

Swelling Behavior of Poly(acrylamide)/Clay Nanocomposite Hydrogels in Acrylamide Aqueous Solution

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ABSTRACT: The swelling behaviors of poly(acrylamide) (PAAm)/clay nanocomposite hydrogels (hereinafter abbreviated as NC gels) in acrylamide (AAM) aqueous solution have been investigated. As-prepared PAAm/clay hydrogels (S-M gels) were posttreated by immersing them in AAM aqueous solution. It was found that the swelling ratio of the NC gels increased greatly when the concentration of the solution is below a critical concentration (c^*), whereas the gels were disintegrated in the solution when the concentration of the solution is above the c^* . Some

disc-like particles were found in the AAM solution accompanying with the unusual swelling behaviors. This unusual swelling behavior is resulted from the change of network structure of the NC gels in AAM aqueous solution, which was further convinced by transmission electron microscopy and element analyses. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 353–358, 2009

Key words: nanocomposites; hydrogels; clay; swelling; disintegrated

INTRODUCTION

In recent years, polymer/clay nanocomposite (NC) gels have attracted much attention because of their excellent properties such as very large deformability, amazing toughness, and better resilience.^{1–5} It consists of poly(*N*-isopropylacrylamide) (PNIPAAm) and clay Laponite XLG (Clay-G). Clay-G, a synthetic hectorite clay, forms disc-like particles with a diameter of 20–30 nm, a thickness of 1–2 nm, and a negative surface charge density stabilizing dispersions when it is suspended in water.^{6,7} Indeed, with increasing clay content, the mechanical strength of the gels increases. However, most NC gels have been synthesized with low clay content because of the high viscosity of the aqueous clay dispersion at high clay concentration. Recently, high clay content PNIPAAm hydrogels (S-N gels) and PAAm hydro-

gels (S-M gels)^{8–10} have been successfully prepared by using Laponite XLS (Clay-S), a kind of synthetic hectorite modified by tetrasodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$). This Laponite XLS can be easily dispersed in water up to about 15% (w/v) with no need for a special mixer and complicated procedure, unlike the preparation of similar NC gels with Laponite XLG. S-M gels based on AAM as the monomer and Clay-S as the inorganic crosslinker are very tough and can withstand high levels of elongation without damage, when compared with the weak and fragile hydrogels started with AAM and *N,N'*-methylenebisacrylamide (NMBA, as organic crosslinker). Interestingly, the properties can be modulated by heat posttreatment.⁴ The swelling ratio of the hydrogels increases greatly after heat treatment, much higher than that of any other reported NC gels.¹¹ Although many efforts have been made to clarify the precise mechanisms and interaction between clay and polymer chains,^{12–20} no direct evidence has been reported up to now.

Unusual swelling behaviors of S-M hydrogels in AAM aqueous solution were found in this study, which gives some direct evidences to clarify the precise mechanism and interaction between clay and polymer chains. The as-prepared hydrogels after posttreatment become water-swollen or disintegrated in AAM aqueous solution. The origin of this unexpected swelling behavior is discussed on the basis of the results of the swelling, TEM, and EA.

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TABLE I
State of the S-M, OR-PAAm Hydrogels in AAm Aqueous Solution

Samples	Concentration of AAm aqueous solution (w/v)								
	1%	2%	5%	8%	10%	12.5%	15%	18%	20%
S10M5	+	+	-	-	-	-	-	-	-
S10M10	+	+	+	+	-	-	-	-	-
S10M15	+	+	+	+	+	+	-	-	-
S10M20	+	+	+	+	+	+	+	+	-
OR-PAAm	+	+	+	+	+	+	+	+	+

⁺represents the hydrogels are swollen; ⁻represents the hydrogels are disintegrated.

EXPERIMENTAL PART

Materials

Acrylamide (AAm) (98.5%, chemically pure; Shanghai Fine Chemical Material Institute, Chemical Purity, Shanghai, China), synthetic hectorite Laponite XLS (Clay-S) (Rockwood, USA, 92.32 wt % Mg_{5.34}Li_{0.66} Si₈O₂₀ (OH)₄Na_{0.66} and 7.68 wt % Na₄P₂O₇], NMBA, potassium persulfate (KPS), and *N,N,N',N'*-tetramethyldiamine (TEMED) (analytical reagent; Shanghai Chemical Reagent) were used as received. All solutions used in the experiments were prepared in deionized water.

Preparation of the S-M hydrogels

The hydrogels were prepared with initial solutions consisting of a monomer (AAm), a crosslinker (Clay-S or NMBA), an initiator (KPS), and an accelerator (TEMED). In all cases, the water/initiator ratio and the volume of the accelerator were fixed at 1000/1 (w/w) and 24 μ L, respectively. First, a transparent aqueous solution consisting of water (28 mL), clay (1.5–3.0 g) or NMBA (0.015 g), and AAm (3–6 g) was prepared. Then, the accelerator (TEMED, 24 μ L) and an aqueous solution of the initiator (KPS; 0.03 g in 2 mL of water) were added to the former solution with stirring at room temperature. Next, free radical polymerization was carried out at room temperature for 120 h. All the hydrogels were synthesized in air-tight glass tubes (interior size: 5 mm in diameter and 60 mm in length).

Posttreatment of S-M hydrogels

The as-prepared hydrogels (sample size: 5 mm in diameter and 20 mm in length) were immersed in 50 mL AAm aqueous solution with different concentrations at room temperature. After fully swelling, the SxMy hydrogels were put in a large excess of deionized water for at least 2 weeks at room temperature. The deionized water was changed repeatedly to remove AAm molecules until reaching a new equilibrium over the time.

In this article, the NC hydrogels are expressed as SxMy where S and M stand for the Clay-S concentration, PAAm content, respectively; and x, y stand for 100 \times clay/water (w/w) and 100 \times monomer/water (w/w), respectively. For example, S5M20 stands for the hydrogel containing Clay-S with a Clay-S/water ratio of 5/100 (w/w), PAAm with a polymer/water ratio of 20/100(w/w). A traditional PAAm hydrogel crosslinked by organic reagents (i.e., NMBA) is called an OR-PAAm gel.

Measurement of swelling properties

The swelling ratios of SxMy hydrogels in AAm aqueous solution and in water were investigated.

As-prepared gels (initial size of 5 mm in diameter and 20 mm in length) were immersed in a large excess of solution at certain time until the gel weight approached saturation. The fully swelling gels were taken out of the solution at certain time and blotted with wet filter paper to remove excess solution on the hydrogel surface and weighed. The equilibrium swelling ratio (SR) was calculated with the following equation:

$$SR = (W_s - W_d)/W_d \quad (1)$$

where W_s is the weight of the swollen hydrogel and W_d is the weight of the dry hydrogel; samples were dried under atmospheric conditions (25°C) for 3 days and then at 80°C under vacuum for 24 h. The swelling ratios of OR-PAAm gels were measured by the same procedures as control.

Transmission electron microscopy

Changes of the property of the AAm aqueous solution having immersed SxMy hydrogels were observed by TEM (H-800, Hitachi, Japan) testing. After immersed in 5 % (w/v) AAm aqueous solution for about 50 h, the S10M10 gel was removed from the solution and the solution was subjected to TEM testing.

Element analyses

Changes of the component of the AAm aqueous solution having immersed SxMy hydrogels were measured by EA (ELIII, Vario, Germany). The samples were treated by the same procedure as earlier for EA.

RESULTS AND DISCUSSION

Preparation of S-M gels

Uniform PAAm hydrogels (S-M gels) were prepared by *in situ* free radical polymerization in solutions containing different amounts of AAm, in all cases without any phase separation or precipitation. In all S-M gels, it was found that the shape of the resulting hydrogel was the same as that of the vessel used. Polymerization yields, evaluated from the weights of dried gels,¹ were nearly 100% in all cases.

Swelling properties

The states of as-prepared S-M hydrogels are different with the change of AAm concentration in aqueous solution. The hydrogels swell and still remain noncolor, transparent, and complete shape at low concentration. They become disintegrated before fully swollen and lose their initial shapes at high concentration. As shown in Table I, there is a critical concentration c^* ([AAm] in w/v %) for a certain hydrogel. When the concentration c is lower than c^* , hydrogels swell fully and have no disintegration, as shown in Figure 1(b), (e.g., c^* is 10% for S10M10, while it is 20% for S10M20). It seems that c^* is related to the content of PAAm (c_p in w/w) in the hydrogel. When c is the same with or higher than c_p , the hydrogel is disintegrated. Especially, the hydrogels almost dissolved in the solution and the solution became very viscous when the [AAm] is too high, as shown in Figure 1(c).

This special behavior has not been reported according to our information. To understand the origin of this unusual swelling behavior, the SR of a serial of S-M gels in AAm aqueous solution were measured. As shown in Figure 3(a), almost all hydrogels have a higher equilibrium swelling ratio after posttreatment.

As a rule, the equilibrium swelling ratio of a hydrogel depends on the hydrophilicity of the polymer chains and the physical structure of the hydrogels.²⁰ In AAm aqueous solution, the chemical components of the SxMy hydrogels do not change, so the remarkable increase of the swelling ratio of the SxMy hydrogels should be ascribed to the change in the physical structure of the hydrogels.

Generally, the interaction between PAAm and Clay-S is regarded as a combination of hydrogen

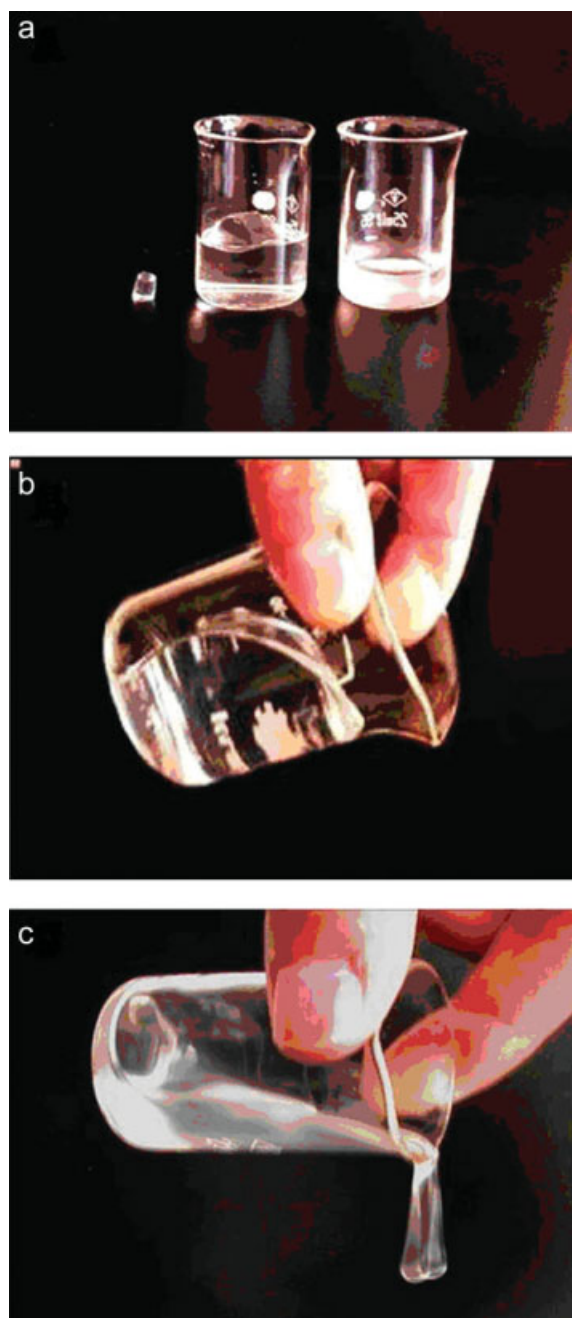


Figure 1 Comparison of the as-prepared, swollen and disintegrated S10M10 hydrogels: (a) as-prepared hydrogels (left); hydrogel in water (middle); hydrogel in 40% (w/v) AAm aqueous solution (right); (b) swollen hydrogel in water; (c) disintegrated hydrogel in AAm aqueous solution. [Color figure can be viewed in the online issue, which is available at www.interscience.com.]

bonding and ionic interaction. The oxygen atoms of the clay surface may be able to form hydrogen bonds with the amide proton of AAm, and the metal atoms on the clay surface may form a complex with the carboxyl oxygen of AAm.^{1,2} After preparation, the polymer chains in the gel are in a dynamic adsorption/desorption equilibrium with the clay

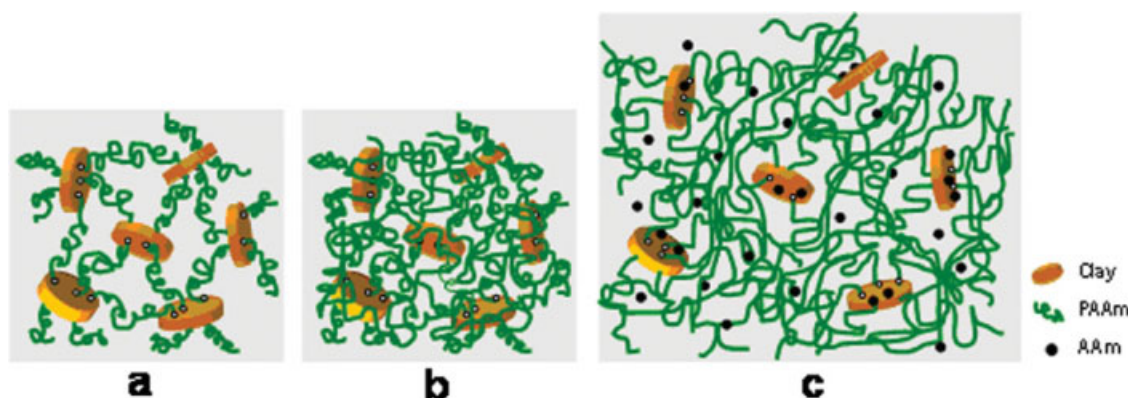


Figure 2 Cartoon demonstration of (a) primary bone structure of S-M gel on the earlier formation; (b) state of the resulting S-M gels; (c) swollen S-M gels in AAm aqueous solution with the concentration below a critical concentration (c^*). Only a part of the nanocomposite hydrogel is drawn for clarity. [Color figure can be viewed in the online issue, which is available at www.interscience.com.]

particles.¹⁷ As AAm molecules and PAAm chain have the same functional group to interact with clay particles, the original equilibrium is destroyed in AAm aqueous solution. Some PAAm chains may separate from the surface of the clay particles and the active sites are taken up by AAm molecules.

However, as suggested by Haraguchi et al.,^{1,2,5} the polymer chains growing from the surface of the individual clay during gelation may form bridges between the particles. The clay particles are already surrounded by the polymer chains after the state of hydrogel preparation. Therefore, we suggest that the earlier formed polymer chains (abbreviated as Chain I) can distribute uniformly on the surface of clay as the primary network structure of the gels. This situation is schematically illustrated in Figure 2(a). As the polymerization reactions proceed, the later formed polymer chains (abbreviated as Chain II) can cover only the surface of the former polymer chains,

resulting in inhomogeneous network structure, even some repeat units of one polymer segment may anchor on the same clay particles [as shown in Fig. 2(b)]. The uneven network structure will result in some polymer chains becoming useless or negative for the swelling of the gels. Hence, it is possible that under the effect of AAm molecules, the Chain II being useless or negative for the swelling of the gels detach first from the surface of the clay. Consequently, the AAm molecules occupy the active sites, as shown in Figure 2(c). This endows hydrogels with a larger effective chain length for swelling, as shown in Figure 3(a) (e.g., from 67 g/g for S10M20 in water to 1006 g/g for S10M20 in 18% AAm aqueous solution).

The SR of all SxMy hydrogels is concentration-dependent in AAm solution. With the increase of the concentration, the SR of all SxMy gels increase greatly (e.g., from 520 g/g for S10M10 in 1% AAm

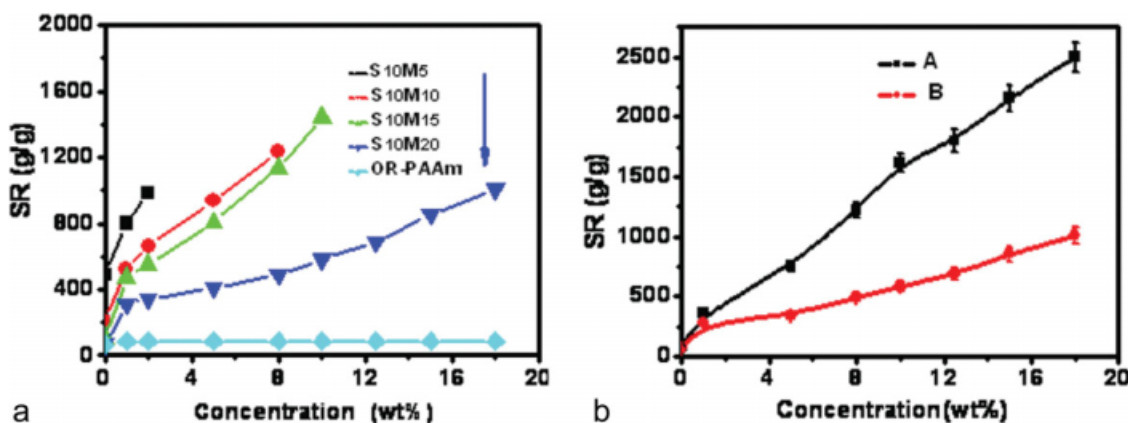


Figure 3 (a) Effects of the concentration of AAm aqueous solution on the equilibrium swelling ratio of the S-M hydrogels; (b) equilibrium swelling ratio of S10M20 hydrogels posttreated in different AAm aqueous solution A: the swelling ratio of the gel in water; B: the swelling ratio of the gel in the posttreating solution. [Color figure can be viewed in the online issue, which is available at www.interscience.com.]

TABLE II
The Results of Element Analyses

Element of Laponite XLS	Na (μg)	Mg (μg)	Si (μg)	Li (μg)
Element mass ratio in theory	4.94	27.74	48.48	1
Element mass ratio of the sample	51.91	29.96	45.47	1

aqueous solution to 1235 g/g for S10M10 in 8% AAm aqueous solution), indicating that the higher the concentration of AAm solution, the more polymer chain detach from the clay surface. According to the context, the concentration of the solution corresponding to the maximum SR is c^* . Thus it is understandable that when the concentration c is higher than c^* , too many polymer chains will separate from the clay particles and the main network structure of the S-M gels is disintegrated. This result further verifies the relationship between c^* and c_p .

In contrast, OR-PAAm gels swell slightly in AAm aqueous solution regardless of the AAm concentration (e.g., from 67 g/g in water to 87 g/g in AAm aqueous solution). This is due to that the structures of the hydrogels with chemical crosslink do not change in AAm solution.

The SRs of the posttreated SxMy hydrogels in water are given in Figure 3(b). As shown in Figure 3(b), the SR of the posttreated SxMy hydrogels in water increase further (e.g., from 1006 g/g for S10M20 in 18% AAm aqueous solution to 2500 g/g for the gels in water). It is possible that a higher osmotic pressure for the posttreated hydrogel in water than that of in AAm solution¹⁰ was obtained. So the swelling ratio of posttreated gels increases further in water when compared with that of in AAm solution.

EA

As aforesaid, if the polymer chains separate from the surface of the clay particles under the action of AAm molecules, there must be some clay

particles that isolate and enter into the solution. To confirm the existence of some free Clay-S particles in the AAm aqueous solution during posttreating the gels, the AAm aqueous solution having immersed SxMy hydrogels were measured by EA. The results are given in Table II. It is clear that the values of the element mass ratio of the sample in this study are quite close to those of theory calculation of Clay-S except the value of element Na, which is much higher than that of theory calculation. A possible reason is that the excess of Na is being brought in when the solution is diluted during EA.

TEM analyses

Figure 4 shows TEM images of pure clay aqueous solution and the AAm aqueous solution after immersing as-prepared hydrogels. As shown in Figure 4(b), some discs can be observed clearly. They are isolated individually or combined with others. According to the results of EA, there are some clay particles in the solution by posttreatment. So it is quite possible that the discs are clay particles. The monodisperse discs have a diameter of 20–30 nm, which agrees with the size of Laponite XLS according to former reports.^{6,7} Thus we can safely say that these discs are clay particles. It is very interesting to note that the contours of Laponite XLS in TEM images, which dispersed in pure water or in normal AAm aqueous solution, cannot be seen clearly, while they are quite clear in the AAm solution as seen in this work. A possible reason for this is that some PAAm chains detached from the

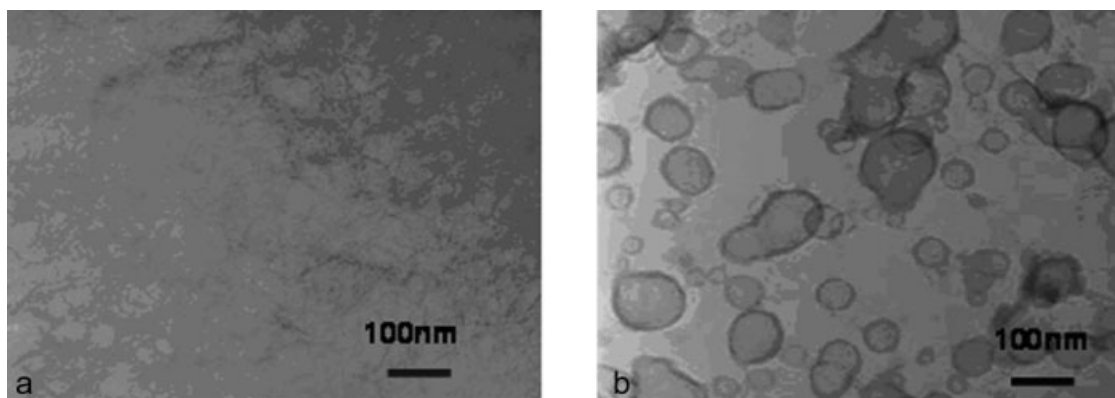


Figure 4 TEM images of (a) pure clay aqueous solution; (b) the AAm aqueous solution after immersing as-prepared hydrogel.

clay surfaces and entered into the solution as free chains, which act as background in TEM images. As a result, the clay discs can be observed clearly.

CONCLUSIONS

NC hydrogels based on PAAm as the hydrophilic polymer components and Clay-S as crosslinkers were posttreated in AAm aqueous solution. The SxMy hydrogels exhibit unusual swelling behaviors over posttreatment. When the concentration of the solution is below c^* , the swelling ratio of NC hydrogels increased constantly until they reach a swelling equilibrium after about 120 h. When the concentration of the solution is above the c^* , the gels became disintegrated before they fully swell. Swelling measurements combined with TEM and EA tests show that the physical structure of PAAm/Clay NC hydrogels changes as the result of posttreatment. The polymer chains detach from clay surfaces and some free Clay-S particles enter into the solution, which proves clay particles and polymer chains in polymer/clay NC gels connected by physical crosslinking, a kind of interaction weaker than chemical bond. This result also confirms that the properties of S-M gels can be modulated successfully besides the methods of heating or monomer aqueous solution posttreatment by controlling suitable conditions. The studies of other properties of the S-M gels posttreated by AAm aqueous solution are in progress.

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