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Unusual swelling behavior of polymer–clay nanocomposite hydrogels

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Abstract

The swelling behavior and the elastic properties of nanocomposite hydrogels have been investigated. The hydrogels were prepared by free-radical polymerization of the monomers acrylamide (AAm), *N*,*N*-dimethylacrylamide (DMA), and *N*-isopropylacrylamide (NIPA) in aqueous clay suspensions at 21 °C. Laponite with a radius of gyration in distilled water of 20 nm was used as clay particles in the hydrogel preparation. The reactions with AAm monomer were carried out in the presence of the chemical crosslinker *N*,*N*′-methylenebis(acrylamide) (BAAm). It was found that the volume of nanocomposite hydrogels immersed in water rapidly increases and attains a maximum value after about one day. Surprisingly, further increase in the swelling time results in the deswelling of the gels until they reach a limiting swelling ratio after about 5 days. This unusual swelling behavior is observable only when the clay concentration in the hydrogel is above the overlap threshold c^*. Swelling measurements combined with the elasticity tests show that the effective crosslink density first decreases, but then increases with increasing time of swelling of the hydrogels. The results were explained in terms of the rearrangements of the highly entangled polymer chains and clay particles during the gel volume change.

Keywords: Nanocomposite hydrogels; Clay; Swelling

1. Introduction

Design of hydrogels with a good mechanical performance is crucially important in many existing and potential application areas of soft materials. Several attempts have been made in recent years to design hydrogels with excellent mechanical performance [1]. Haraguchi et al. prepared such hydrogels starting from acrylamide (AAm)-based monomers together with Laponite as a physical crosslinker, replacing the traditional chemical crosslinkers [2–5]. Laponite, a synthetic hectorite clay, when suspended in water forms disc-like particles with a thickness of 1 nm, a diameter of about 25 nm, and a negative surface charge density stabilizing dispersions in water [6,7]. Formation of a crosslinked polymer network using a small amount of Laponite indicates that these nanoparticles act as a multifunctional crosslinker with a large effective functionality. The action of Laponite as a crosslinker seems to be due to strong interactions at the clay–polymer interface and the combination of polymer and inorganic components within a single material on a nanoscale level. Such nanocomposite hydrogels are attractive for a wide range of applications [8,9].

Contrary to the conventional chemically crosslinked hydrogels, the nanocomposite hydrogels formed using Laponite as a crosslinker exhibit extraordinary mechanical toughness, tensile moduli, and tensile strengths [2–5]. Haraguchi explained this unusual feature of Laponite hydrogels with the uniform distribution of the clay particles within the hydrogel sample [2–4]. Shibayama et al. investigated the structure and molecular dynamics of the nanocomposite hydrogels by SAXS, X-ray scattering, dynamic light scattering and contrast-matched SANS experiments [10–12]. Although the chain dynamics of nanocomposite hydrogels is similar to the conventional chemically crosslinked gels, it was shown that the inhomogeneity in these

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hydrogels is mainly due to the clay–clay and the clay–polymer scatterings. They suggested that the action of Laponite as a multifunctional crosslinker is responsible for the good mechanical performance of such materials. More recently, Okay and Oppermann have observed by rheological experiments that a large energy dissipation occurs during the deformation of the nanocomposite hydrogels that contain Laponite [13]. These results suggest that the polymer chains in the gel are in a dynamic adsorption/desorption equilibrium with the clay particles. An order of magnitude with a larger value of the loss factor tan δ of nanocomposite hydrogels compared to the chemically crosslinked hydrogels is an indication of such dynamic processes and requires an extensive rearrangement of the highly entangled polymer material close to the clay surface [13]. This rearrangement during deformation is likely to equalize the force acting on the gel among the polymer chains and, thus, is responsible for the excellent mechanical performance of these materials. Considering that the dynamics in the nanocomposite hydrogels needs diffusive motion of both the nanoparticles and the polymer chains, one may expect that swelling of the gel in a good solvent should enhance the rearrangements inside the gel network. As the nanocomposite gel swells, the particles will move apart to contact more chain segments, which would induce variation in the network structure and physical properties of the gel.

This study aims to observe the structural response of nanocomposite hydrogels subjected to swelling tests. Here, we report unusual swelling behavior of nanocomposite hydrogels based on polyacrylamide (PAAm), poly(*N*,*N*-dimethylacrylamide) (PDMA) and poly(*N*-isopropylacrylamide) (PNIPA) as the hydrophilic polymer components and Laponite XLS as the clay component. When the nanocomposite hydrogel after preparation is immersed in water, it first swells but then deswells again until attaining a thermodynamic equilibrium state with the surrounding water phase. The origin of this unexpected self-deswelling behavior is discussed on the basis of the results of the swelling and elasticity test conducted at various swelling times.

2. Experimental section

2.1. Materials

Acrylamide (AAm, Merck), *N*,*N*-dimethylacrylamide (DMA, Aldrich), *N*-isopropylacrylamide (NIPA, Aldrich), *N*,*N*′-methylenebis(acrylamide) (BAAm, Merck), ammonium persulfate (APS, Merck), and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED, Merck) were used as received. The synthetic hectorite clay, Laponite XLS $Na^{+}_{0.7}[(Si_8Mg_{5.5}Li_{0.3})O_{20}(OH)_4]^{0.7-}$, modified with pyrophosphate ions ($P_2O_7^{4-}$) was provided by Rockwood Ltd. Note that both the surfaces and the edges of Laponite XLS discs are negatively charged, leading to electrostatic repulsion among the discs and efficiently prohibiting the formation of a gel structure [6,7]. Indeed, Laponite XLS can be easily dispersed in water up to about 10% concentration. Suspensions of Laponite XLS were prepared by dispersing the white powder at the preset concentrations in deionized water with vigorous stirring for one week.

2.2. Polymerization

Nanocomposite hydrogels were prepared in a similar manner to that reported previously [13], i.e., by free-radical polymerization of the monomers in aqueous clay suspensions using APS–TEMED redox initiator system at 21 °C. The initial concentration of the monomers AAm, DMA, and NIPA was set to 5 w/v % (grams of monomer/100 ml solution), while the Laponite concentration was varied over a wide range. The monomer AAm, DMA, or NIPA and the accelerator TEMED (0.25 v/v %) were first dissolved in Laponite XLS aqueous suspensions. The reactions using the monomer AAm were carried out in the presence of BAAm crosslinker at different chemical crosslinker ratios X, the molar ratio of the chemical crosslinker BAAm to the monomer AAm. After bubbling nitrogen, the initiator APS (3.51 mM) was added to the reaction solution and the polymerization was conducted in plastic syringes of about 4 mm internal diameter for 24 h. In this way, several series of PAAm, PDMA, and PNIPA nanocomposite hydrogels were prepared at various clay contents. Clay concentrations were expressed as grams of Laponite XLS/100 ml reaction solution (w/v %).

2.3. Extraction of clay particles

The Laponite concentration in the gel network was determined by the extraction of the hydrogels in an excess of water and then drying the insoluble material to constant mass. For this purpose, the hydrogel samples after preparation in the form of rods of 4 mm in diameter were placed in an excess of water at 21 °C. To achieve good precision, three measurements were carried out on samples of different lengths taken from the same gel. The samples were immersed in water for at least three months replacing the water every week. Thereafter, the hydrogel samples equilibrium swollen in water were carefully deswollen in a series of water–methanol mixtures with increasing methanol contents. This solvent exchange process facilitated final drying of the hydrogel samples. They were then washed several times with methanol and dried at 80 °C to constant weight. Assuming that the conversion of the monomers AAm, NIPA and DMA to the crosslinked polymer is complete [14–16], Laponite concentration C^b_{clay} (in w/v %) inside the gel after extraction can be calculated as

$$C^b_{\text{clay}} = 10^2 \frac{\left(m_{\text{dry}} - m_0 C_M/100\right)}{m_0} \tag{1}$$

where m_0 and m_{dry} are the weights of the gel sample after preparation and after drying, respectively, C_M is the initial concentration of the monomer (5 w/v %). Note that Eq. (1) gives the Laponite concentration inside the gel with respect to the after preparation state. In Fig. 1, the concentration of Laponite C^b_{clay} remaining in the PAAm gel ($X = 1/80$) after extraction is plotted against its concentration C_{clay} in the reaction mixture. If $C^b_{\text{clay}} = C_{\text{clay}}$, all the particles remain inside the gel network, indicating that the particles are bound strongly to the polymer chains. This condition is represented in the figure by the

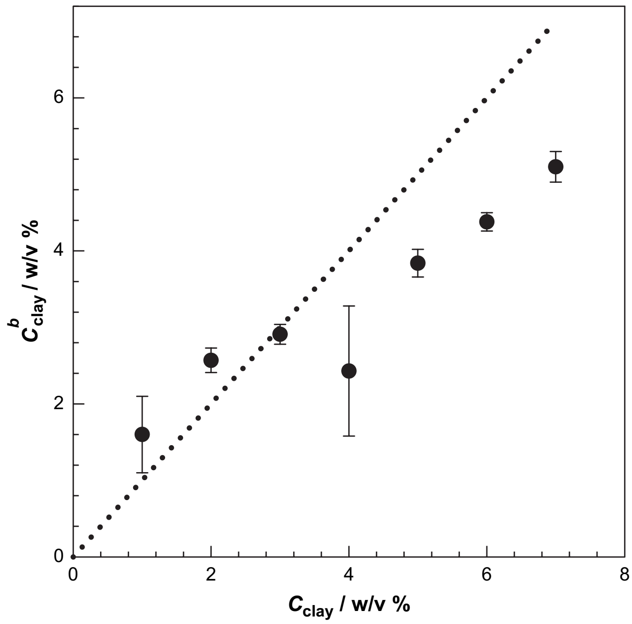

Fig. 1. Concentration of Laponite C^b_{clay} remaining in the PAAm gel network after extraction shown as a function of its concentration C_{clay} in the reaction mixture. The dotted line represents the relation $C^b_{clay} = C_{clay}$.

diagonal dotted line. Moreover, smaller values of C^b_{clay} indicate escape of some Laponite particles from the gel network. It is seen that, at or below $C_{clay} = 3\%$, most of the Laponite used in the gel preparation remains inside the gel as bounded to the polymer chain. Deviation from the dotted line mainly appears above 3% Laponite, indicating that some clay particles can be extracted from the gel network. Moreover, within the limits of experimental error of about 8%, C^b_{clay} was found to be equal to C_{clay} for both PNIPA and PDMA hydrogels over the range of concentration investigated (5–9 w/v %).

2.4. Swelling measurements

The nanocomposite hydrogels formed in syringes of about 4 mm internal diameter were cut into samples of about 10 mm length. Then, each sample was placed in an excess of water at 21 ± 0.5 °C and water was replaced every day. The gel volume change during the course of swelling was monitored by measuring the diameter of the gel samples by using an image analyzing system consisting of a microscope (XSZ single Zoom microscope), a CDD digital camera (TK 1381 EG) and a PC with the data analyzing system Image-Pro Plus. The swelling ratio V_{rel} at a given swelling time t was calculated as

$$V_{rel} = (D/D_0)^3 \tag{2}$$

where D and D_0 are the diameters of the gel sample at time t and just after its preparation, respectively.

2.5. Elasticity tests

Uniaxial compression measurements were performed on nanocomposite hydrogels in water after certain swelling times. All the mechanical measurements were conducted in a thermostated room of 21 ± 0.5 °C. The stress–strain isotherms were measured by using an apparatus previously described [14,17]. The elastic modulus G was determined from the slope of linear dependence

$$f = G\left(\lambda - \lambda^{-2}\right) \tag{3}$$

where f is the force acting per unit cross-sectional area of the undeformed gel specimen and λ is the deformation ratio (deformed length/initial length).

3. Results and discussion

Fig. 2 shows the diameter D of the nanocomposite PAAm (A) and PDMA (B) hydrogel samples as a function of swelling time in water. The measurements were carried out by online monitoring of the diameter of the gel samples immersed in water under an optical microscope coupled with an automatic image analyzing system. In addition to the clay, the chemical crosslinker BAAm was also used in the preparation of PAAm hydrogels. This is due to the fact that (i) PAAm nanocomposite hydrogels without BAAm crosslinker were too weak to withstand the mechanical tests, especially at low clay contents and (ii) they become invisible under the microscope after about 6 h of swelling time so that their swelling process cannot be monitored. The chemical crosslinker ratio X given in Fig. 2 denotes the molar ratio of the crosslinker BAAm to the monomer AAm. Fig. 2A also shows pictures of a gel sample with 7 w/v % Laponite taken at different swelling times. For all the gel samples, no distortion in the cylindrical shape of the gels was observed during the course of swelling. It is seen that the diameter of the nanocomposite hydrogels rapidly increases with increasing time of swelling and attains a maximum value after about one day. Surprisingly, further increase in the swelling time results in the deswelling of the gels until they reach a limiting swelling ratio after about 5 days. This self-deswelling behavior was also observed in PNIPA hydrogels with a clay content of 5% or above.

The appearance of a maximum in the swelling curve of the nanocomposite hydrogels has not been reported before. To understand the origin of this unusual swelling behavior, both the swelling ratio V_{rel} and the modulus of elasticity G of the hydrogels were measured at different swelling times. For this purpose, the samples were taken out of the solution at certain time intervals and they were subjected to swelling and elasticity tests. The measurements with PAAm gels ($X = 1/80$) containing 7 w/v % Laponite were conducted by two separate techniques: (i) using a single gel sample subjected to several (at least eight) swelling and compression tests at various swelling times and (ii) using a set of gel samples (at least eight) subjected to swelling and compression tests only once, after a certain time of swelling. It was observed that both techniques gave the same results.

Fig. 3 shows V_{rel} and G of PAAm hydrogels with various clay contents plotted against the swelling time. The crosslinker ratio is 1/80. At a clay content of less than 4 w/v % (left

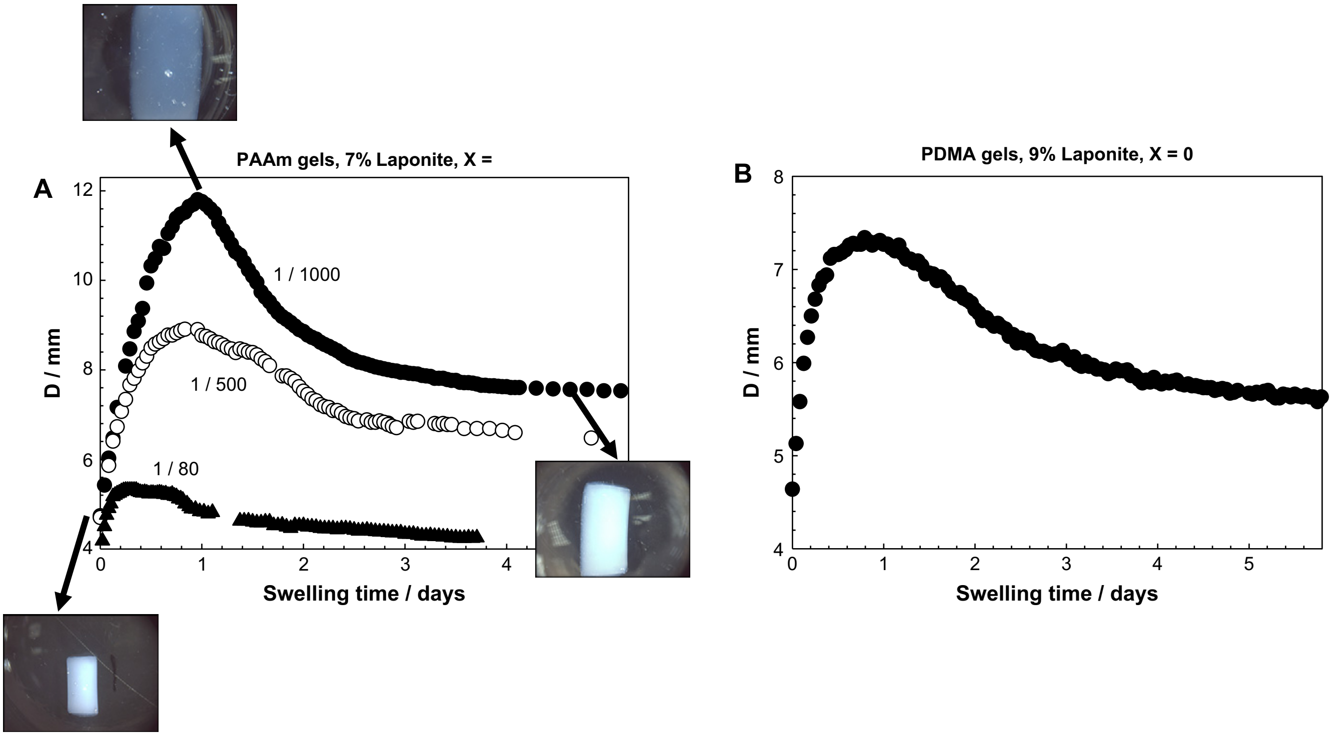

Fig. 2. Diameter D of nanocomposite hydrogel samples shown as a function of the swelling time in water. (A) PAAm gels with various chemical crosslinker ratios X indicated in the figure. Laponite = 7 w/v %. The pictures are from the hydrogel sample with $X = 1/1000$ after 1, 25, and 100 h of swelling time in water. (B) PDMA hydrogels with 9 w/v % Laponite and without a chemical crosslinker ($X = 0$).

panel), the gel swells up to a critical time and then attains a constant volume. This is expected from the usual swelling kinetics of gels. However, for gels prepared at higher clay content (right panel), swelling and modulus curves exhibit a maximum and a minimum, respectively. The higher the clay content, the higher is the maximum swelling ratio observed after about one day of swelling time. In Fig. 4, V_{rel} and G are plotted against the swelling time for PAAm hydrogels with 7 w/v % Laponite but with various chemical crosslinker ratios X. As the crosslinker ratio X is decreased, the gel attains a larger volume, i.e., the maximum swelling ratio increases while the minimum value of the elastic modulus decreases. Thus, the extent of deswelling increases as the crosslinker ratio is decreased. For example, at $X = 1/1000$, the gel first swells up to about ninefold volume and then deswells to attain an equilibrium volume of about only twice the initial gel volume. V_{rel} and G versus swelling time plots of both PDMA and PNIPA hydrogels prepared at $X = 0$ and with 5–9% Laponite (not shown) exhibited similar behavior. The results thus demonstrate that the appearance of a maximum in the swelling curves is a characteristic feature of nanocomposite hydrogels.

From the swelling and elasticity data of the hydrogels, one may calculate the effective crosslink density ν_{e} using the equation [18,19]

$$G = A\nu_{\mathrm{e}}RT\left(\nu_2^0\right)^{2/3}\left(\nu_2\right)^{1/3} \tag{4}$$

where the front factor A equals to 1 for an affine network and $1 - 2/f_{\mathrm{e}}$ for a phantom network, f_{e} is the average functionality of the crosslinkers, ν_2^0 and ν_2 are the volume fractions of the crosslinked polymer in the gel after preparation and at the state of the elasticity tests, respectively, R and T are in their usual meanings. Since the average functionality of the nanoparticles is in the range of 10^1–10^2 [20], the prefactor A is close to unity, even for phantom networks. For the following calculations, we set $A = 1$. Further, assuming the conversion of the monomer to the crosslinked polymer is complete, using the polymer densities 1.35 g/ml for both PAAm and PNIPA [14], 1.21 g/ml for PDMA [16], ν_2^0 was calculated as 0.037, 0.037, and 0.041, respectively. The polymer volume fraction relates to V_{rel} by $\nu_2 = \nu_2^0/V_{\mathrm{rel}}$. Fig. 5A and B shows the variation of the effective crosslink density ν_{e} of PAAm hydrogels with various clay and BAAm contents, respectively, as a function of the swelling time. As usual in chemically crosslinked gels, for clay contents below 4 w/v %, no change in ν_{e} was observable during the whole course of the gel volume change. However, if the clay content is 4 w/v % or above, ν_{e} first decreases and then rapidly increases during gel swelling. The extent of the variations in ν_{e} becomes significant as the clay content is increased or the chemical crosslinker ratio X is decreased. Fig. 5C and D shows the crosslink density ν_{e} of PDMA and PNIPA hydrogels, respectively, as a function of the swelling time. The hydrogels were prepared with 5–9 w/v % Laponite but without the chemical crosslinker BAAm. It is seen that, although the extent of the variation in ν_{e} is relatively small compared to PAAm gels, a similar behavior is also observable for both PDMA and PNIPA nanocomposite hydrogels.

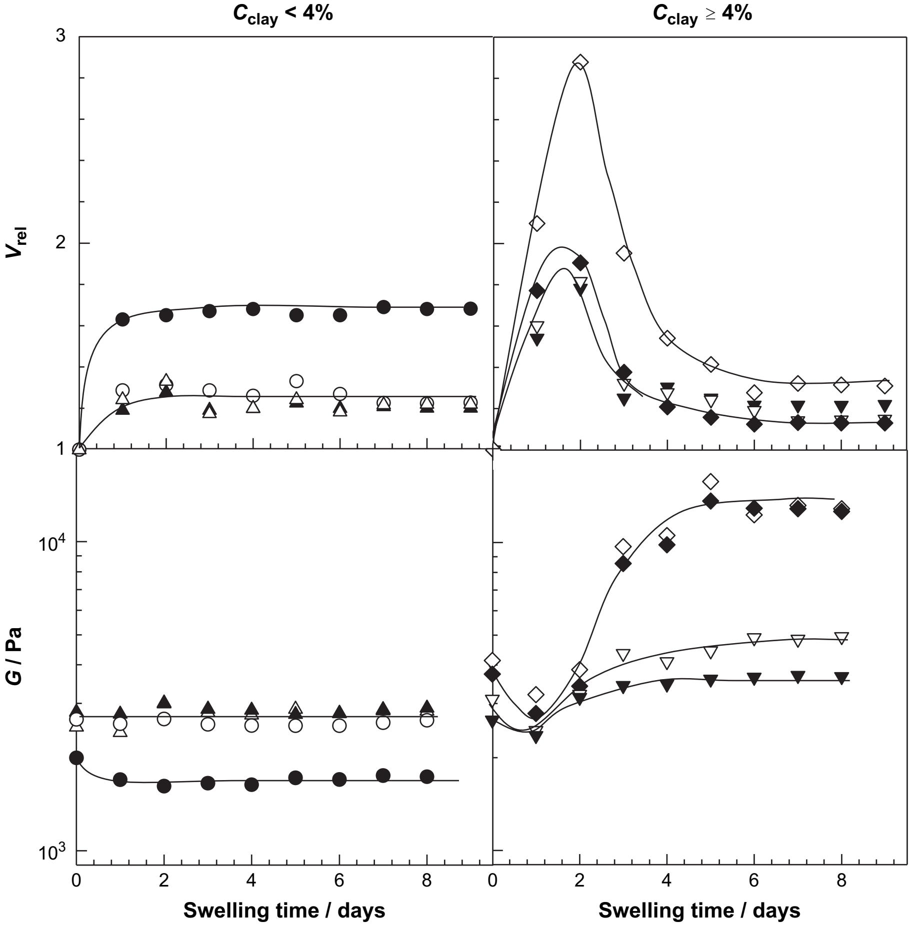

Fig. 3. Volume swelling ratio V_{rel} and the elastic modulus G of PAAm hydrogels shown as a function of the swelling time in water. $X = 1/80$. Laponite w/v % = 0 (●), 1 (○), 2 (▲), 3 (△), 4 (▼), 5 (▽), 6 (◆), 7 w/v % (◇). The curves show the trend of data.

The results thus indicate that the increasing degree of dilution during swelling leads to a change in the network structure of the hydrogels. To visualize the volumes occupied by the clay particles in the gel network during swelling, the so-called overlap threshold c^* where the particles start to overlap was calculated using the equation [21]

$$c^* = \frac{\overline{M}_w / N_A}{\left(\frac{4}{3}\pi R^3\right)} 10^2 \qquad (5)$$

where N_A is the Avogadro's number, $\overline{M}_w$ is the weight-average molecular weight and R is the radius of clay disks. The molecular weight and the radius of gyration R_g of Laponite particles were reported recently as 2.5 (±0.3) $\times 10^6$ g/mol and 20 (±2) nm, respectively [13]. Provided the clay particles form thin circular disks of uniform density, the radius of the disks is $R = \sqrt{2}R_g = 28$ (±3) nm. Thus, using Eq. (5), the overlap concentration was estimated to be 4.5 (±1) w/v %, which is in reasonable agreement with the value 4 w/v % reported by Nie et al. [20]. Furthermore, PAAm chains formed under the same experimental conditions but without Laponite have a molecular weight $\overline{M}_w = 6.9 \times 10^5$ g/mol and a radius of gyration in water $R_g = 42$ nm, which lead to $c^* = 0.4$ w/v % [22]. This means that the polymer chains are in the semi-dilute regime, both after preparation and after equilibrium swelling in water.

Comparison of the overlap concentration of Laponite with the experimental results shows that the unusual swelling behavior of the nanocomposite hydrogel is observable only when the initial concentration of clay is above its overlap concentration. Our experimental results are thus consistent with the following scenario:

If the clay content is below 4%, clay particles in the reaction solution are in the dilute regime. Thus, as suggested by Haraguchi [2–5], the polymer chains growing from the surface of the individual clay particles during gelation may form bridges between the particles and constitute the network chains in the resulting nanocomposite hydrogels. Since the clay particles are already surrounded by the polymer chains after the state of gel preparation, the gel swelling does not induce a substantial change in the overall clay–polymer adsorption/desorption equilibria.

However, when the clay concentration becomes larger than c^*, the nanoparticles start to overlap so that they form several agglomerates in the suspension. In this range of clay concentration, the polymer chains start to grow mainly from the surface of the agglomerates, but they are excluded from the region between the nearby particles within the agglomerates.

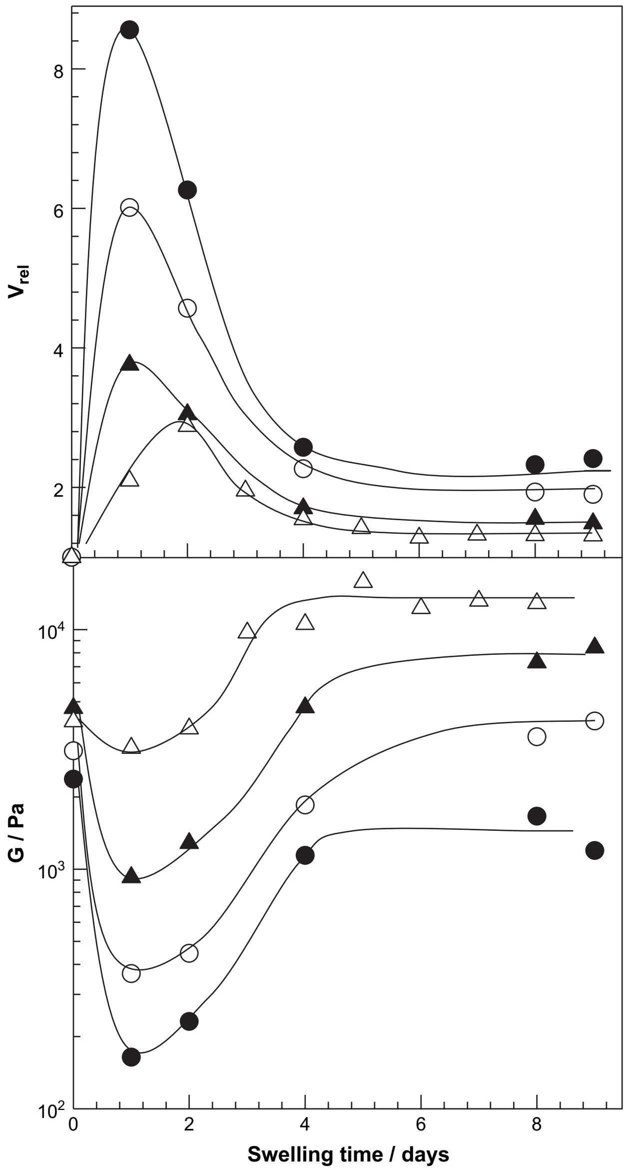

Fig. 4. Volume swelling ratio V_{rel} and the elastic modulus G of PAAm hydrogels shown as a function of the swelling time in water. Laponite = 7 w/v %. $X = 1/1000$ (●), 1/500 (○), 1/200 (▲), 1/80 (△). The curves show the trend of data.

Thus, the particle surfaces exhibit an unequal distribution of polymer concentration, which leads to an unbalanced osmotic pressure pushing the particles further together. This type of interparticular attraction forces is called depletion attractions [23,24]. As the polymerization reactions proceed, that is, as the number of polymer chains increases, the newly formed polymer chains can only cover the surface of the agglomerates so that the polymer is distributed more and more unevenly on the particles resulting in an increase in the cluster density due to the increasing extent of depletion attractions. This situation corresponds to the state of the nanocomposite gel after preparation and is schematically illustrated in Fig. 6A. However, as the gel swells in water, the particles move apart to assume a new equilibrium state in the gel solution. This leads to a substantial increase in the gel volume (Fig. 6B). At the same time, some individual particles separated from the agglomerates diffuse out of the gel solution leading to a decrease in the crosslink density of the nanocomposite hydrogel. The free sites generated on the surface of the newly separated particles during swelling can now be covered by polymer chains, which lead to an increase in the gel crosslink density and a decrease in the gel volume (Fig. 6C). Thus, the decrease of the crosslink density during the initial period of swelling is due to the escape of some clay particles into the external solution while subsequent increase of the crosslink density is due to the generation of free sites on the particle surfaces interacting with the polymer segments. It should be noted that the entire nanocomposite hydrogels prepared with a clay content of above c^* concentration were opaque, both after preparation and after equilibrium swelling in water, while they were less opaque or transparent at maximum swelling. This behavior can also be seen from the pictures of the gel sample given in Fig. 2. One may expect that the clay agglomerates are responsible for the opacity of the gels after preparation state, while the disintegration of the agglomerates during swelling leads to a more homogeneous distribution of the particles along the gel volume so that the opacity decreases. Formation of additional crosslinks and subsequent decrease in the gel volume lead to the reappearance of opacity in the equilibrium swollen hydrogels.

The decrease of the crosslinker ratio X increases the mesh size of the network, thereby facilitating the escape of the particles from the gel to the outer solution. As a consequence, the initial decrease of the crosslink density during swelling becomes significant at low crosslinker ratios (Fig. 5B). Furthermore, as seen from Fig. 5, the effective crosslink densities of both PDMA and PNIPA hydrogels are much higher than those of PAAm hydrogels. For example, after the gel preparation state, that is, at the swelling time = 0, the crosslink densities ν_e are 45, 40 and 26 mol m^{-3} for PNIPA, PDMA, and PAAm ($X = 1/1000$) hydrogels, respectively, with 7 w/v % Laponite. Thus, although PAAm hydrogel contains, in addition to Laponite, extra chemical crosslinks, it exhibits the lowest effective crosslink density compared to PDMA and PNIPA hydrogels. This indicates that the attractive interactions between the clay particles and AAm segments are much weaker than clay–DMA or clay–NIPA interactions. As a result, the nanoparticles and the polymer chains in PAAm gel network reorganize much easier during the course of swelling so that the deswelling occurs at a much higher extent. We may conclude that the net result of the swelling process of nanocomposite hydrogels with a clay content above c^* concentration is the rearrangement of the clay particles to produce a much more homogeneous distribution of the nanoparticles along the gel volume.

4. Conclusion

Nanocomposite hydrogels based on PAAm, PDMA and PNIPA as the hydrophilic polymer components and Laponite XLS as the clay component exhibit unusual swelling behavior in water. They first rapidly swell and attain a maximum

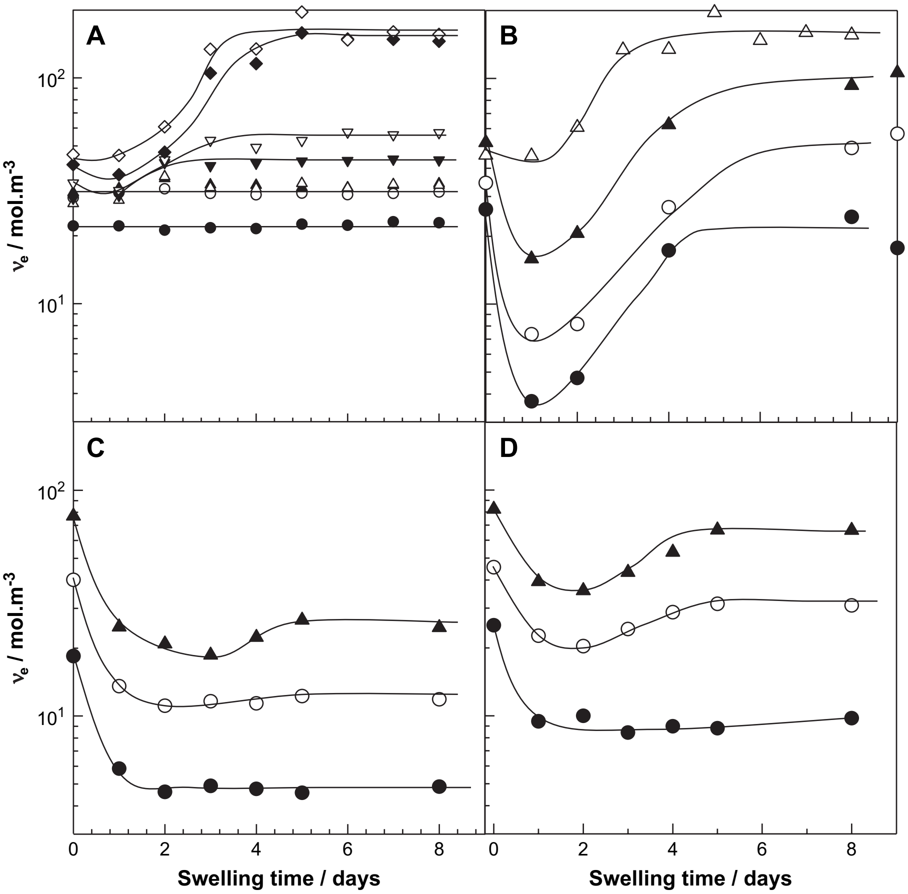

Fig. 5. Effective crosslink density ν_e of the nanocomposite hydrogels shown as a function of the swelling time in water. (A) PAAm gels. $X = 1/80$. Laponite w/v % = 0 (●), 1 (○), 2 (▲), 3 (△), 4 (▼), 5 (▽), 6 (◆), 7 w/v % (◇). (B) PAAm gels. Laponite = 7 w/v %. $X = 1/1000$ (●), 1/500 (○), 1/200 (▲), 1/80 (△). (C and D) PDMA and PNIPA hydrogels, respectively. $X = 0$. Laponite w/v % = 5 (●), 7 (○), and 9 (▲).

swelling ratio after about one day. Further increase in the swelling time results in the deswelling of the gels until they reach a limiting swelling ratio after about 5 days. This type of swelling behavior is observable only when the clay concentration in the hydrogel is above the overlap threshold c^*. Swelling measurements combined with the elasticity tests show that the effective crosslink density ν_e of the hydrogels first decreases, but then increases with increasing time of swelling. The extent of the variations in ν_e becomes significant as the clay content is increased or the chemical crosslinker ratio X is decreased. The results were explained in terms of the rearrangements of the highly entangled polymer chains and clay particles during the course of swelling.

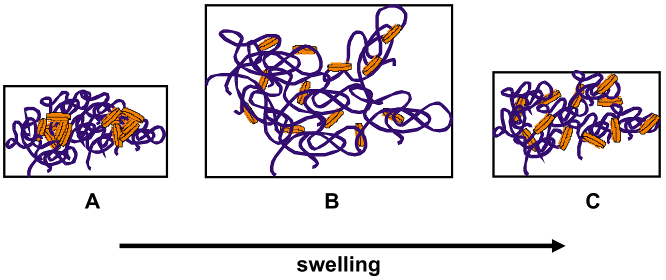

Fig. 6. Cartoon demonstrating the effect of swelling on the state of dispersion of clay particles in hydrogels. Blue lines and orange disks indicate polymer chains and clay particles. Only a part of the nanocomposite hydrogel is drawn for clarity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Since Laponite nanoparticles produce physical crosslinks inside the hydrogel, these particles should be detached from the gel network under suitable conditions weakening the attractive interactions between the polymer segments and the particles. This work shows that the hydrogels are stable in water. The studies about the stability of the nanocomposite hydrogels in aqueous solutions of salts, acetone, and poly(ethylene oxide) of molecular weight 10,000 g/mol are in progress.

Acknowledgements

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