

# Effect of Intercalant Content of Mica on the Various Properties for the Charged Nanocomposite Poly(*N*-Isopropyl acrylamide) Hydrogels

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**ABSTRACT:** In this study, we intend to adjust the charge properties of the poly(*N*-isopropylacrylamide) [Poly(NIPAAm)] gel by using anionic clay and cationic monomer. Hence, two series of nanocomposite hydrogels bearing different charges were designed from NIPAAm, intercalated mica (IM) (NIM-series) and NIPAAm, IM, trimethyl (acrylamido propyl) ammonium iodide (TMAAI) (NTIM-series), respectively. The mica was first intercalated with different contents of intercalant, trimethyl (acrylamido propyl) ammonium chloride (TMAACl), based on the cationic exchange capacity (CEC) of mica. The effect of the CEC value of IM and IM content on the charge property, swelling behaviors, mechanical properties, and drug-re-

lease behaviors of the present gels were investigated. Results showed that the negative charges for NIM series gels decrease with increase in CEC values of the IM (from  $-11$  to  $-6$  mV), the positive charges for NTIM series gels also decrease with increase in CEC values of the IM (from  $+36$  to  $+18$  mV). The swelling behaviors and mechanical properties for the NTIM gels were significantly enhanced by IM content and CEC values of the IM. The microstructures, morphologies, and drug-release behaviors in these two series gels are also investigated. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2277–2287, 2007

**Key words:** nanocomposites; hydrogels; intercalated mica

## INTRODUCTION

Hydrogels are crosslinked, three-dimensional hydrophilic polymeric networks that swell but do not dissolve when brought into contact with water. There are some hydrogels that sometimes undergo a volume change in response to a change in surrounding conditions such as temperature,<sup>1,2</sup> pH,<sup>3–5</sup> solvent composition,<sup>6</sup> and salt concentration. Poly(*N*-isopropylacrylamide) [poly(NIPAAm)] hydrogel exhibits a volume-phase transition phenomenon about  $32$ – $33^\circ\text{C}$ .<sup>7,8</sup> This temperature is defined as the critical gel transition temperature (CGTT). It is well-known that NIPAAm gel has swell–deswell behavior; it is widely used in many fields, such as in drug-delivery systems,<sup>9</sup> extraction,<sup>10</sup> and enzyme-activity control.<sup>11</sup>

In recent years, the study of organic–inorganic nanocomposites has become a very important field. Currently, reinforcing polymer with small amounts of smectite clays has been attracted increasing interest, because the derived heterostructural materials exhibit impressive mechanical, thermal, optical, and other properties that increase their technological value.<sup>12–26</sup>

Clays have sandwich types of structures with one octahedral Al sheet and two tetrahedral Si sheets, the so-called phlo-silicate. There are many types of phlo-silicates: kaolinite, montmorillonite, hecrite, saponite, mica, etc. Mica is a plate-like crystalline aluminosilicate and has been widely used as reinforcing filler in polymeric matrices due to its excellent mechanical, electrical, and thermal properties.<sup>27</sup> The intercalated reactive mica was prepared by the intercalation of cationic monomer TMAACl and the effect of pure  $\text{K}^+$ -mica and intercalated reactive mica on water absorbency and the initial absorption rate in deionized water for poly(sodium acrylate) composite superabsorbents were investigated in our previous report.<sup>28</sup> To investigate the influence of CEC value of IM and IM content on the swelling behavior, physical property, and drug release behavior for the non-ionic poly(NIPAAm) hydrogel, two series of nanocomposite hydrogels with negative and positive charges were, respectively, prepared from NIPAAm, intercalated mica (IM) (NIM-series) and NIPAAm, IM, trimethyl (acrylamido propyl) ammonium iodide (TMAAI) (NTIM-series).

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## EXPERIMENTAL

### Materials

*N*-isopropylacrylamide (NIPAAm) (Wako Pure Chemical, Osaka, Japan) was recrystallized in *n*-hexane

**TABLE I**  
**Feed Composition, Yield, and Equilibrium-Swelling Ratio for Present Hydrogels with Different CECs**

Sample codes	Mica content (wt %)	Intercalation content (CEC)									
		0		0.5		1.0		1.5		2.0	
		Yield (%)	Q (g/g)	Yield (%)	Q (g/g)	Yield (%)	Q (g/g)	Yield (%)	Q (g/g)	Yield (%)	Q (g/g)
NT <sup>a</sup>	0	88.3	10.1	–	–	–	–	–	–	–	–
NM <sup>a</sup>	1	92.6	6.0	–	–	–	–	–	–	–	–
NTM <sup>a</sup>	1	92.1	9.0	–	–	–	–	–	–	–	–
NIM <sup>b</sup>	1	–	–	90.3	7.0	89.1	7.3	91.8	7.7	87.7	7.8
NTIM <sup>a</sup>	1	–	–	94.2	9.0	91.7	9.3	89.4	8.7	88.8	9.1
	3	–	–	87.6	9.5	93.7	9.7	91.6	9.5	87.2	9.4
	5	–	–	92.5	10.0	91.2	10.2	94.7	10.0	89.8	10.2
	7	–	–	95.3	10.6	89.4	10.9	91.9	11.1	88.2	11.5

N: NIPAAm; T: TMAAI; M: mica; IM: intercalated mica.

<sup>a</sup> Composition is NIPAAm 99 mol %, TMAAI 1 mol %, NMBA 5 mol %, APS 1 mol %, and TEMED 5 mol %.

<sup>b</sup> Composition is NIPAAm 100 mol %, NMBA 5 mol %, APS 1 mol %, TEMED 5 mol %.

before used. *N,N'*-methylene-bisacrylamide (NMBA) (Sigma Chemical, St. Louis, MO) as a crosslinker, ammonium persulfate (APS) (Wako Pure Chemical) as an initiator, and *N,N,N',N'*-tetramethylethylene diamine (TEMED) (Fluka Chemical, Buchs, Switzerland) as an accelerator were used as received. Swollen mica was purchased from Wako Pure Chemical. The cation exchange capacity (CEC) of the mica is about 80 meq/100 g. (3-acrylamidopropyl) trimethylammonium chloride (TMAACl) as an intercalatant was purchased from TCI (Tokyo, Japan). The formula of mica is  $K\{Al_2[AlSi_3O_{10}](OH)_2\}$ . Caffeine and crystal violet (CV) as model drugs were obtained from the Fluka Chemical Co.

### Intercalation of mica

Quaternary alkyl ammonium exchanged mica was synthesized as follows: various ratios of  $K^+$ -mica and TMAACl based on CEC of mica were mixed in 500 mL of deionized water as suspension solution. The suspension solution was stirred at 30°C for 1 day. Then, the intercalated mica (IM) was separated by centrifugation and washed with large volumes of water to remove unreacted TMAACl, then dried in the vacuum oven at 35°C.

### X-ray diffraction analysis

Powder XRD analyses were performed by using a Shimadzu X-ray powder diffractometer with Cu anode (model XRD-6000, Kanagawa, Japan), running at 40 kV and 30 mA, scanning from 2 to 13° at 3°/min. The IM 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.

The Bragg's Eq. (1) was used to calculate the distance of mica interlayers (d).

$$n\lambda = 2d \sin \theta \quad (1)$$

where  $n = 1$  and  $\lambda = 3.6151E$ .

### Synthesis of TMAAI

The cationic monomer trimethyl (acrylamido propyl) ammonium iodide (TMAAI), synthesized from dimethylaminopropyl acrylamide (DMAA), methyl iodide and butanone as a solvent in 0°C ice bath was reported as previous study.<sup>29</sup>

### Preparation of anionic and cationic nanocomposite hydrogels

The anionic nanocomposite hydrogels were prepared as follows. NIPAAm was dissolved in deionized water in a 10-mL sample vial. To this solution, 5 mol % of NMBA, 1 mol % of APS, 5 mol % of TEMED, and 1 wt % mica or IM based on total monomer weight was added and mixed thoroughly. The mixture was then injected into the space between two glass plates with a 1-mm silicone rubber as a spacer. Polymerization was carried out at 25°C for 1 day. When the gelation was completed, the gel membrane was cut into disks, 10 mm in diameter, and 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.

The cationic nanocomposite hydrogels were prepared as the same as the anionic nanocomposite hydrogels except that the NIPAAm (100 mol %) was

replaced into NIPAAm (99 mol %) and TMAAI (1 mol %). The feed composition, yield, and equilibrium-swelling ratio of cationic nanocomposite hydrogels are also listed in Table I. The sample codes, X-y-z, represent the gel composition (X), mica content (y) (wt %), and intercalation content (z) (based on CEC). For example, NTIM-1-0.5 represents NTIM containing 1 wt % mica with intercalation content of 0.5 CEC.

### Thermogravimetric analysis

The organic intercalant content in mica interlayer was measured by thermogravimetric analysis with Perkin–Elmer Pyris 1 TGA (Boston, MA). The experiments were carried out on approximately 4–6 mg of samples in air atmosphere (flow rate 30 cm<sup>3</sup>/min) at a heating rate of 20°C/min from 100 to 780°C.

### Equilibrium swelling ratio measurement

The preweighed dried gels ( $W_d$ ) were immersed in deionized water at 25°C until swelling equilibrium was attained. Each gel was removed from the water bath, tapped with delicate task wipers to remove excess surface water, and weighed as the wet weight of gel ( $W_w$ ). The equilibrium-swelling ratio ( $Q$ ) was calculated from eq. (2):

$$Q = (W_w - W_d)/W_d \quad (2)$$

### Zeta potential measurement

The samples were immersed in 20 mL deionized water for 12 h and were suspended in colloidal solution by homogenizer (Polytron, PT3100, Littau, Switzerland). The zeta potentials of the hydrogels were measured with Zeta-meter microscope 3.0+ (Staunton, VA).

### Swelling kinetics measurement

The swelling ratio was obtained by weighing the initial and swollen samples at various time intervals. The amount of water absorbed,  $W_t$ , was reported as a function of time and the equilibrium absorption at infinitely long time was designated as  $W_\infty$ . Equation (3) was used to calculate the diffusion coefficient  $D$  for  $W_t/W_\infty \leq 0.8$ .<sup>30</sup>

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

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 eq. (4) for  $W_t/W_\infty \leq 0.6$ .<sup>31,32</sup>

$$W_t/W_\infty = Kt^n \quad (4)$$

where  $K$  is a characteristic constant of the gel and  $n$  is a characteristic exponent of the mode transport of the penetrate. In addition, Eq. (5) was used to determine the penetration velocity ( $v$ ) of water in each gel, which was described by Peppas et al.:<sup>33,34</sup>

$$v = \frac{1}{2\rho_w A} \left( \frac{dw}{dt} \right) \quad (5)$$

where  $dw/dt$  is the slope of the weight gain versus time curve,  $\rho_w$  is the density of water,  $A$  is the area of the one face of the disk, and factor 2 accounts for the fact that penetration takes place through both sides of disk.

### Physical properties measurement

The gel strengths of these completely swollen gels were measured by uniaxial compression experiment with universal tester (LLOYD LRX; J.J. Lloyd, Poole, UK). The shear modulus ( $G$ ) can be calculated with eq. (6):<sup>35,36</sup>

$$\tau = F/A = G(\lambda - \lambda^{-2}) \quad (6)$$

where  $\tau$  is the compression stress,  $F$  is the compression load,  $A$  is the cross-sectional area of swollen gels, and  $\lambda$  is the compression strain ( $L - L_0/L_0$ ). At low strains, a plot of  $\tau$  versus  $-(\lambda - \lambda^{-2})$  would yield a straight line whose slope is  $G$ . The effective crosslink density ( $\rho_x$ ) can be calculated from the  $G$  and polymer volume fraction ( $v_2$ ) as eq. (7):

$$\rho = G/v_2^{1/3}RT \quad (7)$$

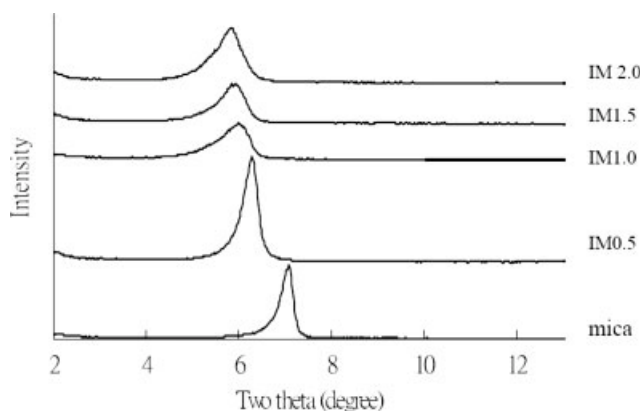
where  $R$  is the ideal gas constant and  $T$  is the absolute temperature.

### Equilibrium-swelling ratio at different temperatures

The equilibrium-swelling ratios of the gels were measured after wiping off water on the surface with filter paper in the temperature range from 25 to 45°C. Gel samples were immersed into an excess of deionized water for 24 h at every temperature. The  $Q$  at every temperature was calculated by eq. (2).

### Drug release of the composite gels

The dry gels were equilibrated in 300 ppm of drug solution at 25°C for 24 h to load drug into the gels. The drug release experiments were carried out by transferring the previously incubated-drug gels into 10 mL deionized water at 37°C. The gels were repeatedly removed and transferred into 10 mL fresh deionized water at each fixed time interval. The releases of



**Figure 1** The XRD patterns of mica and intercalated mica with different CEC values.

drug were analyzed by ultraviolet spectrophotometer (JASCO V-530, Tokyo, Japan) at 272 and 598 nm for caffeine and crystal violet (CV), respectively.

### Morphologies

Samples were equilibrated in deionized water for 24 h and then the swollen gels were frozen-dried for 48 h. The gels were immersed in liquid nitrogen and fractured. A gold metal layer coated on the specimens to provide proper surface conduction. The cross-sectional morphology of the fractured specimens was examined with scanning electron microscopy (SEM) (JEOL JSM5300, Tokyo, Japan) with an acceleration voltage of 15 kV.

## RESULTS AND DISCUSSION

### Identification of the intercalated mica (IM)

The XRD patterns of various intercalated-mica samples are shown in Figure 1. A typical XRD pattern of mica, with a strong peak at  $7.1^\circ$  corresponding to a basal spacing of  $12.52 \text{ \AA}$ , is shown in Figure 1. After intercalating with various content of TMAACl into the mica, the peak shifted to a low angle at  $6.32^\circ$ ,  $6.12^\circ$ ,  $6.02^\circ$ , and  $5.92^\circ$ , corresponding to basal spacing of  $14.03$ ,  $14.78$ ,  $14.88$ ,  $15.03 \text{ \AA}$  for IM0.5, IM1.0, IM1.5, and IM2.0, respectively. This shows that the inter-layer of mica was intercalated by the short chain acrylamido trimethyl ammonium ion during the cation-exchange process.

### Thermogravimetric analysis

Figure 2 shows the dynamic thermogravimetric curves of IM with various CEC values. Thermogravimetric curves show that the weight percentage remaining at  $780^\circ\text{C}$  for the intercalated mica decreases with an increase of intercalant in mica. That

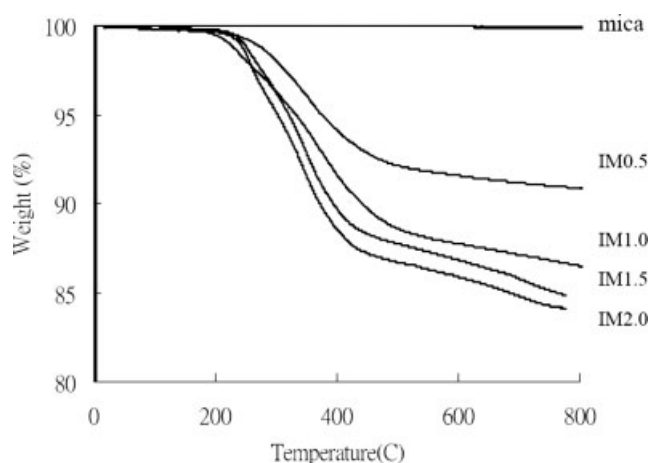
is, the residual weight percentage for pure mica, IM0.5, IM1.0, IM1.5, and IM2.0 are 100, 87.13, 84.7, 82.62, and 81.92%, respectively. These results equivalent to the intercalation ratios are 92.2, 75, 61.1, and 52.1% for IM0.5, IM1.0, IM1.5, and IM2.0, respectively.

### Effect of TMAAI and IM content on swelling ratio for the composite gels

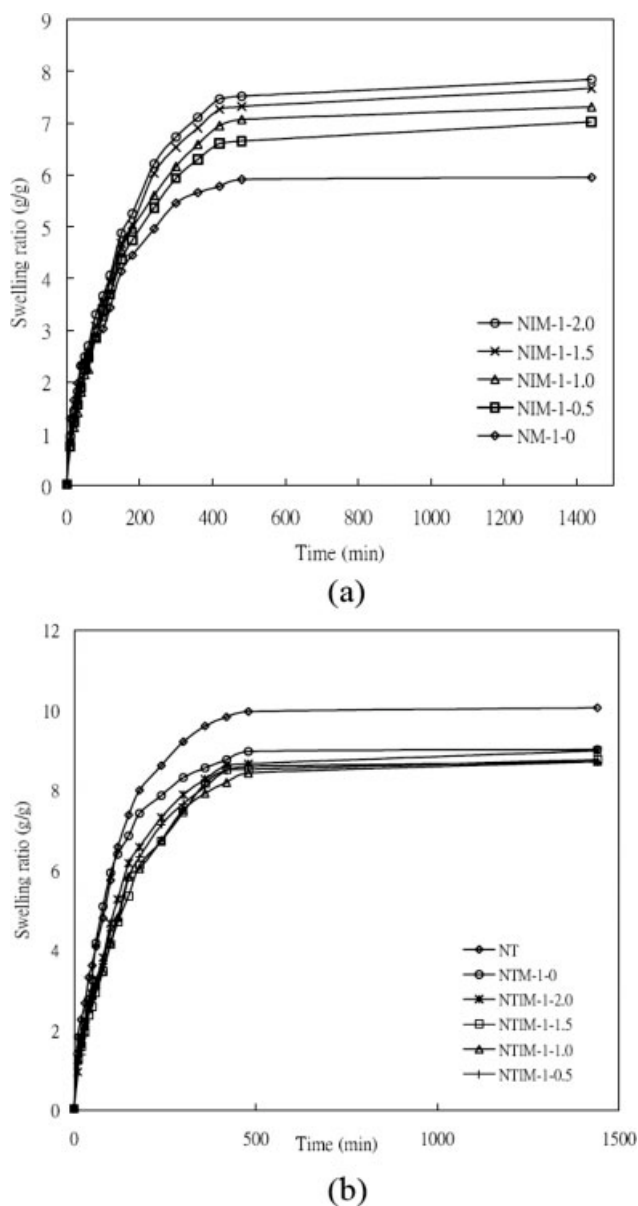
The effect of TMAAI and IM content on the swelling ratios for the present hydrogels is shown in Figures 3 and 4. The results shown in Figure 3(a) indicate that the  $Q$  increases from 6.0 for NM gel containing 1 wt % mica to 7.0, 7.3, 7.7, and 7.8 for NIM-series gels with different CEC values (also see Table I). This result explicitly indicates that the layer space of the intercalated mica could accommodate more water when IM was incorporated into the NIPAAm gel. On the other hand, the results shown in Figure 3(b) indicate that the  $Q$  values for the NTIM-1-z series gel with different intercalant contents are 9.0, 9.3, 8.7, and 9.1, respectively. From Table I, we also find that the  $Q$  values for NT and NTM gels are 10.1 and 9.0, respectively, and for NTIM-series gels increase with increase of IM content such as 9.0, 9.5, 10.0, and 10.6 for NTIM-y-0.5 containing 1, 3, 5, and 7 wt % IM content, respectively. From these results, we find that the  $Q$  values for the present gels are not significantly affected by the intercalant content of mica (CEC value)[CEC effect], but significantly affected by cationic monomer, TMAAI (cationic effect). That is, the  $Q$ s for NTIM gels are higher than those for NM and NIM gels.

### Investigation of water diffusion in xerogels

The swelling ratios as a function of time for NIM-series gels and NTIM-series gels in deionized water at



**Figure 2** TGA curves of pure mica and intercalated mica with different CEC values.



**Figure 3** Swelling ratio as a function of time for (a) NIM and (b) NTIM hydrogels containing 1 wt % IM with different CEC values in deionized water at 25°C.

25°C are shown in Figures 3 and 4, respectively. The  $n$ ,  $k$ , and  $D$  values obtained from eqs. (3) and (4) are listed in Tables II and III. The results indicate that the swelling exponents,  $n$ , for NIM-series gels range from 0.38 to 0.40 and for NTIM-series gels range from 0.31 to 0.46, respectively. This evidence indicates that the swelling transport mechanism for all the gels belongs to Fickian diffusion ( $n < 0.5$ ) according to the classification of diffusion mechanism presented by Alfrey et al.<sup>37</sup> This evidence also shows that the swelling transport mechanisms for all the gels are not obviously affected by the addition of different IM contents into the gels. In addition, the  $D$  values for NIM-1- $z$  series gels (Table II) decrease

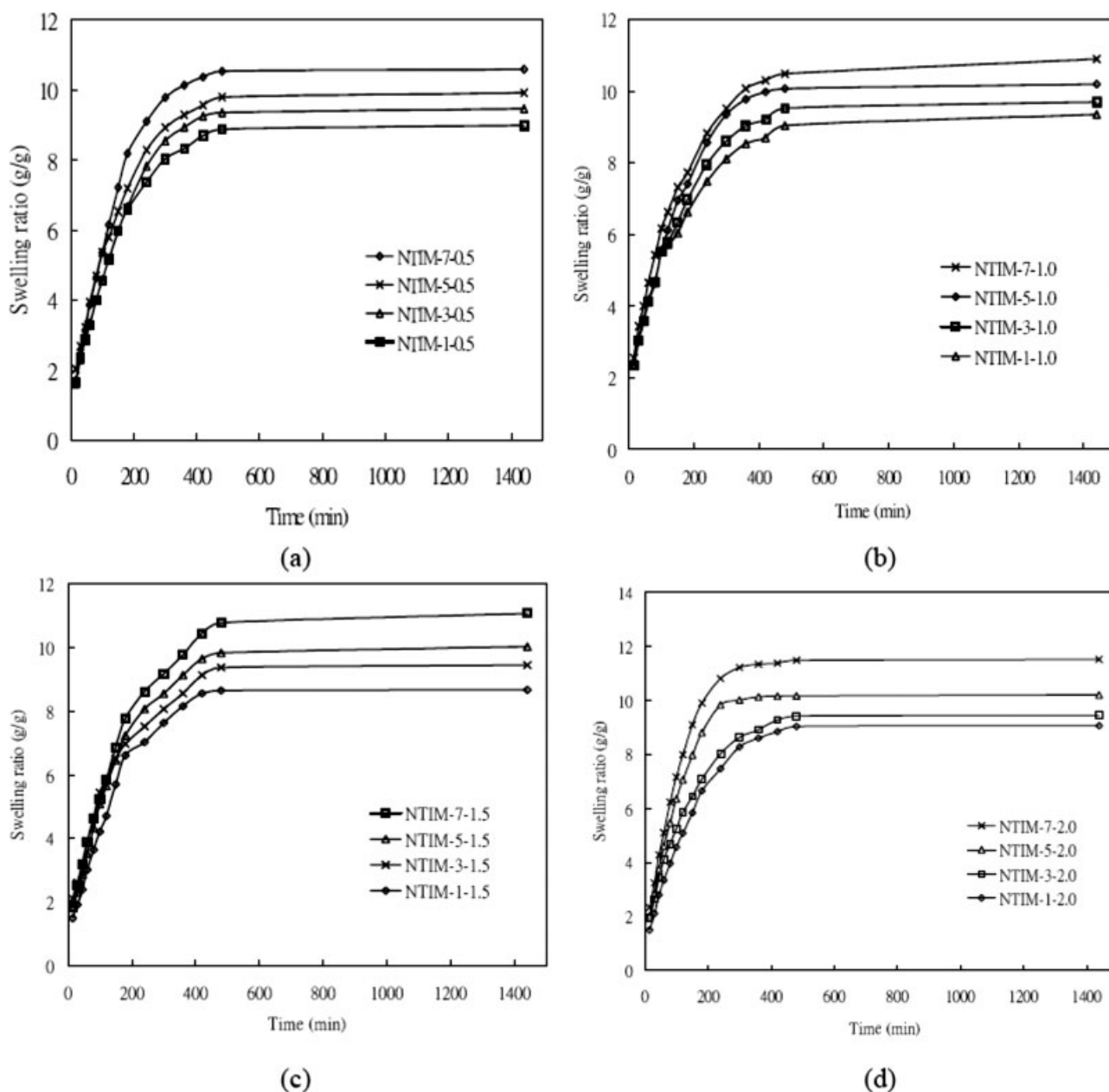
with an increase of the CEC value of the mica from 0.82 to  $0.61 \times 10^{-7}$  ( $\text{cm}^2/\text{s}$ ). But, the  $D$  values for NTIM-series gels in Table III increase with increase in IM content and CEC values of the IM. The penetration velocities ( $v$ ) for these two series gels have similar tendencies as their  $D$  values. Compare these two series gels, we can find that the cationic TMAAI monomer incorporated into the NIM gels can significantly enhance the diffusion coefficient and penetration velocity of the gels.

#### Effect of intercalant content of IM on gel strength and crosslinking density

The gel strength was accessed by the shear modulus ( $G$ ) and crosslink density ( $\rho_x$ ) calculated from eqs. (6) and (7). The results in Table III indicate that the  $\rho_x$  values for NTIM- $y$ -0.5, NTIM- $y$ -1.0, NTIM- $y$ -1.5, and NTIM- $y$ -2.0 series hydrogels increase from  $2.22 \times 10^{-6}$  to  $5.06 \times 10^{-6}$  mol/cm<sup>3</sup>; from  $4.06 \times 10^{-6}$  to  $5.17 \times 10^{-6}$  mol/cm<sup>3</sup>; from  $4.75 \times 10^{-6}$  to  $6.09 \times 10^{-6}$  mol/cm<sup>3</sup>; from  $5.15 \times 10^{-6}$  to  $7.35 \times 10^{-6}$  mol/cm<sup>3</sup>, respectively. And, the  $G$  values are significantly enhanced by IM content and CEC values of IM. This behavior conforms to the intercalated hydrotalcite (HT) that was incorporated into the poly(acrylic acid-*co*-NIPAAm)/HT hydrogels, which showed that the crosslinking density and gel strength increased with an increase of the intercalant content in the gels.<sup>38</sup> However, these tendencies are not observed in NIM-1- $z$  series gels. The  $\rho_x$  values of the NIM-1- $z$  series hydrogels ranged from  $1.41 \times 10^{-6}$  to  $1.79 \times 10^{-6}$  mol/cm<sup>3</sup> and the  $G$  values ranged from 25.22 to 29.13 g/cm<sup>2</sup>. This may be attributed to the IM not dispersed well in the NIPAAm gel system. But, incorporating TMAAI into the NIPAAm gel can improve the dispersity of the IM in the NTIM gel system. From above discussion, the CEC effect is more significant in the charged hydrogels.

#### Effect of temperature on swelling ratio for NTIM-series and NIM-series composite gels

The effect of temperature on the equilibrium-swelling ratio for NIM-series and NTIM-series gels is shown in Figures 5 and 6. The results shown in Figure 5 indicate that the higher the intercalant content, the lower the swelling ratio for the NIM series gels under the temperature above 40°C. It is well-known that PNIPAAm gel has swelling-deswelling behavior at below and above its CGTT. From Figure 5, the CGTT shifted to higher temperature when the IM was incorporated into the NIPAAm gel. This result indicates that the intercalated mica is more hydrophilic than pristine mica. The result also shows that the swelling ratios for the NIM series gels are lower than the NM gel above CGTT. This behavior



**Figure 4** Swelling ratio as a function of time for (a) NTIM-*y*-0.5, (b) NTIM-*y*-1.0, (c) NTIM-*y*-1.5, and (d) NTIM-*y*-2.0 hydrogels in deionized water at 25 °C.

indicates that the interlayer in IM can provide the channel of water release out of the NIM gels at higher temperature. The results for NTIM gels

shown in Figure 6 also indicate that higher the temperature the lower is the swelling ratio, but the CGTTs for the NT gel system are not significantly

**TABLE II**  
Fundamental Properties of the NIM Series Nanocomposite Hydrogels

Sample code	$\rho_x$ ( $10^6$ wet gel (mol/cm <sup>3</sup> ))	$G$ (g/cm <sup>2</sup> )	$n$	$K$ ( $10^2$ )	$D$ ( $10^7$ ) (cm <sup>2</sup> /s)	$v$ (cm/min)
NM-1-0	1.72 ± 0.05	25.66 ± 1.3	0.38	1.82	0.82	0.78
NIM-1-0.5	1.63 ± 0.06	29.13 ± 0.7	0.4	1.48	0.88	0.79
NIM-1-1.0	1.79 ± 0.08	25.99 ± 1.0	0.4	1.49	0.88	0.79
NIM-1-1.5	1.41 ± 0.05	27.25 ± 0.8	0.4	1.63	0.75	0.80
NIM-1-2.0	1.58 ± 0.05	25.22 ± 0.6	0.39	1.67	0.61	0.75

**TABLE III**  
**Fundamental Properties of the NTIM Series Nanocomposite Hydrogels**

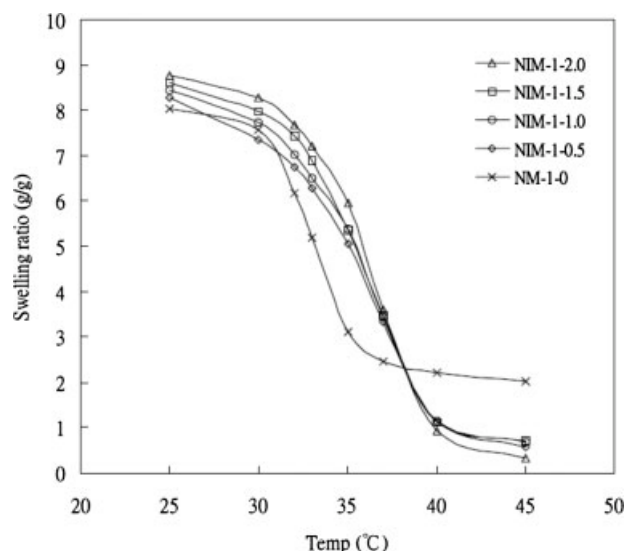
Sample code	$\rho_x$ ( $10^6$ ) (mol/cm <sup>3</sup> )	G (g/cm <sup>2</sup> )	n	K ( $10^2$ )	D ( $10^6$ ) (cm <sup>2</sup> /s)	v (cm/min)
NT	1.22 ± 0.07	20.22 ± 0.8	0.38	1.93	0.13	1.17
NTIM-1-0	1.78 ± 0.09	27.98 ± 1.1	0.39	1.85	0.81	1.16
NTIM-1-0.5	2.22 ± 0.07	44.03 ± 1.2	0.36	2.16	2.32	1.08
NTIM-3-0.5	4.13 ± 0.05	78.13 ± 2.1	0.4	1.59	3.08	1.13
NTIM-5-0.5	4.92 ± 0.08	92.37 ± 1.8	0.37	2.1	4.21	1.14
NTIM-7-0.5	5.06 ± 0.1	101.36 ± 2.4	0.44	1.13	4.92	1.23
NTIM-1-1.0	4.06 ± 0.03	83.76 ± 1.2	0.31	3.81	3.28	1.16
NTIM-3-1.0	4.23 ± 0.1	84.49 ± 1.4	0.32	3.54	4.82	1.18
NTIM-5-1.0	4.87 ± 0.11	96.53 ± 2.2	0.36	2.43	5.69	1.26
NTIM-7-1.0	5.17 ± 0.09	100.73 ± 1.7	0.34	2.74	6.42	1.30
NTIM-1-1.5	4.75 ± 0.04	89.93 ± 1.3	0.41	1.42	3.87	1.17
NTIM-3-1.5	5.08 ± 0.1	96.18 ± 1.1	0.36	2.44	5.03	1.19
NTIM-5-1.5	5.46 ± 0.08	104.78 ± 1.5	0.41	1.46	6.18	1.25
NTIM-7-1.5	6.09 ± 0.05	133.02 ± 0.9	0.43	1.2	6.94	1.33
NTIM-1-2.0	5.15 ± 0.11	97.79 ± 2.1	0.43	1.3	4.66	1.20
NTIM-3-2.0	5.46 ± 0.07	104.87 ± 1.7	0.41	1.72	5.12	1.25
NTIM-5-2.0	6.4 ± 0.09	118.64 ± 1.4	0.46	1.12	5.97	1.40
NTIM-7-2.0	7.35 ± 0.14	134.184 ± 2.5	0.48	0.97	7.27	1.51

changed when the IM was added into the NT gel. From above results, the hydrophilicity of the cationic TMAAI is higher than anionic intercalated mica.

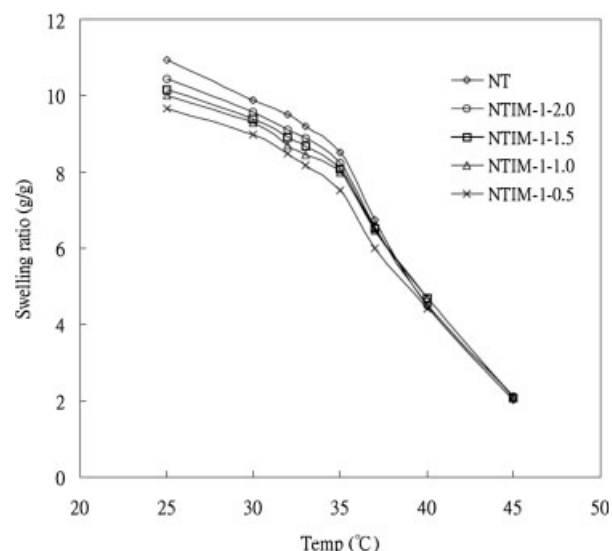
### Zeta potential

To confirm the charged property of the NIPAAm gel when IM and/or TMAAI were added, the zeta potentials of the gels were measured. Figure 7 shows the CEC value of IM on the zeta potentials of NTIM-1-z and NIM-1-z series hydrogels containing 1 wt % IM. The results indicate that zeta potentials decrease from +36 to +18 mV for NTIM-series

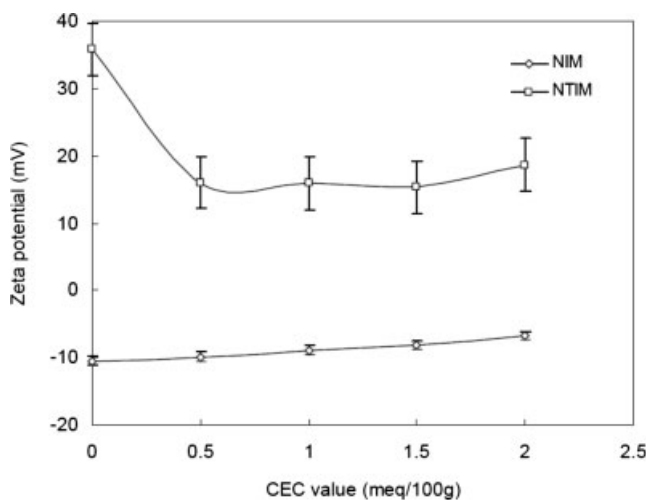
gels, but increase from -11 to -6 mV for NIM-series gels with increase in intercalating content of mica. This is because the cationic intercalant (TMAAI) neutralized negative charges of mica. This resulted in making the charge density of the mica decreases with increasing intercalating content (-42.5, -39.0, -38.3, -37.9, and -32.2 mV for 0 CEC, 0.5 CEC, 1.0 CEC, 1.5 CEC, and 2.0 CEC, respectively). Hence, the zeta potential of the NIM decreased while the IM was added into NIPAAm gel. Similarly, the zeta potential for the cationic NT gel decreases due to charge neutralization of the cationic NT gel and anionic IM.



**Figure 5** Effect of temperature on equilibrium swelling ratio for the NIM series hydrogels containing 1 wt % IM with different CEC values.

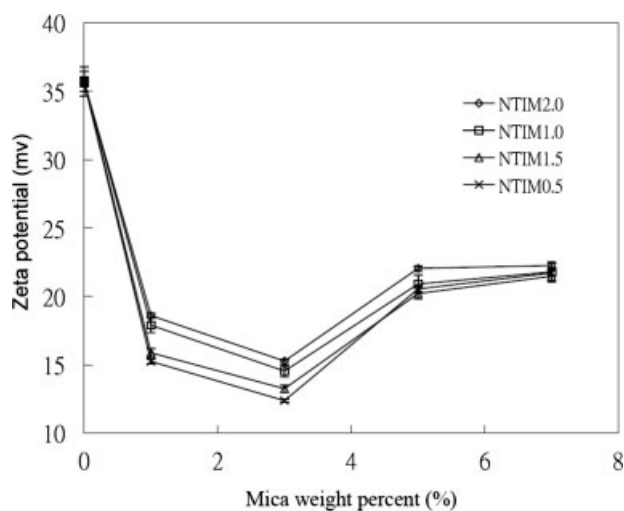


**Figure 6** Effect of temperature on equilibrium swelling ratio for the NTIM series hydrogels containing 1 wt % IM with different CEC values.



**Figure 7** Effect of CEC value of IM on the zeta potential for NIM and NTIM series hydrogel containing 1 wt % IM.

The results for NTIM series gels shown in Figure 8 indicate that the zeta potentials, respectively, decrease from 35.7 mV for NT gel to 12.4, 13.2, 14.5, 15.3 mV, and for NTIM-y-0.5, NTIM-y-1.0, NTIM-y-1.5, and NTIM-y-2 containing 3 wt % IM, then increase to 21.4, 21.7, 21.7, and 22.2 mV for corresponding gels containing 7 wt % IM. That is, the minimum zeta potential for NTIM gels appears at 3wt% IM during the experimental range. The charge inversion for the colloid gel was observed in this Figure. This result also shows that the zeta potentials for NTIM series gels approach to constant at 7 wt % IM added into the gels. This result can describe why the swelling ratio of NTIM-7-z series gels approach to constant at 7 wt % IM (Table I). From above results, the charge density of the pres-

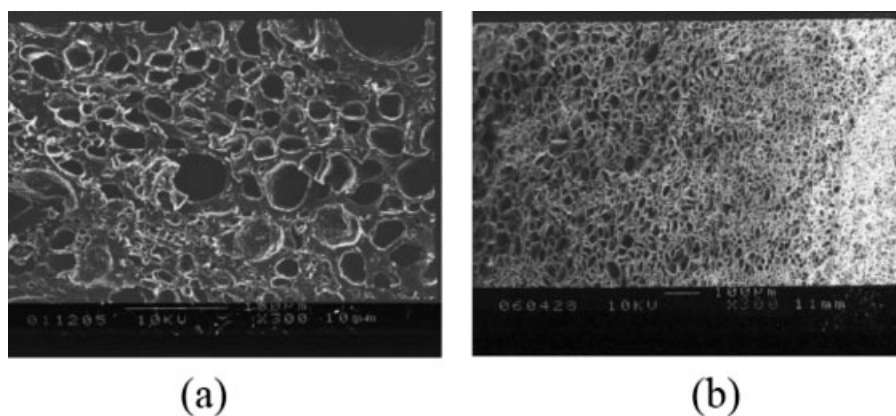


**Figure 8** Effect of IM content on the zeta potential of the NTIM-series gels with different CEC values.

**TABLE IV**  
Drug-Loading Amount and Fractional Release of the Composite Hydrogels

Drug	NM-1-0	NIM-1-0.5	NIM-1-1.0	NIM-1-1.5	NIM-1-2.0	NTIM-1-0.5	NTIM-1-1.0	NTIM-1-1.5	NTIM-1-2.0	NT
Caffeine										
Loading amount (ppm/g)	787.88	942.95	939.95	1145.26	1378.29	1015.44	1233.6	834.48	758.95	763.3
Fractional at release 600 min (%)	61.06	58.22	56.27	55.42	50.14	72.01	74.99	80.27	84.02	85.67
CV(+)										
Loading amount (ppm/g)	1176.12	1998.36	1947.5	2183.75	1783.44	1067.77	1175.2	930.59	682.25	663.8
Fractional release at 600 min (%)	29.57	32.42	38.13	40.7	44.38	90.4	92.82	94.22	95.02	95.42





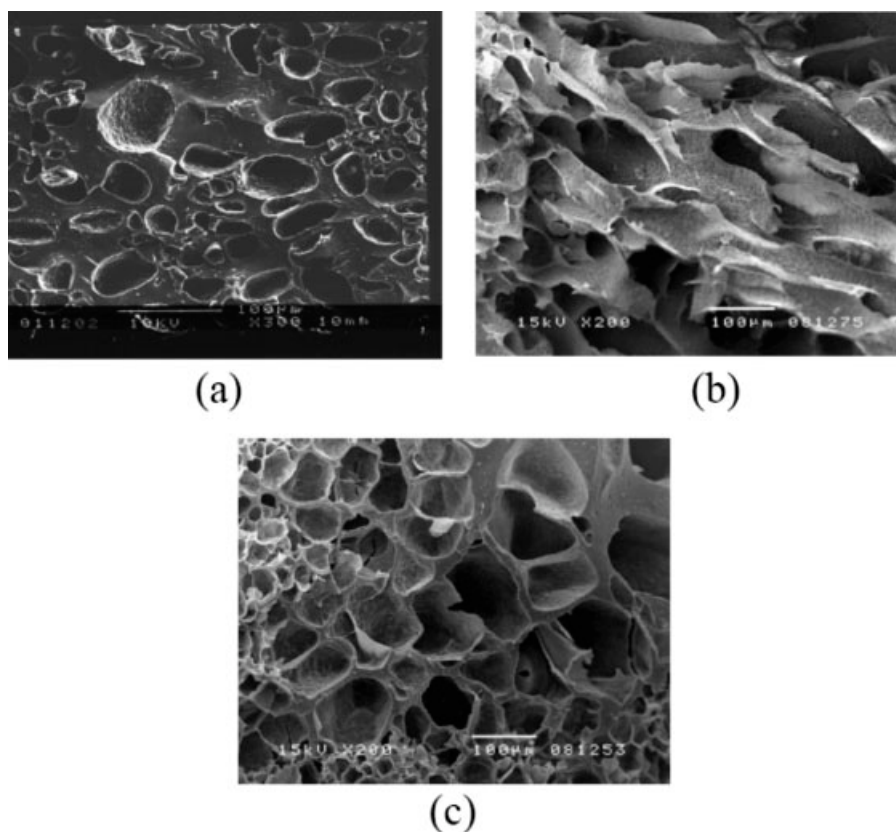
**Figure 9** Cross-sectional microphotographs of the NIM-series hydrogels (a) NM-1-0 and (b) NIM-1-2.0.

ent hydrogels can be varied by the incorporation of IM into the gels.

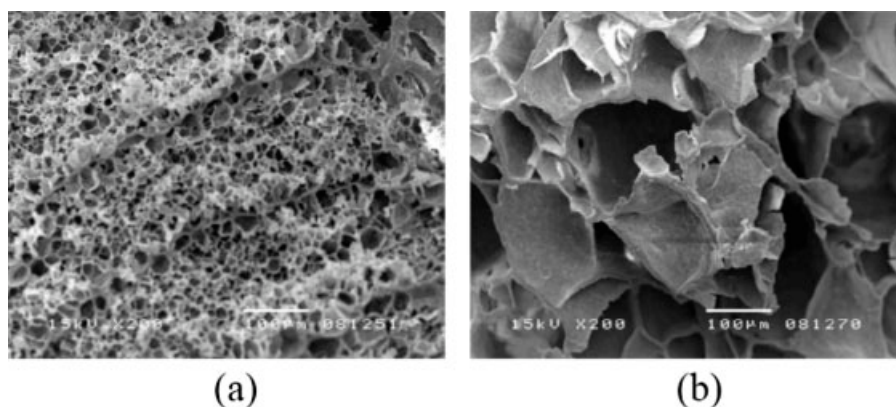
#### Effect of CEC values on drug release for NTIM and NIM gels

Generally, the loading amount and fractional release of drugs depends upon the swelling ratio, charge density, and the affinity of the gel. The loading amount and fractional release of the model drugs at

600 min for the NTIM and NIM hydrogels containing 1 wt % IM with various CEC values were summarized in Table IV. The results shown in Table IV indicate that the loading amount of caffeine for NIM series gels increases with an increase of CEC value of IM, but fractional release of caffeine decreases with increase in CEC value of IM. However, a contrary result for NTIM series gels in caffeine loading and fractional release behavior was obtained. Hence, loading amount and fractional release of the non-



**Figure 10** Cross-sectional microphotographs of the NTIM-series hydrogels (a) NT (b) NTM-1-0 and (c) NTIM-1-2.0.



**Figure 11** Cross-sectional microphotographs of the NTIM-series hydrogels (a) NTIM-7-0.5 and (b) NTIM-7-2.0.

ionic caffeine mainly depend on the swelling ratio and affinity of the gels. In addition, the fractional release of cationic CV in anionic NIM gels increases with decrease of charge density NIM series gels (NIM-1-0 < NIM-1-0.5 < NIM-1-1.0 < NIM-1-1.5 < NIM-1-2.0). On the contrary, the fractional release of cationic CV in cationic NTIM gels increases with increase of charge density of NTIM series gels (NTIM-1-2.0 > NTIM-1-1.5 > NTIM-1-1.0 > NTIM-1-0.5) due to charge repulsion. These results conform to our previous results.<sup>39</sup>

### Morphologies

The cross-sectional microphotographs for NTIM-series and NIM-series hydrogels were shown in Figures 9 and 10. From these microphotographs, we can find that the pore size decreases with increasing of the CEC of mica for NIM series gels. But, the pore size become larger when the cationic TMAAI monomer was added into the NIM series gels (Fig. 10). However, the effect of the CEC on the pore size for the NTIM series gels is not significant. This can prove that the swelling ratios for NTIM gels cannot significantly increase with the CEC of mica. But, the pore size for NTIM-7-z gels significantly increases with increase in the CEC of mica (Fig. 11). That resulted in increasing the swelling ratio of the composite gels (Table I).

### CONCLUSIONS

The charge character of the poly(NIPAAm) gel can be adjusted by incorporating intercalated mica and/or cationic monomer, TMAAI, into the NIPAAm during polymerization. The anionic NIM and cationic NTIM series composite hydrogels were successfully synthesized in this study. Some conclusions can be drawn from above discussion. Mica can be intercalated with TMAACl under low CEC value. The intercalating ratio of mica decreased from 90 to 50%

when the intercalation with higher CEC value was used. The equilibrium-swelling ratios for the present gels are not significantly affected by the intercalant content of mica, but significantly affected by cationic monomer, TMAAI. The cationic TMAAI monomer incorporated into the NIM gels can significantly enhance the diffusion coefficient and penetration velocity of the gels. In mechanical properties, adding IM into the gel composition enhanced the gel strength and crosslinking density for NTIM-series gels. The zeta potential of the NIM decreased while the IM was added into NIPAAm gel. Similarly, the zeta potential for the cationic NT gel decreased due to charge neutralization of the cationic NT gel and anionic IM. The CGTT shifted to higher temperature when the intercalated mica or TMAAI was added into the NIPAAm gel. The drug release behaviors in these hydrogels were related with the charge properties of the gels and drugs.

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