPAAm gels become the key for increasing the fracture strength of these gels further.

In this paper, we prepared nanocomposite PNIPAAm/clay hydrogels by choosing a kind of hectorite modified by tetrasodium pyrophosphate (i.e. ionic dispersant). This kind of clay can be easily dispersed in water and can form a low viscous aqueous dispersion at high content under 10 wt%. We successfully prepared high clay content nanocomposite hydrogels by simple mixture and solution polymerization, which have extremely high tensile strength, such as 1 MPa at clay content: 15/100(clay/water weight ratio), three times higher than for reported products [25], and even higher than extremely tough double-network hydrogels (tensile strength

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0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.11.030

0.68 MPa) reported by Gong [28,29]. It was also found that the swelling ratios of these composite hydrogels are high, and the deswelling kinetics of them is interesting and complicated due to the presence of ionic dispersant. We believe the high hectorite content nanocomposite hydrogels with surprising mechanical strength and interesting deswelling kinetics will have wide potential applications, such as man-made parenchyma and microchannel opponents etc.

2. Experimental part

2.1. 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%$Na_4P_2O_7$), potassium persulfate(KPS)(Shanghai Chemical Reagent, Analytic Reagent), *N*,*N*,*N*′,*N*′-tetramethyldiamine (TEMED). All reagents were used as received. All solutions used in experiments were prepared in deionized water.

2.2. Preparation of nanocomposite hydrogels

Hydrogels were prepared using initial solutions consisting of monomer (NIPAAm), crosslinker (Clay-S or Clay-G), initiator (KPS), and accelerator (TEMED). In all cases, the water/monomer ratio, the monomer/initiator ratio, and the volume of accelerator were fixed at 10/1(w/w), 100/1(w/w), and 24 μL, respectively. First, a transparent aqueous solution consisting of water (28 ml), clay (0.6–4.5 g), and NIPAAm (3 g) was prepared. Then, the accelerator (TEMED, 24 μL) and the aqueous solution of initiator (KPS 0.03 g in water 2 ml) were subsequently added to the former solution with stirring at 0 °C. Next, free-radical polymerization was carried out at 5 °C for 72 h. Hydrogels were synthesized in glass tubes (interior size = 5 mm diameter × 500 mm length). For measurements of mechanical properties, deswelling rate, hydrogels were used as-prepared in order to retain the equal water/polymer ratio for all gel samples.

In this paper, hydrogels are expressed as S*m* gel and G*n* gel, which is S and G stand for gels containing Clay-S and Clay-G, respectively, and *m* and *n* stand for 100 × clay/water(w/w), for example, S2 stand for gels containing Clay-S with clay/ water weight ratio:2/100.

2.3. Measurements of mechanical properties

Tensile strength measurements were performed on hydrogels of the same size (5 mm diameter × 80 mm length) and the same polymer/water weight ratio (1/10) 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. Compressive measurements were performed on hydrogels of the size (8.5 × 8.5 × 11 mm (thickness)) and the polymer/water weight ratio (1/10). The cubic sample were compressed by the upper plate, which was connected to a load cell, at a strain rate of 5%/min.

The strain under stress (or compression) is defined as the change in length (or thickness) relative to the initial length (or thickness) of the specimen. The strength and modulus were calculated on the basis of the initial cross section.

2.4. Measurement of swelling ratio

As-prepared gels rods were cut in the same size (5 mm diameter × 30 mm length), and were immersed in a large excess water to attain swelling equilibrium at 5 °C for 1 week prior to measurement, changing the water several times. Swelling ratios are represented by the ratio of weights of the swollen gel (W_s) to the corresponding dried gel (W_d).

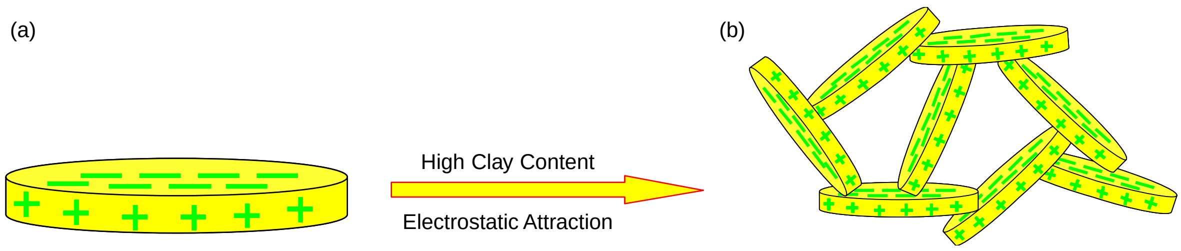
2.5. Measurements of deswelling kinetics

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 same water/polymer ratio (10/1(w/w)) and sample size (5 mm diameter × 30 mm length).

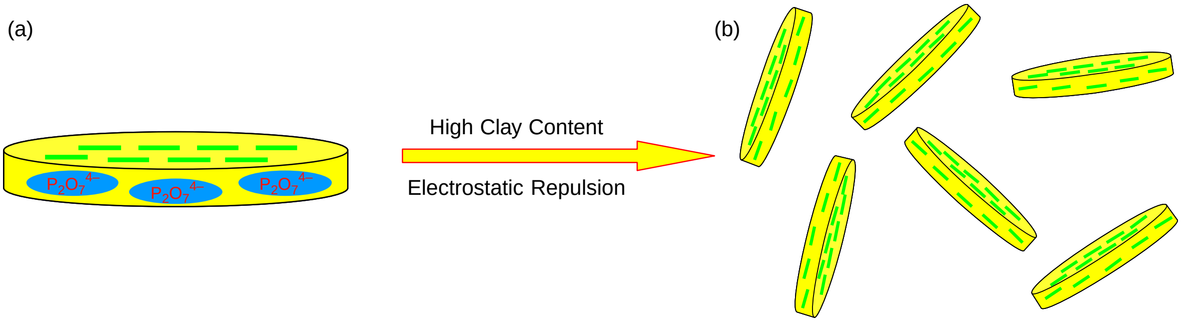
3. Results and discussion

3.1. Mechanical properties of high hectorite content nanocomposite hydrogels

When the pure synthetic hectorite (Clay-G) with a thin disc structure, as shown in Scheme 1a, is dispersed in water, its surface and edges are negatively charged and positively charged, respectively. Thus, at a high clay concentration



Scheme 1. Dispersion and Gel Formation of Pure Hectorite (Clay-G) in water. (a) A single disc of Clay-G, diameter 30 nm, thickness 1 nm; (b) Gel formation-‘House of Cards’.



Scheme 2. Dispersion of Hectorite Modified by tetrasodium pyrophosphate (Clay-S) in water. (a) A single disc of Clay-S in water, diameter 30 nm, thickness 1 nm; (b) Stable dispersion of Clay-S in water.

(2 wt% for Clay-G) or after a definite time (different time for different concentration), the discs will form a 'House of Cards' structure, as shown in Scheme 1b, due to the electrostatic attraction among surfaces and edges of different discs, and become a very viscous gel-like dispersion. This problem makes it hardly to mix with monomer or other reagents by normal mixing methods. This was the reason for the limitation the Clay-G Content on 2 wt%.

However, as to the synthetic hectorite modified by tetrasodium pyrophosphate (Clay-S), the edges of discs modified by tetrasodium pyrophosphate are negatively charged (illustrated in Scheme 2a), so the surfaces and edges of discs exhibit the same charge, leading to electrostatic repulsion among discs and efficiently prohibiting the formation of 'House of Cards' structure. Therefore, the Clay-S dispersions can form a uniform dispersion in water (illustrated in Scheme 2b) and still sustain a low viscosity at high hectorite concentrations, making it easy to mix with monomer and other reagents by simple magnetic stirring. Using Clay-S as crosslinker, the most difficult problem for preparing pre-polymer solutions with high clay content is settled completely.

Fig. 1 shows effects of different hectorite content on mechanical properties of hydrogels. As shown in Fig. 1, the load and strain of S2 are very close to that of G2; moreover they almost show the same load-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 S2 gel are not affected by ionic dispersant. As shown in Fig. 1, the load of S-gels increase with increasing clay content, for example, the load increases from 1.45N of S2 to 19.64N of S15.

Swelling ratio, tensile strength, tensile modulus, and elongation at break for S and G-gels with different clay content are summarized in Table 1. As shown in Table 1, the swelling ratio of G 2 gel is much lower than of S2, S5, and S10 gels. This phenomena may be due to the presence of dispersant (i.e. tetrasodium pyrophosphate) contained in S-gels. This makes the ion concentration in S-gels larger than in G-gels, resulting in the osmotic pressure of S-gels larger than these of G-gels. So the swelling ratios of S-gels are larger than these of G-gels. Elongations at break for S-gels are almost independent on clay content, and the elongations of all S-gels change between 1300 and 1430%. On the other hand, the strength and the modulus changed markedly with clay content, as shown in Fig. 2. Both properties are improved quickly with increasing clay content. At high clay content (>10), the strength and the modulus of S-gels are very high, for instance, the strength and the modulus of S15 gels are larger than 1 MPa and 74 kPa, respectively. The tensile strength of S15 gels is even larger than that of the extremely tough double network gels (tensile strength 0.68 MPa at break strain 75%) reported by Gong et al. [28].

We also investigated the compressive strength of S-gels. As shown in Fig. 3, the stress of S15 gel increases at lower rate up to 75% strain, from 0 to 2 MPa, and increases more quickly between 75 and 92% strain, from 2 to 20 MPa. Moreover, in the whole compressive process the gel was not damaged, and it was found that it can recover to about 50% of its original length at room temperature after the compressive process. The result indicates that the S15 gel is hardly damaged by compressive deformation, similar to rubber. This phenomenon is probably caused by two reasons. One is that polymer chain segments retain high mobility in water, so the polymer is in the elastic state. Another reason is that the S-gels have a narrow molecular weight distribution between crosslinks due to the uniform dispersion of hectorite in water, and the crosslink density of the nanocomposite gels is much lower than that of traditional gels crosslinked by *N*,*N′*-methylenebisacrylamide or other chemical crosslinkers, which has been proved recently [24–26].

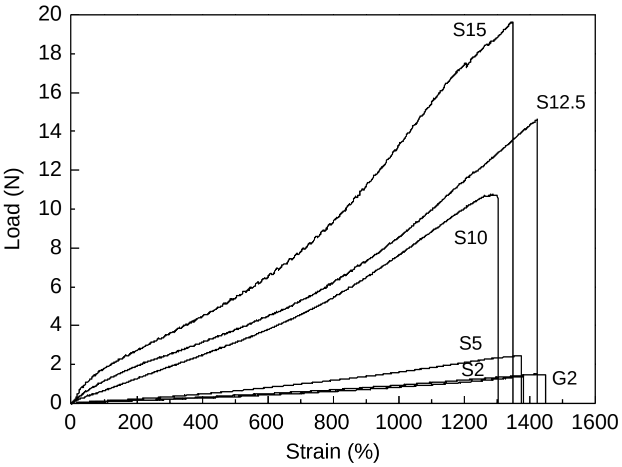


Fig. 1. Effects of different hectorite content on mechanical properties of S-gels and G-gels.

Table 1
Swelling ratio, mechanical properties of hydrogels

Hydrogel	Swelling ratio (W_w/W_d)	Tensile strength (kPa)	Elongation (%)	Modulus (kPa)
G2	47	74	1445	5.12
S2	66	70	1381	5.07
S5	61	125	1375	9.09
S10	48	547	1304	41.95
S12.5	42	744	1424	52.22
S15	26	1000	1348	74.18

Therefore, the mechanical behavior of S-gels is similar to that of rubber with low crosslink density.

3.2. Deswelling kinetics

Fig. 4 shows deswelling kinetics at 50 °C for S-gels. As shown in Fig. 4, the deswelling kinetics of S2 gel is the same as that of traditional PNIPAAm gels–the water retention (W_t/W_0) decreases with increasing deswelling time. However, other deswelling kinetic curves of S-gels are quite different from that of traditional chemical crosslinked PNIPAAm gels and NC gels crosslinked by Clay-G reported by Haraguchi [24–26]. S5 and S10 gels deswell initially (0–10 min for S5, 0–5 min for S10), and then begin to swell during the subsequent period (10–30 min for S5, 5–45 min for S10). After a definite time (30 min for S5, 45 min for S10), the gels deswell again, and the deswelling rate of S5 during this period is faster than that of

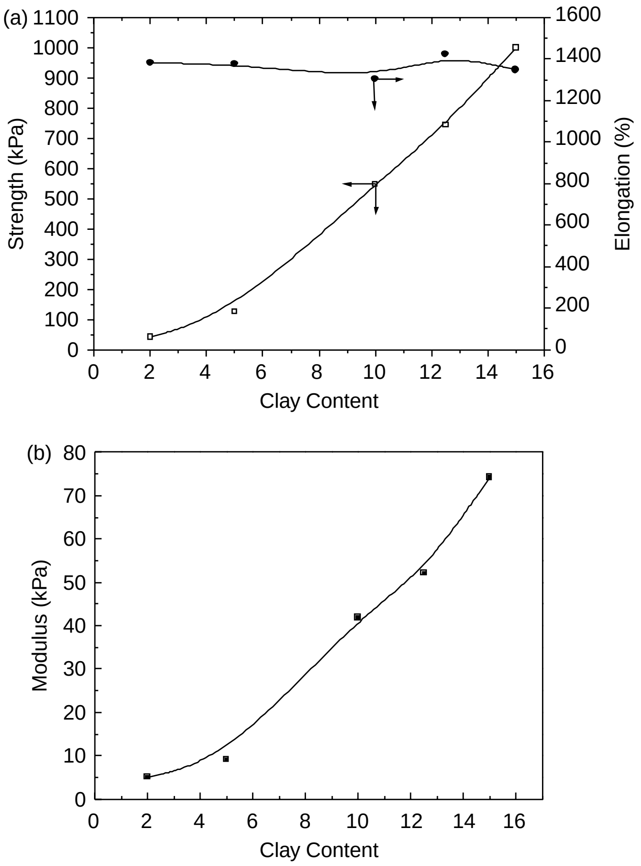


Fig. 2. Changes of mechanical properties, such as (a) tensile strength and elongation at break, and (b) modulus, by altering Clay-S contents of S-gels. Initial cross-sectional area (19.63 mm^2) was used for calculating the modulus and strength.

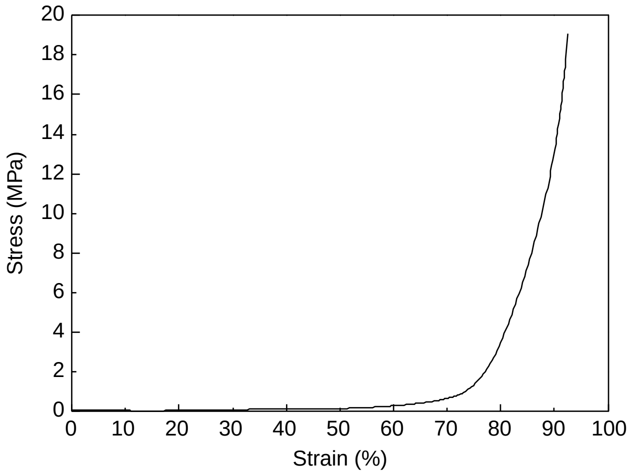


Fig. 3. Stress-strain curves for S15 gel (water/polymer ratio: 10/1(w/w), 25 °C, 5%strain/min, sample (11 mm (thickness) ×8.5×8.5 mm)) under uniaxial compression.

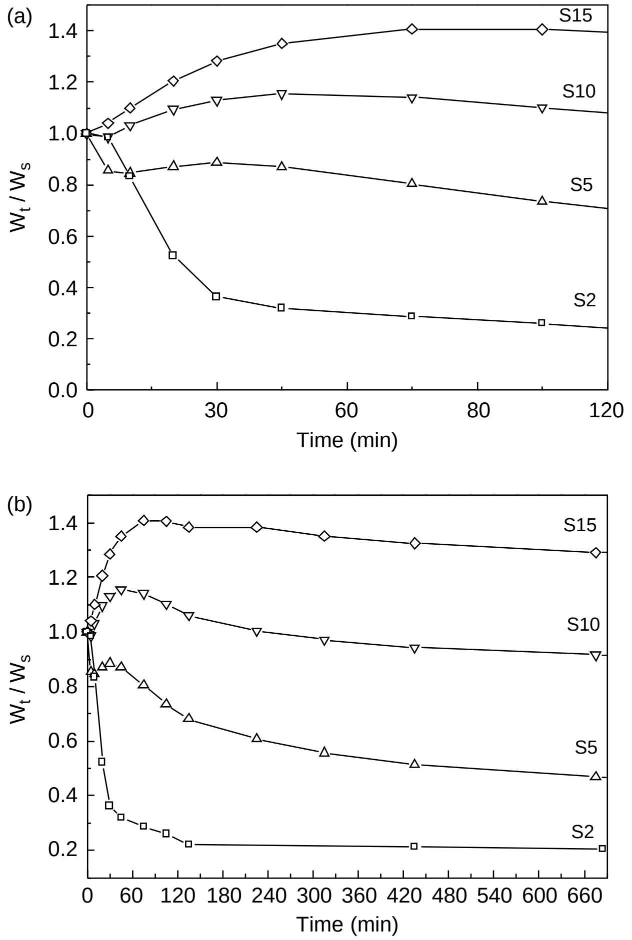


Fig. 4. Deswelling kinetics at 50 °C for S-gels. Deswelling kinetics at 50 °C for S-gels in initial period; (b) Deswelling kinetics at 50 °C for S-gels in 11 h.

S10. But S15 swells firstly during the initial period(0–75 min), while it begins to deswell slowly after 75 min.

The interesting and complicated deswelling kinetics for S-gels is due to the presence of ionic dispersant–tetrasodium pyrophosphate contained in Clay-S. This makes the ion concentration in S-gels larger and the osmotic pressure higher, resulting in a strong swelling trend of S-gels. The trend is independent on temperature. When S-gels are immersed in water at 50 °C, the high ion concentration in S-gels change gels to swell more; on the other hand, the phase transition trend of PNIPAAm molecules causes gels to collapse. Therefore, the behavior of S-gels is determined by the competition of two opposite effects. For S2 gel, the ion concentration is not high enough to overcome the trend to collapse, so it deswells during the whole testing process. For S15 gel, during the initial period, the ion concentration is high enough to overcome the trend to collapse, so it swells during the initial period. Meanwhile, some free pyrophosphate anionic groups and sodium ions diffuse in water from the gel, changing the decrease of ion concentration in gels. This leads to a decrease in osmotic pressure, and the phase transition trend of PNIPAAm becomes predominant, resulting in deswelling behavior of S15 gel. However, for S5 and S10 gels, the deswelling kinetics is more complicated. During the initial period, the trend of collapse is driven by phase transition and is slightly stronger than the swelling trend caused by ion osmotic pressure. So the gels initially deswell. Ions diffuse continuously from the surface of gels into water with increasing time. The ion concentration inside the gels increases a little due to diffusion of ions from the central part of the gels up to the surface. This makes the swelling trend to overcome the collapsing trend, resulting in gels swell. Finally, during the next period S5 and S10 gels deswell again due to the same reason which is responsible for the deswelling behavior of S15 gel described above.

4. Conclusion

A series of high clay content PNIPAAm hydrogels (S-gels) have been successfully synthesized for the first time by choosing a special kind of synthetic hectorite modified by tetrasodium pyrophosphate (Clay-S), which can be easily dispersed in water and form a low viscous dispersion at high clay content. These hydrogels show improved mechanical properties, much larger than any PNIPAAm gels reported before. The compressive strength of S15 gel also has been investigated, and we found that the S15 gel is hardly damaged by compression, like rubber. Moreover, the deswelling kinetics of S-gels is very interesting and complicated. This phenomenon is due to the influence of ionic dispersant contained in Clay-S. We are planning to investigate systematically the effect of ionic dispersant on the deswelling kinetics of S-gels, the diffusion of ionic dispersant in gels, and the interaction between tetrasodium pyrophosphate and gels in our future research.

Acknowledgements

This research is financially supported by the National Natural Science Foundation of China (Project No.50473002), and the Cultivation Fund of the Key Scientific and Technical Innovation Project, Ministry of Education of China(No.704021).

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