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Study on the synthesis and performance of hydrogels with ionic monomers and montmorillonite

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Abstract

Two series of the nanocomposite hydrogels were synthesized by in-situ solution polymerization. One pre-gel solution was obtained by directly dispersing the montmorillonite (MMT) powder into aqueous monomer solution and the other pre-gel solution was obtained by mixing monomer aqueous solution and the dispersion of MMT. The structure and performance of two series of hydrogels in dry state were studied by XRD, Raman spectroscopy, TEM and ^{27}Al MAS NMR. Compressing test results showed that the gel strength of the hydrogels prepared by the latter method was much higher than that by the former method. When acryloyloxyethyl trimethyl ammonium chloride (DAC) was introduced into the system, hydrogels with excellent nanostructure could be synthesized. The result of ^{27}Al MAS NMR suggested that the chemical environment of aluminum in MMT was changed by the introduction of DAC due to the interaction between the groups of DAC and MMT layers. Thus, the combination of copolymerizing with strong polar monomers and using the dispersion of MMT were the effective ways to obtain nanocomposite hydrogel of MMT and ionic monomers. The nanostructure of the hydrogel improved the gel strength, while the swelling ratio of the hydrogel depended on synergic effects of multifunctional groups.

Keywords: Nanocomposite hydrogel; Gel strength; Structure analysis

1. Introduction

Superabsorbent polymeric gel, consisting of three-dimensional polymer network and water-filled inner of network, has attracted much attention as functional soft materials. And it has been used in sanitary napkins and disposable diapers, amendments in greening and agriculture, refrigerants in medical and food industries (Omidian et al., 1998; Xue et al., 2001; Tong and Zhang, 2005; Zhao et al., 2005). However, the mechanical properties of conventional superabsorbent polymer were mostly off target because the large proportion of water in the polymers and its randomly cross-linked network structure often make the hydrogel inevitably weak and fragile (Kim et al., 1995).

To improve the mechanical performance of the hydrogel, an inorganic component was introduced and the nanocomposite hydrogels with excellent mechanical performance were firstly created by Haraguchi and Takehisa (2002). In recent years, a large number of hydrogels with excellent gel strength were obtained by

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the introduction of inorganic components, such as AAm/MMT (Starodoubsev et al., 2003, 2006), PNIPA/clay (Haraguchi and Li, 2006; Liu et al., 2006). Hydrogels exhibited great potential as advanced soft materials as reported elsewhere, such as temperature-sensitive actuators (Liang et al., 2000), biocompatible materials (Darder et al., 2003), tough hydrogels with their surface friction sensitive to atmosphere (Haraguchi and Matsuda, 2005), and raw materials for layered porous solids (Haraguchi and Matsuda, 2005). It was well known that during the synthesis of nanocomposite hydrogels, the viscosity of MMT dispersion would increase seriously due to the aggregation of the clay mineral platelets when the ionic monomer was introduced. Thus it was more difficult to obtain the nanocomposite hydrogel with ionic monomers and clay by the conventional method. To solve this problem, different methods, such as using the modified clay or the suspension of clay, could be employed. However, the effect of methods of preparation on the structure of hydrogels with ionic monomers and clay minerals was rarely discussed in detail. At the same time, based on the structure model of hydrogel with nonionic monomers and layer silicate, the dispersed platelets of clay in the polymer matrix were considered as cross-linking agent (Haraguchi and Takehisa, 2002; Wu et al., 2003; Tanaka et al., 2005). Thus, many researchers concluded that the improvement of the swelling ratio and gel strength of hydrogel should be contributed to the formation of nanostructure in polymer matrix. However, the relationship between performance and structure of hydrogel with ionic monomer and clay was rarely studied.

In this paper, hydrogels composed of sodium acrylate, DAC and MMT were synthesized by in-situ polymerization in aqueous solution and the performance of the hydrogels was investigated. A relationship between structure and performance of the hydrogel with ionic monomers and MMT was studied in detail.

2. Experiments

2.1. Materials

Acrylic acid (AA) was supplied by YiLi chemical Co. Ltd (Beijing, China). Sodium montmorillonite (Na^+-MMT) with a cation exchange capacity (CEC) of 92 mEq/100 g was supplied by Zhejiang Linan Bentonite Factory (Zhejiang province, China). The size of the MMT aggregates was less than 75 μm. Acryloyloxyethyl trimethyl ammonium chloride (DAC) were selected as cationic monomer, which was supplied by Sanyo Chem. Industries (Sanyo, Japan). *N*,*N*′-methylenebisacrylamide (NMBA) and ammonium persulfate (APS) used as cross-linking agent and initiator respectively, were supplied by Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All agents were used directly without further purified.

2.2. The synthesis of the nanocomposite hydrogels

The mixture of MMT (3.00 g) and distill water (80.00 g) was stirred for 10 h by mild magnetic stir to obtain the dispersion of MMT. A certain weight of AA (30.00 g) was dissolved in 30 mL distilled water, and the sodium hydroxyl solution (30 wt.%) was added into the AA aqueous under stirring in a cool water bath. The neutralization degree was controlled to be around 80%. Then, the appropriate mass of DAC in aqueous solution (80 wt.%) and NMBA were added to the above solution. The mixture was slowly added to the dispersion of MMT. After N_2 gas was introduced into the reactor for 1 h, a quantity of initiator was added at 60 °C under stirring, and the reaction was carried out for 20 h until the hydrogel was obtained.

The samples for structure analysis were extracted with distill water and methanol (50/50 wt/wt) for at least 40 h and then dried to constant weight in a vacuum oven at 50 °C.

2.3. Swelling ratio

0.10 g dry sample powder (mesh 30–40) was immersed into 400 mL distilled water for approximate 24 h to reach the equilibrium of swelling. The sample was filtered through a 100-mesh screen and the excess water was wiped superficially with filter paper. The swelling ratio was determined by:

$$Q = (M - M_0)/M_0$$

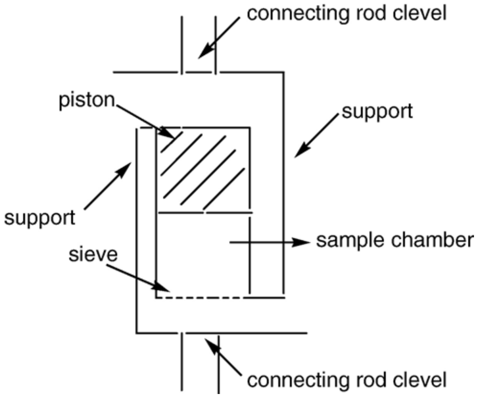
where M was the mass of gel and M_0 was the mass of dry sample powder.

2.4. Gel strength

To measure the gel strength of hydrogel, many methods had been employed (Dubrovskii et al., 1994; Ramazani-Harandi et al., 2006). In this paper, the gel strength was obtained by as follows: sample with a size of 30–40 mesh was selected to avoid the effect of powder size on gel strength, the swollen hydrogel particles (the swelling ratio was controlled at 400 g/g) were placed into the sample chamber as shown in Scheme 1. The compression utensil was connected with an INSTRON-1121 testing machine and the compressing test was carried out with a speed of 10 mm/min to a constant strain of 30 mm. By calculating the area under the stress–strain curve, the work (Y) of squeezing out a certain mass (M) hydrogel was obtained. The antipressure energy (E_{press}) could be calculated by:

$$E_{\text{press}} = Y/M$$

Here, E_{press} was defined as gel strength by Yang et al. (1993).



Scheme 1. Compression utensil.

2.5. Analysis

XRD patterns were obtained by a D/max 2500 X-ray diffraction meter (Tokyo, Japan), a conventional copper target X-ray tube set to 40 kV and 200 mA. The X-ray source was Cu Kα radiation. Data were collected from 2θ of 1.50 to 30.00° (θ being the angle of diffraction) with a step width of 0.02° and step time of 0.4 s, scanning speed of 8°/min, divergence slit width of 0.2 mm, scatter slit width of 0.6 mm, receiving slit width of 0.2 mm at room temperature. A JEM-2000EX TEM operated at 200 kV was used to study the morphology of the samples. Slices of 50 nm were cut with a Leica Ultracut UCT microtome by a glass knife for the TEM studies. Raman spectroscopy was carried out using a Nicolet 960 FT-Raman spectrometer (USA) with 2 cm^{-1} resolution and excitation source of Nd:YVO_4 laser (1.5 W, $\lambda = 1064$ nm). ^{27}Al MAS NMR measurements were carried out on Bruker AV-400 NMR spectrometer operating at 100.58 MHz. The MAS spinning rate was 5 kHz. In this section, the samples for XRD, FT-Raman and TEM analysis were nanocomposite hydrogels with different MMT content in dry state.

3. Results and discussion

3.1. Raman spectra

Fig. 1 corresponds to the Raman spectra of MMT, copolymer of DAC and poly (sodium acrylate) and dry nanocomposite hydrogel. MMT is characterized by bands located at 270 cm^{-1}, 450 cm^{-1}, 710 cm^{-1} and 1090 cm^{-1}, but the peaks were weaker and broader (Frost and Rintoul, 1996). As to the spectra of copolymer shown in Fig. 1(2), the peak located as 3030 cm^{-1}, 2970 cm^{-1} and 1730 cm^{-1} were found, which were attributed to ν_{as}C–H, ν_sC–H and C=O of DAC, respectively. The peak located at 1410 cm^{-1} corresponds to COO^- of sodium acrylate. In the spectrum of the nanocomposite hydrogel (Fig. 1(3)), the absorption bands at 270 cm^{-1} and 1090 cm^{-1} belonged to MMT and all absorption bands mentioned at the spectrum of copolymer (Fig. 1(2)) were found. The result manifested that the sample 3 was the composite of MMT, DAC and poly (sodium acrylate).

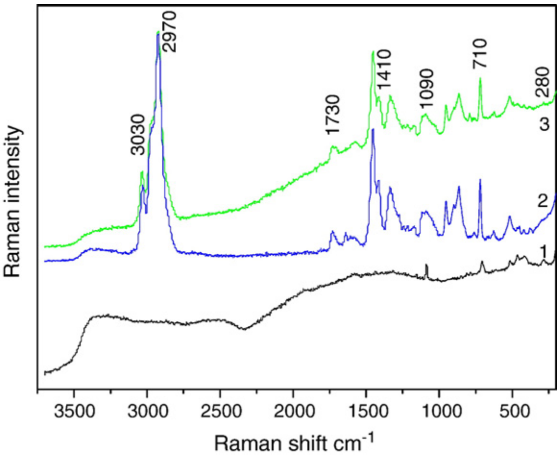


Fig. 1. Raman spectra of MMT (1), the copolymer with DAC and sodium acrylate (2), and the composite from dispersed MMT and sodium acrylate (3).

3.2. The effect of dispersion of MMT

Many researchers found that hydrogels can be synthesized from dispersed MMT and nonionic water-soluble monomers, such as AAm, NIPAAm, etc. (Zhu et al., 2006; Zhang et al., 2006). However, it was difficult to synthesize the hydrogels with ionic monomers and

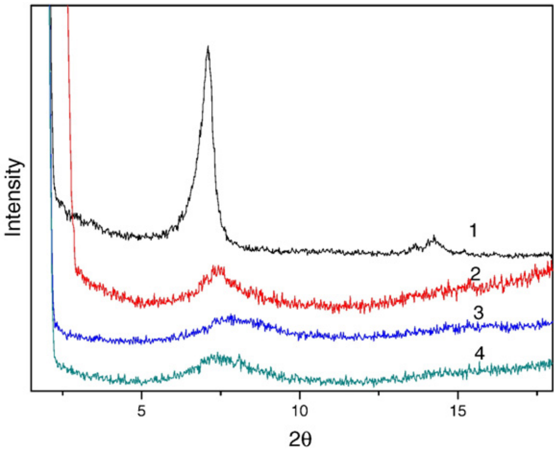


Fig. 2. XRD patterns of the composites with different MMT after drying. 1) MMT, 2) composite with 9.0 wt.% MMT dispersed into the aqueous monomer solution; 3) composite with 4.5 wt.% MMT, 4) composite with 9.0 wt.% MMT.

MMT by the same method because of aggregation of the clay mineral platelets caused by the electrostatic interaction between the platelets and ionic monomer.

Two series of hydrogels were synthesized by in-situ solution polymerization. One pre-gel solution was obtained by dispersing the MMT powder into aqueous sodium acrylate solution (sample 2). The other was obtained with sodium acrylate and the dispersion of MMT (sample 3, 4).

The XRD pattern profiles of both dry hydrogels and MMT powder are shown in Fig. 2. As to sample 2 and sample 4, reflections at 6.56° could be found at diagram 2 and 4, which was similar to diagram 1 (MMT). The position and strength of the reflections of all samples showed little difference, which indicated that, the MMT particles in the hydrogel consisted of relatively large numbers of layers. In diagram 3 that the reflection of MMT became weaker and the width of reflection became wider when the MMT content in the composite with poly (sodium acrylate) and MMT was decreased to 4.5 wt.%. This suggested that there exist some disorder of the MMT platelets in the composite, in agreement with the results obtained by Chen et al. (2005).

The difference in morphology of two dry nanocomposite hydrogels was also seen by TEM (Fig. 3). A large number of aggregated MMT platelets was found in Fig. 3(a) and (c). It suggested that a nanostructure rarely existed in the hydrogels. On the contrary, some intercalated structures were found in Fig. 3(b) and the

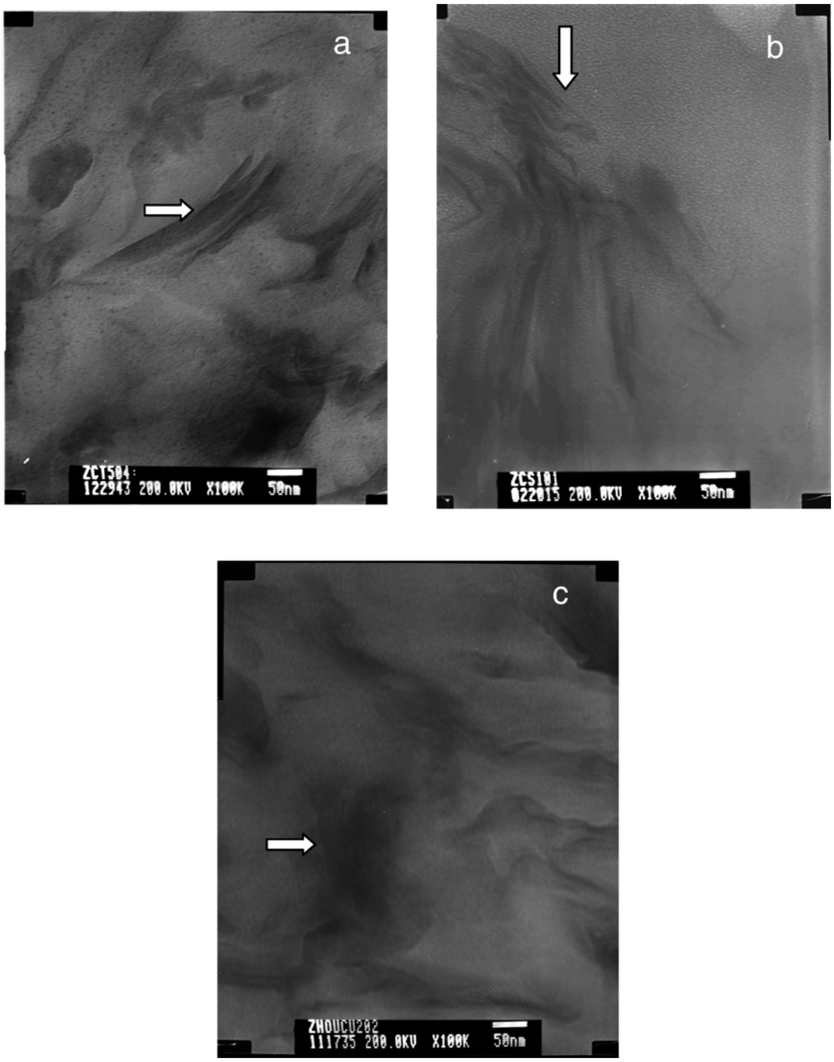


Fig. 3. TEM images of dried hydrogels: sample 2 (a); sample 3 (b); sample 4 (c). The black section represents MMT and the white section the polymer matrix.

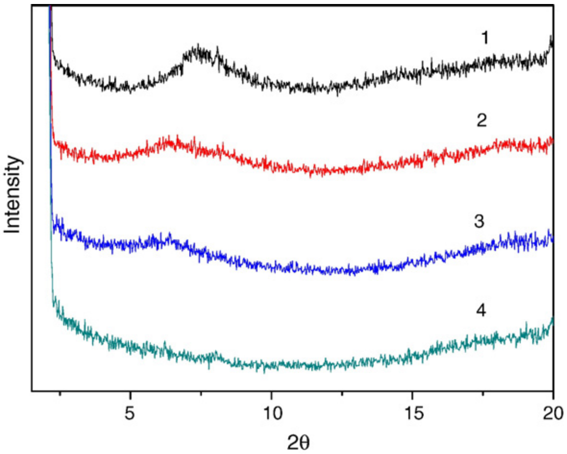


Fig. 4. XRD patterns of the hydrogels with 9.0 wt.% MMT and different DAC/AAcNa mass ratios after drying. 1) DAC/AAc = 0, 2) DAC/AAc = 5/25, 3) DAC/AAc = 10/20, 4) DAC/AAc = 20/10.

clay mineral platelets were better dispersed into the matrix indicating a nanocomposite hydrogel.

3.3. Effect of co-monomer

An investigation carried out by Vaia and Liu (2002) suggested that copolymerizing with a polar monomer could promote the formation of nanostructure in the hydrogel. In this paper, DAC was selected as co-monomer.

The XRD pattern profiles of the dry nanocomposite hydrogels were shown in Fig. 4. When DAC content was low, the band width of d_{001} became wider and the intensity weaker (Fig. 4(2)). In the each diagram (from 1 to 3) was a weakly pronounced band at $2\theta = 3–6°$ whose position shifted to higher angels with increasing DAC content. When the molar ratio of DAC to AAc was 1:1 mol/mol (Fig. 4(4)), the band disappeared completely. The feature manifested that the order of the MMT layers was seriously destroyed by the interaction between the cationic monomer and the MMT platelets.

The TEM indicated when few DAC was introduced, a slightly intercalated structure (Fig. 5). With increasing DAC content, a pronounced intercalated structure was found (Fig. 5).

In the ^{27}Al MAS NMR diagrams (Fig. 6), the peaks located at 60 ppm and 6 ppm could be distinguished from each other, which was attributed to 4-coordinated (tetrahedral) and 6-coordinated (octahedral) aluminum, respectively (Wang and Scrivener, 2003). Comparing the spectrum of poly (sodium acrylate)/MMT composite (diagram 2) with MMT (diagram 1), the shape and chemical shift of peaks located at 60 ppm and 6 ppm were almost constant. Thus the chemical environment of aluminum in MMT platelets was not changed by the introduction of sodium acrylate. However, as shown in Fig. 6 (from diagram 3 to diagram 6), an obvious change occurred in the spectrum when the DAC was introduced. Intensity of the peak located at 6 ppm obviously increased, while the intensity of the peak located at 60 ppm decreased with increasing content of DAC. The chemical environment of aluminum in MMT platelets was changed by the introduction of DAC due to the interaction between DAC and MMT

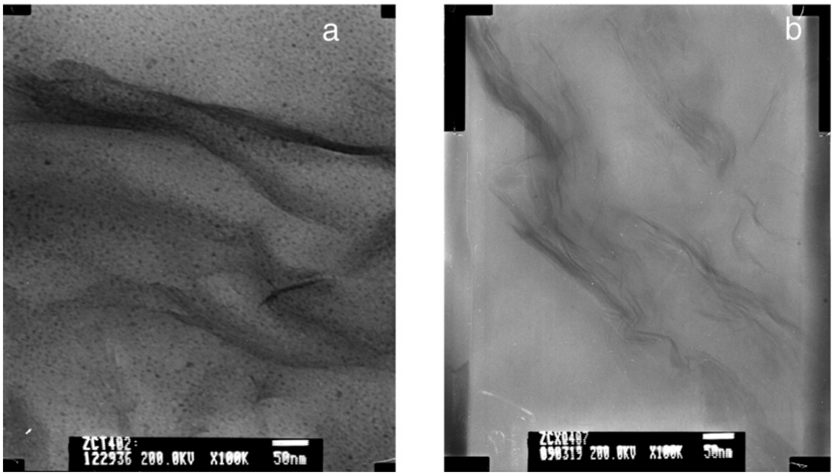


Fig. 5. TEM images of the dried hydrogels (a) hydrogel with 9.0 wt.% MMT and copolymer of DAC and sodium acrylate, DAC/AAcNa = 5 g/25 g, (b) hydrogel with 9.0 wt.% MMT and copolymer of DAC and sodium acrylate, DAC/AAcNa = 10 g/20 g, The black section represents MMT, the white section represents the polymer matrix.

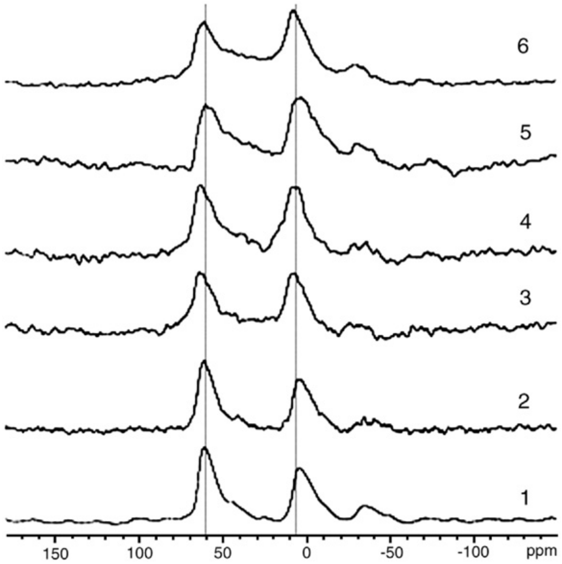


Fig. 6. ^{27}Al MAS NMR spectra of MMT (1), AAc/MMT = 30 g/3 g (2), DAC/AAc/MMT = 1 g/29 g/3 g (3), DAC/AAc/MMT = 5 g/25 g/3 g (4), DAC/AAc/MMT = 10 g/20 g/3 g (5), DAC/AAc/MMT = 20 g/10 g/3 g (6).

platelets. The interaction between DAC and MMT platelets promoted the formation of the nanostructure in the hydrogel.

In conclusion, during the synthesis of nanocomposite hydrogels the properties of co-monomers were important factors, which can control the structure of the nanocomposite hydrogel. The stronger the interaction between MMT platelets and monomer was, the easier the hydrogels with the nanostructure could be obtained.

3.4. The effect of nanostructure on performances of the hydrogels

The properties of all the composites used in our study are listed in Table 1. The gel strength of sample 4 was 15.67 mJ/g, which was lower than that of the matrix (sample 1, gel strength 18.60 mJ/g). As for sample 4, the clay mineral platelets were not dispersed into the matrix and the gel strength was reduced due to the phase separation between MMT and polymer. As sample 5 contains some intercalated MMT particles, the gel strength reached 29.36 mJ/g, which was higher than for the matrix (sample 1). Sample 8 containing well-dispersed MMT mineral platelets showed a gel strength up to 45.04 mJ/g, which was about two times of the corresponding copolymer (sample 2, gel strength 24.36 mJ/g). Thus the nanostructure of the composites improved the gel strength distinctly due to the good dispersion of the MMT platelets in the matrix. On the other hand, the gel strength of the sample synthesized by using an aqueous MMT dispersion and sodium acrylate was higher than the sample synthesized by dry MMT (sample 3, gel strength 20.36 mJ/g).

Comparison of the data of sample 2 (1250 g/g) and sample 8 (750 g/g) (Table 1), indicates that the swelling ratio of the hydrogel was reduced due to the cross-linking of MMT platelets. This agrees with the results of Haraguchi and Takehisa (2002) who considered that the exfoliated clay mineral platelets in the matrix could act as cross-linking agent. As shown in Table 1, the swelling ratio of the hydrogel with 9.0 wt.% MMT dispersion (sample 6, swelling ratio 2100 g/g) was close to that of the hydrogel with 9.0 wt.% MMT powder (sample 4, swelling ratio 2030 g/g) and both of them were higher than the matrix (sample 1, swelling ratio 1000 g/g). Thus, increasing swelling ratio of the hydrogel shows a synergic effect of multifunctional groups due the introduction of the MMT.

4. Conclusion

The gel strength of the hydrogel synthesized by using aqueous montmorillonite dispersions was higher than

Table 1
Performance of the hydrogels

No.	Sample	Conc. of monomers (wt.%)	Conc. of MMT (wt.%)	Ratio of DAC to AAc (g/g)	Status of MMT	Swelling ratio (g/g)	Gel strength (mJ/g)
1	AAcNa	15	–	–	–	1000	18.60
2	AAcNa–DAC	15	–	10/20	–	1250	24.36
3	MMT–AAcNa	15	4.5	–	Precipitation	1480	20.35
4	MMT–AAcNa	15	9.0	–	Precipitation	2030	15.67
5	DMMT–AAcNa	15	4.5	–	Slurry	1700	29.36
6	DMMT–AAcNa	15	9.0	–	Slurry	2100	19.30
7	DMMT–AAcNa–DAC	15	9.0	5/25	Slurry	1260	26.39
8	DMMT–AAcNa–DAC	15	9.0	10/20	Slurry	750	45.04

MMT represents MMT powder and DMMT represents dispersed MMT. The gel strengths were measured at the swelling ratio of 400 g/g.

that of the hydrogel synthesized by applying dry montmorillonite. When DAC was introduced, the chemical environment of aluminum in the MMT platelets was changed due to the interaction with DAC functional groups. The gel strength of hydrogel can be increased up to two times of the matrix. The nanostructure of hydrogels improved the gel strength.

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