Effect of Montmorillonite on the Properties of Thermosensitive Poly(N-Isopropylacrylamide) Composite Hydrogels

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ABSTRACT: Thermosensitive composite hydrogels containing various amounts of sodium montmorillonite (NaMM) and poly(N-isopropylacrylamide) (pNIPAAm) were synthesized. Their equilibrium degree of swelling (DS) was measured in NaCl solutions of different ionic strength and at various temperatures. The DS decreased when increasing the clay content and no substantial shift in the phase transition temperature was noticed. The composite hydrogels investigated had a NaMM content ranging between 1.0 and 5.7 wt % (in 0.1M NaCl at 25°C). A considerable enhancement in the response to thermal stimuli was observed for NaMM contents >2–3 wt %. It is suggested that when the NaMM concentration approaches a critical value, the clay platelets can inhibit the formation of the hydrophobic skin layer that hinders shrinking in conventional pNIPAAm hydrogels. The effect of montmorillonite on the mechanical properties of the hydrogels was investigated by uniaxial compression tests, which showed that the modulus increases with the NaMM content. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1964–1971, 2004

Key words: clay; hydrogels; modulus; nanocomposites; stimuli-sensitive polymers

INTRODUCTION

Poly(N-isopropylacrylamide) (pNIPAAm) is a well-known thermosensitive polymer that in aqueous media shows a lower critical solution temperature (LCST) at ~ 32°C.[1] Hydrogels obtained by cross-linking pNIPAAm swell at low temperatures while they shrink abruptly when heated above their LCST. This behavior has attracted great attention for possible technological applications such as drug delivery,[2–4] solute separation,[5] or preparation of sensors[6,7] and actuators.[8,9]

The properties of pNIPAAm hydrogels can be modified in several ways. For instance, the degree of swelling (DS) and the LCST values can be altered by cross-linking NIPAAm in the presence of comonomers of various degrees of hydrophilicity[10–12] or by changing the medium properties through the addition of cosolvents,[13] salts,[14] or surfactants.[15] The response rate can be enhanced by preparing hydrogels with a porous structure,[16,17] containing dangling chains,[18] or, finally, by copolymerizing NIPAAm with suitable monomers.[19] Recently, thermoresponsive composite materials were synthesized by incorporating montmorillonite into pNIPAAm gels.[20,21]

Montmorillonite is a layered silicate that is actively investigated for the preparation of polymer nanocomposites.[22] In comparison with unfilled polymers, these materials exhibit an unusual improvement in the mechanical properties for filler contents as low as 5 wt % or even lower.[23] Therefore, the incorporation of montmorillonite into hydrogels might improve their mechanical properties, which represent a weak point of these materials. Liang et al. used organically modified montmorillonite to prepare hydrogels that exhibited higher DSs and enhanced thermal response compared with conventional pNIPAAm gels.[21] Messersmith et al. synthesized materials containing two different amounts of sodium montmorillonite (NaMM) and they found that at relatively high NaMM loadings (10.7 wt %), pNIPAAm/NaMM composites did not exhibit appreciable themosensitivity.[20] However, extensive investigations on the influence of NaMM

TABLE I
Composition of Polymerizing Mixtures

Hydrogel	NaMM (g)	NIPAAm (g)	MBA (g)	Water (g)	TEA (μL)	AMPS[a] (mL)
NIP10	—	0.584	0.016	5.10	76	0.30
NIP10-MM10	0.067	0.584	0.016	5.04	76	0.30
NIP10-MM20	0.150	0.584	0.016	4.95	76	0.30
NIP10-MM30	0.258	0.584	0.016	4.84	76	0.30
NIP10-MM40	0.400	0.584	0.016	4.70	76	0.30
NIP12.5	—	0.876	0.024	5.85	110	0.45
NIP15	—	0.876	0.024	4.65	110	0.45
NIP12.5-MM20	0.225	0.876	0.024	5.63	110	0.45
NIP15-MM20	0.225	0.876	0.024	4.43	110	0.45

[a] AMPS solution with concentration of 20.4 mg/mL.

content on swelling were not performed by these authors; in addition, the effect of clay on the response rate and mechanical properties was not studied. Therefore, in this work, gels with five NaMM loadings were synthesized. Experiments were performed to study their equilibrium swelling behavior and their response rate at different temperatures and ionic strengths. Finally, uniaxial compression tests were performed to investigate the effect of NaMM on the modulus of the hydrogels.

EXPERIMENTAL

Materials

NIPAAm (97%) was purchased from Aldrich Co., Inc. (Milwaukee, WI), and the other reagents were from Fluka Chemie GmbH (Buchs, Switzerland). All reagents were used as received, with the exception of triethylamine (TEA), which was distilled under reduced pressure. NaMM was a kind gift from Laviosa S.p.A. (Livorno, Italy). This was an especially purified NaMM with a cation exchange capacity of 128 mEq/100 g and a particle size of 4–6 μm.

Hydrogel synthesis

Materials with NaMM contents in the dry state ranging from 0 to 40 wt % were synthesized at a fixed monomer concentration (10 wt %). For two compositions, gels also were obtained from 12.5 and 15 wt % monomer concentrations. Typical recipes are described in the following sections; the amount of each reagent is reported in Table I.

Synthesis of pNIPAAm hydrogels

NIPAAm and N,N'-methylenebisacrylamide (MBA) were put in a reaction tube (diameter, 14 mm) and dissolved in bidistilled water. The solution was degassed under vacuum and flushed with nitrogen

three times. Then, TEA and ammonium persulfate (AMPS) solution ($c = 20.4$ mg/mL) were added under nitrogen stream. The tube was sealed at 18°C for 24 h. The gel was washed thoroughly with 0.1M NaCl for 4 d and cut into discs 2 mm thick. The discs were washed with bidistilled water for 3 d and dried over P_2O_5 up to constant weight.

Synthesis of pNIPAAm/NaMM composite hydrogels

A suspension of NaMM in bidistilled water was sonicated for 4 h in a reaction tube (diameter, 14 mm). NIPAAm and MBA were dissolved in the tube and the mixture was degassed under vacuum and flushed with nitrogen three times. Then, TEA was added under nitrogen stream and the suspension was stirred for 60 min and sonicated for 15 min at 25°C. Finally, the AMPS solution ($c = 20.4$ mg/mL) was added under nitrogen stream. The tube was sealed and at a temperature of 18°C for 24 h. Purification and drying were performed as described for pNIPAAm.

Instruments and methods

Fourier transform–infrared (FT-IR) spectra were run on dry films using a Jasco 5300 FT-IR spectrophotometer (Easton, PA) equipped with a diffuse reflection attachment (model DR-81). To obtain the films, the hydrogels first were equilibrated in bidistilled water and then micronized and finally spread over the sample holder and dried in vacuo.

Scanning electron microscopy (SEM) investigations were performed with a Cambridge S260 microscope (ComScan Ltd., Waterbeach, UK) on gold sputtered specimens of freeze-dried hydrogels.

X-ray diffraction (XRD) patterns were obtained from a Siemens Kristalloflex-180 diffractometer (Bruker GmbH, Karlsruhe, Germany) with a Cu anode running at 40 kV and 50 mA, scanning from 2 to 25° at 0.016°/s.

TABLE II
Composition, DS, and Shear Modulus of Hydrogels

Hydrogel	Monomer concentration	NaMM content (wt %)		DS[c]	G (kPa)[d]
		Dry Material[a]	Hydrogel[b]		
NIP10	10	0	0	10.4	9.5
NIP10-MM10	10	10	1.0	9.4	11.5
NIP10-MM20	10	20	2.1	8.4	14.1
NIP10-MM30	10	30	3.7	7.2	15.6
NIP10-MM40	10	40	5.7	6.0	22.0
NIP12.5	12.5	0	0	8.2	—
NIP15	15	0	0	7.0	—
NIP12.5-MM20	12.5	20	2.4	7.2	—
NIP15-MM20	15	20	2.7	6.4	—

[a] NaMM content in dry materials. Values calculated from the composition of the reaction mixture.
[b] NaMM content in hydrogels equilibrated at 25°C in 0.1M NaCl. Values calculated from the composition of the reaction mixture and from the DS.
[c] DS at 25°C in 0.1M NaCl.
[d] Shear modulus of hydrogels equilibrated at 25°C in 0.1M NaCl.

Swelling measurements

The DS was determined through the following equation:

$$DS = \frac{w_s - w_d}{w_d}$$

where w_s and w_d were the weights of the swollen and dried sample, respectively. The weight w_s was determined removing the specimen from the bath, wiping rapidly its surface with filter paper, and weighing the hydrogel in a stoppered tared vial.

Shear modulus measurements

Uniaxial compression measurements were performed at 25°C on hydrogels previously equilibrated in 0.1M NaCl at the same temperature. The diameter and thickness of the specimens were 13 and 8 mm, respectively. The apparatus was similar to that described by Sayil and Okai.[24] A cylindrical gel of cross-sectional area A was coated with a thin film of silicone grease to minimize water loss and placed on a digital balance with a 0.01-g sensitivity. A rod was used to apply a compressive vertical displacement of 100 μm to the hydrogel. The displacement was measured using a comparator with 1×10^{-3}-mm sensitivity. The force F necessary to obtain such displacement was calculated from the mass value recorded by the balance. The sample was allowed to relax for 60 s before mass reading. The procedure was repeated several times, each time applying a displacement of 100 μm, up to a final deformation of $\sim$ 20%. The shear modulus G was determined as the slope of the plot of the stress $\sigma = F/A$ versus $(\lambda - 1/\lambda^2)$, where λ is the deformed length divided by the initial length of the specimen.

RESULTS AND DISCUSSION

PNIPAAm/NaMM composite hydrogels with different compositions and obtained from different monomer concentrations were prepared by polymerizing NIPAAm and MBA in aqueous clay suspensions. NaMM was sonicated previously to promote delamination in water. In all experiments, the MBA content was 2 mol % compared with NIPAAm. Yields were always >98%; therefore, the NaMM content in the gels was very close to that of the corresponding reaction mixture. The composition of dry materials and gels equilibrated in 0.1M NaCl at 25°C is reported in Table II.

The FT-IR spectra run on dry films showed the presence of typical bands of pNIPAAm (3290–3300 cm^{-1}, N—H stretching; 2973, 2934, and 2876 cm^{-1}, C—H stretching; 1649 cm^{-1}, amide I; 1539 cm^{-1}, amide II) and NaMM (1033 cm^{-1}, Si—O stretching). No evidence for band shifts compared with pNIPAAm and NaMM, which might provide useful indications on matrix-filler interactions, was found.

XRD experiments were run to gather information on the structure of pNIPAAm/NaMM composites. The XRD pattern of NaMM powder exhibited a peak for $2\theta = 8.9°$, which corresponds to a basal spacing of 0.99 nm. The intensity of the peak was reduced in the patterns of freeze-dried gels, suggesting that the clay was delaminated only partially.

The effect of the NaMM content on the thermosensitivity of pNIPAAm/NaMM hydrogels was investigated by equilibrium swelling experiments, which were run first at a fixed temperature (25°C) in NaCl solutions of different ionic strengths and then at different temperatures and a fixed ionic strength (0.1M NaCl). The response rate was investigated both in "slow-heating" experiments, where the specimens were heated gradually at 0.1°C/min from 5 to 70°C,
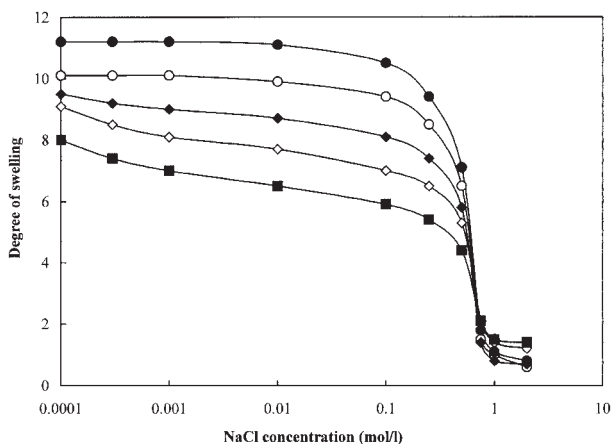
Figure 1 DS at 25°C versus NaCl concentration for NIP10 (●), NIP10-MM10 (○), NIP10-MM20 (♦), NIP10-MM30 (◇) ,and NIP10-MM40 (■).

and in "fast-heating" experiments, where the specimens first were equilibrated at 25°C and then allowed to deswell at 45°C. Finally, the effect of NaMM on the mechanical properties of the gels was investigated by uniaxial compression tests.

Effect of ionic strength on swelling

The behavior of aqueous clay dispersions is largely influenced by the presence of salts and polymers.[25] In fact, montmorillonite suspensions owe their stability to mutual repulsion of diffuse double layers existing around the particles. The thickness of the double layer decreases with increasing the concentration of salts dissolved in the medium. At high enough concentrations, clay particles approach each other so closely that they flocculate.

Polymers can be adsorbed on clay surfaces and alter particle interactions; therefore, depending on their structure, they can either sterically stabilize or flocculate clay suspensions.

On the other hand, pNIPAAm gels undergo a phase transition in NaCl solutions when the salt concentration exceeds a critical value, which is ~ 0.7M at 25°C.[26] For this reason, the effect of NaCl concentration on the DS of pNIPAAm/NaMM composite hydrogels was investigated.

First, the gels were equilibrated in $1 \times 10^{-4}M$ NaCl at 25°C, and then the ionic strength was increased gradually every 48 h up to 2M. The equilibration time was selected on the basis of preliminary experiments, which indicated that at 25°C dry materials reached a constant DS in 36 h. Figure 1 shows that all hydrogels exhibit a phase transition at the concentration typical of pNIPAAm (~ 0.7M). Therefore, the clay neither suppresses nor shifts noticeably the NaCl-induced transition compared with the unfilled gel. However,

the salt concentration being the same, the DS decreases with increasing the NaMM content. A possible explanation for this trend is that as a consequence of the adsorption of pNIPAAm chains on clay surfaces, the NaMM platelets act as physical cross-link sites thus reducing the DS.

It may be noticed that for all composite hydrogels except NIP10-MM10, the slope of the curves increases at low concentrations ($<10^{-3}M$). Probably, in NIP10-MM10, which has low clay loading, swelling is dominated by pNIPAAm, the platelets being highly dispersed among polymer chains. However, NaMM interactions are no longer neglectable in the gels with higher loadings and, for NaCl concentrations less than ~ $10^{-3}M$, the electrostatic repulsion between diffuse double layers produces the expansion of the hydrogels.

Effect of temperature on swelling

The influence of temperature on the DS was investigated by means of equilibrium experiments, which were run at a fixed ionic strength (in 0.1M NaCl). The temperature was increased step by step and the hydrogels were weighed after 48 h of equilibration at each temperature. Figure 2 shows that all hydrogels exhibit a phase transition between 30 and 35°C, which is in the typical range of pNIPAAm. Therefore, the introduction of NaMM does not shift appreciably the phase transition temperature. As observed in the experiments at variable ionic strength, the DS is lower the higher the NaMM content, so that the transition becomes less sharp with increasing the clay loading. This would explain why Messersmith et al. did not detect any LCST in hydrogels with 10.7 wt % of NaMM, a much higher content compared with our materials, which contain <5.7 wt % of clay (see Table II).
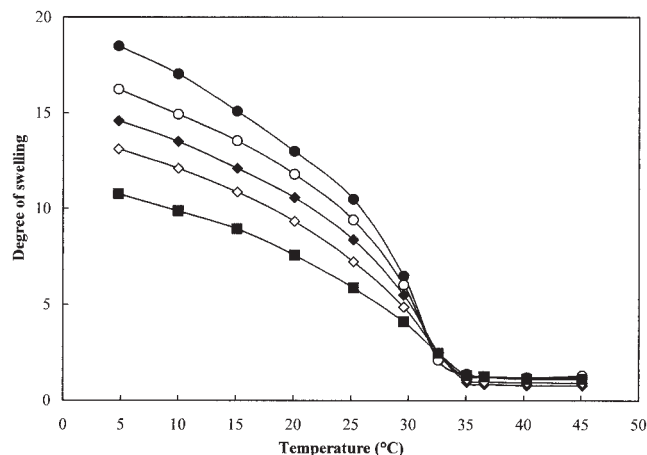

Figure 2 DS in 0.1M NaCl versus temperature for NIP10 (●), NIP10-MM10 (○), NIP10-MM20 (♦), NIP10-MM30 (◇), and NIP10-MM40 (■).
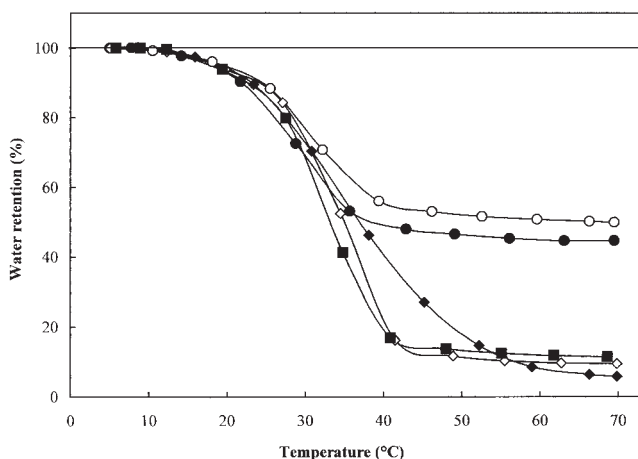
Figure 3 WR% versus temperature for hydrogels equilibrated in 0.1M NaCl at 5°C and heated at 0.1°C/min up to 70°C: NIP10 (●), NIP10-MM10 (○), NIP10-MM20 (◆), NIP10-MM30 (◇), and NIP10-MM40 (■).

Response to thermal stimuli

The equilibrium swelling curves, although important to evidence the thermosensitivity of the hydrogels, were obtained under conditions seldom encountered in practical applications. For this reason the response to thermal stimuli was assessed by slow-heating experiments, where the gels were first equilibrated in 0.1M NaCl at 5°C and then gradually heated at 0.1°C/min and weighed at intervals.

Figure 3 shows the resulting deswelling curves. They are expressed in terms of percent water retention (WR %), which represents the percentage of the water present in the hydrogel at the starting temperature T_0 that is retained at the temperature T. The WR % is related to the DS through the following relationship:

$$\text{WR \%}(T) = \frac{\text{DS}(T)}{\text{DS}(T_0)} \times 100$$

From inspection of the curves, three distinct behaviors can be recognized. The gels with no or low clay content, NIP10 and NIP10-MM10, retained 40–50% of water even when heated at 70°C; it can be calculated from Figure 2 that in equilibrium experiments residual water was already as low as 10% at 35°C. In contrast, the NaMM-rich hydrogels, NIP10-MM30 and NIP10-MM40, exhibited a much sharper transition, attaining water contents very similar to those of equilibrium experiments for $T > 40$–45°C. NIP10-MM20, which had an intermediate clay loading, showed also an intermediate deswelling curve, being able to shrink completely, but only at high temperatures.

The same trend was observed in "fast-heating" experiments, where the gels were first equilibrated in 0.1M NaCl at 25°C and then allowed to deswell at

45°C. Figure 4 a shows that NIP10 and NIP10-MM10 exhibited initially fast shrinking followed by very slow deswelling. After 24 h, they retained ~ 75% of water while the equilibrium retention at 45°C was nearly 10%. In contrast, NIP10-MM30 and NIP10-MM40 reached the equilibrium in roughly 100–150 min and NIP10-MM20 did the same but required longer times.

In Figure 4 b the deswelling curves of hydrogels having the same composition (0 and 20 wt % of NaMM in the dry material) but prepared using different monomer concentrations in the polymerizing mixture are compared. A considerable increase in the deswelling rate is observed in the composite hydrogels when the monomer concentration passes from 10
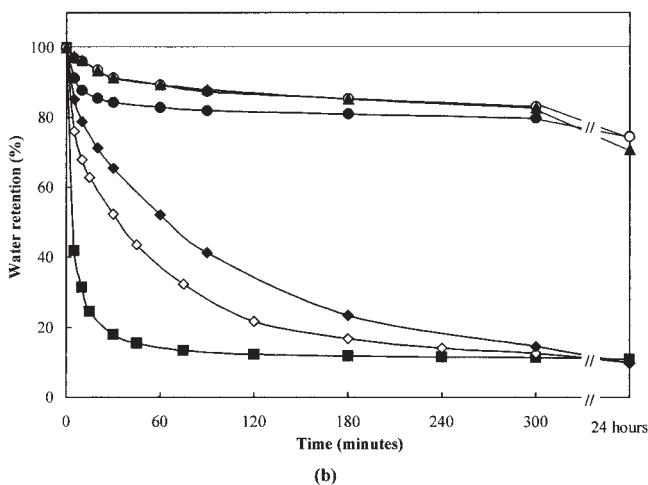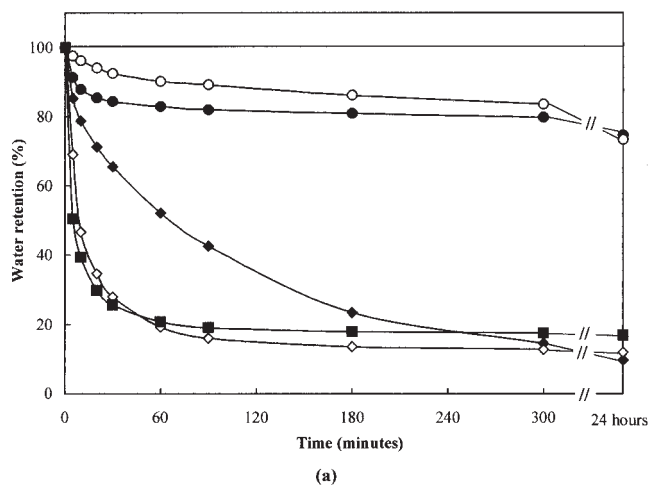

(a)

(b)

Figure 4 WR% versus time for hydrogels equilibrated in 0.1M NaCl at 25°C and shrunk at 45°C. (a) Hydrogels obtained from 10 wt % monomer concentration in the polymerizing mixture: NIP10 (●), NIP10-MM10 (○), NIP10-MM20 (◆), NIP10-MM30 (◇), and NIP10-MM40 (■). (b) Hydrogels obtained from different monomer concentrations: NIP10 (●), NIP12.5 (○), NIP15 (▲), NIP10-MM20 (◆), NIP12.5-MM20 (◇), and NIP15-MM20 (■).
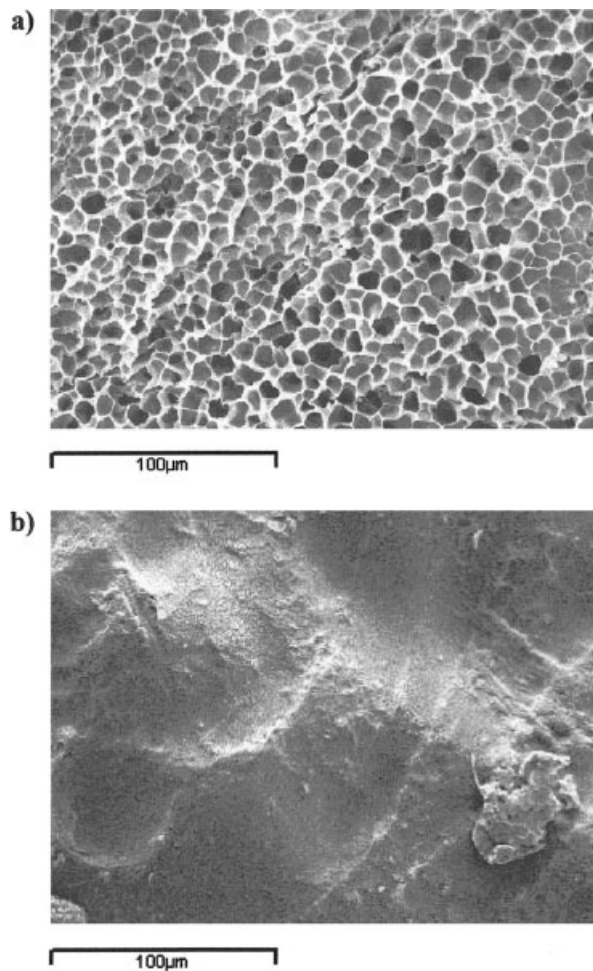
Figure 5 SEM micrograph of NIP10 (a) equilibrated at 25°C and (b) shrunk at 45°C for 30 min. Similar SEM images were obtained when the other gels were analyzed under the same conditions.

to 15 wt %, while a weaker and reverse effect is noticed in pNIPAAm specimens. Because the clay/polymer ratio is the same in the three composite gels and no substantial effect of the monomer concentration is observed in the pNIPAAm specimens, these results strongly suggest that the NaMM content has a dramatic influence on the shrinking kinetics of the gels. In fact, as shown in Table II, it is evident that a great enhancement of the deswelling rate is observed when the NaMM concentration passes from 2.1 wt % (NIP10-MM20) to 2.7 wt % (NIP15-MM20).

The same conclusion is valid also for the gels with different clay/polymer ratios (Figure 4 a), because NIP10-MM10 (1.0 wt % of NaMM) shows a behavior similar to NIP10, whereas shrinking becomes much faster passing from NIP10-MM20 (2.1 wt % of NaMM) to NIP10-MM30 (3.7 wt % of NaMM). Interestingly, deswelling of NIP10-MM40 (5.7 wt % of NaMM) follows almost the same kinetics as NIP10-MM30, in spite of the higher clay loading. Summarizing, our

data suggest that pNIPAAM/NaMM hydrogels undergo fast (or slow) deswelling according to whether their NaMM concentration is significantly greater (or lower) than a critical value, which is $\sim$ 2–3 wt %.

The observation that the gels with higher clay contents exhibit higher shrinking rates may appear surprising, because deswelling of thermosensitive hydrogels is a diffusion-limited process[27] and polymer-clay nanocomposites generally exhibit reduced permeability to solvents compared with unfilled polymers.[28] As suggested by other authors,[29] the limited deswelling shown by pNIPAAm hydrogels on rapid heating can be explained by assuming that shrinking of the external part of the specimens produces a hydrophobic surface layer that suppresses the diffusion of water from the inner part of the hydrogels to the surrounding medium. Therefore, the enhanced shrinking rate exhibited by the gels with higher NaMM contents might be explained assuming that NaMM prevents the formation of this skin layer. In fact, when pNIPAAM and pNIPAAm/NaMM hydrogels were equilibrated in water at 25°C, frozen in liquid nitrogen, freeze-dried, and analyzed by SEM, they displayed a cell-like surface (Figure 5 a). In contrast, if they were fixed at 45°C for 30 min before freeze-drying, a smooth surface was observed because of hydrogel shrinking (Figure 5 b). As shown in Figure 4 a, when NIP10 and NIP10-MM10 are fixed at 45°C, they expel only a small fraction of their water in 30 min, and their deswelling rate even decreases over the following period of time. Thus, deswelling of their surface produces a hydrophobic layer that hinders further shrinking. In contrast, the high water loss exhibited by the gels with higher NaMM loadings indicates that substantial and more uniform deswelling takes place in these specimens. Therefore, NaMM
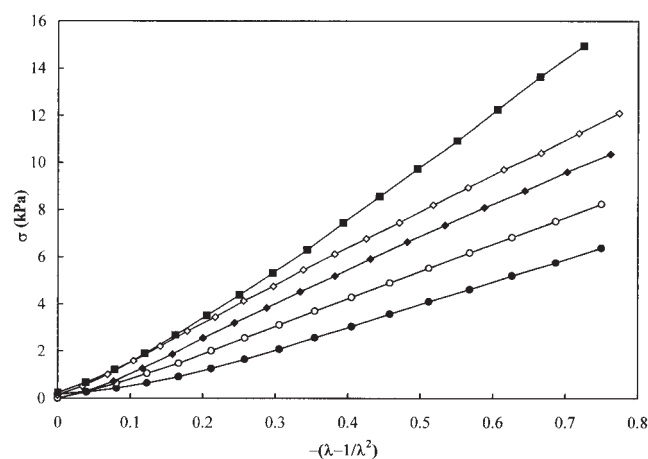

Figure 6 Stress versus $(\lambda - 1/\lambda^2)$ curves for uniaxial compression tests performed on hydrogels equilibrated in 0.1M NaCl at 25°C: NIP10 (●), NIP10-MM10 (○), NIP10-MM20 (◆), NIP10-MM30 (◇), and NIP10-MM40 (■).

seems to prevent the formation of the skin layer if its concentration is at least 2–3 wt %.

Interestingly, it is known that NaMM aqueous dispersions undergo sol-gel transitions for clay contents between 2 and 4 wt %, the exact value depending on the type of clay and on the salt concentration.[30] For NaCl concentrations greater than $\sim 0.01M$ the gel formation has been ascribed to attractive interactions occurring between the NaMM platelets. Therefore, a possible explanation for the different behavior exhibited by the hydrogels is that when the clay content approaches a critical value, the NaMM platelets form a physical network, which is able to hinder the hydrophobic association of pNIPAAm chains above the LCST. Studies are underway to confirm this hypothesis and to evaluate if the role of NaMM is just to limit the hydrophobic association or also to promote deswelling when attractive interactions of the clay platelets lead to their aggregation.

Shear modulus of hydrogels

The effect of montmorillonite on the mechanical properties of the hydrogels was evaluated by uniaxial compression tests run at 25°C on specimens previously equilibrated in $0.1M$ NaCl at the same temperature. Assuming the validity of the classical equation of rubber elasticity,[31]:

$$\sigma = G \left(\lambda - \frac{1}{\lambda^2} \right)$$

where σ is the compressive stress, λ is the deformed length divided by the initial length of the specimen, and the shear modulus G was determined as the slope of the plot of σ versus $(\lambda - 1/\lambda^2)$. The experimental curves (Figure 6) evidence a deviation from linearity at small deformations, which, as suggested by literature data,[32] probably is related to imperfections in the surface of the specimens. The values of G increase with the NaMM content from 9.5 kPa for NIP10 up to 22 kPa for NIP-MM40 (see Table II). Figure 7 shows that a linear relationship exists between shear modulus and water content, thus suggesting that the increase in modulus is a consequence the reduced DS. In turn, as previously discussed, the reduction of the water content is probably a consequence of attractive interactions occurring between the NaMM platelets and pNIPAAm chains.

CONCLUSION

The pNIPAAm/NaMM composite investigated showed both the thermally induced and the NaCl-induced phase transitions typical of pNIPAAm. The incorporation of clay did not shift appreciably the
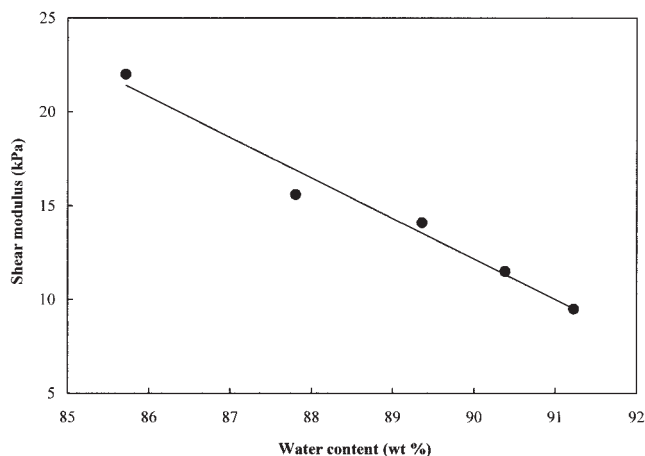

Figure 7 Shear modulus variation as a function of the water content for pNIPAAm/NaMM composite hydrogels of different compositions.

position of these transitions compared with unfilled hydrogels, but it reduced substantially the DS. When the clay content approached a critical value, a substantial enhancement of the response rate was observed. It is suggested that when the NaMM concentration is high enough, the clay platelets can establish a physical network that hinders the hydrophobic association of pNIPAAm chains and therefore the formation of the hydrophobic skin layer typical of pNIPAAm hydrogels. The shear modulus increased with the NaMM content and this was ascribed essentially to the reduction of the DS induced by the presence of clay.

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