Polyacrylate/(Carboxymethylcellulose Modified Montmorillonite) Superabsorbent Nanocomposite: Preparation and Water Absorbency

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ABSTRACT: Montmorillonite (MMT) was modified with carboxymethylcellulose (CMC). The X-ray diffraction (XRD) and FTIR analyses showed that the CMC chains had intercalated into the MMT sheets, and the strong chemical interaction between the ether bonds from CMC and Si—O bonds from MMT was the driving force for intercalation. Polyacrylate (PAA)/modified MMT superabsorbent nanocomposites were fabricated by effectively dispersing the modified MMT in acrylic acid solution and polymerizing the acid. The superabsorbent composites were characterized by XRD, TEM, and FTIR. The influence of modified MMT, weight ratio of CMC to MMT, and modified MMT content in the nanocomposites on the water absorbency was investigated. Results showed that the introduction of pure MMT could decrease the water absorbency of the gel, but adding modified MMT could not only effectively increase the water absorbency of the gel, but also improve its water retention ability. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 118–123, 2008

Key words: superabsorbents; nanocomposites; montmorillonite; carboxymethylcellulose

INTRODUCTION

Superabsorbent polymers (SAPs) can absorb large amounts of water and retain it even under pressure. Because of their excellent characteristic, SAPs are widely used in many fields such as sanitary goods, agriculture, and medicine for drug-delivery systems.[1–3] Among already developed SAPs, Polyacrylate (PAA)-based ones play an important role. A number of researchers attempted to modified PAA to enhance their water absorbency, gel strength, and water retention ability.[4–6]

Montmorillonite (MMT) is a kind of loose-layer silicate made up of two tetrahedral sheets fused to an edge-shared octahedral sheet of aluminum hydroxide, with a thickness of ∼ 1 nm and a length of ∼ 100 to several 100 nm. Polymer/MMT nanocomposites are novel materials based on the intercalation of polymer chains into MMT layers. They have evoked intense research interest because of their remarkable mechanical, thermal, and molecular barrier improvements when compared with conventional composite.[7–9]

Because of its hydrophilic nature, MMT is suitable for use in SAPs as additives. The preparation of PAA/MMT nanocomposites have been reported by several researchers aimed at improving properties of PAA in one or more aspects.[10,11] To render MMT more organophilic and increase interlayer spacing, MMT is usually treated with organic cations in the preparation of polymer/MMT nanocomposites. Therefore, the organic modification of MMT is the most important process before PAA/MMT superabsorbent nanocomposites are prepared. However, in the preparation of PAA/MMT superabsorbent nanocomposites, the commonly used cations (alkyl ammonium salts) present the drawback of poor water absorbency.[10,11] To overcome this problem, we prepared PAA/MMT nanocomposites using chitosan, a hydrophilic cationic polysaccharide, as the MMT modifier.[12]

Although the modification of MMT with different organic cations have been reported in the preparation of PAA/MMT nanocomposites, no reports have discussed the modification of MMT with organic anionics. As a continuation of our work, we used carboxymethylcellulose (CMC), a hydrophilic anionic polysaccharide, as the MMT modifier in this study. One reason is that CMC can intercalate into MMT sheets[13] and it has good compatibility with PAA because of the hydrophilic —COO⁻Na⁺, —OH groups on its backbone. The intercalation of CMC into MMT makes the MMT nanolayers more hydrophilic,

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enabling them to be exfoliated by acrylate molecules more easily. Another important reason for CMC as the modifier is that CMC has high water absorbency and it can be used to prepare SAP, the incorporation of CMC to the nanocomposites may improve the water absorbency. The objectives of this work were (i) to prepare PAA/(CMC modified MMT) nanocomposite and (ii) to study the influences of the modified MMT on the water absorbency and the water retention ability of the nanocomposites.

EXPERIMENTAL

Materials

Acrylic acid (AA, chemically pure, Tianjin Chemical Reagent Factory, China) was distilled under reduced pressure before use. Sodium carboxymethylcellulose (CMC, Special Reagent Factory of Nakai University, China) with a nominal degree of substitution of 0.75–0.85 and a viscosity-average molecular weight of 4.6×10^5 was used without prior purification. Na^+-MMT (Zhejiang Linan Bentonite Compancy, China) with a cationic exchange capacity of 90 mequiv/100 g was milled through a 300-mesh screen. Potassium persulfate (Tianjin Chemical Reagent Factory, China) was recrystallized from water and N, N-methylene bisacrylamide (Tianjin Chemical Reagent Factory, China) was recrystallized from methanol.

Wide-angle X-ray diffraction (XRD) measurements were performed with a Japan Rigaka diffractometer using Cu, Ka radiation($\lambda = 0.154$ nm) at a generator voltage of 40 kV and a generator current of 100 mA. FTIR spectra of the samples were recorded on a Nicolet-170SX FTIR spectrometer using KBr pellets. Samples were ultramicrotomed on a LKB5 ultracut microtome to give sections with a nominal thickness of 80–100 nm. TEM images were obtained with a Philips-EM400SP transmission electron microscope.

Preparation of modified MMT

A series of modified MMT with different CMC content were prepared by the following procedure. Typically, 0.5 g Na^+-MMT was added to 50 mL distilled water and mechanically stirred, followed by ultrasonic treatment for 15 min, which resulted in good MMT dispersion. The CMC solution, obtained by dissolving 1 g CMC in 50 mL distilled water, was added to the MMT suspension and the mixture was stirred vigorously for 2 h at 70°C. The modified MMT suspension was dried in an oven at 70°C to a constant weight and milled through a 300-mesh screen.

Preparation of PAA/modified MMT superabsorbent nanocomsites

AA (10 g) was dissolved in 10 mL distilled water and then neutralized in an ice bath with 30 wt % NaOH until the neutralization was 75% complete on a mole basis in a three-neck flask equipped with a stirrer, a condenser, and a thermometer. One gram of modified MMT was added to the above neutralized monomer solution and stirred vigorously until the modified MMT was well dispersed. Potassium persulfate (0.020 g + 2.0 mL H_2O) was used as initiator and N, N-methylene bisacrylamide (0.015 g + 1.5 mL H_2O) as the crosslinker. They were both added to the AA-modified MMT mixed solution. Then the mixture was stirred and heated to 70°C in a water bath for 4 h. After polymerization, the gel was washed with ethanol and water and dried in an oven at 70°C to constant weight. The dried gel was pulverized into particles, whose average size was between 0.2–0.3 mm. PAA/modified MMT nanocomposites were designated as PAA/mMMT in this article. The feed compositions of samples were listed in Table I.

Preparation of PAA/MMT, PAA/CMC, and PAA/CMC/MMT superabsorbent composites

The preparation procedure of PAA/MMT and PAA/CMC composites differed from that of PAA/mMMT composites only in replacing modified MMT with MMT and CMC, respectively. PAA/CMC/MMT composite was obtained by introducing CMC and MMT to acrylic acid polymeric solution one by one, and then the mixture was stirred. Polymerization was carried out under the same conditions as those of PAA/mMMT composites.

Measurement of water absorption

The accurately weighted SAP (0.1 g) was immersed in distilled water at room temperature until equilibrium had reached, then the unabsorbed liquid was filtered with a nylon bag, the gel was allowed to drain on a sieve for 10 min, and the bag was weighed to determine the weight of water swollen gel. The water absorption (Q) was calculated using the following equation:

$Q = (w_2 - w_1)/w_1$, where w_1 is the weight of dried absorbent and w_2 is the weight of swollen absorbent after absorption.

Measurement of water retention

The water retention (WR) capacity was determined in an oven at 25°C. The water swollen gels were put on petri plates and dried at 25°C. The swollen hydrogels were weighted and the decreases in their weight were measured as a function of time by gravimetry. The values of WR were obtained by following equation:

TABLE I
Feed Composition and Water Absorbency of the Superabsorbents

| Sample | AA | Modified MMT | | MMT | CMC | Water absorption (g/g) |
		CMC	MMT			
PAA	10	–	–	–	–	614
PAA/MMT1	10	–	–	0.34	–	512
PAA/MMT2	10	–	–	0.50	–	406
PAA/mMMT1	10	0.34	0.66	–	–	610
PAA/mMMT2	10	0.50	0.50	–	–	698
PAA/mMMT3	10	0.66	0.34	–	–	844
PAA/mMMT4	10	0.75	0.25	–	–	681
PAA/mMMT5	10	0.85	0.15	–	–	627
PAA/CMC	10	–	–	–	0.66	598
PAA/CMC/MMT	10	–	–	0.34	0.66	416

$$WR(\%) = M_t/M_0 \times 100\%$$

where M_0 is the initial weight of the hydrogel in water and M_t is its weight after lost of water at each time.

RESULTS AND DISCUSSION

Identification of PAA/mMMT superabsorbent nanocomposite

The XRD patterns of MMT, PAA, and PAA/mMMT3 composite were shown in Figure 1. In the scattering curve for pure MMT, a prominent peak corresponding to the basal spacing of MMT occurred at a d-spacing of 1.25 nm ($2\theta = 7.07°$). This peak was not observed in PAA/mMMT3 composite, indicating that MMT were exfoliated in PAA matrix. The broad, low intensity peak in PAA/mMMT3 composite can be assigned to PAA. As can be observed from the XRD pattern for PAA, the peak position of PAA is approximately equal to that of PAA/mMMT3 composite.

Effect of CMC macromolecular on the formation of the nanocomposite

There are two effects of CMC on the formation of the nanocomposite. Firstly, CMC macromolecular intercalated into the MMT gallery, expanded the gallery distance, which can be evidenced from the XRD pattern of modified MMT with weight ratio of CMC to MMT of 2 (Fig. 1, curve b). For modified MMT, the basal reflection of MMT move to lower angle and gallery spacing is 1.47 nm, which is higher than that of unmodified MMT; it indicates intercalation of CMC into MMT. The peak broadening and weakness most likely indicate the disordered intercalated structure. The expanded gallery distance in modified MMT make acrylate molecules enter into MMT gallery more easily for *in situ* polymerization.

The intercalation may be attributed to the chemical interaction between ether bonds and Si—O bonds,

which can be evidenced from FTIR analysis. Figure 2 shows the FTIR spectra of MMT, CMC, and modified MMT with the weight ratio of CMC to MMT of 2. The characteristic vibration bands of MMT are shown at 3630 cm^{-1} (—OH stretch from lattice hydroxyl), 3349 cm^{-1} (—OH stretch from free H$_2$O), 1649 cm^{-1} (—OH bending), 1439 cm^{-1} (asymmetric stretch of CO$_3^{2-}$ ion), 1042 cm^{-1} (Si—O stretch), and 796 cm^{-1} (Al—O stretch).[14] Those of CMC are shown at 3263 cm^{-1} (—OH stretch), 1589 cm^{-1} (asymmetric stretch of COO$^-$ ion), 1415 cm^{-1} (symmetric stretch of COO$^-$ ion), 1019 cm^{-1} (stretch of ether bond). In the spectrum of modified MMT, a band around 1042 cm^{-1} due to the Si—O stretching vibrations of MMT was split apart into 1104 and 1040 cm^{-1}. A peak at around 1019 cm^{-1} corresponding to the stretching of ether bond of CMC disappeared.

Secondly, large interactions on the surface of MMT make it easy to agglomerate in acrylic acid polymeric solution, the intercalation of CMC to
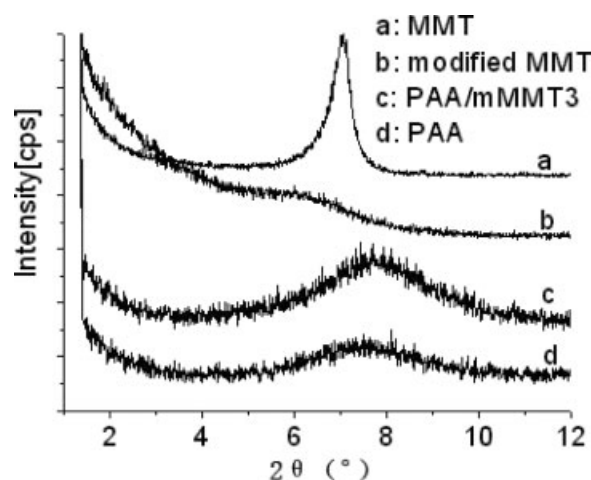

Figure 1 XRD patterns of MMT, modified MMT, PAA, and PAA/mMMT3 composite.
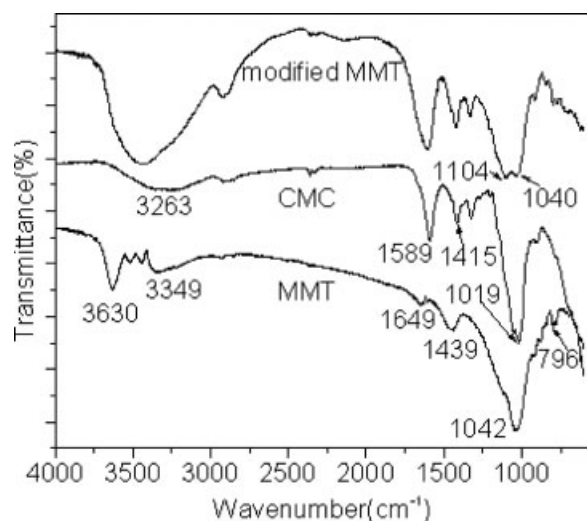
Figure 2 IR spectra of MMT, CMC, and modified MMT.

MMT can overcome this problem to some extent. Figures 3 and 4 show the photogragh of PAA/MMT1 and PAA/mMMT3 composites, respectively. In the photogragh of PAA/MMT1, the clay particles are in agglomerated form. In PAA/mMMT3, it can be seen that some of the clay particles are having platelet-like layer structures.

Effect of the introduction of modified MMT on the water absorbency of PAA

Table I shows the feed compositions and properties of the PAA, PAA/MMT, and PAA/mMMT superabsorbents. Compared with PAA, the water absorbency of PAA/MMT1 and PAA/MMT2 were decreased by 102 g/g and 208 g/g, respectively, which may be attributed to the high crosslink density caused by the MMT particles in the composites.[15–17]

The pure MMT content in PAA/mMMT3 composite was identical to that of PAA/MMT1, but the water absorbency of the former was increased by 332 g/g when compared with that of the latter. This can be explained as follows: Firstly, according to our previous report,[17] the lower water absorbency of PAA/MMT composites when compared with that of PAA was mainly resulted from the increase of crosslink density caused by the formation of hydrogen bonds between the Si—O bonds from MMT and —COOH groups from PAA. It can be concluded from the FTIR analysis of modified MMT in above discussion that some of the Si—O bonds of MMT were consumed by CMC in modified MMT, which would reduce the Si—O bonds of MMT to form crosslinking points with PAA in PAA/mMMT composites. The decrease of crosslink density will result in the increase of water absorbency.[18]

To confirm these results, PAA/CMC/MMT composite, which differed from PAA/mMMT3 compos-
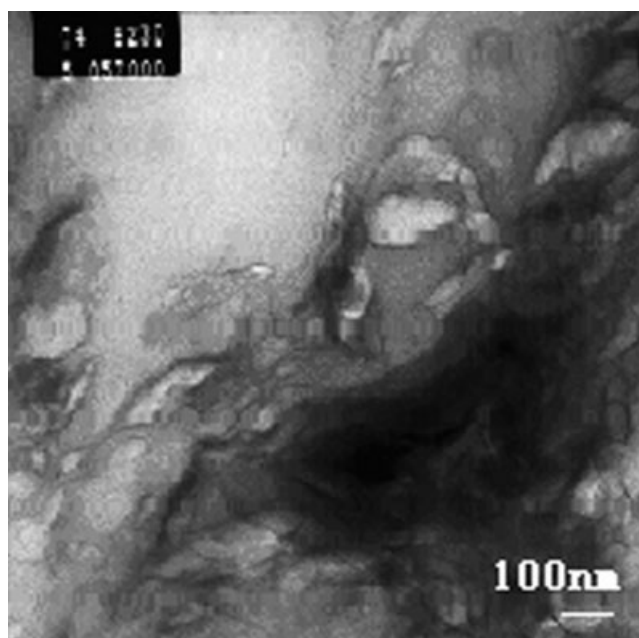

Figure 3 TEM of PAA/MMT1 composite.

ite only in preparing procedure, was synthesized. PAA/CMC/MMT composite was prepared by introducing CMC and MMT to acrylic acid solution one by one, while in the preparation procedure of PAA/mMMT3 nanocomposite, MMT was modified with CMC before being added to acrylic acid solution. It was obvious that the reaction probability between CMC and MMT was less in the PAA/CMC/MMT than in PAA/mMMT3, which resulted that the Si—O bonds of MMT in the former composite would
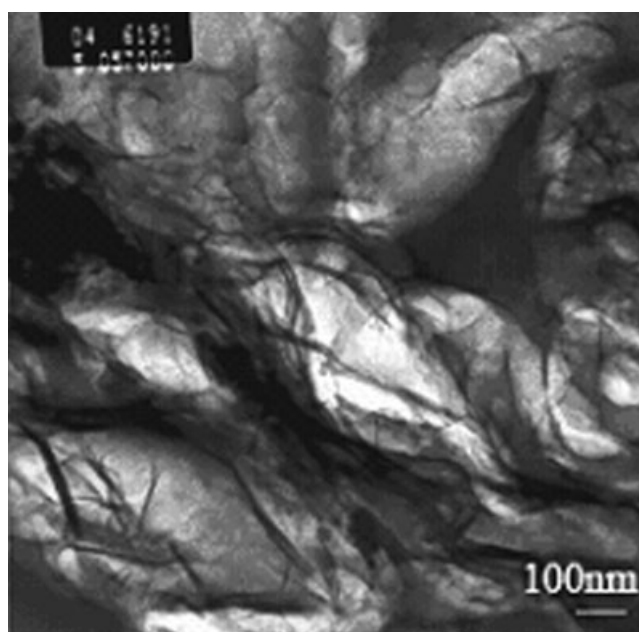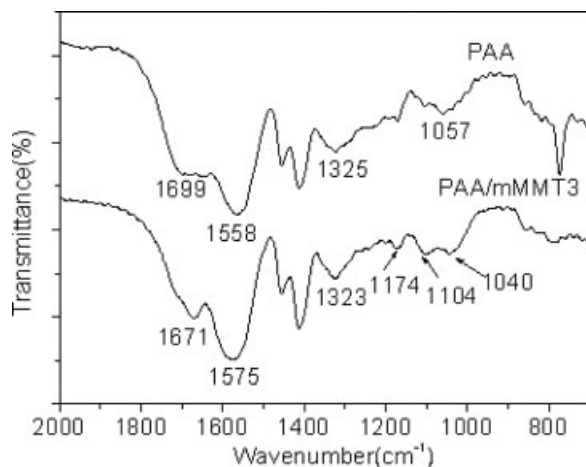

Figure 4 TEM of PAA/mMMT3 composite.

Figure 5 IR spectra of PAA and PAA/mMMT3 composite.

not be effectively consumed by CMC chains as those in the latter composite. Therefore, the crosslinking points arised from Si—O bonds and PAA was higher in the former composite than those in the latter composite. It might be expected that the water absorbency of PAA/CMC/MMT would be lower than that of PAA/mMMT3, the result shown in Table I was consistent with our prediction.

Secondly, the increase in water absorption could arise from the strong chemical interaction between modified MMT and PAA, which can be evidenced from the FTIR spectrum. Figure 5 illustrates the FTIR spectra of PAA and PAA/mMMT3. The characteristic vibration bands of PAA are shown at 1699 cm^{-1} (C=O stretch), 1558 cm^{-1} (COO$^-$ asymmetric stretching), 1325 cm^{-1} (C—O—H bending stretching), 1057 cm^{-1} (C—O asymmetric stretching). In the spectrum of PAA/mMMT3 composite, bands around 1104 and 1040 cm^{-1} due to the characteristic bands of modified MMT were not changed, which suggested that the interaction between CMC and MMT in modified MMT was too strong to be destroyed by PAA. Bands around 1699, 1558, and 1325 cm^{-1} in the spectrum of PAA shifted to 1671, 1575, and 1323 cm^{-1}, respectively. A band at 1057 cm^{-1} corresponding to the C—O asymmetric stretching vibration of PAA disappeared and a new peak at 1174 cm^{-1} appeared, indicating a strong chemical interaction between modified MMT and PAA.

Thridly, the coeffect of hydrophilic groups such as —OH, —COO$^-$Na$^+$ from CMC, —COOH, —COO$^-$Na$^+$ from PAA, and —OH from MMT sheets would increase the water absorption.

Effect of CMC content in modified MMT on the water absorbency of PAA/mMMT composites

PAA/mMMT composites of the 10 wt % modified MMT content with different weight ratio of CMC to

MMT were illustrated in Table I, sample PAA/mMMT1-PAA/mMMT5. The results showed that the water absorbency increased with increasing weight ratio of CMC to MMT when the value is <2. However, at weight ratio >2, the greater the content of CMC is, the lower the water absorption is although it remained higher than that of pure PAA. This can be explained as follows: Firstly, the amount of Si—O bonds consumed by CMC chains was increased with the increase of CMC content. Hence, the crosslink points arised from Si—O bonds and PAA became lower in the composites at higher content of CMC. According to Flory's swelling theory, decreasing the crosslink density would increase the water absorbency. However, when the weight ratio >2, the Si—O bonds might be completely consumed by CMC chains. As a result, the interaction between MMT and PAA was greatly weaken, therefore the coeffect of CMC, MMT, and PAA might not be well exhibited. This result also indicated that appropriate interaction among CMC, MMT, and PAA would benefit the increase of water absorbency.

PAA/CMC composite had lower water absorbency than that of PAA. The reason might be that the structure of PAA/CMC composite was a semi-interpenetrating network and the entanglements between CMC chains and PAA chains might increase the physical crosslink points.

Influence of the content of modified MMT on the water absorbency of PAA/mMMT composites

Figure 6 shows the content of modified MMT on the water absorbency of PAA/mMMT composites (the weight ratio of CMC to MMT was two in modified MMT). The water absorbency of the composites was increased with the increase of modified MMT when the value is below 10 wt %. Further increasing the
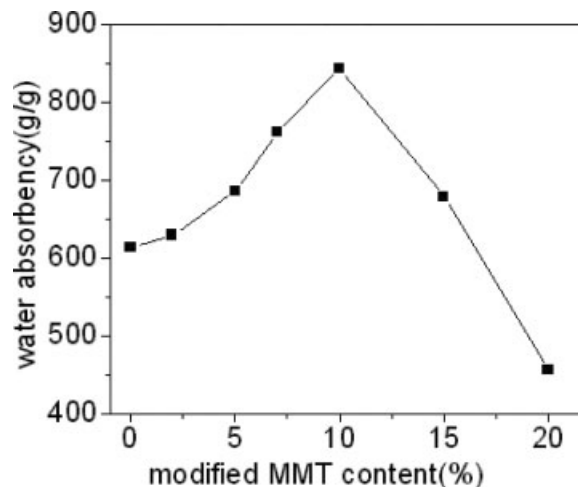

Figure 6 Effect of modified MMT content on water absorbency in deionized water.
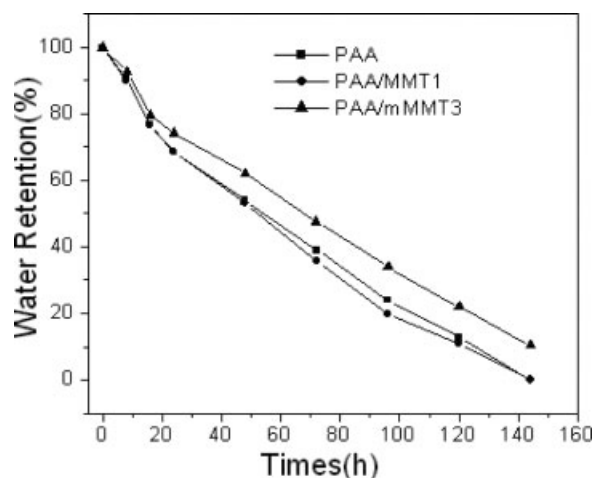
Figure 7 Water retention of swollen samples as a function of time at 25°C.

modified MMT content caused a water absorbency loss. The reasons were: Firstly, although MMT was a hydrophilic clay, but its water absorbency was much lower than that of PAA. The higher the modified MMT is, the higher the MMT content is, and so the lower water absorbency is. Besides, it was difficult to disperse modified MMT in acrylic acid solution homogeneously at higher modified MMT content, which would also decrease the water absorbency.

Water retention ability of the nanocomposite

The water retention ability is an important parameter for SAP used in agriculture, especially the effective utilization of water in dry and desert regions. Figure 7 shows the water retention ability under nature conditions for PAA, PAA/MMT1, and PAA/mMMT3 composite at 25°C. It could be seen that PAA, PAA/MMT1, and PAA/mMMT3 had a decreasing tread of water retention with prolonging the time, but the water retention ability for PAA/mMMT3 was higher than those of PAA and PAA/MMT1, about 17.1, 0.2, and 0.15% of distilled water for PAA/mMMT3, PAA, and PAA/MMT1, respectively, maintained at 25°C after 96 h. This can be explained from the barrier effect of polymer/MMT nanocomposites.[19,20] The nanodispersed MMT sheets in the composite impede the diffusion of the water molecules and make the diffuse path for water vapor

longer than that in PAA and PAA/MMT1 composite, and then decrease the dewatering rate in the gel.

CONCLUSIONS

MMT was modified with CMC. XRD and FTIR analyses showed that CMC chains had intercalated into MMT sheets and reaction occurred between the Si—O bonds from MMT and ether bonds from CMC. PAA/modified MMT nanocomposites were prepared. XRD and TEM analyses confirmed the formation of nanocomposites. FTIR analysis showed the strong interaction between PAA and modified MMT. The water absorbency and the water retention ability under nature conditions of the nanocomposites were higher than those of PAA and PAA/MMT composite. The effects of the content of CMC and modified MMT on the water absorbency of the composites were researched.

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