# Antipolyelectrolyte Superabsorbing Nanocomposites: Synthesis and Properties

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**ABSTRACT:** Novel polyampholytic superabsorbing nanocomposites based on the zwitterionic sulfobetaine monomer [3-(methacrylamido)propyl)]dimethyl(3-sulfopropyl)ammonium hydroxide were synthesized through *in situ* polymerization in aqueous solution with different contents of an organo-modified clay (OMMT, Cloisite 30B). Structural and thermomechanical properties of hydrogels were characterized by FT-IR, XRD, and DMTA, respectively. Swollen gel strength of hydrogels was determined by a rheological method. Storage modulus of the hydrogels was considerably improved in comparison with its the clay-free counterpart. The nanocomposite hydrogel containing 15% OMMT possessed the highest gel strength. The glass transition temperature was increased from 58.4 to 67.0°C for the clay-free and nanocomposite hydrogel containing 8% OMMT, respectively. The swelling behavior of the hydrogel in various salt solutions was investigated. Antipolyelectrolyte behavior was observed with enhancement of concentration of mono- and multivalent salts. Swelling in the various pH media was nearly pH-independent over a wide range of pH. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 3542–3547, 2009

**Key words:** hydrogel; nanocomposite; sulfobetaine; superabsorbent; zwitterion

## INTRODUCTION

Amphoteric polyelectrolyte (polyampholyte) hydrogels are hydrophilic networks that contain both positively- and negatively-charged functional groups on their structure in which the ionic groups are located on separate monomer units[1] [Fig. 1(a)] or incorporated into a zwitterionic monomer [Fig. 1(b)].[2] They exhibit antipolyelectrolyte behavior in salt solutions swelling significantly more in saline solutions than in pure water.[3–5] The conventional superabsorbent hydrogels based on poly(potassium acrylate-*co*-acrylamide) were nearly collapsed in multivalent cation solutions.[6–8]

Polysulfobetaines are the most important type of polyampholytes which have been extensively studied.[4,9–11] Copolymers of sulfobetaines with cationic,[12–14] anionic,[3,4,15] and nonionic[5,16–18] monomers have also been investigated.

Sulfobetaines were reported to be used in surface modification of biomaterials with good blood compatibility.[19] Their zwitterionic characteristics can be retained at all pH values.[20] However, these hydrogels exhibited poor gel strength causing limitation of their applications.

There are four ways for gel strength improvement: surface-crosslinking,[21] formation of cyclic structures such as oligo fumarate,[22] preparation of interpenetrating polymer networks (IPNs),[23] and making nanocomposite polymers, particularly layer silicates.[24–26] Recently, much attention has been focused on the preparation of nanocomposite hydrogels with high gel strength and lower cost using organomodified clays.[27]

The organomodified clays considerably improve mechanical properties, because of intercalated or exfoliated structure formed in the polymer nanocomposite.[28–30] There are some interactions between functional groups of the clay surface and polymer chains, particularly in nanocomposite hydrogels, which lead to improving mechanical properties.[26,27,31] In other word, modified clay is not a noneffective (inert) filler during polymerization, instead, covalent bonding between inorganic and organic phase can occur. Since modified clays have a crosslinker role to play, they are sometimes referred to as crosslinking points or multifunctional crosslinkers.

To the best of our knowledge, study on nanocomposite sulfobetaine hydrogels was not reported up to now. Xu investigated polyampholyte superabsorbent nanocomposites prepared from an ion pair comonomer in which the ionic groups are located on separate monomer units.[26]

The aim of this work was the preparation and characterization of novel polysulfobetaine nanocomposite
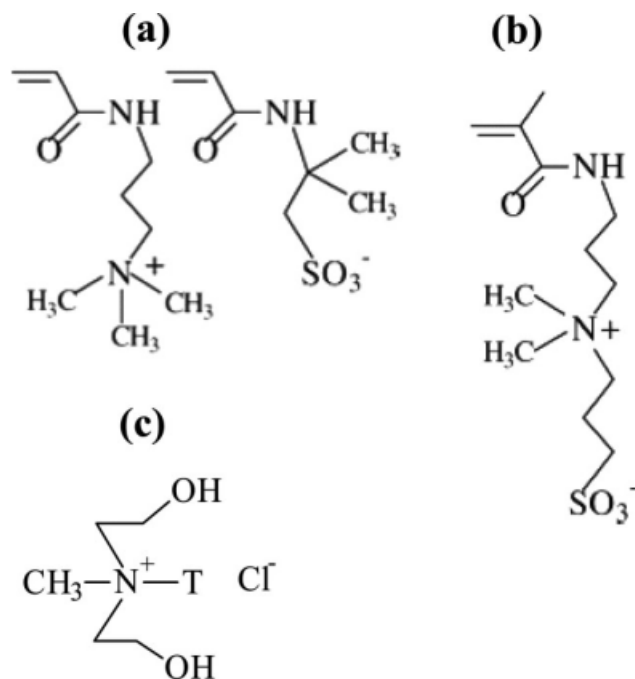
**Figure 1** Chemical structure of two types of ampholytic monomers. (a) ion pair 3-methacrylamido-propyltrimethylammonium 2-acrylamido-2-methylpropanesulfonate, (b) [3-(methacrylamido)propyl)]dimethyl(3-sulfopropyl)ammonium hydroxide (MPDSAH); a zwitterionic monomer used in the present work, (c) modifier quaternary ammonium salt intercalated in the silicate layers of Cloisite® 30B (T = Tallow; ~ 65% C18; ~ 30% C16; ~ 5% C14).

hydrogels based on the inner salt [3-(methacrylamido)propyl)]dimethyl(3-sulfopropyl)ammonium hydroxide (MPDSAH) [Fig. 1(b)] using an organo-modified caly, OMMT [montmorillonite intercalated with a special type of quaternary ammonium salt, Fig. 1(c)] through an *in situ* polymerization method. Swelling behavior of the nanocomposite polysulfobetaine is discussed. In addition, the effect of OMMT content on the hydrogel properties was investigated by FTIR, dynamic mechanical thermal analysis (DMTA), x-ray diffraction (XRD) and rheology.

## EXPERIMENTAL

### Materials

MPDSAH (supplied by Aldrich) and $N,N''$-methylenebisacrylamide as a crosslinker, ammonium persulfate (APS) as an initiator were purchased from Merck, OMMT (Cloisite® 30B, containing 90 meq modifier/100 g clay) purchased from Southern Clay Co., and salts NaCl, CaCl$_2$ and AlCl$_3$ (supplied by Merck) were used without purification.

### Hydrogel synthesis

The general reaction conditions were followed according to Ref 3. Briefly, MPDSAH monomer

(10.00 g) that was dissolved in distilled water (10.0 g). OMMT (0–15 wt %) was added to the monomer solution and stirred for 4 h. Then the crosslinker (65 m$M$) and initiator (44 m$M$) solutions were added to the slurry, respectively. The reactor was put in a water bath (80°C) to start polymerization. After the gelation point, the reactor was kept for 30 min in the bath. The elastic gel product was cut into small pieces, oven-dried (60°C, 4 h) and stored away from light and moisture.

### Swelling measurement

Powdered dried gel samples (0.20 g) were dispersed in distilled water and salt solutions (NaCl, CaCl$_2$, AlCl$_3$) with different concentrations (0.1, 0.15, 0.3, 0.5, 0.9 $M$). Equilibrium swelling (g/g) was determined after 30 min until the swelling reached to equilibrium (eq. 1).

$$\text{Swelling} = (M - M_0)/M_0 \qquad (1)$$

where, $M_0$ is the initial dried gel weight and $M$ is the weight of the hydrated gel.

The media with acidic and basic pHs were prepared by addition of appropriate standard solutions of hydrochloric acid and sodium hydroxide to distilled water, respectively.

### Instrumental analysis

X-ray diffraction spectra of nanocomposites was recorded with a diffractometer (Siemens D5000) at a voltage of 40 kV and a current of 30 m$A$ with Cu-k$_\alpha$ line ($\lambda$ = 0.1541 nm). Thermal analysis was performed by a DMTA type DMA-triton (Trite C2000 DMA). Powdered samples were heated with a rate of 5°C/min. A paar-physica oscillatory rheometer (MC R300, Germany) with parallel plate geometry (plate diameter of 25 mm, gap of 2 mm) was used at 25°C to determine the gel strength of nanocomposites.[32] FTIR spectra of dried samples as KBr tablets were recorded by an ABB-Bomem MB-100 FT-IR spectrophotometer. The pH values of aqueous solutions were determined by a pH-meter type Consort C533 (Belgium, accuracy ±0.1).

## RESULTS AND DISCUSSION

### Swelling studies

Swelling in distilled water and ionic environments

Polyampholyte nanocomposite hydrogels based on MPDSAH showed improved saline-swelling properties, i.e., antipolyelectrolyte behavior. Swelling of hydrogels containing 6 wt % OMMT versus salt concentration in different saline solutions is shown in Figure 2. Swelling capacity of polysulfobetaine
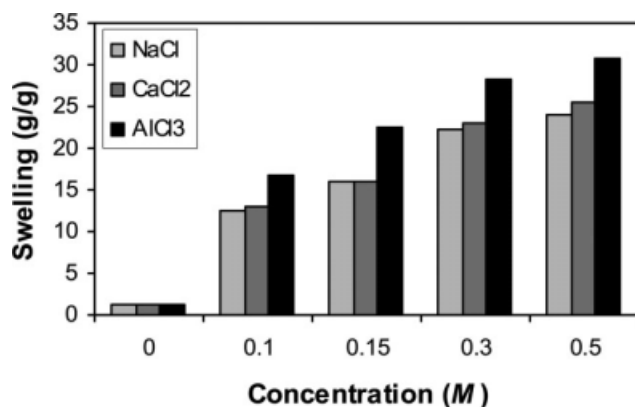
**Figure 2** Swelling capacity of the nanocomposite hydrogel (having 6 wt % OMMT) in deionized water (concentration 0) and saline solutions (NaCl, CaCl$_2$ and AlCl$_3$) with different concentrations.

nanocomposite hydrogel in distilled water was only 1.26 g/g. It was considerably increased in salt solutions. It reached to 24.12 g/g in 0.5 M NaCl solution. In multivalent salt solutions, swelling capacity was even more enhanced. For instance, it was increased to 25.39 and 30.67 g/g at 0.5 M CaCl$_2$ and AlCl$_3$, respectively. As expected, such behavior is total contrast with that of conventional hydrogels based on the usual acrylic monomers, i.e. acrylamide (AM), acrylic acid (AA) and its salts. For instance, swelling capacity of a superabsorbent based on potassium acrylate (KA), AA and AM was reported to be less than 4 g/g in 0.15 M AlCl$_3$.[7] This considerable dissimilarity between the polysulfobetaine nanocomposites and conventional superabsorbent hydrogels are attributed to the ionic interaction difference in the swelling media.

In distilled water, intrachain attractions between opposite charges are stronger than interchain forces in the zwitterionic-type hydrogels.[33] The attractive force between the cationic quaternary ammonium group and the anionic sulfonate group of poly-(MPDSAH) chain caused the inter- and intrachain associations. As a result, swelling capacity was lower than 2 g/g in water, whereas it was exceedingly enhanced in aqueous salt solutions. In fact, addition of salt breaks up the ionic associations leading to the swelling enhancement.[3,5] Moreover, higher swelling in aqueous multicharged environments (e.g., AlCl$_3$) in comparison with aqueous monovalent solutions (e.g., NaCl) may be attributed to cation exchange incapability of zwitterionic groups.[3] Response of these hydrogels was significantly different from polyelectrolyte behavior in the aqueous multivalent solutions. Absorption in the polyelectrolyte was decreased due to complexing multicharged ions with them.[34] Inversely, the complexation between zwitterionic groups of antipolyelectrlolytes was broken more easily by multicharge ions.[5] Thus, this phenom-

enon led to increasing swelling capacity. On the other hand, swelling was not particularly changed at higher salt concentration (e.g., 0.9 M). This may be attributed to the limitation of the swelling capacity of the nanocomposite poly(MPDSAH) which originated from the charge shielding effect that diminishes the anion–anion and cation–cation repulsive forces.[6]

Swelling capacity of the nanocomposites was less than that of the clay-free counterpart [Clay 0%, Fig. 3(a)]. The swelling was decreased significantly when the clay content was more than 6%. This may be attributed to two reasons. First, it is related to OMMT action during *in situ* crosslinking polymerization. Particles of OMMT can act as crosslink points or multifunctional crosslinker sites leading to higher crosslink density and loss of swelling.[27] Second, since less hydrophilic material (i.e., OMMT) is incorporated to the hydrophilic network, the swelling loss will be reasonable to some extent.[35]

Swelling in various pH media

Swelling capacity versus pH of swelling environment is shown in Figure 4 for the nanocomposite polysulfobetaine contained 6 wt % OMMT. The highest absorption (6.0 g/g) was observed at pH 1.6. With pH enhancement, the swelling capacity was reduced to 3.5 g/g at pH 2.5 then it was nearly leveled off from pH 2.5 to 11.5. At pH 12.7, swelling capacity was increased to 4.4 g/g.

The sulfonate group in MPDSAH will be deprotonated above pH 2.5.[20] So, the polymer achieved a positive charge due to the presence of ammonium group, and then the polycationic nature of the network caused the swelling improvement. A pH-independent behavior between pH 2.5 and 11.5 is obviously related to the presence of equal numbers of both negative (sulfonate) and positive (ammonium) charges. At very high pH (e.g., 12.7),
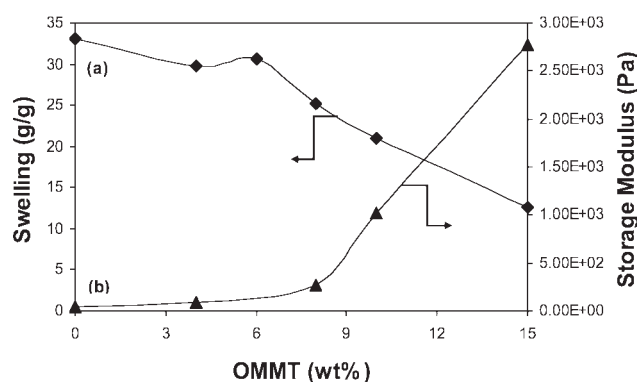


**Figure 3** Effect of the incorporated OMMT content on (a) swelling capacity of poly(MPDSAH) hydrogels with various OMMT% in 0.5 M AlCl$_3$ and (b) storage modulus of the hydrogels (preswollen in 0.3 M AlCl$_3$) recorded at angular frequency 7.5 s$^{-1}$.

however, the ammonium groups are partially surrounded by OH anions. Therefore, polymer acquired a little negative charge due to the sulfonate groups. Swelling enhancement at very low and very high pHs was attributed to appear the ionic nature of hydrogel network which caused osmotic pressure difference between gel and the solvent phase.

## Rheological studies

A rheological method was carried out to determine gel strength of prepared hydrogels with the amount of various amounts of OMMT. It had previously shown that the swollen gel strength can accurately be determined by oscillatory rheometer with parallel plate geometry.[32] The storage modulus can be taken as a measure of the mechanical strength of nanocomposite poly(MPDSAH).
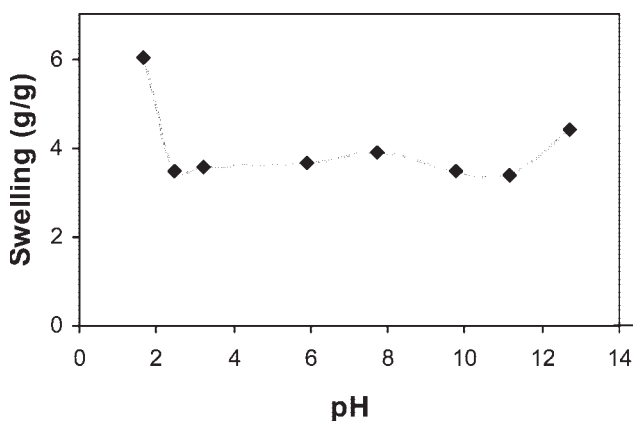
Figure 5 shows storage modulus of the hydrogels (comprising 0–15 wt % OMMT) preswollen in 0.3 $M$ AlCl$_3$. It was observed that storage modulus was gradually increased with angular frequency enhancement for individual samples.

Increase of storage modulus at higher frequencies exhibits that hydrogel becomes stiffer; because the polymer chains do not have enough time for relaxation, thus the chain flexibility is reduced.[32] According to Figure 5, at a given frequency (e.g., 7.5 s$^{-1}$), the storage modulus was increased with OMMT percentage increases. The modulus for the noncomposite (clay-free) sample at frequency 7.5 s$^{-1}$ was 43.4 Pa. It was appreciably increased to 2780 Pa in the nanocomposite containing 15 wt % OMMT.
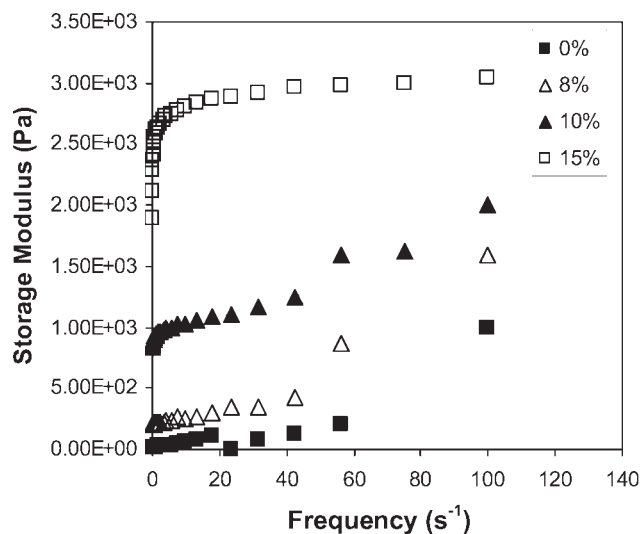
The relation of storage modulus with the average molecular weight between crosslinks ($M_c$) is introduced by the following eq. (2).

$$G' = \rho R T / M_c. \qquad (2)$$

where $G'$ is the relaxed rubbery modulus, $\rho$ is density, $R$ is the gas constant and $T$ is temperature.



**Figure 5** Storage modulus vs. angular frequency for nanocomposite hydrogels containing 0–15 wt % OMMT. The samples had already been preswollen in 0.3 $M$ AlCl$_3$.
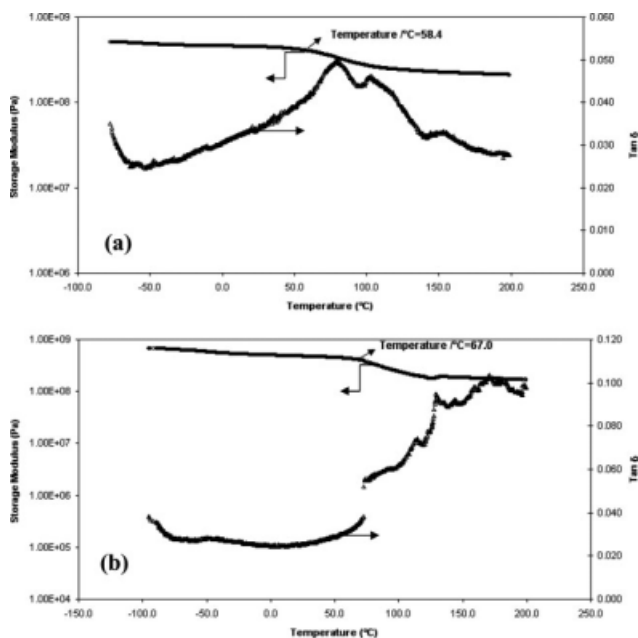
According to this equation, higher crosslink density leads to higher storage modulus.

Decrease of $M_c$ (i.e., higher crosslink density) results in swelling loss followed by enhancement of gel strength [Fig. 3(b)]. In another aspect, since absorbed water inside of the hydrogel can act as a plasticizer,[36] therefore, a less-swollen gel exhibits higher modulus. According to Figure 3, swelling reduction and modulus enhancement of the nanocomposite poly(MPDSAH) was observed with OMMT increase. According to eq. (2), these results confirm that gel strength was improved due to presence of OMMT nanoparticles assumed to contribute partially as crosslinking points.

## Dynamic mechanical thermal analysis

DMTA thermogram for the clay-free sample is shown in Figure 6(a). It was observed that glass transition temperature (Tg) of the noncomposite was 58.4°C. It was increased in nanocomposite hydrogels with OMMT enhancement. Tg was increased to 61.7°C (not shown) and 67°C [Fig. 6(b)] in poly(MPDSAH) nanocomposite hydrogels containing 4 and 8% OMMT, respectively.

Here, the chemical crosslinker was identical for the nanocomposite samples. Increase of Tg may indicates that crosslink density was increased. It was described in previous sections that clay could act as a multifunctional crosslinker or crosslink point in hydrogels which led to increase crosslink density in the gel structure.[37,38] Webster mentioned crosslink action of clay particles in hydrophobic systems such as urethane-acrylate which led to increase effective crosslink density.[39] Chain mobility was decreased



**Figure 4** The swelling capacity of nanocomposite (having 6 wt % OMMT) versus pH of the swelling environment.

**Figure 6** DMTA thermograms of (a) free-clay hydrogel and (b) nanocomposite hydrogel containing 8 wt % OMMT.

with increase of crosslink density which caused Tg enhancement.

According to Figure 6, modulus below Tg was 421.3 and 447.4 MPa at 50.7°C for the clay-free and nanocomposite with 8% OMMT, respectively. It was observed that modulus below Tg exhibited 6.2% enhancement in comparison with the clay-free sample.

### Structural investigations

FT-IR spectroscopy

Structure of the polysulfobetaines was preliminary characterized by FT-IR spectroscopy. The spectra of OMMT and polysulfobetaine hydrogel with 6% OMMT are exhibited in Figure 7. Peaks at 1204,
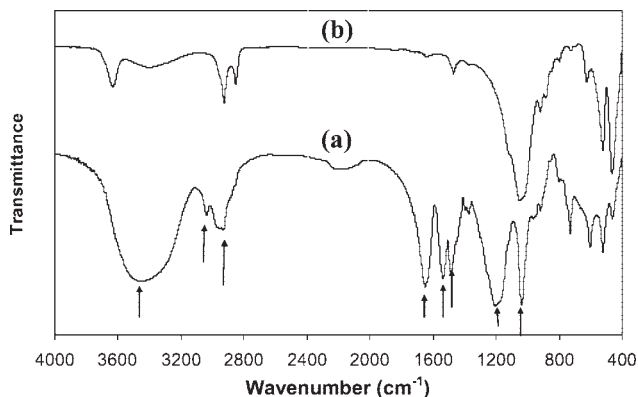


**Figure 7** FT-IR pattern of (a) nanocomposite with 6 wt % OMMT and (b) pure OMMT (Cloisite 30B).

**TABLE I**
**XRD Properties of Pure OMMT and Nanocomposites with Different Percentages of OMMT**

| OMMT (wt %) | Peak position (2θ°) | d-spacing (°A) |
|---|---|---|
| 2 | 3.917 | 22.53 |
| 4 | 4.252 | 20.76 |
| 6 | 4.444 | 19.86 |
| 8 | 4.153 | 21.26 |
| 10 | 4.414 | 20.00 |
| 100 | 4.822 | 18.30 |

1035, and 1651 cm$^{-1}$ in the nanocomposite spectrum are due to stretching vibration of C—N, S—O and the amide C=O, respectively. Peaks appeared at 1538 cm$^{-1}$ is attributed to bending vibration of the secondary amide N—H. Weak asymmetric stretching vibration band of S(=O)$_2$ is appeared at 1372 cm$^{-1}$. Different vibration modes of C—C and C—C—H bonds located in fingerprint area of spectra are appeared at 2932 and 3037 cm$^{-1}$. The broad band OH is appeared at around 3443 cm$^{-1}$ that is due to the moisture absorbed by the polysulfobetaine hydrogel. The secondary amide N—H stretching band is overlapped by the broad band OH.

Figure 7(b) exhibited FT-IR spectrum of OMMT. The very strong band at 1046 cm$^{-1}$ is attributed to stretching vibration of Si-O and medium bending vibration band Si-O is appears at 465 cm$^{-1}$ and the weak band around 918 cm$^{-1}$ is related to stretching vibration Al-O. Two bands at 2926 and 2852 are attributed to stretching vibration modes C—H and C—C—H due to the intercalated ammonium alkyl salt of OMMT. The broad band around 3399 is corresponding to OH linked to Si.

### X-ray diffraction

XRD data are given in Table I and Figure 8. Diffraction angle (2θ) and interlayer distance (d-spacing) for OMMT was 4.82 and 18.30°A, respectively. *In situ* crosslinking polymerization of MPDSAH caused an interlayer distance increase in nanocomposite
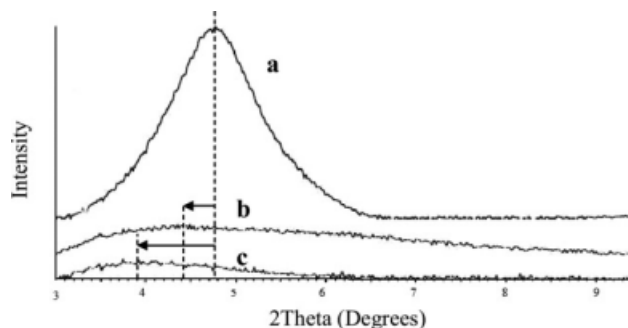


**Figure 8** XRD profiles of (a) OMMT and (b) nanocomposite hydrogel containing 10 wt % OMMT, (c) nanocomposite hydrogel containing 2 wt % OMMT.

hydrogels. The distance for the nanocomposite containing 2 and 10% OMMT was determined to be 22.53 and 20.0°A, respectively. The data confirmed intercalated structure in the nanocomposite hydrogels. The interlayer distance of the nanocomposites was decreased with OMMT increase. The MPDSAH probably could not enter between all clay layers when the clay content was elevated. As a result, the d-spacing was decreased with the clay content enhancement. The extent of interlayer enhancement in nanocomposite hydrogel was not too high in comparison with OMMT. This could be probably related to the hydrophobically modified clay (organomodified MMT, i.e., OMMT). The hydrophobic alkyl ammonium salts used usually in the clay modification, do not favor the entrance of hydrophilic monomers such as MPDSAH. As a result, the interlayer distance was only increased up to a maximum 4.2°A in the nanocomposite sample with 2% OMMT (Table I).

## CONCLUSIONS

Novel nanocomposite hydrogels based on a zwitterionic monomer (MPDSAH) and organo-madified montmorillonite can be synthesized by the thermally dissociated initiator under normal atmospheric conditions.

Swelling studies of the products in different aqueous media indicated an antipolyelectrolyte behavior, so that swelling capacity was increased with both mono- and multivalent salt solution concentrations. This behavior was attributed to breaking up inter- and intrachain associations between the sulfonate and ammonium groups of the sulfobetaine monomer, MPDSAH. Swelling in the various pH media of the polysulfobetaines was nearly pH-independent at a wide range of pH.

Incorporation of OMMT into the composite led to swelling loss and storage modulus enhancement due to taking it part in crosslinking. Hence, the gel strength and Tg enhancement varied directly with OMMT weight percent.

XRD patterns of prepared nanocomposites preliminarily confirmed an intercalated nanocomposite structure in the hydrogel products.

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