

## Gelation performance of poly(ethylene imine) crosslinking polymer-layered silicate nanocomposite gel system for potential water-shutoff use in high-temperature reservoirs

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**ABSTRACT:** Polymer gels have been widely used for water shutoff in mature oil fields. In this paper, polyacrylamide (PAM)–montmorillonite (MMT) nanocomposites (NC) were prepared through in situ intercalative polymerization. Fourier transform infrared spectroscopy and X-ray diffraction were conducted to characterize the prepared PAM/MMT nanocomposites. The gelation performance of poly(ethylene imine) (PEI) crosslinking PAM/MMT nanocomposite gel system (NC/PEI gel system) was systematically investigated by bottle testing and viscosity measurement methods. The results showed that the gelation performance of the NC/PEI gel system was greatly affected by the total dissolved solids, PAM/MMT nanocomposite concentration, and PEI concentration. The NC/PEI gel system exhibited much better thermal stability and gelation performance than the PAM/PEI gel system at the same conditions. The gelation performance after flowing through porous media of the NC/PEI gel system before injection and that of the subsequently injected gel system was different. The gel strength decreased and the gelation time was delayed after the gel system before injection was flowed through porous media. However, the gel strength of the subsequently injected gel system did not decrease, and only the gelation time was delayed after flowing through porous media. This study suggests that the NC/PEI gel system can be used as a potential water-shutoff agent in high-temperature reservoirs. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 44243.

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### INTRODUCTION

Excessive water production is a common problem for oil production, which can lead to rapid productivity decline and increased operating costs. Chemical water-shutoff treatments have been widely used in mature oil fields.<sup>1–3</sup> Polymer gels have become the mainstream of chemical water-shutoff agents because of their relatively low cost and effective plugging properties.<sup>4–8</sup> Most of the polymer gels are usually prepared with polyacrylamide or acrylamide-based copolymers and an inorganic or organic crosslinker. Inorganically crosslinked gels are formed by ionic bonding between the negatively charged carboxylate groups and inorganic crosslinkers such as Cr(III) or Al(III) salt. However, the inorganically crosslinked gels have a relatively short gelation time and unsatisfactory thermal stability due to the rapid forming rate and weak stability of the ionic bonding. Organic crosslinkers can form covalent bonds with polymers, which provides to the organically crosslinked gels a higher thermal stability and longer gelation time than inorganically

crosslinked gels. Nevertheless, most of the common organic crosslinkers, such as phenolformaldehyde, hydroquinone-hexamethylenetetramine, terephthalaldehyde, and dihydroxynaphthalene, are toxic and environmentally unfriendly, which limits the application of these crosslinkers in oil fields. Recently, the organic crosslinker poly(ethylene imine) (PEI), which has low toxicity and excellent crosslinking ability, has been widely reported.<sup>9–11</sup> The polymer gel system that consists of PEI and copolymer *tert*-butyl acrylate (PAtBA) has been successfully applied for water shutoff in Mexico.<sup>12,13</sup> The gel system that contains 7.0 wt % PAtBA and 0.3 wt % PEI can remain stable with high strength even at temperatures above 120 °C. But PAtBA showed some compatibility problems with high-salinity brines.<sup>14</sup> Moreover, the relatively high cost and the required high concentration of PAtBA make the PAtBA/PEI gel system uneconomic, which limits wide application. Polyacrylamide (PAM) has lower cost and better compatibility than PAtBA, so crosslinking PAM with PEI to form a water shutoff gel has more advantages. The gelation mechanism of the PAM/PEI gel system can be explained as the nucleophilic amine nitrogen on PEI attacking the carbonyl

carbon attached to the amide group and substituting the acrylamide pendant groups on the PAM chain.<sup>15</sup> Al-Muntasheri *et al.*<sup>16–19</sup> studied the gel performance and gelation kinetics of the PAM/PEI gel system at high temperature and proved that the PAM/PEI gel system can remain stable at 130 °C for 8 weeks. However, the PAM/PEI gel system was not stable enough when the concentration of PAM was relatively low. It was observed that a syneresis phenomenon occurred when the gel system that contained 5.0 wt % PAM and 0.3 wt % PEI remained at 100 °C after 3 weeks.<sup>19</sup> The PAM concentration should be as high as 7.0 wt % or even 9.0 wt % to guarantee the thermal stability of the PAM/PEI gel system. However, a high polymer concentration will result in short gelation time and high initial viscosity, which makes it difficult to inject gels into reservoirs successfully.<sup>14,20</sup> Previous studies<sup>11,14,16,21,22</sup> indicated that the gelation time of the PAM/PEI gel system could be delayed when inorganic salt was utilized as a retarder. The shrinkage of the polymer network caused by charge shielding resulted in fewer accessible crosslinking sites for PEI because PEI macromolecule coils were not easily permeated intermolecularly into the contracted polymer network. Nevertheless, sometimes the delayed effect of inorganic salt is limited at high temperature, and too much inorganic salt has a negative effect on gel strength.<sup>22,23</sup>

Recently, organic–inorganic composite materials have been widely studied because of their excellent performance. Therefore, the introduction of inorganic materials to improve the performance of water-shutoff gels has attracted great interest.<sup>24–26</sup> As a common and low-cost inorganic material, clay is very suitable for preparing water-shutoff gels because it can significantly improve the mechanical properties and thermal stability of the gel.<sup>27–29</sup> Tongwa *et al.*<sup>25</sup> obtained a high-strength water-shutoff gel by mixing partially hydrolyzed polyacrylamide (HPAM) and Laponite XLG, and the gel showed a good thermostability through thermogravimetric analysis. Nevertheless, the gel can be formed by electrostatic attraction of HPAM and Laponite XLG only under high-speed blending conditions, which is hard to achieve in practical applications in oil fields. Polymer-layered silicate (PLS) nanocomposites can be obtained by intercalating polymer between the montmorillonite (MMT) layers through in situ intercalative polymerization or melt intercalation. The performance of the polymer can be improved by the incorporation of MMT. Zolfaghari *et al.*<sup>26</sup> prepared nanocomposite hydrogels (NC gels) by crosslinking the PAM/MMT nanocomposite with chromium(III). The NC gels showed higher strength and elastic modulus compared with the similar but unfilled PAM gel. Accordingly, it is possible to form a thermally stable water-shutoff gel with high strength by crosslinking a relatively low concentration of PAM/MMT nanocomposite (NC) with PEI. However, little work has been done to systematically examine the NC/PEI gel system.

In this work, a PAM/MMT nanocomposite was prepared through an in situ intercalative polymerization method. The structure of the prepared PAM/MMT nanocomposite was characterized through Fourier transform infrared (FTIR) and X-ray diffraction (XRD) spectroscopy. The gelation performance of the NC/PEI gel system and the effects of PAM/MMT nanocomposite concentration, PEI concentration, and inorganic salt concentration on the gelation performance were investigated. The

thermal stability of the NC/PEI gel system and the gelation performance of the gel system after flowing through porous media were also evaluated.

## EXPERIMENTAL

### Materials

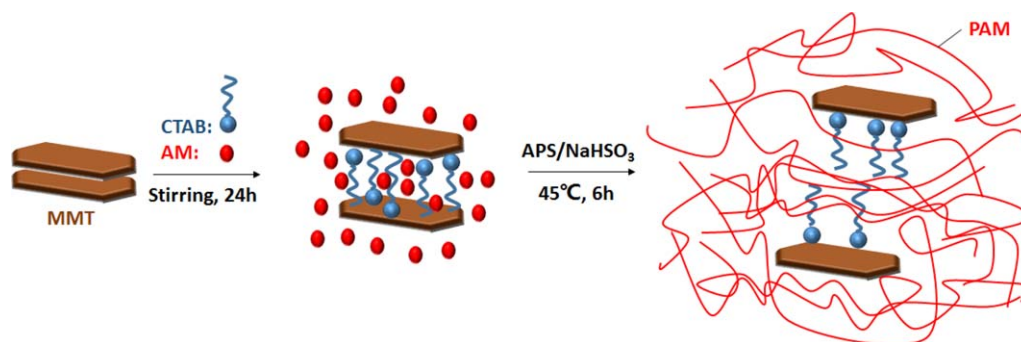
Acrylamide (AM), hexadecyl trimethyl ammonium bromide (CTAB), ammonium persulfate (APS), sodium hydrogen sulfite (NaHSO<sub>3</sub>), and sodium chloride (NaCl) were of analytical grade as obtained from KeLong Chemical Reagent Co., Ltd. (Chengdu, China). Sodium montmorillonite (MMT-Na) with a cation exchange capacity of 90 meq/100 g was provided by Yanfeng Mineral Co., Ltd. (Shijiazhuang, China). PEI with an average molecular weight of 70 kDa was purchased as a 50 wt % aqueous solution from Aladdin Reagent Co., Ltd. (Shanghai, China). PAM with an average molecular weight of 5,000 kDa was provided by Hona Chemical Co., Ltd. (Guangzhou, China). The degree of hydrolysis of PAM was less than 5%. Water was double-deionized with a Millipore Milli-Q system (Massachusetts, United States) to produce the 18 MΩ deionized water. Saline water was prepared from double-distilled water and NaCl. All gelant solutions were prepared with saline water [total dissolved solids (TDS) 5000 mg/L] in this study without special description.

### Preparation of PAM/MMT Nanocomposite

The PAM/MMT nanocomposite was prepared by the following procedure. A 20-g amount of AM and a certain amount of CTAB (32.8 wt % relative to the MMT-Na) were placed in a 250-mL three-necked round flask and completely dissolved by the addition of an appropriate amount of distilled water. Then a certain amount of MMT-Na was added into the three-necked round flask and stirred with a mechanical agitator for 24 h. After that, the initiator APS/NaHSO<sub>3</sub> (molar ratio 1.2:1) was added with the concentration of 0.1 wt % relative to the AM, and the solution was heated to 45 °C under a nitrogen atmosphere for 6 h, after which a white, gelatinous PAM/MMT nanocomposite was obtained. The PAM/MMT nanocomposite was washed and extracted with ethanol to remove residual monomers and initiator. Finally, the PAM/MMT nanocomposite was further dried in a vacuum oven at 50 °C for 48 h. Two types of PAM/MMT nanocomposite were obtained by adjusting the mass ratio of AM and MMT-Na. The PAM/MMT nanocomposite is referred to as NC1 and NC2 in this paper when the mass ratio of AM and MMT-Na is 3:1 and 1:1, respectively. The synthesis process is shown in Figure 1.

### Characterization

XRD patterns were obtained to measure the degree of clay exfoliation and determine the polymer intercalation between the clay layers using a PANalytical X-ray diffractometer (Almelo, Holland) with Cu-Kα radiation at 40 kV and 40 mA. The samples were scanned over 2θ ranges from 1 to 40° with a step size of 0.02°. Infrared spectra of MMT-Na, NC1, and NC2 were obtained in the 400–4000 cm<sup>-1</sup> region using a Nicolet Nexus 170SX Fourier transform infrared spectrophotometer (Madison, United States) on a KBr tablet. Static light scattering measurements were conducted to evaluate the weight-average molar mass of PAM that was contained in the PAM/MMT



**Figure 1.** Synthesis of PAM/MMT nanocomposite. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

nanocomposite. The PAM aqueous solution was obtained by centrifuging and filtering the aqueous solution of PAM/MMT nanocomposite. The static light scattering measurements were performed on a BI-200SM light scattering detector (New York, United States) at the wavelength of 532 nm. The refractive index increments of PAM in aqueous solutions were determined at 25 °C.

### Evaluation of the Gelation Performance

To investigate the effects of PAM/MMT nanocomposite concentration, PEI concentration, and inorganic salt concentration on the gelation performance, bottle test and apparent viscosity

measurement methods were both conducted. The bottle test method provides a semiquantitative measure of gelation performance.<sup>30</sup> Gel strength during development of gelation kinetics was expressed as an alphabetic code of A to I, as shown in Table I. The specific process of the bottle test is as follows. The PAM/MMT nanocomposite and PEI were dissolved in a saline solution with complete stirring to prepare a gelant solution. Then a 20-mL volume of the gelant solution was transferred to a 50-mL volume Westwood bottle. The bottle was sealed and placed in an oven that was set at 120 °C. After that, the bottle was inverted and observed at different intervals, and the gel strength code was recorded. For the bottle test method, the gelation time is considered to be the period of time when the gelant solutions in a code A state turn into a flowing gel code C. Simultaneously, the accurate gelation time was determined by the viscosity measurement method. For this method, the gelation time is defined as the time needed to reach the inflection point on the viscosity versus time curve. This method has been widely used.<sup>15,17,24</sup> The viscosity of the gel system was measured through a Brookfield viscometer DV-III (New York, United States) in this study.

Thermal stability is an important property of a water-shutoff gel system. The destabilization of the gel system could result in a decrease in the gel strength, which shows in the continuous decreasing of the syneresis and the viscosity. However, for a bulk gel, the viscosity cannot be measured accurately. Therefore, the bottle test method, which can be used to observe the gel strength and syneresis phenomenon directly, was also used to evaluate the long-term gel thermal stability.

### Gelation Performance Study after Flowing through Porous Media

The experimental setup mainly consisted of a constant-speed pump and a core holder. The simplified schematic of the experimental setup is shown in Figure 2. A synthetic core was used as the porous media. The permeability of the core ( $\phi$  3.8 cm  $\times$  7.5 cm) to saline water (TDS 5000 mg/L) was determined to be about 1100 mD. The porosity of the core was about 24%. The core was vacuumed before use. The procedure described below was followed for all tests.

- (1) PAM/MMT nanocomposite and PEI were dissolved in saline water (TDS 5000 mg/L) to prepare the gelant solution. Then the gelant solution was divided into three

**Table I.** Gel Strength Codes

Gel strength code	Gel description
A	No detectable gel formed: The gel appears to have the same viscosity as the original polymer solution.
B	Highly flowing gel: The gel appears to be only slightly more viscous than the initial polymer solution.
C	Flowing gel: Most of the gel flows to the bottle cap by gravity upon inversion.
D	Moderately flowing gel: Only a small portion (5–10%) of the gel does not readily flow to the bottle cap by gravity upon inversion (usually characterized as a tonguing gel).
E	Barely flowing gel: The gel can barely flow to the bottle cap, or a significant portion (>15%) of the gel does not flow by gravity upon inversion.
F	Highly deformable nonflowing gel: The gel does not flow to the bottle cap by gravity upon inversion.
G	Moderately deformable nonflowing gel: The gel deforms about halfway down the bottle by gravity upon inversion.
H	Slightly deformable nonflowing gel: Only the gel surface slightly deforms by gravity upon inversion.
I	Rigid gel: There is no gel surface deformation by gravity upon inversion.

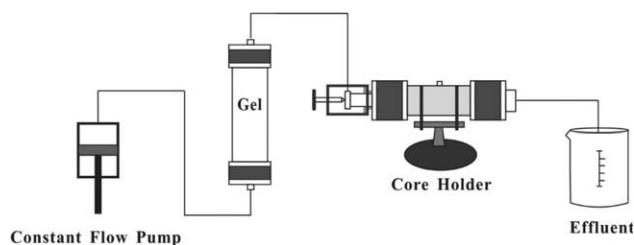


Figure 2. Simplified schematic of the experimental setup.

samples, which were referred to as the original gel sample, gel sample 1, and gel sample 2. Each sample was 50 mL. After that, gel sample 1 was allowed to flow through the synthetic core at a constant flow rate of 1 mL/min. The effluent was collected and rejected at a constant flow rate of 1 mL/min for full shearing three times. Then gel sample 1 after flowing through the core was collected, and the collected gel sample was referred to as gel sample 1A. Subsequently, gel sample 2 was injected and flowed through the same core following the same procedure as gel sample 1, and gel sample 2 after flowing through the core (gel sample 2A) was also collected.

- (2) A drop of gel sample (original gel sample, gel sample 1A, or gel sample 2A) was placed on a sample stage. Subsequently, the gel sample was frozen by liquid nitrogen and freeze-dried for 24 h followed by metal spraying treatment. Then the microstructure of the gel sample was observed by a scanning electron microscope (SEM).
- (3) The original gel sample, gel sample 1A, and gel sample 2A were removed in the same amount (20 mL) and sealed in three individual 50-mL Westwood bottles. Then the bottles were placed in the oven at 120 °C. The gel strength code was recorded regularly.

## RESULTS AND DISCUSSION

### Characterizations

The chemical structures of MMT-Na, NC1, and NC2 were confirmed by FTIR spectroscopy, as shown in Figure 3. In the spectrum of MMT-Na, the bands observed at 3621 and 1638  $\text{cm}^{-1}$  are attributed to the stretching vibration and bending vibration of structural hydroxyl in MMT-Na, respectively. The absorption peak at 3448  $\text{cm}^{-1}$  is related to the  $\text{H}_2\text{O}$  adsorbed on MMT-Na. The band at 1038  $\text{cm}^{-1}$  is attributed to the stretching vibration of Si—O. In the spectra of NC1 and NC2, strong absorption peaks at 3446  $\text{cm}^{-1}$  and 3447  $\text{cm}^{-1}$  are attributed to the stretching vibration of N—H. Furthermore, the peaks at 2926 and 1630  $\text{cm}^{-1}$  are the characteristic absorption peaks of C—H and C=O, respectively. The peaks at 1038  $\text{cm}^{-1}$  and 1039  $\text{cm}^{-1}$  are attributed to the stretching vibration of Si—O. Therefore, a conclusion can be drawn from the FTIR data that the target nanocomposites NC1 and NC2 were synthesized successfully.

Figure 4 presents the XRD patterns of MMT-Na, NC1, and NC2. The interplanar distance can be determined by Bragg's law:  $\sin \theta = n\lambda/2d$ , where  $\lambda$  corresponds to the wavelength of the X-ray radiation used in the diffraction experiment,  $d$  represents the spacing between diffractive lattice planes, and  $\theta$  is the measured diffraction angle or glancing angle.<sup>31</sup> The decrease of  $\theta$ , which

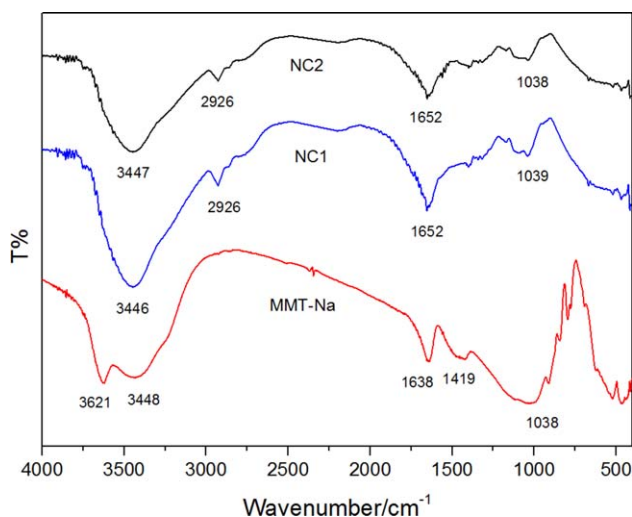


Figure 3. FTIR spectra of MMT-Na, NC1, and NC2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

corresponds to the peak of the sample, indicated an increase in the interplanar distance of the MMT. A strong diffraction peak at  $2\theta = 6.9^\circ$  in the MMT-Na powders corresponded to the layered structure (spacing between clay sheets  $d = 1.28$  nm). Complete exfoliation was observed for NC1 and NC2, as was evidenced by the absence of the basal peak. This was related to the huge amount of energy produced by the polymerization process. The XRD results indicated that the MMT layers have been dramatically exfoliated and well dispersed in the PAM/MMT nanocomposites.

Figure 5 and Figure 6 show the static Zimm plots of PAM of NC1 and of NC2, respectively. Extrapolating to infinite dilution and taking the intercept, the weight-average molar mass  $M_w$  of PAM of NC1 and NC2 was determined to be  $4.89 \times 10^6$  and  $3.12 \times 10^6$  g/mol, respectively.

### Effect of PAM/MMT Nanocomposite Concentration on Gelation Performance

To investigate the effect of PAM/MMT nanocomposite concentration on the gelation performance, the crosslinker PEI was

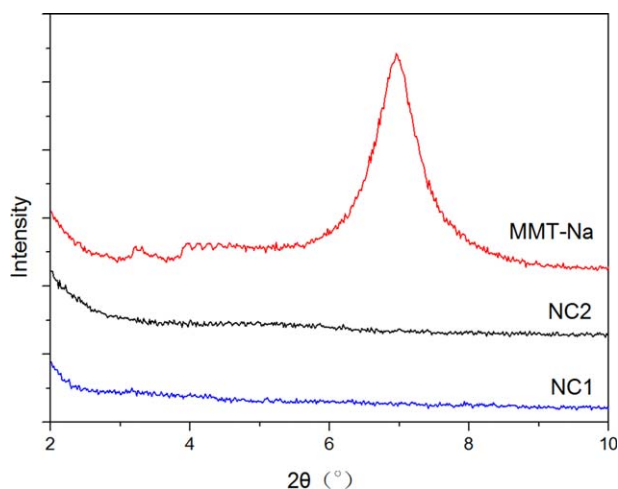


Figure 4. XRD spectra of MMT-Na, NC1, and NC2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

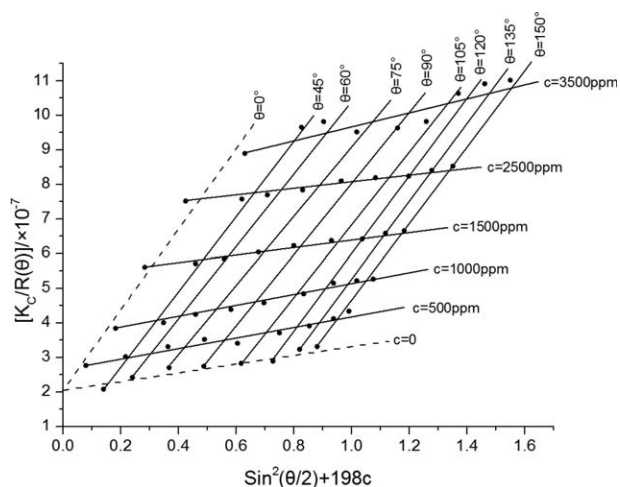


Figure 5. Zimm plot for PAM of NC1.

kept at a constant concentration of 0.3 wt %. The concentrations of NC1 and NC2 were varied from 1.0 to 4.0 wt %. PAM was also used to prepare a gelant solution for comparison. The experimental results are shown in Table II and Figure 7.

Table II shows that the strength of the NC/PEI gel increased with the increase of the PAM/MMT nanocomposite concentration, which was similar to the variation trend of the PAM/PEI gel. It is easy to understand that more crosslinking units can be achieved at a higher PAM/MMT nanocomposite or PAM concentration. In addition, the final strength of the NC1/PEI gel was significantly higher than that of the PAM/PEI gel at the same conditions. This is mainly because the presence of MMT can reinforce the strength of the gel. The phenomenon that the strength of a gel can be reinforced by compositing inorganic materials was also found in previous studies.<sup>24,32</sup> Generally, the strength of a gel can be higher when the clay content of the polymer/clay composite increases.<sup>25,26</sup> However, the final strength of the NC1/PEI gel system was higher than that of the NC2/PEI gel system under the same concentrations of NC1 and NC2. Two factors led to this result. On one hand, a high MMT content resulted in a low PAM content when the total

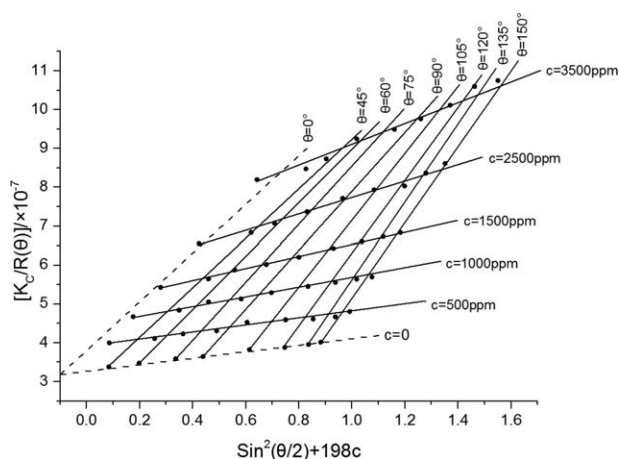


Figure 6. Zimm plot for PAM of NC2.

Table II. Effect of PAM/MMT Nanocomposite or PAM Concentrations on Gelation Performance

Type	Gel polymer concentration (wt %)	Strength code of gel (h)						
		0.5	1	2	3	5	8	12
NC1	1.0	A	A	A	A	G	H	H
	2.0	A	A	A	E	H	H	H
	2.5	A	A	A	E	I	I	I
	3.0	A	A	A	F	I	I	I
	4.0	A	A	C	G	I	I	I
NC2	1.0	A	A	A	A	A	G	G
	2.0	A	A	A	A	G	H	H
	2.5	A	A	A	A	H	H	H
	3.0	A	A	A	C	H	I	I
	4.0	A	A	A	F	I	I	I
PAM	1.0	A	A	A	B	E	E	de <sup>a</sup>
	2.0	A	A	E	F	F	F	F
	2.5	A	B	F	G	G	G	G
	3.0	A	C	F	G	G	G	G
	4.0	B	D	G	H	H	H	H

See gel strength codes in Table I. PEI concentration is 0.3 wt %.  
<sup>a</sup>“de” represents dehydrated gel.

concentration of PAM/MMT nanocomposite was constant, which meant that fewer crosslinking units could be achieved. On the other hand, the  $M_w$  of PAM of NC1 was larger than the  $M_w$  of PAM of NC2. The molecular coil size of PAM was larger when the  $M_w$  was higher, which resulted in a stronger three-dimensional structure.<sup>21</sup>

It can be observed in Figure 7 that the gelation time decreased as the PAM/MMT nanocomposite concentration increased. This can be explained by the high PAM/MMT nanocomposite concentration providing more crosslinking units, accordingly accelerating the gelation rate. Besides, it is noticeable that the

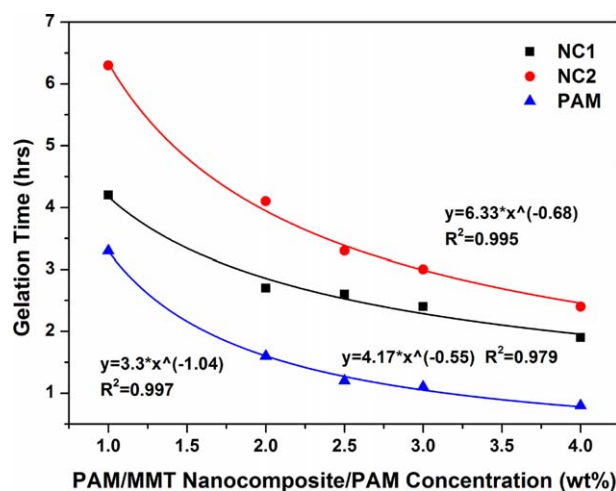


Figure 7. Power exponential relationship of gelation time versus PAM/MMT nanocomposite or PAM concentrations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

**Table III.** Effect of PEI Concentration on Gelation Performance

Type	Gel PEI concentration (wt %)	Strength code of gel (h)						
		0.5	1	2	3	5	8	12
NC1	0.30	A	A	A	E	H	H	H
	0.45	A	A	B	G	H	H	H
	0.60	A	A	D	G	I	I	I
	0.75	A	A	F	I	I	I	I
	0.90	A	B	F	I	I	I	I
NC2	0.30	A	A	A	A	G	H	H
	0.45	A	A	A	C	H	H	H
	0.60	A	A	A	E	I	I	I
	0.75	A	A	B	G	I	I	I
	0.90	A	A	E	H	I	I	I
PAM	0.30	A	A	E	F	F	F	F
	0.45	A	B	E	G	G	G	G
	0.60	A	D	H	H	H	H	H
	0.75	B	E	H	H	H	H	H
	0.90	B	E	H	H	H	H	H

See gel strength codes in Table I. Polymer concentration is 2.0 wt %.

gelation time of the NC/PEI gel system was remarkably longer than that of PAM/PEI gel system, which mainly resulted from the smaller PAM content of the NC/PEI gel system compare to the PAM/PEI gel system. In addition, MMT layers may have shielding effects on the acrylamide pendant groups of PAM, so the carbonyl carbon attached to the amide group is not easily attacked for PEI. This conjecture was suggested because the gelation time of the NC1/PEI gel system was longer than the PAM/PEI gel system even though the concentration of NC1 was about 1.34 times higher than that of PAM, which means the gelation time of both gel systems was not the same even though the PAM content of both gel systems was about equal. The gelation time can be represented by power exponential equations, as shown in Figure 7, in which  $x$  is the PAM/MMT nanocomposite or PAM concentration (wt %) and  $y$  is the gelation time (h). The reaction order of PAM is 1.04, which is similar to the result obtained by Al-Muntasheri *et al.*<sup>16</sup> In their study, the reaction order was around 1.0 for the PEI crosslinking PAM gel systems. However, the reaction orders of PAM/MMT nanocomposites are quite different. The reaction orders of NC1 and NC2 are 0.55 and 0.68, respectively. A previous study indicated that the value of the reaction order is greatly dominated by the polymer hydrolyzing degree.<sup>21</sup> Therefore, the existence of MMT layers may have effects on the reaction order similar to the polymer hydrolyzing degree.

#### Effect of PEI Concentration on Gelation Performance

In this section, the concentrations of NC1 and NC2 were kept at 2.0 wt %. The PEI concentrations were varied from 0.30 to 0.90 wt %. Meanwhile, PAM was also used for comparison. The experimental results are summarized in Table III and Figure 8.

The results show that the gelation time decreased as PEI concentration increased. This is because the chance of PEI attacking the

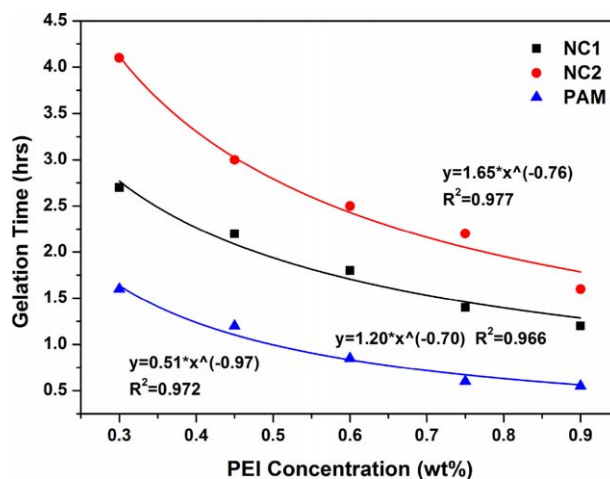
carbonyl carbon attached to the amide group increases with the increase of the PEI concentration, which results in a higher cross-linking reaction rate. Moreover, it can be found that the final gel strength was significantly improved when the PEI concentration was increased from 0.3 to 0.6 wt % for all gel systems, but there is no obvious change when the PEI concentration was increased from 0.6 to 0.9 wt %. This indicates that an extra-high concentration of PEI has a limited effect on improving gel strength. Besides, gel syneresis may result from explosive crosslinking when the PEI concentration is rather high. Therefore, too high of a PEI dosage is not recommended.

The gelation time can also be represented by power exponential equations as shown in Figure 8, in which  $x$  is the PEI concentration (wt %) and  $y$  is the gelation time (h). The reaction orders were 0.70, 0.76, and 0.97 for NC1, NC2, and PAM, respectively. The reaction order of the PAM/MMT nanocomposite was rather different from that of PAM, which further demonstrates that the existence of MMT layers has effects on the reaction order.

#### Thermal Stability

The thermal stability of gel systems was measured by the bottle test method at 120 °C. The experimental results are summarized in Table IV.

For NC2/PEI gels, a syneresis phenomenon was observed for all gels before 10 days, and syneresis occurred in just one day for most of the gels. This is because the stability of gels has much to do with the concentration of PAM.<sup>19</sup> But the PAM content of NC2 was relatively low and could not provide enough cross-linking units and thereby led to a weak gel structure. Also, the low  $M_w$  of PAM of NC2 resulted in a smaller effective hydrodynamic volume, which is the other reason for the instability of NC2/PEI gels.<sup>21</sup> NC1/PEI gels, which have more PAM content and higher  $M_w$  of PAM than NC2/PEI gels, showed superior thermal stability when the concentration of NC1 was higher than 2.0 wt %. Quite stable gels were obtained when the concentration of NC1 was increased to 4.0 wt %. The gels could



**Figure 8.** Power exponential relationship of gelation time versus PEI concentrations. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table IV.** Gelation Performance of NC/PEI Gel Systems

Type	Gel composition		Strength code of gel (days)											
	Polymer concentration (wt %)	PEI concentration (wt %)	1	2 <sup>a</sup>	3	4	5	10	20	30	40	50	60	90
NC1	1.0	0.3	H	de	—	—	—	—	—	—	—	—	—	—
		0.6	H	H	de	—	—	—	—	—	—	—	—	—
		0.9	I	de	—	—	—	—	—	—	—	—	—	—
	2.0	0.3	H	H	H	H	de	—	—	—	—	—	—	—
		0.6	I	I	I	I	de	—	—	—	—	—	—	—
		0.9	I	I	I	de	—	—	—	—	—	—	—	—
	3.0	0.3	I	I	I	I	I	I	I	de	—	—	—	—
		0.6	I	I	I	I	I	I	I	de	—	—	—	—
		0.9	I	I	I	I	I	de	—	—	—	—	—	—
4.0	0.3	I	I	I	I	I	I	I	I	I	I	I	I	
	0.6	I	I	I	I	I	I	I	I	I	I	I	I	
	0.9	I	I	I	I	I	I	I	de	—	—	—	—	
NC2	1.0	0.3	G	de	—	—	—	—	—	—	—	—	—	—
		0.6	H	de	—	—	—	—	—	—	—	—	—	—
		0.9	H	de	—	—	—	—	—	—	—	—	—	—
	2.0	0.3	H	H	de	—	—	—	—	—	—	—	—	—
		0.6	I	I	de	—	—	—	—	—	—	—	—	—
		0.9	I	de	—	—	—	—	—	—	—	—	—	—
	3.0	0.3	I	I	I	I	de	—	—	—	—	—	—	—
		0.6	I	I	I	I	de	—	—	—	—	—	—	—
		0.9	I	I	de	—	—	—	—	—	—	—	—	—
4.0	0.3	I	I	I	I	I	de	—	—	—	—	—	—	
	0.6	I	I	I	I	I	de	—	—	—	—	—	—	
	0.9	I	I	I	I	de	—	—	—	—	—	—	—	

See gel strength codes in Table I.

"—" is the simple form of "de"

<sup>a</sup>"de" represents dehydrated gel.

remain stable with a high strength for 90 days when the concentration of PEI was 0.3 or 0.6 wt %. According to the research of Al-Muntasheri *et al.*,<sup>33</sup> a PAM/PEI gel system can remain stable at 120 °C for more than 2 weeks only when the concentration of PAM is no less than 7.0 wt %. The reason that NC1/PEI gels could remain stable with a relatively low NC1 concentration is related to the MMT layers that were dispersed in the gels. On one hand, the incorporation of MMT into the polymer matrix can enhance the thermal stability by playing a role in insulation and as a barrier during decomposition.<sup>34,35</sup> On the other hand, gel syneresis is the process in which the gel compresses the liquid in its network structure and shrinks its volume. The existence of MMT layers in a gel structure can improve the rigidity of the gel structure and restrains the volume shrinkage, which results in a good thermal stability. A high PEI concentration is unnecessary when the gel is stable and strong enough with relatively low PEI concentration. Therefore, the gel system that consists of 4 wt % NC1 and 0.3 wt % PEI is recommended as a water-shutoff agent in high-temperature reservoirs.

#### Effect of Inorganic Salt Concentration on Gelation Performance

The gel system containing 4.0 wt % NC1 and 0.3 wt % PEI had a good thermal stability at high temperature, which was proved in the previous section. So this gel system was used to investigate the effect of TDS on the gelation performance in this experiment. The TDS of the prepared gelant solution was increased from 5000 to 35,000 mg/L by increasing the concentration of NaCl.

From Figure 9, it can be observed that the apparent viscosity of the NC1 solution at room temperature decreased with the increase of the TDS of the solution. This is because the PAM coils of NC1 will contract at high TDS, and the hydrodynamic volume of the polymer molecules becomes smaller. This characteristic of the NC1 solution has a positive effect on obtaining good injectivity of the NC1/PEI gel system.

The effect of TDS on gelation time is shown in Figure 10. The gelation time of the NC1/PEI gel system increased as the TDS

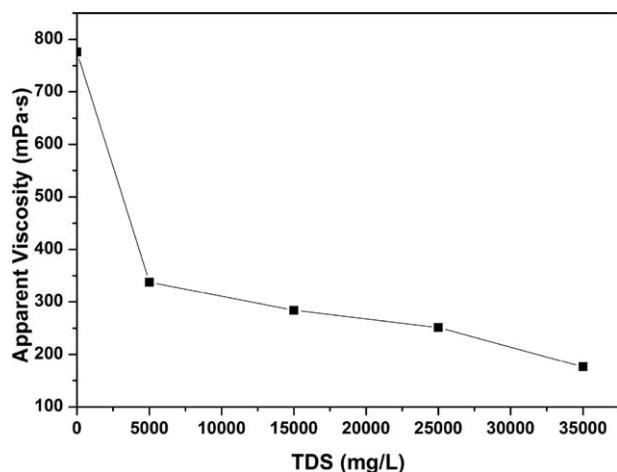


Figure 9. Effect of TDS on the viscosity of NC1 solution.

of the solution increased. This can be explained by the contracted PAM coils of NC1 making it difficult for PEI to permeate into it intermolecularly because of the macromolecule coil structure of PEI. The shrinkage degree of PAM is greater when the TDS is higher. As a consequence, the permeation ability of PEI constantly decreases, and thereby the gelation time increases correspondingly. The relationship of gelation time versus TDS for the PAM/PEI gel system at 120 °C was obtained from the study of Al-Muntasheri *et al.*,<sup>16</sup> which is also shown in Figure 10. Fitted lines were obtained by linear fitting of the experimental data from Al-Muntasheri's experiments and the present experiments. It can be found that the slope of the fitted line in the present experiments is larger than that of the fitted line of Al-Muntasheri's experiments, which means the effect of TDS on the NC1/PEI gel system is larger than on the PAM/PEI gel system. This phenomenon can be explained as follows. The negative charge on the MMT surface can generate electrostatic repulsion among the MMT layers, which results in a more stretched macromolecule network of NC1 than that of PAM. But the charge-screening effect on NC1 will be more and more obvious as the TDS of the solution increases, so the shrinkage degree of NC1 is greater than that of PAM, which makes NC1 more sensitive to TDS.

#### Gelation Performance Study after Flowing through Porous Media

The same NC/PEI gel system that consists of 4.0 wt % NC1 and 0.3 wt % PEI was used for the study in this section.

The microstructure of the original gel sample, gel sample 1A, and gel sample 2A is shown in Figure 11. The microstructure of the original gel sample, gel sample 1A, and gel sample 2A all present a network structure that contains a connected skeleton and many cavities. The entanglement of polymer chains was the main reason for the formation of the microstructure of the gel samples. The PAM chains that contained NC1 entangled together in the aqueous solution and formed the connected skeleton. Simultaneously, the MMT layers dispersed in aggregate in the network structure. Thus, some small, irregularly shaped particles can be seen attached to the skeleton. However, although the microstructure of the gel samples was similar, some difference could also have been found. The cavity sizes of gel sample 1A

and gel sample 2A were both bigger than that of the original gel sample, which may be because the disentanglement and degradation of polymer chains occurred when gel samples flowed through the core. Besides, the cavity shapes of gel sample 1A were more inhomogeneous than that of the original gel sample and gel sample 2A. This interesting phenomenon indicated that gel sample 1A was more affected than gel sample 2A when the gel samples flowed through the core. This finding was also reflected in the gelation performance of the original gel sample, gel sample 1A, and gel sample 2A, as shown in Table V. The final gel strength and gelation time of gel sample 1A were lower and longer than that of the original gel sample, whereas gel sample 2A could achieve the same gel strength (code I) as the original gel sample and only exhibited delayed gelation time. Generally, dilution, absorption, and shearing have significantly impacted the gelation performance of the gel system when the gel system has flowed through the porous media. However, after the gel sample 1A was flowed through the core, the saline water content in the core and the absorption capacity of the core were both decreased, so the effects of dilution and absorption on the gel sample 2A were weakened. As a result, gel sample 2A exhibited a different gelation performance from gel sample 1A. Generally, the effect of shearing on the gelation performance of a gel system is significant because shear degradation of the polymer takes place. Therefore, the gelation performance of a gel system will be obviously affected by the shearing.<sup>21,36</sup> Nevertheless, gel sample 2A could also achieve the same high gel strength as the original gel sample, which may result from the reinforcing effect of the dispersed MMT layers in gel.

From the gelation performance of the original gel sample, gel sample 1A, and gel sample 2A, a useful understanding can be obtained to guide the well-site application of the NC1/PEI gel system. When the gel system is injected underground, the concentration of NC1 and PEI should be relatively high in pre-slug to ensure that the gel strength can achieve a satisfactory state, and the concentration of NC1 and PEI in post-slug (the subsequent part of the injected gel solution) can be lower than that in pre-slug (the former part of the injected gel solution) to save costs.

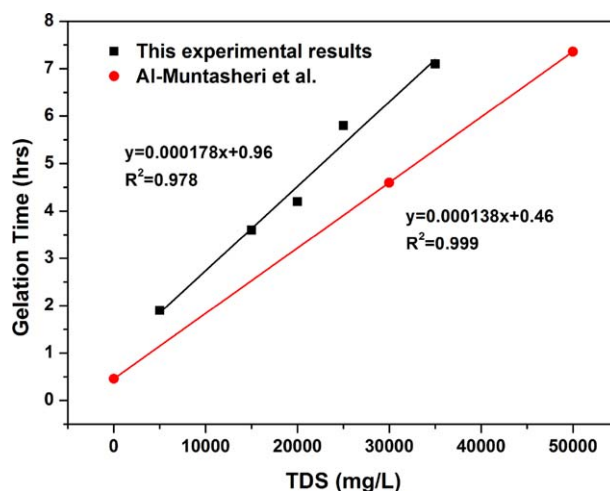
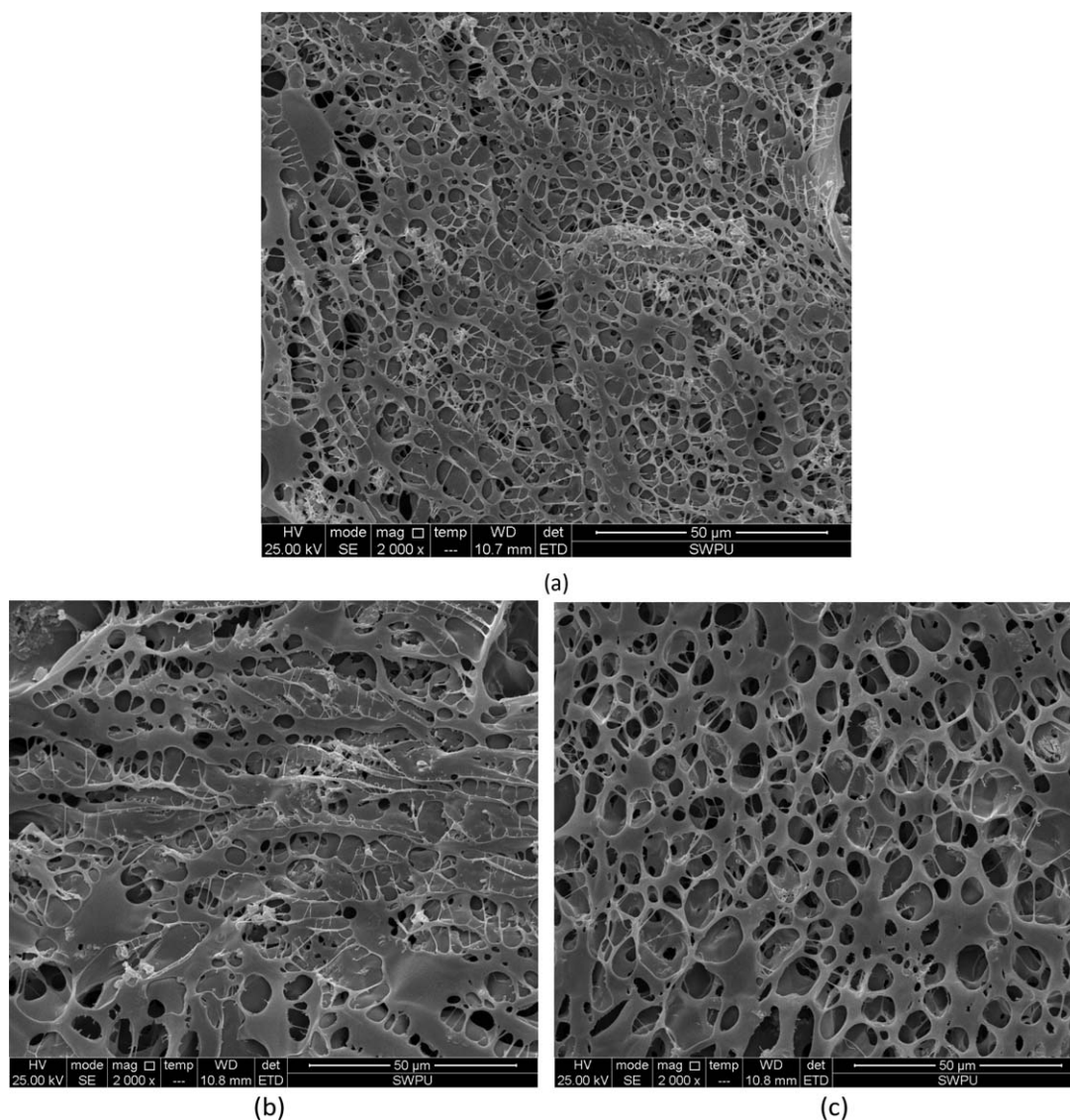


Figure 10. Effect of TDS on the gelation time. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]





**Figure 11.** Microscopic structure of gel samples (code A state): (a) original gel sample, (b) gel sample 1A, (c) gel sample 2A.

## CONCLUSIONS

The gelation performance of an NC/PEI gel system at the high temperature of 120 °C was investigated systematically in this study. The following conclusions are obtained:

- (1) The concentration of PAM/MMT nanocomposite and PEI has a great effect on the strength and gelation time of the NC/PEI gel system. The gelation performance of the NC/PEI gel system is much better than that of the PAM/PEI gel system under the same conditions.
- (2) Power exponential equations were obtained by fitting the relationship of PAM/MMT nanocomposite or PEI concentration versus gelation time curves. The reaction order of the NC/PEI gel system is different from the reaction order of the PAM/PEI gel system, which is related to the existence of MMT in the PAM/MMT nanocomposite.

**Table V.** Gelation Performance of NC1/PEI Gel Samples

Type	Strength code of gel (h)									
	0.5	1	2	3	4	5	6	8	10	12
Original gel sample	A	A	C	G	I	I	I	I	I	I
Gel sample 1A	A	A	A	D	H	H	H	H	H	H
Gel sample 2A	A	A	A	E	I	I	I	I	I	I

See gel strength codes in Table I.

- (3) The NC/PEI gel system that consists of 4.0 wt % NC1 and 0.3 wt % or 0.6 wt % PEI can remain thermally stable at 120 °C for 90 days. The dispersed MMT layers in the gel contribute a lot to the thermal stability of the gel.
- (4) The gelation time of the NC/PEI gel system can be delayed by increasing the TDS. The TDS has a greater effect on the gelation time of the NC/PEI gel system than that of PAM/PEI gel system.
- (5) The gelation performance after flowing through porous media of the NC/PEI gel system before injection and that of the subsequently injected gel system is different. The final gel strength decreases and the gelation time is delayed after the gel system before injection flows through porous media. However, the gel strength of the subsequently injected gel system does not decrease, and only the gelation time is delayed after flowing through porous media.

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