

Chitosan Modified MMT-Poly(AMPS) Nanocomposite Hydrogel: Heating Effect on Swelling and Rheological Behavior

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ABSTRACT: Vulnerability of hydrogels against thermal circumstances may be substantially eliminated via incorporating nanoclay to prepare nanocomposite hydrogels. In this research, chitosan-intercalated montmorillonite (ChitoMMT) was used as a bionanoclay to yield novel nanocomposite hydrogels based on 2-acrylamido-2-methylpropanesulfonic acid. The bionanoclay is suitable especially for preparing biomaterials used in biomedical, food, and pharmaceutical applications, unlike conventional commercial nanoclays (alkyl ammonium-intercalated MMT) which are not appropriate for bio-applications due to toxicity of the intercalant particularly where the clay content is high. Two different crosslinkers (i.e., methylene

bisacrylamide, and polyethyleneglycol dimethacrylate) were employed to synthesize the nanocomposites. The variations in swelling, rheological and thermal properties of the hydrogels were essentially attributed to thermally induced crosslink cleavage/formation depending upon the crosslinker nature. The nanocomposites comprised superior thermal properties in comparison with the clay-free hydrogel counterpart. They can preserve substantially their swelling ability for longer heating periods. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 2548–2556, 2010

Key words: hydrogel; nanocomposite; AMPS; chitosan; swelling

INTRODUCTION

Hydrogels with superabsorbing properties are lightly crosslinked hydrophilic polymers, which can absorb and retain a large amount of water and other physiological fluids.¹ They can be used in hygienic^{1,2} and agricultural applications,^{1–5} drug delivery,^{1–3,6,7} water sealing with swellable rubbers,⁸ coal dewatering,⁹ food packaging,¹⁰ fire protection,¹¹ and artificial snows.¹⁰

Nanocomposite hydrogels have been developed greatly in recent years due to superior properties in comparison with neat hydrogels. Mechanical properties have essentially been improved in these hydrogels.^{12,13} They can be particularly used in drug delivery,^{14,15} enhanced oil recovery,¹⁶ electronic,^{17,18} and optical¹⁹ devices.

Nanocomposite hydrogels were made using organo-modified clays^{15,20–22} or metal nanoparticles such as gold, silver, and copper.^{23–25} Clays such as montmorillonite (MMT) and bentonite are mostly modified with cationic intercalants such as alkylammoniums.^{15,26–28} These intercalants are mostly toxic,

therefore, the resulting modified clays are not proper for biomedical and food applications particularly when the organo-modified clay content in polymer matrix is high.²⁹

As an early stage of this work, MMT was intercalated with chitosan to prepare a biomodified nanoclay; ChitoMMT. Chitosan is extensively used in bio-related applications due to its biocompatibility^{30,31} and antibacterial properties.³² It has already been used as an intercalant for the nanoclay preparation.³³

The majority of nanocomposite and composite hydrogels are reported to be based on *N*-isopropylacrylamide monomer due to induction of reversible thermoresponsive properties by this monomer.^{13,14} Acrylamide (AM)^{16,23} and acrylic acid (AA)^{20,14} have also been employed in several researches. 2-Acrylamido-2-methylpropanesulfonic acid (AMPS) is another attractive monomer due to its good reactivity and acidity. The AMPS-based hydrogels comprise electroresponsive properties and can be used in electrical applications.^{34,35} It may also be employed in biochemical purposes for skin contact electrodes³⁶ and muscle actuators, for example, gel robots.^{11,37} To the best of our knowledge, there is no report on synthesis of biomodified clay nanocomposites fully composing AMPS; even full-AMPS hydrogel composites have not been studied vastly. On the other hand, since homopoly(AMPS) hydrogels are

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more susceptible against heating comparing to conventional AM- and AA-based hydrogels, incorporation of the nanofillers may compensate the thermal vulnerability.

In this article, ChitoMMT-contained poly(AMPS) hydrogel nanocomposites were synthesized. Thermally induced variations of swelling and rheological properties of the synthesized gels were studied in detail.

EXPERIMENTAL

Materials

AMPS (Merck, Germany), ammonium persulfate (APS, Merck), polyethylene glycol dimethacrylate (PEGDMA 330, Aldrich, USA), chitosan with molecular weight 280,000 (Fluka), methylene bisacrylamide (MBA, Fluka, Switzerland), montmorillonite K10 (Fluka) and water-miscible solvents (all from Merck) were used as received.

Clay modification to prepare ChitoMMT

MMT (0.50 g) was dispersed in 50 mL distilled water. Chitosan (2.0 g) was separately dissolved in 312 mL of 1% v/v acetic acid aqueous solution. Both mixtures were then poured in a 1-L flask and heated (9 h, 70°C) while gently stirring. The mixture was centrifuged and thoroughly washed with 1% acetic acid solution and distilled water, respectively. The product was dried in a forced draft oven (60°C, 6 h). It was ground and kept in a capped bottle.

Synthesis of biomodified hydrogel nanocomposite

Monomer AMPS (30.0 g) was dissolved in 30.0 g water. The biomodified nanoclay (ChitoMMT) was added to the reactor containing AMPS solution. The mixture was stirred for 24 h at room temperature to disperse clay. Subsequently, fixed amounts of initiator (0.15 g APS) and crosslinker (0.24 g PEGDMA) were added to the reactor. It was stirred while heating in a water bath (70°C) to initiate polymerization. After gelation, the reactor was kept in the bath for 30 min. Then, the elastic gel was cut in the form of small pieces that subsequently dried in a forced draft oven (60°C, 6 h). The dried product was ground with a hammer-type minigrinder and screened.

Swelling measurements

A 0.200 g sample of dried polymer (mesh 35–100) was dispersed in 100 mL of water and allowed to swell for 1 h to reach equilibrium swelling. Each dispersion was filtered through a polyester gauze to

remove the excess water, and then hydrated gels were weighed. Swelling (g/g) was calculated by dividing the weight of swollen gel to the weight of dried gel.

X-ray diffraction

X-ray diffraction of samples was obtained by a X-ray diffractometer (X'Pert, Philips, Netherlands) at wavelength $\text{Cu-K}\alpha = 1.54 \text{ \AA}$ operating at a voltage of 40 kV and a current of 40 mA at the rate of $2^\circ/\text{min}$ in the range of $1\text{--}10 2\theta$.

Rheometry

The rheological measurements were performed using a Paar-Physica oscillatory rheometer (MCR300, Germany) at 25°C with parallel plate geometry (plate diameter of 25 mm, gap of 3 mm). The detailed procedure was previously reported.³⁸

Transmission electron microscopy

TEM images were observed with Zeiss model (EM 900) at 80 kV. Nanocomposite hydrogel was dispersed in acetone. Some droplets of dispersion was added to grid and allowed to dry at room temperature. Then the grid put in a chamber of the device to observe images.

Elemental analysis

Elemental analysis was performed by a CHNOS analyzer system (elementar, model vario EL III).

FTIR

FTIR spectra of dried samples as KBr tablets were recorded by an ABB-Bomem MB-100 FTIR spectrophotometer.

RESULTS AND DISCUSSION

Structure of ChitoMMT and nanocomposite hydrogel

Figure 1(a) shows XRD pattern of unmodified MMT. The interlayer distance between the clay galleries was recorded to be 9.87 \AA ($2\theta = 8.85$). After the bio-modification, the peak was shifted to $2\theta = 3.90$ indicating that the interlayer distance of MMT was increased from 9.87 to 22.6 \AA .

Elemental analysis was also used as another proof for the chitosan intercalation. Nitrogen percent for unmodified MMT was 0.03% which was increased to 0.65% in ChitoMMT. This nitrogen content enhancement is related to $-\text{NH}_3^+$ groups of chitosan, which have been intercalated in MMT.

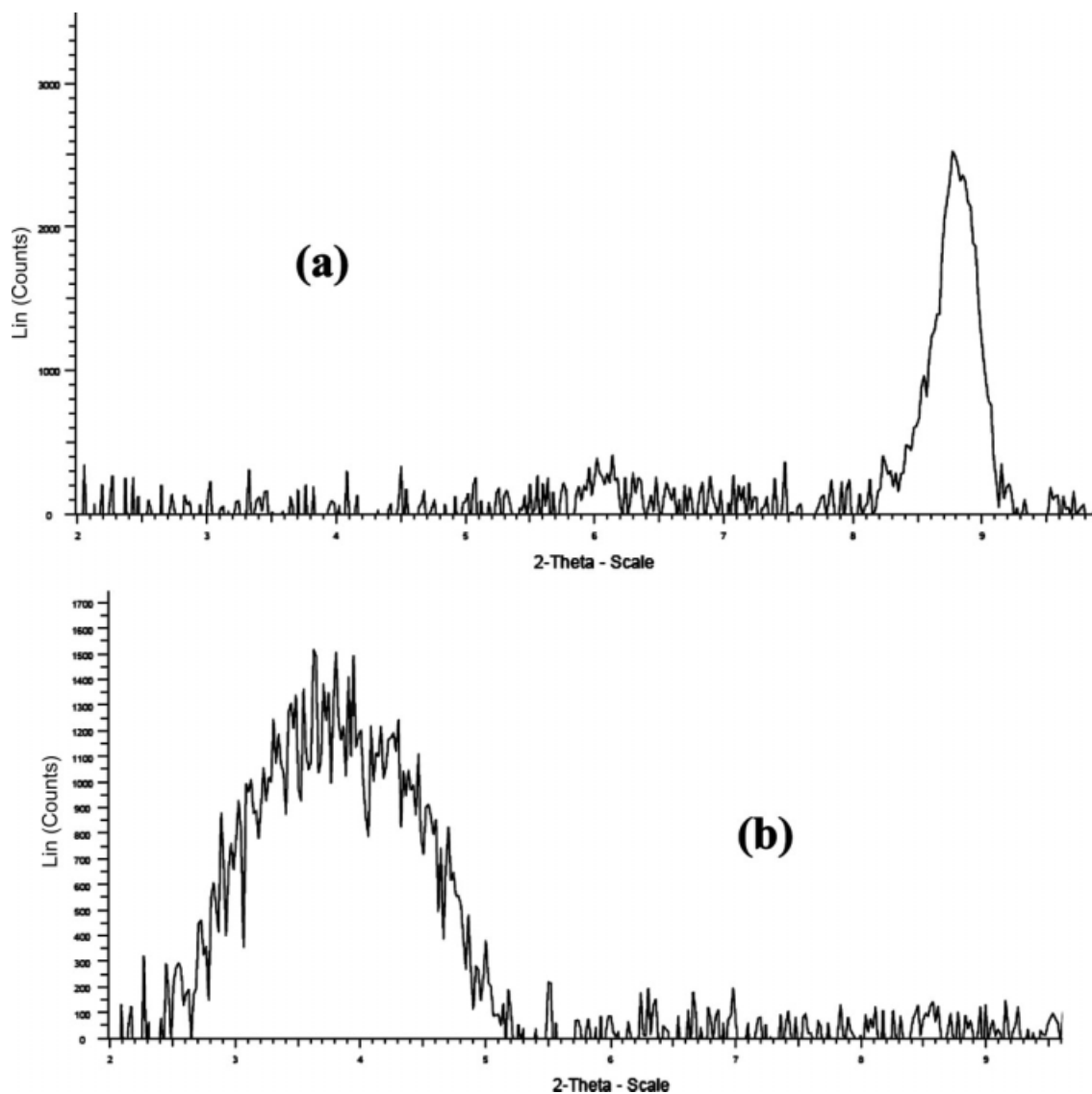


Figure 1 XRD pattern of (a) unmodified MMT and (b) chitosan-modified MMT (ChitoMMT).

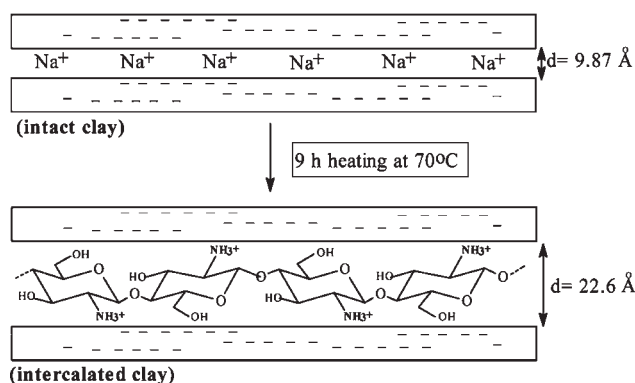
Clay surface contains a lot of negative charges, which are counterbalanced with cations such as Na^+ and Ca^{2+} in the interlayer spaces. Cation exchange reactions can take place in intercalation process between Na^+ and chitosan in slightly acidic media. It should be pointed out that this cation exchange reaction is thermodynamically favorable.^{33,39} So, it proceeds at a mild heating (70°C) during a rather long time (9 h). Scheme 1 exhibits the chitosan entrance between the clay galleries to increase the clay interlayer distance.

Figure 2 shows TEM micrograph of the nanocomposite hydrogel. The image showed that nanocomposite hydrogel comprised an intercalated structure. Jana reported three factors involving clay exfoliation in a polymer nanocomposite: electrostatic attractive, elastic, and van der Waals forces.⁴⁰ If elastic force overcomes attractive force, exfoliation of clay occurs.

This fact implied that the polymerization process of AMPS monomer could not arrange enough elastic force for exfoliation of clay.

Studies on swelling capacity-heating relation

The effect of heating time and temperature on swelling capacity of poly(AMPS)-biomodified clay nanocomposite (contained 6% ChitoMMT) and its clay-free counterpart (noncomposite sample) were comparatively studied while two different kinds of crosslinkers (i.e., MBA and PEGDMA) were used for preparing the hydrogels. Since super-swelling hydrogels contain extremely low density of crosslinking, the crosslink formation or cleavage cannot be detected easily by normal techniques. On the other hand, the clay particles somehow act as crosslink points and, therefore, the crosslinking system



Scheme 1 Schematic structure of unmodified clay (MMT) and its conversion to the chitosan-modified MMT.

becomes too complicated to be quantitatively studied. Instead, as successfully practiced before,⁴¹ swelling capacity measurements were simply used to provide valuable information about the thermal vulnerability of the hydrogels. Rheometrical measurements were performed on the swollen gels to typically confirm the interpretations.

MBA-crosslinked poly(AMPS)-biomodified MMT nanocomposite

Figure 3 shows swelling capacity variation of the two clay-free and nanocomposite hydrogel samples heated at 80°C for 0–18 h. Two distinctive regions can be seen in the swelling-heating time profile for clay-free sample. In the first region, swelling capacity was increased from 44 g/g after 2 h to 281 g/g after 12 h oven drying. In the second region, swelling capacity was vastly increased with increase of drying time. It was increased to 505 and 900 g/g after 13 and 15 h oven drying, respectively. Then,

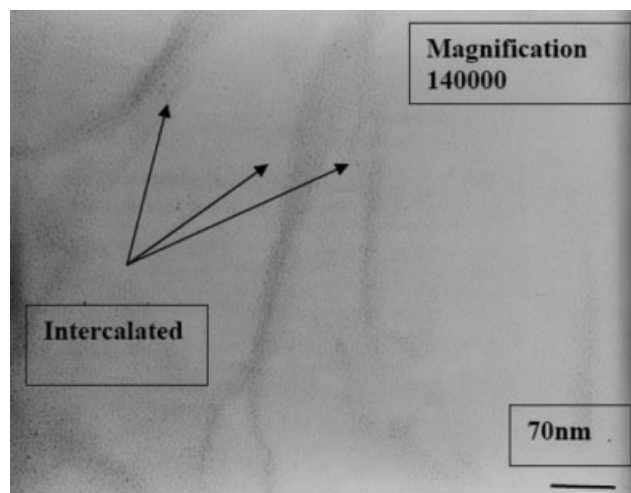


Figure 2 TEM pattern of ChitoMMT-poly(AMPS) nanocomposite hydrogel.

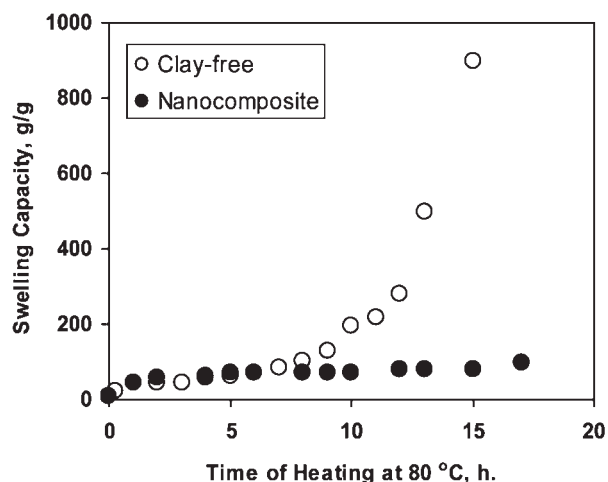


Figure 3 Swelling capacity vs. time of heating at 80°C for MBA-crosslinked hydrogels of ChitoMMT-poly(AMPS) nanocomposite in comparison with the clay-free counterpart.

the clay-free sample became soluble in water after heating for 15 h.

Swelling capacity for the nanocomposite hydrogel was increased from 59 to 71 g/g after 2 and 5 h oven drying at 80°C. Then swelling capacity very mildly increased with the enhancement of the oven drying time. Finally, swelling capacity was increased to 100 g/g after heating for 17 h. It showed that the nanocomposite hydrogel was more stable than the noncomposite sample. Nanocomposite hydrogel can preserve its absorbency after 17 h heating at 80°C, whereas the clay-free sample turns out to be soluble in swelling media after 15 h heating.

Thermo-accelerated enhancement of swelling versus drying temperature was also examined at higher temperatures. According to Figure 4, swelling capacity of the clay-free sample was increased initially from 10 to 161 g/g after 2 h heating at 100°C.

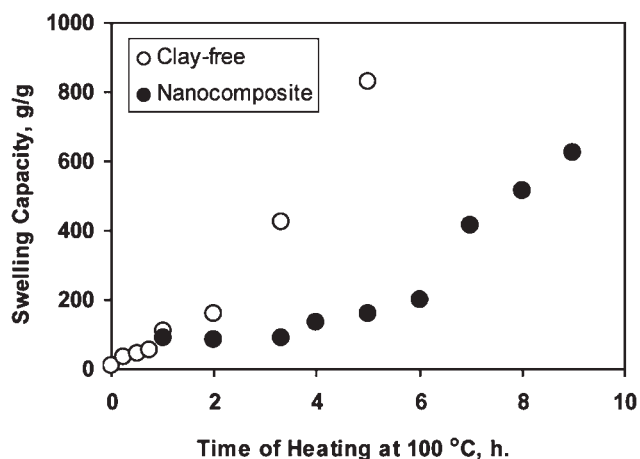


Figure 4 Swelling capacity vs. time of heating at 100°C for MBA-crosslinked hydrogels of ChitoMMT-poly(AMPS) nanocomposite in comparison with the clay-free counterpart.

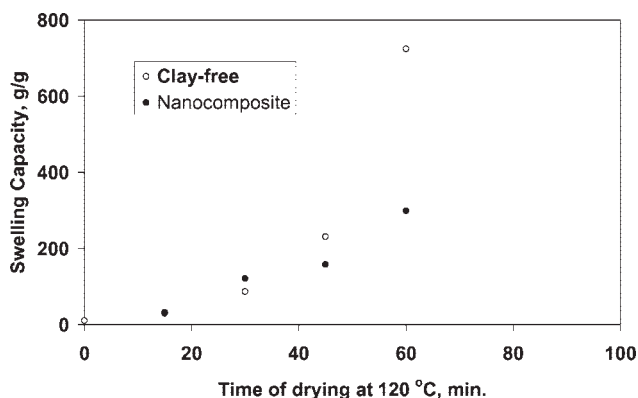


Figure 5 Swelling capacity vs. time of heating at 120°C for MBA-crosslinked hydrogels of ChitoMMT-poly(AMPS) nanocomposite in comparison with the clay-free counterpart.

Then, the swelling was immensely increased with the drying time, so that it was enhanced to 427 g/g after 3.20 h. This sharp swelling increase was continued to reach to 790 and 945 g/g after 4 and 6 h, respectively. After 6 h heating at 100°C, the poly (AMPS) hydrogel sample was totally soluble in water.

As shown in Figure 4, swelling capacity of the nanocomposite sample was increased from 87 to 133 g/g after 2 and 4 h of heating at 100°C, respectively. Then it was enhanced to 200 g/g after 6 h. Subsequently, swelling capacity was vastly increased with heating time raise, so that it eventually reached to 625 g/g after heating for 9 h.

It is clearly observed that at higher temperature (100°C), enormous enhancement of swelling has been delayed for the nanocomposite hydrogel. Although swelling increase of the clay-free hydrogel was perceived after 3 h, it was delayed to 6 h for its nanocomposite counterpart. It can be seen that the nanocomposite has higher thermal stability against crosslink degradation than the clay-free hydrogel.

Severer destructive effect of temperature was observed when the hydrogel was heated at 120°C (Fig. 5). At this temperature, swelling capacity of the clay-free sample was enhanced up to 231 and 724 g/g just after 45 and 60 min, respectively. Therefore, at 120°C, the time required for thermal decrosslinking of the MBA-crosslinked poly(AMPS) hydrogel network (leading to the complete dissolution) was immensely reduced to just about 1 hour. Swelling capacity of the nanocomposite sample was increased from 32 to 121 g/g after heating at 120°C for 15 and 30 min, respectively. The swelling capacity reached to 158 and 300 g/g after heating at 120°C for 45 and 60 min, respectively. The absorbency of the nanocomposite after heating for 1 h (300 g/g) was considerably lower than that of the clay-free sample (724 g/g). This significant difference in swelling-heating behavior was related to the stabilization effect of the

biomodified clay incorporated into the hydrogel structure.

Increase of thermal stability of polymer-clay composites or nanocomposites has been observed in a number of works.⁴²⁻⁴⁷ Broadly speaking, the chemical nature of studied polymeric material and its degradation mechanism play an important role.⁴² There are some explanations about improvement of thermal stability in polymer-clay nanocomposites. Galeski reported that the clay layer acts as a physical barrier, lowering gas transport at the interface. As a result, oxygen diffusion toward the bulk is reduced, which lead to decrease of thermo-oxidative degradation.^{43,44} Galeski⁴³ also mentioned that the heat conductivity of nanocomposite sample is reduced due to insulation action of the clay layer at the surface. Dubis described that the inactivation effect has an important role to increase thermal stability of the polymer nanocomposites. Active centers due to polymer chain decomposition can probably react with clay.⁴² Meanwhile, crosslinking reaction between polymer and clay can also occur. These reactions can also increase thermal stability of the material.⁴² Yoon and coworkers⁴⁵ explained that the shielding effect of the clay layer lead to increased thermal stability. Modified silicate layers are impermeable to degradation products formed during thermo-decompositions. Therefore, release rate of decomposed parts become slower. As a result, the weight loss of the polymer composite is delayed.⁴⁴ The earlier studies have been carried out for different polymer-clay nanocomposites, which are mostly hydrophobic. Wang and coworkers^{46,47} particularly studied thermal stability improvement in hydrogel nanocomposites based on poly(sodium acrylate) and poly(acrylamide). Wang reported improving influence of the clay structure on thermal properties. The clays with 1 : 1 and 1 : 2 layer silicate show 4 and 3 decomposition stages, respectively.⁴⁶ In another article, Wang et al.⁴⁷ mentioned that clay particles can act as the heat barriers causing thermal stability improvement via hindrance against passing the gaseous species produced from the thermal decomposition through the matrix.

Thermogravimetric data (Table I) for clay-free poly(AMPS) hydrogel sample and its nanocomposite counterpart indicates that the main decomposition stage of the samples occurred above 200°C. Since the thermal induced enhancement of swelling was observed during the heat treatment at 80–120°C, which was considerably lower than the temperature required for initiating decomposition (around ~ 200°C), it can be concluded that another phenomenon except polymer decomposition had occurred. Taking into consideration the “huge change of swelling” in the polymer network, it is most likely related to the crosslink density, which is the most effective parameter

TABLE I
Thermogravimetric Data for Clay-Free Sample and Nanocomposite Poly(AMPS) Hydrogel Containing 6.0 wt % Chitosan-Modified MMT

Biomodified clay content, wt%	Temperature (°C) accompanying with weight loss of		
	10% (T ₁₀)	50% (T ₅₀)	70% (T ₇₀)
0.0	200.2	314.8	376.0
6.0	202.8	326.4	407.0

influencing the swelling level of polymer networks; it is inversely dependent to crosslink density following a power law trend.⁴⁸ Considering the swelling “enhancement”, it should be logically related to the crosslink cleavage (decrosslinking). Significant increase of swelling capacity confirms that crosslink density should be reduced, that is, the crosslink disconnection should occur. Rheological studies (the next section) also confirm crosslink density reduction through decrease of storage modulus.

As mentioned before, it should be pointed out that superabsorbent hydrogels contain very low density of crosslinking. Therefore, the crosslink cleavage can be detected neither by conventional spectroscopies (e.g., IR, NMR) nor by thermal techniques such as TGA and DSC. Therefore, these small, but effective, changes of the crosslink density can be simply traced via swelling measurements and confirmed by rheological studies.⁴¹

Therefore, at lower temperature only crosslinks are susceptible to be cleaved. Here, in case of ChitoMMT-poly(AMPS) hydrogel nanocomposites, lower heat conductivity of nanocomposite sample can probably reduce heat flow to the gel. The thermal induced crosslink degradation may be hindered by the modified MMT particles, leading to prolonged time of the crosslink degradation. For instance, as exhibited in Figure 4, considerable crosslink degradation of MBA-crosslinked poly(AMPS) hydrogel was postponed to 7 h in nanocomposite sample at 100°C. This was just 3 h for the clay-free (noncomposite) sample.

Another reason for higher thermal stability of the nanocomposite hydrogel in comparison with the clay-free hydrogel is attributed to some crosslink formation between the clay and growing chains of the polymer. There are some reports about joint formation between functional groups of the clay surface and acrylic polymer chains.⁴⁹ Haraguchi et al.⁵⁰ mentioned that clay can act as a multifunctional plane crosslinker. These additional crosslinks can also be a reason for higher stability of nanocomposite hydrogels.

PEGDMA-crosslinked poly(AMPS)-biomodified MMT nanocomposite

Figure 6 shows swelling of the PEGDMA-crosslinked poly(AMPS) hydrogels versus heating time at

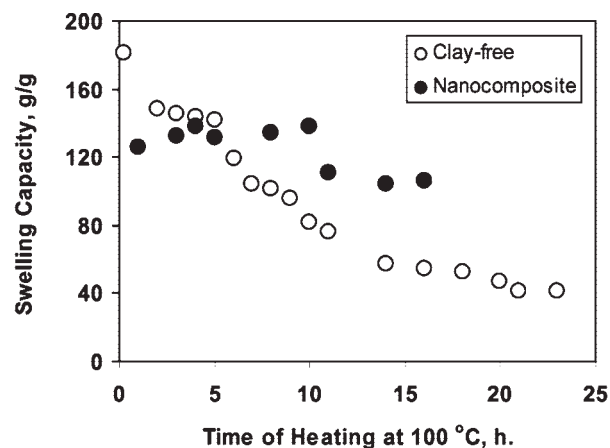


Figure 6 Swelling capacity vs. time of heating at 100°C for PEGDMA-crosslinked hydrogels of ChitoMMT-poly(AMPS) nanocomposite in comparison with the clay-free counterpart.

100°C. It is clearly observed that swelling-heating behavior of this sample is totally different from that of the MBA-crosslinked counterpart illustrated in Figure 4. Swelling capacity of the clay-free sample was measured to be 181 g/g after drying at 100°C for 15 min. It is smoothly decreased to 148 g/g after heating for 2 h. Swelling was then gradually decreased to lower amounts, for example, 81 and 57 g/g after 10 and 14 h drying at 100°C, respectively.

For the nanocomposite hydrogel, however, swelling capacity changes followed a different trend. It was remained nearly constant (~ 130 g/g) during 10 h drying at 100°C. Then, it was mildly decreased with further increase of heating time, so that it reached respectively to 111 and 106 g/g after 11 and 16 h heating.

Similar behavior was observed at 120°C (Fig. 7). The swelling capacity after 15 min heat treatment for

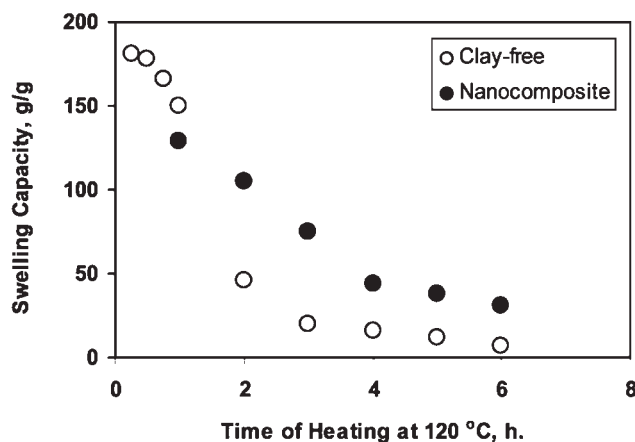
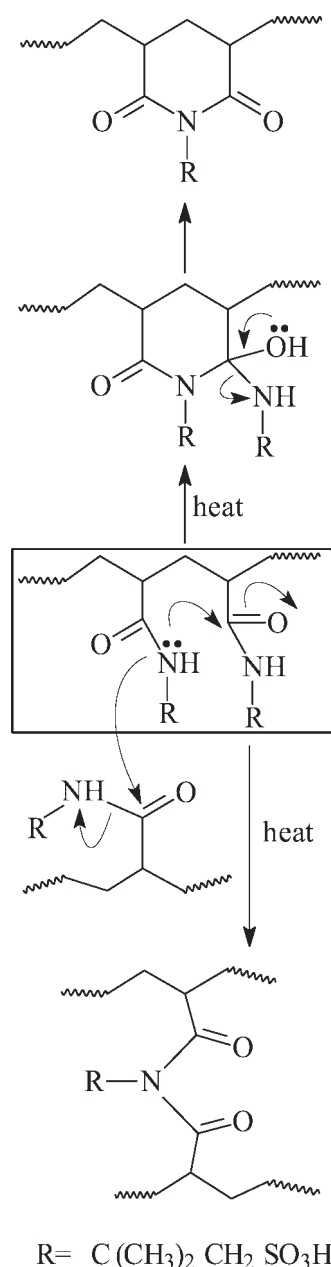


Figure 7 Swelling capacity vs. time of heating at 120°C for PEGDMA-crosslinked hydrogels of ChitoMMT-poly(AMPS) nanocomposite in comparison with the clay-free counterpart.



Scheme 2 Proposed thermal promoted cyclization and re-crosslinking of PEGDMA-crosslinked poly(AMPS) hydrogel.

the clay-free sample was 181 g/g. It was reduced to 46 and 7 g/g after heating for 2 and 6 h, respectively. Again, the hydrogel nanocomposite showed higher resistance against swelling change versus heating temperature and time. Swelling capacity of PEGDMA-crosslinked poly(AMPS) nanocomposite was 105 and 31 g/g after 2 and 6 h heating at 120°C, respectively.

All the obvious visual and behavioral differences between the MBA- and PEGDMA-crosslinked poly(AMPS) hydrogels are rationally attributed to the difference in the chemical nature of the crosslinking agents and absence or presence of clay. It seems that the PEGDMA crosslinker has not been disconnected

during oven drying at high temperature (e.g., 120°C), otherwise, swelling capacity had to be increased as observed in the case of the MBA-crosslinked samples. On the contrary, the swelling capacity is decreased with the increase of drying time. It generally guided us to two probable phenomena occurred during the drying stage: (a) gradual loss of hydrophilicity via removing and/or transforming the hydrophilic groups to hydrophobic functions, (b) formation of a new kind of crosslink.

An intra-molecular cyclization may also be probable, which supports the first occurrence (Scheme 2). Aggour reported the possibility of such reaction during ion beam irradiation of poly(AMPS) resulted in brittleness and insolubility of the irradiated samples.⁵¹ Actually, our samples dried at 120°C are either water-insoluble or brittle, being in agreement with the reported work.⁵¹ Indeed, such reaction is also possible between the pendant groups of adjacent polymer chains. Although such inter-chain reaction (i.e., re-crosslinking) is not very favorable because of some chemical and macromolecular restrictions, this less likely crosslinking interaction would considerably affect the swelling capacity.

Indeed, presence of clay in the hydrogel structure postpones the loss of hydrophilicity of the nanocomposites. The clay insulating nature or its heat barrier effect⁴⁷ reduces effective heat flux through the gel. Therefore, the mentioned intra-molecular cyclization, which is a heat-induced phenomenon is decreased. As a result, the heat-promoted swelling loss is decreased as evidenced in Figure 7.

Rheological study

Rheological studies were carried out to follow swollen gel strength of typical hydrogels heated during

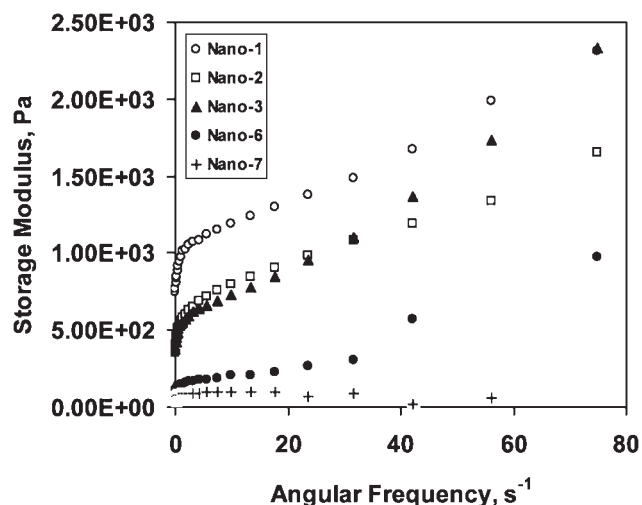


Figure 8 Storage modulus vs. angular frequency for MBA-crosslinked poly(AMPS) hydrogel nanocomposite heated at 100°C for different times (1, 2, 3, 6, and 7 h).

TABLE II
Swelling Capacity and Storage Modulus of PEGDMA-Crosslinked Poly(AMPS) Nanocomposite Hydrogel at Different ChitoMMT Content

ChitoMMT content %	0	2	4	6
Swelling capacity, g/g	188	180	172	165
Storage Modulus (Pa) at angular frequency 31.6 s ⁻¹	630	755	770	985

oven-drying process. It has been previously shown that the gel strength of such super-swelling hydrogels can accurately be determined with an oscillatory rheometer with parallel plate geometry.³⁸ The storage modulus can then be taken as a measure of the mechanical strength of the hydrogel.

Figure 8 representatively shows storage modulus of MBA-crosslinked poly(AMPS) hydrogel nanocomposite dried at 100°C for different times 1, 2, 3, 6 and 7 h. Storage modulus (at frequency 31.6 s⁻¹) of the nanocomposite heated for 1 h was measured to be 1490 Pa. It was reduced to 1110 Pa after 3 h heating, that is, 26% modulus decrease. According to the previous study,⁴¹ the clay-free sample (noncomposite) showed a 70% reduction in the modulus while the heating time was increased from 1 to 3 h at the same temperature. After a 3-hour heating, the clay-free sample become completely water-soluble, whereas the nanocomposite swellability was still preserved. The nanocomposite exhibits a two-fold increase of the time of steadiness against heating at 100°C comparing with the clay-free sample (6 vs. 3 h heating). It implies that overall thermostability of the nanocomposite is higher than that of the clay-free sample.

Storage modulus of the nanocomposite was decreased to 309 Pa after heating for 6 h at 100°C, and it eventually reached to 9.2 Pa after heating for 7 h. Remarkable decrease of modulus indicates that crosslinks in the hydrogel are highly degraded upon heating. It was visibly detected that under longer time of heating, the hydrated strengthened elastic nanocomposite gel was transformed to a loosened slimy state.

Storage modulus is related to the average molecular weight between crosslinks (M_c) through eq. (1)⁵²:

$$G' = \rho RT/M_c \quad (1)$$

where G' is the relaxed rubbery modulus, ρ is density, R is the gas constant, and T is temperature. The storage modulus changes are inversely with M_c . Increase of M_c means lower crosslink density leading to swelling enhancement. It is well known that swelling capacity and gel strength have an inverse relationship, that is, the higher swelling capacity, the lower the gel strength will be.⁵² Here, in the case of

nanocomposite sample, the crosslink density loss upon heating is delayed. Therefore, the storage modulus reduction was observed at longer times of heating.

Crosslink action of clay can be confirmed through swelling measurements. Table II shows swelling capacity of PEGDMA-crosslinked SAPs at different clay content. Swelling capacity of clay-free sample is 188 g/g, which is decreased to 165 g/g at 6% clay content. Swelling capacity is well known to have a reverse relationship with crosslink density. Therefore, the swelling reduction means crosslink density enhancement with increase of the clay content. The clay can act as a crosslinker, which causes to increase crosslink density and the swelling loss.

For the poly(AMPS) itself, CO vibration was appeared at 1641 cm⁻¹. It was shifted to 1654 cm⁻¹ for the sample containing 6% clay. It was attributed to the stronger interactions in superabsorbent nanocomposite sample. The stronger interaction disfavored the efficient delocalization of the carbonyl bonds. As a result, slightly higher energy was needed for the bonds to be vibrated.

CONCLUSION

Chitosan-modified clay containing poly(AMPS) hydrogel nanocomposite was prepared using two different crosslinking agents, that is, MBA and PEGDMA. The thermal/hydrolytic effect on the swelling steadiness was investigated. Thermal stability increment was empirically tracked through swelling and rheological changes. Thermal stability of the hydrogel nanocomposite was improved in comparison with the plain (clay-free) sample. Increase of heating time and temperature caused crosslink density changes depending on nature of the crosslinker employed in the synthesis. MBA-crosslinked samples has tendency to hydrolytic degradation of crosslinkages (decrosslinking), whereas PEGDMA-crosslinked samples exhibits tendency to crosslink formation (re-crosslinking).

Crosslink changes in hydrogels can be tracked through rheological studies. Storage modulus which has a direct relationship with crosslink density was continuously reduced with increase of hydrogel heating time. After heating at 100°C for 1 and 7 h, the modulus was greatly decreased from 1490 to 9 Pa, respectively (angular frequency 31.6⁻¹).

Regarding potential use of the product, the hydrogel may be considered as superior candidate for biomedical applications; in view of the fact that other nanocomposite hydrogels are typically prepared using clays modified often with alkyl ammonium salts which are toxic and not suitable for bio-applications.

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