Effect of Intercalated Hydrotalcite on Swelling and Mechanical Behavior for Poly(acrylic acid-*co*-*N*-isopropylacrylamide)/Hydrotalcite Nanocomposite Hydrogels

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ABSTRACT: A series of nanocomposite hydrogels were prepared from acrylic acid (AA), *N*-isopropylacrylamide (NIPAAm), and intercalated hydrotalcite (IHT) by photopolymerization. The influence of the intercalating content of 2-acrylamido-2-methyl propane sulfonic acid (AMPS) in HT on the swelling and mechanical properties for poly(AA-*co*-NIPAAm)/IHT nanocomposite hydrogels was investigated. The results showed that the higher the content of the AMPS-HT was, the higher the swelling ratio of the gels and the higher the content of the intercalating agent was, the lower swelling ratio. It was also demonstrated that the swelling ratio of the gel was not affected by the counterion in HT. The gel strength and crosslinking density were not enhanced by adding AMPS-HT into the gel composition, but the maximum effective crosslink density and shear modulus of the nanocomposite hydrogels were increased with an increase of the content of the intercalating agent in HT. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 1572–1580, 2005

Key words: nanocomposite; hydrogel; intercalation

INTRODUCTION

Hydrogels are crosslinked hydrophilic polymers with network structures consisting of acidic, basic, or neutral monomers, which are able to imbibe large amounts of water. A variety of hydrogels have been employed for different biomedical applications. Because of their biocompatibility and biodegradability, they are used as bioabsorbable materials in surgeries and biotechnology and in other medical, agricultural, and pharmaceutical applications for delivery of medicines, among other possibilities. For the latter application they are unique carriers for controlled drug delivery.[1,2]

It is well known that *N*-isopropylacrylamide (NIPAAm) is a typical thermosensitive hydrogel because it possesses a lower critical solution temperature.[3,4] The NIPAAm hydrogels suddenly change their shape from a swollen state at the transition temperature by increasing the incubation temperature in water. Therefore, NIPAAm hydrogels are applied in thermosensitive drug delivery systems[5] and separation processes.[6] In those systems, the substrates in the NIPAAm hydrogels are squeezed out at the target tissue in the body by shrinking the gel in response to temperature.[7]

Ionic hydrogels containing high water content are very suitable for applying in biotissues. They have excellent potential as bioresponsive polymers because changing the charge density or the nature of the ionic moieties in the polymer can control the magnitude of their response. Anionic hydrogels contain large amounts of unbound water, allowing a lot of solute release or greater solute transport.[8–11] Hydrogels made of acrylic acid (AA) can be used to develop formulations that release drugs in a natural pH environment.[12,13]

Hydrotalcite (HT) is composed of positively charged layers with interlayer exchangeable anions.[14,15] Its general composition can be represented as $[M^{II}_{1-X}M^{III}_X(OH)_2]^{X+} \cdot [A^{q-}_{x/q} \cdot nH_2O]$, where M^{II} and M^{III} are divalent and trivalent cations, respectively, and A^{q-} is an exchangeable anion. HT is usually chosen as an inorganic filler to prepare HT/polymer nanocomposites.[16–22]

In the past 10 years, most research on nanocomposites has focused on the use of silicate clays as nanoparticles.[23,24] The clays have been widely studied because they are naturally occurring minerals that are commercially available and exhibit a platy morphology with a high aspect ratio and considerable cation exchange capacity. Carlino reported the intercalation

of organic anions into HT,[25] but few reports have discussed the incorporation of HT into a polymer. These studies on HT/polymer nanocomposites have been mainly focused on intercalating behavior. However, the performance of these HT nanocomposites have been seldom reported.

Recently, Hsueh and Chen[26] reported on HT/polyimide nanocomposites. Their basic idea for producing the HT/polyimide nanocomposites is as follows: at first, the organomodified HT was synthesized by incorporating organic anions into HT, followed by polymerization in the interlayer galleries of the HT. After the polymer was generated in the interlayer galleries, the stacking nanolayers of the HT lost their order and then the nanolayers were exfoliated to disperse in the polymer matrix.[26]

Nanocomposite hydrogels containing HT were not investigated in the previous reports. The effect of HT on the physical properties and drug release behavior for nanocomposite hydrogels based on poly(AA-*co*-poly(ethylene glycol)methyl ether acrylate (PEG-MEA))/HT gels was investigated.[27] The results showed that the swelling ratios for the gels were increased with an increase in HT content, but the gel strength and adhesive force were decreased with an increase in the HT content. In this study, the HT was first intercalated by an intercalating agent such as 2-acrylamido-2-methyl propane sulfonic acid (AMPS) with different anion exchange capacity (AEC) of HT, which is referred to as AEC-HT. Then, a series of hydrogels were prepared from AA, NIPAAm, and intercalated HT (IHT) by photopolymerization. The effect of different contents of AEC-HT in the nanocomposite hydrogels on the swelling behavior and physical properties was investigated.

EXPERIMENTAL

Materials

AA, diethoxyacetophenone (DEAP) as a photoinitiator, AMPS, and *N*-dimethylacetamide (DMAc) were purchased from Fluka Chemical Co. (Buchs, Switzerland). Ultrapure water with a conductivity of 18 S/cm was used in all experiments. HT and *N*,*N*-methylenebisacrylamide (NMBA) as a crosslinker were purchased from Aldrich (St. Louis, MO). The AEC of the HT is about 350 mequiv/100 g. NIPAAm was purchased from Wako Pure Chemical Industries (Osaka, Japan).

Intercalation of HT

The quantity of the intercalating agent required was calculated by eq. (1). It means that the equivalence of the ion exchange of HT is equal to the equivalence of intercalating agents (AMPS):

$$AEC \times (W_{HT}/100 \text{ g}) \times 10^{-3} = W_{IA}M_{IA} \times 1/E_{IA}$$

$$(1)$$

$$W_{RIA} = W_{IA} \times \text{multiple}$$

where W_{HT} is the weight of HT (g), W_{IA} is the weight of the intercalating agent (g), M_{IA} is the molecular weight of the intercalating agent (mol/g), E_{IA} is the equivalence of the intercalating agent, and W_{RIA} is the required weight of the intercalating agent (g).

A suspension solution containing 5 g of HT and 3.62 g of AMPS (1-AEC) or 7.24 g of AMPS (2-AEC) was mixed in 500 mL of DMAc. The suspension solution was stirred at 70°C for 24 h. Then, the IHT was separated by centrifugation and washed with a large volume of water to remove unintercalated AMPS. The sample was dried in a vacuum oven at 40°C for 3 days. The obtained IHTs were designated as 1-IHT and 2-IHT for 1-AEC and 2-AEC intercalation, respectively.

Preparation of AA/NIPAAm nanocomposite hydrogels

Monomers (70 mol % AA and 30 mol % NIPAAm) were weighed and mixed in a 20-mL sample vial. Then, 0.1 mol % NMBA, 0.1 mol % DEAP, and IHT with various weight ratios based on the monomer weights were poured into this solution and mixed thoroughly. The mixture was injected into the space between two glass plates with a 1-mm silicone rubber as a spacer. Polymerization was carried out by exposing the monomer solution to UV irradiation for 10 min. After gelation was completed, the gel membrane was cut into 10-mm diameter disks, immersed in an excess amount of deionized water for 3 days to remove residual components, and dried in a 50°C vacuum oven for 1 day. The feed compositions, yields, and equilibrium-swelling ratios of the nanocomposite hydrogels are listed in Table I.

Equilibrium-swelling ratio measurement

The dried gels were immersed in 10 mL of solution at 25°C until swelling equilibrium was attained. The weight of the wet sample (W_t) was determined after removing the surface water by blotting with filter paper. The dry weight (W_d) was determined after drying the gel in a vacuum oven for 2 days. The equilibrium-swelling ratios (Q) of the gels were calculated from eq. (2):

$$Q = (W_t - W_d)/W_d \qquad (2)$$

Swelling kinetics measurement

The swelling ratio was obtained by weighing the initial and swollen samples at various time intervals. The

TABLE I
Feed Compositions and Yield and Equilibrium-Swelling Ratio of Hydrogels

Sample code	AA (mol %)	NIPAAm (mol %)	2-IHT (mol %)	1-IHT (mol %)	HT (mol %)	Yield (%)	Q (g/g)
N0	70	30	—	—	—	96	1.96
0-N1	70	30	—	—	1	94	2.97
0-N3	70	30	—	—	3	97	5.61
0-N5	70	30	—	—	5	95	7.71
0-N7	70	30	—	—	7	93	8.12
1-N1	70	30	—	1	—	94	2.77
1-N3	70	30	—	3	—	97	4.93
1-N5	70	30	—	5	—	95	5.59
1-N7	70	30	—	7	—	94	6.84
2-N1	70	30	1	—	—	94	2.40
2-N3	70	30	3	—	—	96	3.01
2-N5	70	30	5	—	—	94	3.57
2-N7	70	30	7	—	—	92	3.87

1-IHT, intercalated HT (1-AEC); 2-IHT, intercalated HT (2-AEC).

amount of absorbed water (W_t) was reported as a function of time, and the equilibrium absorption at infinitely long time was designated as W_∞. The following equation was used to calculate the diffusion coefficient (D) for $W_t/W_\infty = 0.8$[28]:

$$W_t/W_\infty = (4/\pi^{0.5})(D_t/L^2)^{0.5} \qquad (3)$$

where t is the time and L is the initial thickness of the dried gel. To investigate the diffusion model of the gel, the initial swelling data were fitted to the exponential heuristic equation for $W_t/W_\infty \leq 0.6$[29,30]:

$$W_t/W_\infty = K_t^n \qquad (4)$$

where K is a characteristic constant of the gel and n is a characteristic exponent of the mode transport of the penetrate.

Physical properties measurement

The gel strengths of these samples were measured by a uniaxial compression experiment with a universal tester (Lloyd LRX). Equation (5) was used to calculate the shear modulus (G):

$$\tau = F/A = G(\lambda - \lambda^{-2}) \qquad (5)$$

where τ is the compression stress, F is the compression load, A is the cross-sectional area of swollen gels, and λ is the compression strain (L/L_0). At low strains, a plot of τ versus $-(\lambda - \lambda^{-2})$ would yield a straight line whose slope is G. The effective crosslink density (ρ) was calculated from G and the polymer volume fraction (v_2) as follows:

$$\rho = G/v_2^{1/3}RT \qquad (6)$$

where R is the ideal gas constant and T is the absolute temperature.

Zeta-potential analysis

The dried HT (30 mg) was immersed in 20 mL of deionized water. The zeta potential of the HT was measured by a Zeta-meter microscope 3.0+ (Staunton).

Fourier transform IR (FTIR) analysis

A Horiba FT/IR-720 spectrophotomer (Kyoto, Japan) was used to record the FTIR spectra from pressed KBr pellets containing about 1% HT and 1% IHT.

X-ray diffraction (XRD) analysis

Powder XRD analyses were performed by using a MAC Science X-ray powder diffractometer (Cu anode, model M21X, Osaka, Japan) running at 40 kV and 30 mA and scanning from 2° to 13° at 3°/min. The structure of the HT was determined at different stages of the nanocomposite synthesis. The HT powders were mounted on a sample holder with a large cavity and a smooth surface was obtained by pressing the powders with a glass plate. Analyses of the HT swollen in the gels were performed by spreading the mixture on a gel membrane disk (50-mm diameter, 0.5-mm thickness) used as sample holder. It was designed so that a maximum surface could be irradiated at low angle, giving an optimum intensity to the XRD signal. The nanocomposite plates produced during the molding process had a fairly smooth surface.

RESULTS AND DISCUSSION

Preparation of nanocomposite hydrogels

The conceptual formation of poly(AA-*co*-NIPAAm)/HT nanocomposite hydrogels is shown in Scheme 1. HT
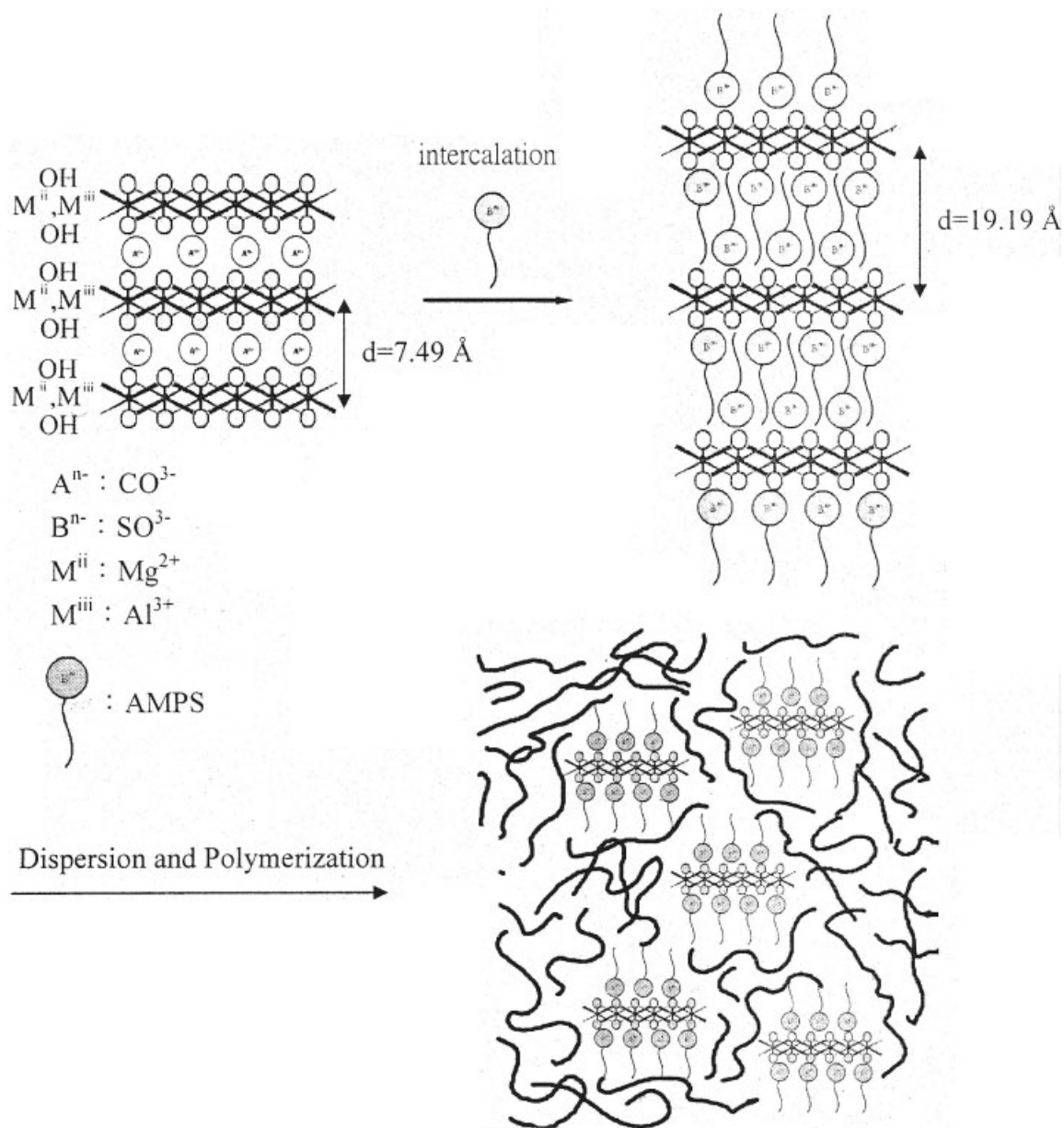
Scheme 1 The conceptual formation of poly(AA-*co*-NIPAAm)/HT nanocomposite hydrogels.

could not disperse in water originally. However, the HT derived through the intercalation of AMPS ionically bonded on the surface of HT by an ion-exchange process can easily disperse in water. Hence, we were successful in using it to prepare a series of nanocomposite hydrogels in aqueous solution. This also implies that the IHT nanolayers with an AMPS side chain were homogeneously dispersed into the poly(AA-*co*-NIPAAm) gel matrix through *in situ* polymerization.

FTIR analysis

The FTIR spectra of AMPS-HT are shown in Figure 1. Strong absorption peaks of asymmetric and symmetric

R—COO$^-$ groups appear at 1610 and 1375 cm^{-1}, respectively. The characteristic absorption peaks of C=O stretching, C=C stretching, N—H bending, asymmetric stretching S=O, and symmetric stretching S=O appear at 1658, 1630, 1558, 1205, and 1049 cm^{-1}, respectively. These peaks demonstrate that AMPS was intercalated into the HT layer (Fig. 1, spectrum b). A broad absorption peak between 3200 and 3600 cm^{-1} is assigned to O—H stretching of both the hydroxide layers and the interlayer water. Strong absorption peaks of C—O at 1375 cm^{-1} disappear in curve c in Figure 1. This result indicated that the carbonate groups were completely exchanged by AMPS in 2-AEC.
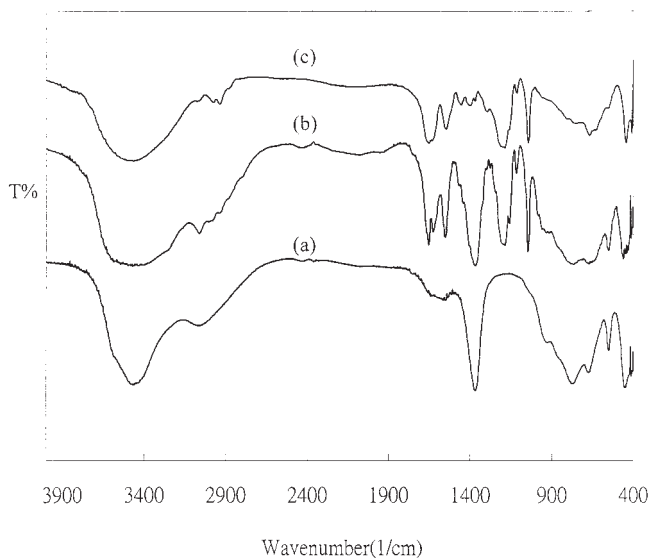
Figure 1 The FTIR spectra of HT (spectrum a), 1-IHT (1-AEC, spectrum b), and 2-IHT (2-AEC, spectrum c).

Identification of HT in nanocomposite hydrogels

The XRD patterns for HT, 1-IHT, 2-IHT, and some typical samples are shown in Figure 2. A typical XRD pattern of HT, with a strong peak corresponding to a basal spacing of 7.49 Å, is shown in curve a in Figure 2. After treatment with AMPS (1-AEC), the peak is shifted to a low angle, corresponding to basal spacing of 16.97 Å in curve b in Figure 2. This result shows that the AMPS are intercalated between the layers during the anion-exchange process, adopting a lateral bilayer structure. For 1-IHT, two peaks appear at 2θ 5.2° and 11.8°. This indicates that both AMPS and a carbonate group are present in the interlayer galleries of the AMPS-HT. Curve b in Figure 2 shows that the equivalent content of the carbonate group is approximately equal to that of AMPS. Therefore, AMPS does not completely exchange carbonate groups. However, after being intercalated by AMPS with 2-AEC, the peak is shifted to a lower angle, corresponding to the basal spacing of 19.19 Å in curve c in Figure 2. For 2-IHT, just one peak appears at 2θ 4.6°. This result explicitly indicates that the equivalent content of the carbonate group was equal to the AMPS content and that AMPS exchanges carbonate groups completely.

The XRD pattern for the gel series containing different HT contents did not exhibit any diffraction at 2θ 3–13°, except for the 0-N7 gel. The 0-N7 gel appeared at a broad peak at 2θ 10.4° (d-spacing = 8.49 Å). This result suggested that a small amount of HT was not completely exfoliated but just intercalated. However, the diffraction peak in 1-N and 2-N series gels disappeared in all samples, such as 1-N7 and 2-N7 sample gels. This result demonstrated that the IHT incorporated into the gels was completely exfoliated.

### Effect of IHT content on swelling and mechanical behavior

The effect of HT and IHT on the fundamental properties, such as the equilibrium-swelling ratio and gel strength, for the nanocomposite hydrogels was investigated.

Effect of different HT contents on equilibrium-swelling ratio in deionized water

The effect of different HT contents on the equilibrium-swelling ratios (Q) for the hydrogels is shown in Figure 3. The results indicate that the equilibrium-swelling ratios for the gel increase with an increase in the content of HT in the gels. This is because the $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{X+}$ nanolayers were exfoliated and well dispersed in the polymer matrix, causing more $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{X+}$ nanolayers to form and providing the stronger hydration ability of the OH group. This leads to the nanocomposite hydrogels becoming more hydrophilic. Hence, the swelling ratio increases with an increase of the content of HT in the gel. Another cause may be the osmotic pressure exerted by the counterions of the incorporated IHT. It is expected that the counterion effect will be observed for poly(AA-co-NIPAAm) gels synthesized in the presence of HT, because the positively charged nanolayers of HT contain the mobile counterions of CO_3^{2-}. In addition, the amount of intercalating agent in the HT will also influence the crosslinking conditions of the gel and the gel network. Figure 3 also shows that the higher the amount of intercalating agent in the feed of the nanocomposite hydrogels is, the lower are the
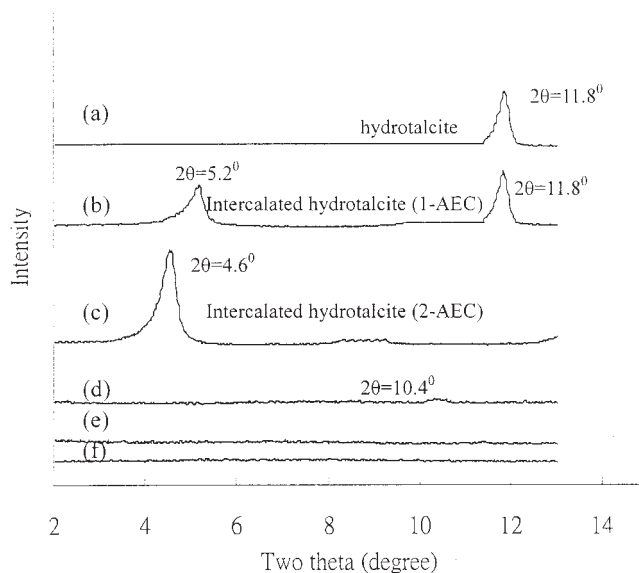
Figure 2 XRD patterns of HT (curve a), 1-IHT (1-AEC, curve b), 2-IHT (2-AEC, curve c), 0-N7 (curve e), 1-N7 (curve d), and 2-N7 (curve f).
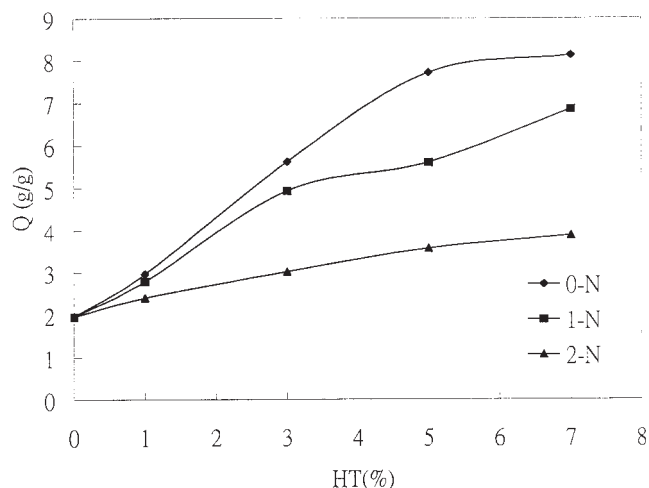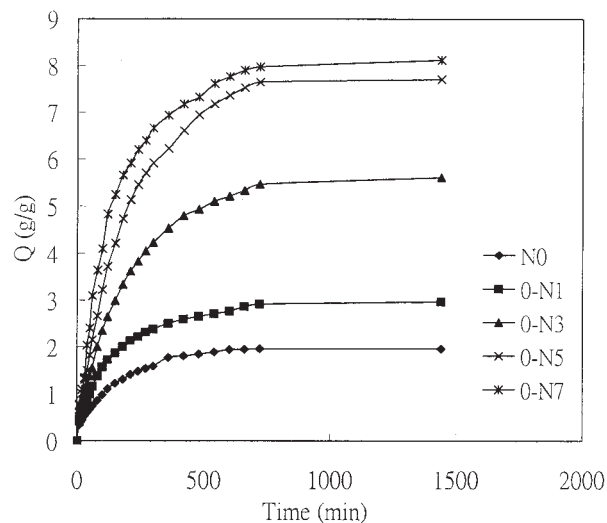
Figure 3 The effect of the HT content on the swelling ratio for 0-N, 1-N, and 2-N series gels in deionized water at 25°C.

Figure 4 The swelling kinetic profiles for the synthesized gels containing various contents of HT (0-AEC) in deionized water at 25°C.

swelling ratios for the gels (0-N > 1-N > 2-N) because of the increase in the degree of crosslinking.

Effect of HT on gel strength

The gel strength was determined from the G obtained from eq. (5). The results in Table II indicate that the G values and the effective crosslink densities (ρ) decrease with an increase of the content of HT. These results conform with those presented by D'Souza et al., who stated that added hydrophilic montmorillonite in the region of small concentrations led to a decrease of G values.[31] They claimed that the result may be attributed to the montmorillonites being well separated and their hydrophilicity. Hence, we think the highly hydrophilic AMPS-HT is well dispersed into the gel system. A decrease in the G is usually accompanied by a decrease in the ρ for hydrogels. The results in Table II also indicate that the ρ values increase with an increase of the content of IHT such as 2-N7

> 1-N7 > 0-N7. This result implies that the content of intercalating agent can enhance the chemical crosslinks between the matrix and dispersed phase. Because the vinyl monomer (AMPS) grafted on the surface of the nanoclay layer provides the crosslinking points between the nanoclay layer and poly(AA-*co*-NIPAAm) matrix through *in situ* polymerization, the compatibility between these two phases can be improved. Thus, the increasing content of IHT can enhance the gel strength and crosslinking density of the nanocomposite hydrogels (see Scheme 1).

Effect of IHT on swelling kinetics

The swelling ratios as a function of time for the gels in deionized water are shown in Figures 4, 5, and 6. The n, K, and D values calculated from eqs. (3) and (4) are listed in Table II. The results show that the diffusion

TABLE II
Fundamental Properties of Poly(AA-*co*-NIPAAm)/IHT Nanocomposite Hydrogels

| Sample code	$D \times 10^7$ (cm^2/s)	n	$K \times 10^2$	G (g/cm^2)	$\rho \times 10^{-1}$ (mol/cm^3)
N0	0.35	0.18	6.5	1553 ± 23	1.32 ± 0.11
0-N1	0.45	0.26	5.1	1127 ± 19	0.94 ± 0.07
0-N3	0.74	0.37	1.9	673 ± 16	0.46 ± 0.05
0-N5	0.83	0.45	1.5	507 ± 19	0.41 ± 0.08
0-N7	0.97	0.48	1.1	433 ± 22	0.37 ± 0.04
1-N1	0.41	0.23	5.4	1383 ± 21	1.11 ± 0.15
1-N3	0.63	0.35	2.7	733 ± 16	0.58 ± 0.07
1-N5	0.77	0.40	2.3	694 ± 16	0.51 ± 0.04
1-N7	0.81	0.43	1.7	588 ± 19	0.44 ± 0.08
2-N1	0.37	0.20	6.1	1436 ± 22	1.23 ± 0.05
2N3	0.55	0.28	4.5	1002 ± 19	0.68 ± 0.03
2-N5	0.58	0.30	3.8	957 ± 17	0.62 ± 0.04
2-N7	0.60	0.33	3.2	843 ± 19	0.60 ± 0.02
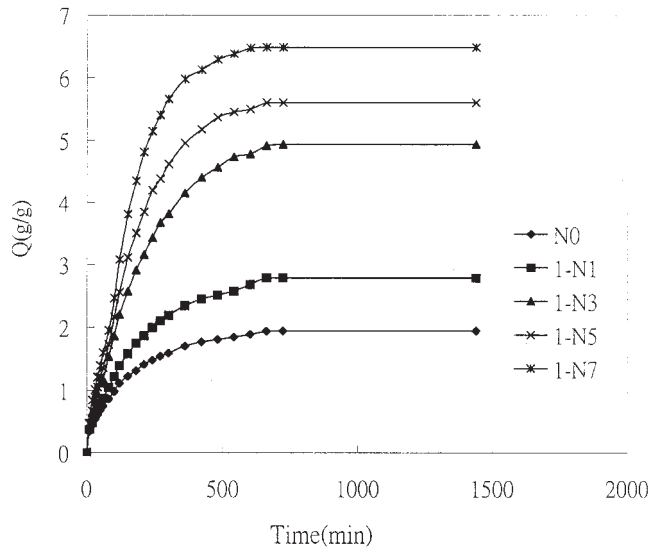
Figure 5 The swelling kinetic profiles for the synthesized gels containing various contents of HT (1-AEC) in deionized water at 25°C.

coefficients for these gels in deionized water decrease with an increase of the content of intercalating agent in IHT of the gel (2-N7 < 1-N7 < 0-N7). This is because increased intercalating agents can enhance the crosslinking density of the gels, making it difficult for water to diffuse into the gels. According to the classification of diffusion mechanism presented by Alfrey et al.,[32] the results shown in Table II indicate that the transport mechanisms for the present nanocomposite hydrogels all belong to Fickian diffusion ($n < 0.5$).
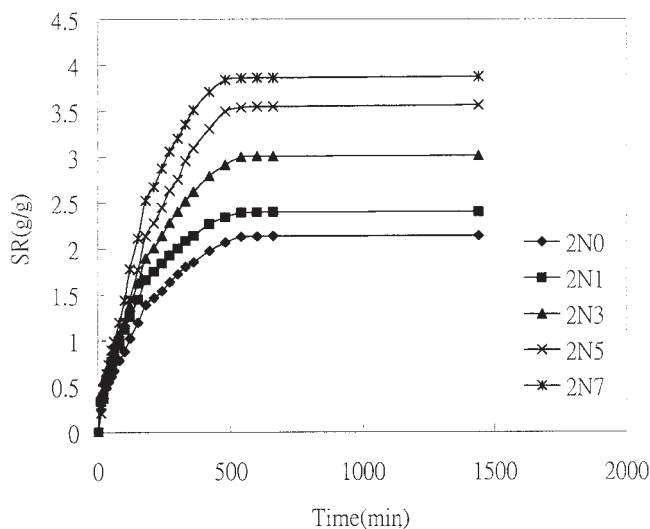
Figure 6 The swelling kinetic profiles for the synthesized gels containing various contents of HT (2-AEC) in deionized water at 25°C.
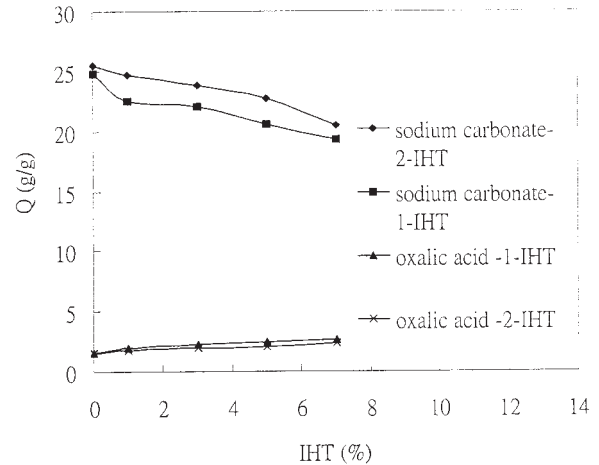

Figure 7 The effect of intercalating agents on the swelling ratio for the synthesized gels in 0.1M sodium carbonate solution (pH 10.7) and 0.1M oxalic acid solution (pH 4.2) at 25°C.

Effect of different IHTs on equilibrium-swelling ratio in 0.1M sodium carbonate and 0.1M oxalic acid solutions

It is known that AMPS completely exchanged the carbonate groups in 2-AEC, as shown in Figures 1 and 2. The carbonate groups do not exist in 2-AEC and do not contribute to the counterion effect. Thus, based on the above concept, the swelling ratio of the gels with 1-AEC should be higher than with 2-AEC in sodium carbonate solution. To confirm this result, the effect of different contents of HT and different contents of intercalating agent in HT on the equilibrium-swelling ratios for the gels in a 0.1M (pH 10.7) sodium carbonate solution were investigated.

The effect of different contents of intercalating agent in HT on the equilibrium-swelling ratios for the gels in sodium carbonate solution are presented in Figure 7. The results show that the swelling ratios for the gels decreased with increased IHT content in sodium carbonate solution (pH 10.7) and the swelling ratios of the gels for 1-AEC IHT were lower than that for 2-AEC IHT in 0.1M sodium carbonate solution. This result is contrary to the expected result. Thus, the swelling ratio of the gel is not affected by the counterion effect but is instead mainly affected by the interaction between the AA segment and the HT. Because the carboxylic acid groups on AA easily ionize at higher pH, inter- or intramolecular ionic bonding occurs between anionic gel and cationic HT nanolayers. Hence, the anionic charge density becomes lower in the gels at higher contents of HT (N7).

In order to confirm that an interaction occurred between the network and HT, the zeta potential of HT intercalated by AMPS with different AEC values of HT was investigated and the results are plotted in Figure 8. The results indicated that the zeta potential
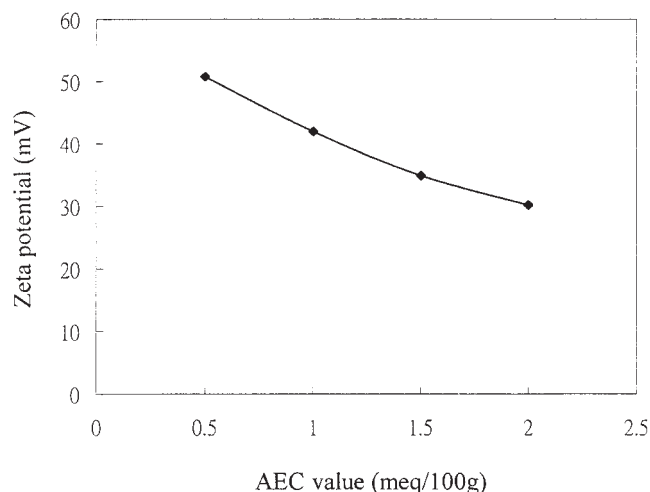
Figure 8 The zeta potential of HT intercalated with different contents of AMPS.

of IHT decreased with an increase in AMPS (AEC). Because the cationic charge density of HT is neutralized by the content of anionic AMPS, the cationic charge density of HT decreased with an increase in the AMPS content.

The results also indicated that the swelling ratio was increased with an increase in the intercalating agent content at higher pH (10.7), that is, 2-IHT > 1-IHT. The intercalating agent content can affect the zeta potential of HT: the higher the intercalating agent content in HT is, the lower the zeta potential (see Fig. 8). Hence, the cationic charge density of the IHT was decreased with the increase in intercalating agent content. This evidence indicates that inter- or intramolecular ionic bonding occurring between the anionic gel and cationic HT nanolayers will decrease with higher intercalating agent content (2-IHT).

In contrast, in oxalic acid (pH 4.2), the swelling ratio increased with an increase in IHT content, as shown in Figure 7. This is because it is difficult to ionize carboxylic acid groups at lower pH. The inter- or intramolecular ionic bonding was diminished, but the $[M^{III}_{1-X}M^{III}_X(OH)_2]^{X+}$ nanolayers could increase the hydrophilicity. However, the results also indicated that the swelling ratio was decreased with an increase in intercalating agent content at lower pH (4.2), that is, 2-IHT < 1-IHT. This is because the increasing content of intercalating agent enhances the crosslinking density of the nanocomposite hydrogels. Thus, the swelling ratio for the gels in oxalic acid solution was decreased with an increase in the intercalating agent content.

From the above results we know that the swelling ratio of the gel is not affected by the counterion effect. Hence, the swelling ratio is only affected by the crosslinking density and the affinity of the HT toward water in deionized water at lower pH. However, the swelling ratio of the gel is influenced by the effect of the interaction between the AA segment and the HT at higher pH.

CONCLUSIONS

A poly(AA-*co*-NIPAAm)/HT nanocomposite hydrogel was successfully synthesized using AMPS as the intercalating content of HT. We concluded that the higher the content of the IHT was, the higher the swelling ratio of the gels and the higher the content of the intercalating agent was, the lower the swelling ratio. The XRD patterns showed that, in the xerogels, the HTs were intercalated and exfoliated but 0-N7 samples were not exfoliated but just intercalated. Adding IHT into the gel composition did not enhance the gel strength and crosslinking density of the gels because of the IHT was well separated and had high hydrophilicity. However, increased intercalating agent enhanced the gel strength and crosslinking density of the gels. This was because the intercalating agent enhanced the chemical crosslinks between the matrix and dispersed phase. The content of intercalating agent affected the cationic charge density of HT. The immersing environment also affected the swelling behavior.

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