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The thermal gelation behavior and performance evaluation of High Molecular Weight Nonionic Polyacrylamide and Polyethyleneimine mixtures for indepth Water Control in Mature Oilfields

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Abstract: A delayed crosslinked polymer gel was developed for indepth water control in mature oilfields. The thermal gelation behavior of nonionic polyacrylamide (NPAM) and PEI was investigated, and sodium citrate (NaCit) was selected as a new retarder to prolong the gelation time. The gelation performance of NPAM/PEI gel system can be adjusted by the variation of NPAM or PEI concentration, and a quadratic model was developed by statistical analysis, which predict the gelation time of NPAM/PEI gel system. The obtained model showed high significance and good reliability as suggested by the F-ratio of 175.16 and high adjusted R-square value (0.9732). The decrease of the initial pH value of gelling solution leads to the weaker gel viscosity and longer gelation time due to the protonation of amine groups on the PEI chains. Increasing temperature resulted in higher gel viscosity but shorter gelation time. The addition of NaCit showed a good delayed gelation effect on the NPAM/PEI gel system, and the gel system in the presence of NaCit exhibited a good compatibility with injected and formation water. A dense three-dimensional structure was observed in matured NPAM/PEI/NaCit gel, and it could keep stable below 150℃. The gel system could effectively reduce the permeability (>95%) and restricted the flow of water after matured in natural cores.

Key Words: nonionic polyacrylamide; gelation time; plugging capacity; water shutoff

1. Introduction

Due to long-term water flooding for enhance oil recovery, a large number of high permeability channels are formed in the reservoir. It results in the increase of water productivity and the reduction of swept volume [1]. Moreover, excessive water production leads to many problems, such as pipeline and equipment corrosion, increased production cost and environmental pollution [2]. Therefore, it is important to reduce the water-cut in mature reservoirs. Due to the adjustable gelation time and gel strength, compatibility with formation fluids and wide range of applicable temperature, crosslinked polymer gels have been extensively used as one of the cost-effective technology for reducing water-cut and improving sweep efficiency in mature oilfield [3,4], especially the polyacrylamide-based crosslinked polymer gels [5].

The polyacrylamide contains a large number of amide groups (-CONH$_2$) and carboxyl groups (-COO$^-$) in its molecular chain after hydrolysis. It could crosslink with different types of crosslinkers, such as Cr^{3+} [6,7], Al^{3+} [8], Zr^{4+} [9] or phenolic resin [10-11] et al.. However, multivalent metal ions and phenolic resin are toxic. Thanks to the eco-friendly and high nucleophilicity of polyethyleneimine (PEI), PEI crosslinked polymer gels have obtained a huge interest for water control treatment [12].

Previous studies have shown that different acrylamide-based polymers were developed to form stable crosslinked polymer gels with PEI. For instance, the copolymer (PAtBA) synthesized by acrylamide (AM) and t-butylacrylate (tBA) could form a rigid gel with PEI at high temperature and exhibited excellent plugging capacity in porous media [13]. In addition, the copolymer prepared with AM and 2-acrylamido-2-methylpropane sulfonic acid (AMPS) [14] and the terpolymer synthesized by AM, AMPS and N-vinylpyrrolidone (NVP) [15] were reported to have the potential application at high temperature reservoirs (>100℃), respectively. However, these polymers are expensive.

As an in-expensive alternative, polyacrylamide (PAM) was utilized to replace the copolymer and terpolymer to crosslink with PEI, and the gel system composed of PEI and various polyacrylamides are suitable for wide temperature (23.3-130℃) [16-22]. To ensure the gelling solution permeate deep into the formation, the inorganic salts, such as NaCl or NH_4Cl, were added into the PAM/PEI gel system to delay the gelation time [16, 17, 21]. However, the retarding effect of NaCl was not satisfactory, while the addition of NH_4Cl reduced the gel strength significantly. Jayakumar et al. pretreated PEI with AMPS or dextran sulfate (DS), respectively, and then cross-linked with partly hydrolyzed polyacrylamide (PHPA), which significantly extended the gelation time of PHPA/PEI gel system [23, 24]. This approach is not conductive to large-scale application in oilfields due to the inconvenience of preparation and high cost.

Moreover, the structure-property of PAM has great influence on the thermal gelation of PAM/PEI gel systems. Jia et al. [19, 20] reported that the gel formed by high molecular weight HPAM and PEI showed better thermal stability than that formed by low molecular weight HPAM at 40 and 65℃ at the same concentration, due to its more complex network skeleton. The larger the molecular weight of polymer, the stronger the gel strength [22]. The dosage of polymer with high molecular weight is relative lower than that of low molecular weight polymer to obtain the same gel strength. It is favor of reducing the expenditure for water shutoff treatment.

However, the larger the molecular weight, the shorter the gelation time [22]. It is well known that the gelling solution prepared with high molecular weight PAM possesses high initial viscosity. It would makes difficult on the injection process for water shutoff treatment. Fortunately, the gel systems prepared with nonionic polyacrylamide (NPAM) were studied. The low initial viscosity before crosslinking and good shearing resistance of NPAM-based gels showed the potential application for indepth water control in mature reservoirs [25, 26].

We notice that the investigations of NPAM-based gel were concentrated in the crosslinking of NPAM and phenolic resin. No systematic investigation was reported on the crosslinking of NPAM and PEI. In addition, based on the existence of ionic interaction between the carboxylate groups ($-COO^-$) of polymer and the ammonium ions (NH_3^+) of PEI [27], organic acid salts may have the potential to be a retarder for prolonging the gelation time of PEI crosslinked gel. In this paper, the thermal gelation behavior of NPAM/PEI gel system is systematically investigated. Sodium citrate (NaCit) is selected as a new retarder to replace the traditional inorganic salts and delay the gelation time of NPAM/PEI system. The statistical analysis is conducted to develop the prediction mathematical model of gelation time, and the compatibility, microstructure, thermal stability and plugging capacity of this gel system are tested for water control treatment.

2. Materials and Methods

2.1. Materials

The nonionic polyacrylamide (NPAM) was purchased from Guangzhou Shuirun Chemical

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Technology Co., Ltd. (China), in which molecular weight is 12 million daltons (as provided by the manufacturer). A liquid form PEI with 50% purity was used as a crosslinker in this study, which provided by Guangzhou Mai Lichen CO., Ltd. (China), and its molecular weight is 70000. Additives including sodium chloride (NaCl), sodium citrate (NaCit), ammonium chloride (NH_4Cl) and hydrochloric acid (HCl) were supplied by Guo Yao Chemical Co., Ltd (China), which were AR grade. Fresh water, injected water or formation water were used in these experiments. The injected and formation water were provided by xinjiang oilfield, and their ionic content were given in **Table 1**. The natural cores used in core flowing experiments were also provided by xinjiang oilfield. No further purification treatment was performed for all chemical agents used in these experiments.

Table 1. The ionic content of injected and formation water

Water type	CO_3^{2-} (mg/L)	HCO_3^- (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^+/K^+ (mg/L)	TDS (mg/L)
Injected water	1216.25	—	274.38	27.03	95.65	15.27	984.6	2613.18
Formation water	6792.4	146.7	52.44	71.69	43.36	27.64	10468.7	17602.93

2.2. Methods

2.2.1. Preparation of Gelling Solutions

All gelling solutions were prepared at room temperature. A certain concentration of NPAM was added into water and stirred until the homogeneous viscous solution was obtained. Then, the prepared polymer solution was aging for 12 hours at room temperature. After that, a predetermined amount of PEI was mixed with the polymer solution with 10 minutes of stirring. Note that PEI was diluted as a 5% aqueous solution prior to use. The pH value of gelling solution was adjusted by adding 1mol/L hydrochloric acid. Note that the salt additives were preferentially soluble in water while prepared the samples.

2.2.2. Determination of Gelation Time and Gel Viscosity of NPAM/PEI Gel System

Apparent viscosity measurements were conducted to quantitatively evaluate the gelation performance of NPAM/PEI gel system. The gelation process transformed from solution to gel was characterized by the variation of apparent viscosity correlated to reaction time. In this study, 80 mL volume of gelling solution was prepared and moved to a sample adapter which could be sealed and set it in oven at specific temperature. the apparent viscosity was measured at regular intervals by brookfield viscometer DVⅡ. **Figure 1** showed the crosslinking reaction process of NPAM/PEI gel system. The gelation time was defined as the time at which corresponds to the inflection point on the plot of apparent viscosity versus time [10]. The gel strength was represented by the viscosity corresponding to the equilibrium period of the gelation curve.

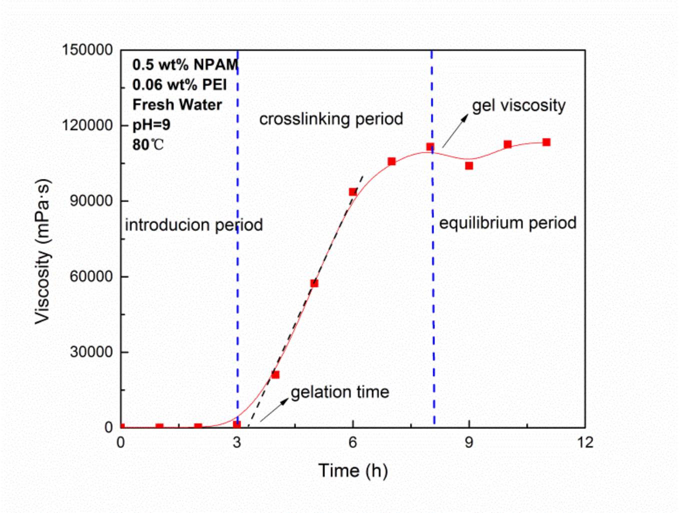


Figure 1. Crosslinking reaction process of the NPAM/PEI gel system

2.2.3. Statistical Analysis

The experiments were designed with two factors (polymer and crosslinker concentration) and five levels, as shown in **Table 2**. All experiments were carried out as designed scheme, and the obtained data of gelation time were fed into the “datafit” software. A mathematical model was obtained by using this approach, which could be utilized to express the comprehensive relationship between the gelation time and NPAM and PEI concentration by the following second-order polynomial equation [28, 29]:

$$GT = \alpha_0 + \sum_{i=1}^{k} \alpha_i C_i + \sum_{i,j=1}^{k} \alpha_{ii} {C_i}^2 + \sum_{i,j=1}^{k} \alpha_{ij} C_i C_j + \varepsilon \qquad (1)$$

where GT is gelation time; $\mathrm{C_i}$ and $\mathrm{C_j}$ are the NPAM and PEI concentration; α_0, α_i, α_{ii}, α_{ij} and ε are intercept, linear, quadratic and interaction constant coefficients, and the statistical random error term, respectively.

The correlation curve of experimental and predicted gelation time was plotted to assess the predictability of the generated model. Moreover, variance analysis (ANOVA) was performed to evaluate the significance of the developed model by Fish’s criterion (F-test), and the accuracy with 95% confidence level was determined using p-value (probability error). The R-square and adjusted R-square were calculated to confirm the reliability of the model.

2.2.4. Scanning electron microscope (SEM)

SEM was performed to observe the microstructure of NPAM/PEI gel. Before examination, the gel samples should be dried and coated with gold palladium film in vacuum. Representative sections were photographed for evaluation.

2.2.5. Differential Scanning Calorimetry (DSC)

The thermal stability of NPAM/PEI gel system was measured by DSC in this study. The matured gel was sliced off and placed in hermetic pan after as the gelling solution matured at 80℃ for three days. The measurement was conducted at the temperature range of 40-200℃ at the scanning rate of 5℃/min.

2.2.6. Core Flowing Experiment

The core flowing experiments were conducted to determine the water control capacity of NPAM/PEI gel by plugging rate. The water flooding rate was set as 0.5 ml/min. The schematic of the core flowing experiment was shown in **Figure 2**, and the detailed experiment steps were given as follow:

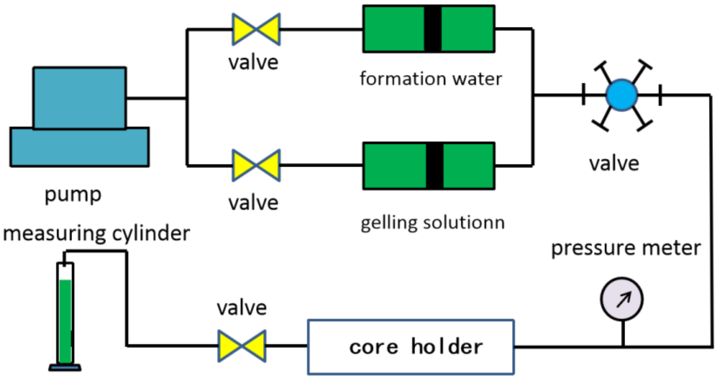


Figure 2. The schematic of core flowing experiment

(1) The cores were washed, dried and weighted. Injected water was used to saturate the cores in vacuum, and their pore volumes (PV) and porosity were determined using weight method.

(2) The water flooding was carried out until the inlet pressure and output fluid reached a stable condition. The initial permeability of the core was calculated according to Darcy's law in the form:

$$k = \frac{q\mu L}{A(P_1 - P_2)} \tag{2}$$

where k is the permeability in mD, q is the flow rate in ml/min, μ is the viscosity of flooding water in mPa•s, L is the core length in cm，A is the cross-sectional area of core in cm^2, P_1, P_2 are the pressure of the core inlet and outlet in MPa, respectively.

(3) A 0.5 PV of gelling solution was injected into the core, and 0.5 PV injected water was injected to replace the gelling solution. After that, the core holder was sealed and placed at 80℃ until the gel matured.

(4) Regained-permeability testing was conducted by water flooding as step (2). The plugging rate (ϕ) of NPAM/PEI gel system was evaluated using the following relation:

$$\phi = \frac{k_0 - k_1}{k_0} \times 100\% \tag{3}$$

The residual resistance factor (RRF) which reflects the ability of plugging agent to reduce the permeability of porous medium was computed as:

$$\mathrm{RRF} = k_0 / k_1 \tag{4}$$

where k_0, k_1 denote the permeability of core before and after gel treatment, respectively, in mD.

3. Results and Discussion

Two main factors, polymer and PEI concentration, were considered to evaluate the gelation performance of NPAM/PEI gel system. Each factor was varied in five levels, while other influencing parameters were kept constant. All gelling solutions were prepared in fresh water at room temperature, and the experiments were conducted at 80℃. The specific experimental scheme and results are illustrated in **Table 2**. The low initial viscosity is observed as the NPAM concentration varies from 0.3 to 0.7 wt%, which gives a good injectivity of the gelling solutions.

Table 2. Experimental scheme and results

NPAM concentration (wt%)	PEI concentration (wt%)	Initial Viscosity (mPa·s)	Gelation time (hour)	Gel viscosity ($\times 10^3$ mPa·s)
0.3	0.02	11.8	11	27.02
	0.03	11.4	9.4	33.726
	0.04	11.4	7.2	40.081
	0.06	10.7	5	69.547
	0.08	10.5	3.9	55.242
0.4	0.02	16.0	8.8	32.254
	0.03	15.8	6.5	38.274
	0.04	15.3	5.1	70.508
	0.06	16.5	3.9	80.832
	0.08	14.8	3.4	102.587
0.5	0.02	22.3	6.6	46.676
	0.03	22.5	5.3	70.641
	0.04	23.4	4.2	102.708
	0.06	25.2	3.2	111.609
	0.08	22.6	3	137.169
0.6	0.02	46.9	6.2	49.249
	0.03	43.2	4.5	87.003
	0.04	43.9	3.6	123.668
	0.06	45.4	3	135.19
	0.08	44.8	2.8	203.426
0.7	0.02	73.0	6	53.054
	0.03	73.1	4.4	105.372
	0.04	72.7	3.5	160.43
	0.06	74.3	2.8	182.256
	0.08	71.4	2.5	267.564

3.1. Mathematical modeling of NPAM/PEI Gel System

Based on the data of gelation time (GT) in **Table 2**, the attempt was conducted on fitting the data of GT with a quadratic polynomial model (**equation (1)**). A prediction model of gelation time is developed that is represented by the following equation:

$$\mathrm{GT} = 25.93 - 43.18\mathrm{C}_A - 316.42\mathrm{C}_B + 165.17\mathrm{C}_A\mathrm{C}_B + 27.14\mathrm{C}_A{}^2 + 1598.19\mathrm{C}_B{}^2 \qquad (5)$$

In this model, the variables C_A and C_B represent polymer and crosslinker concentration, respectively. $\mathrm{C}_A\mathrm{C}_B$ is considered as the interaction of the two variables. It can be seen that the interaction between two variables has significant effects on the response (GT). In addition, the coefficients of the crosslinker terms in the model are higher than that of polymer terms, so that the effect of PEI on GT is greater than NPAM.

The predicted and experimental gelation time were plotted in **Figure 3**. The slop of the linear fitting curve is, 0.9787, very close to 1. This indicates that the predicted data is fitted well with the experimental data. The coefficients of multiple determination (R^2) and adjusted multiple determination ($\mathrm{R_a}^2$) for the developed model are 0.9788 and 0.9732 (given in **Table 3**), respectively, which are verified the reliability of this model.

The statistical significance of the developed mathematical model was further assessed by ANOVA. As shown in **Table 3**, it can be concluded form high F-ratio value (175.16), the obtained model is highly significant. Furthermore, the p-value of <0.05 indicates the quadratic model is able to explain 95% of the variability in gelation time for the designed NPAM/PEI gel system.

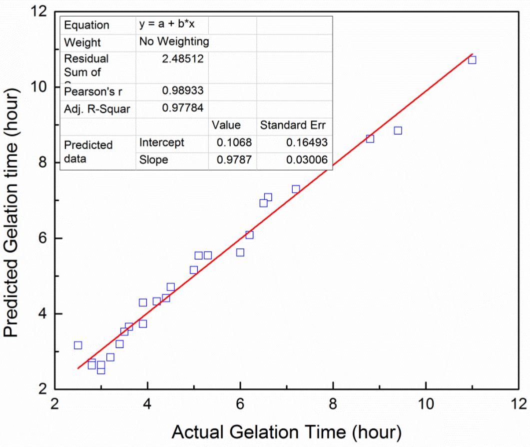


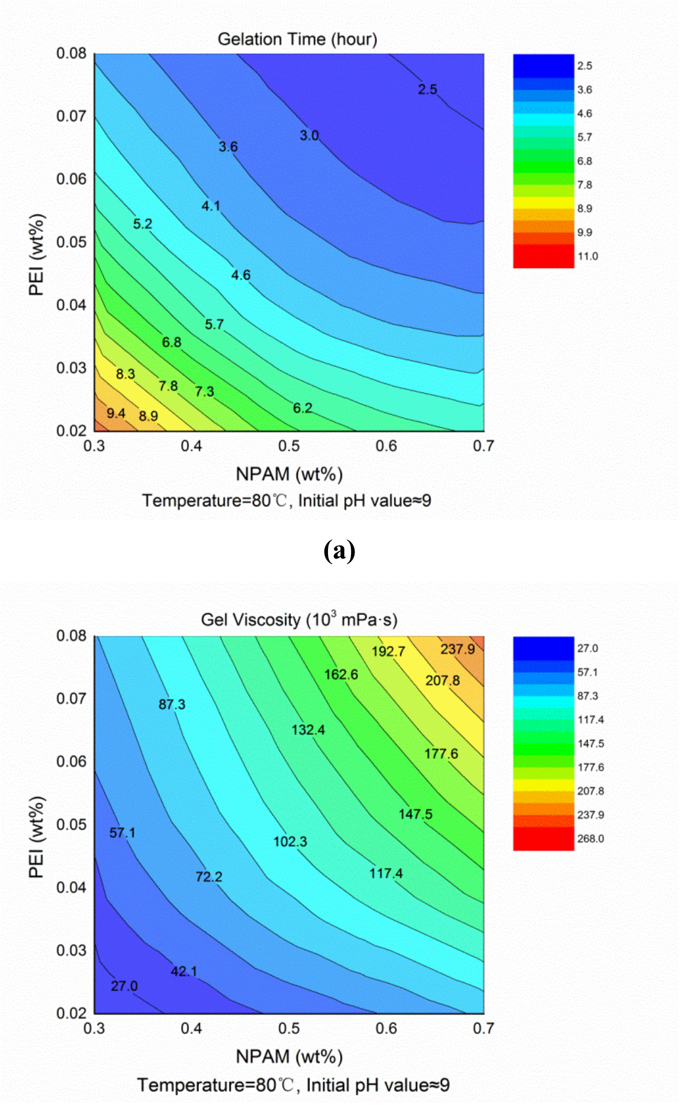
Figure 3. Predicted value based on the obtained model vs. actual value of GT

Table 3. The results of ANOVA

ANOVA	Sum of square	DOF	Mean square	F-ratio	p-value
Regression	117.04	5	23.41	175.16	<0.0001
Residual	2.54	19	0.1336		
total	119.58	24			
Data fit	R^2	R_a^2	Residual error		
	0.9788	0.9732	0.3656		

3.2. Effects of polymer and crosslinker concentration

The experimental data in **Table 2** were extracted and plotted as a function of NPAM and PEI concentration, respectively. **Figure 4(a)** and **4(b)** present the contour maps of gelation time and gel viscosity, respectively, which reflect the interaction between polymer and crosslinker concentration. It is observed that the contour of gelation time varies from 11 to 2.5 hour from bottom left to top right in **Figure 4(a)**, while the contour of gel viscosity correspondingly increases from 27.02 to 267.56 Pa·s in **Figure 4(b)**. The shorter gelation time and higher gel viscosity were obtained with the increment of NPAM concentration as high polymer concentrations provide more crosslinking sites, which accelerate the crosslinking rate and make the crosslinking networks more strength. The increase of PEI concentration has a similar effect to that of polymer on the gelation performance of NPAM/PEI gel system. That is because that more amine groups are available for crosslinking with increasing PEI concentration. It should be noted that excessive PEI would cause the occurrence of over-crosslinking [19].



(a)

(b)

Figure 4. Contour map of gelation time and gel viscosity for NPAM/PEI gel system. (**a**) Contour map of gelation time; (**b**) Contour map of gel viscosity

3.3. Effect of Initial pH Value

Five samples composed of 0.7wt% NPAM and 0.08wt% PEI were prepared with fresh water. The pH value of these gelling solutions was adjusted from 9 to 5 by adding hydrochloric acid. The gelation performance of all samples were measured at 80℃, and the results were shown in **Figure 5**. It can be seen that the NPAM/PEI gel system in acidic has a longer gelation time than that in alkaline and neutral. However, the gel viscosity tenders to be weaker when the initial pH value varies from alkaline to acidic. The gelation time varies slightly as the initial pH value decreases from 9 to 7, while an obvious elongation is observed on the gelation time as the initial pH value changes from 7 to 5. This observation is due to the fact that a large number of amine groups (-NH_2) on the PEI chains are protonated in acidic and lost the activity of nucleophilic substitution, which lead to the decrease of the available crosslinking sites. Consequently, the longer gelation time and weaker gel viscosity are obtained. As reported by Suh et al., the protonation ratios of PEI at pH value of 9 and 7 were 97% and 85%, respectively, while that at pH 5 was 52% [30]. This result provides an effective evidence for the above explanation.

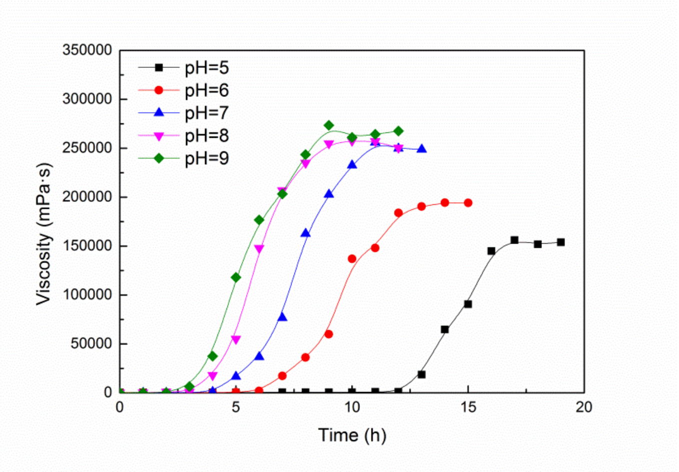


Figure 5. Gelation performance of NPAM/PEI gel system at different initial pH values

3.4. Effect of Temperature

Two NPAM/PEI gel systems were selected with the formulations of 0.5/0.06 wt% and 0.7/0.08 wt%. The effect of temperature on the gelation process of NPAM/PEI gel system were performed at the range of 50 to 80℃. The experimental results are given in **Table 4**. As compared with the samples at 50℃, the gelation time of two formulas at 80℃ are decreased by 5.5 and 5 times, respectively. It is revealed that high temperature plays an accelerative effect on the gelation process of NPAM/PEI gel system. Moreover, increasing temperature is contributed to form a stronger gel. It is believed that the effective collision between polymer and PEI molecular enhances with increasing temperature, which improves the crosslinking rate and crosslinking density. Therefore, the higher gel viscosity and shorter gelation time are obtained.

Table 4. Experimental results at different temperatures

Gel systems	Temperature (℃)	Gelation Time (hour)	Viscosity ($\times 10^3$ mPa·s)	R^2	E_a (kJ/mol)
Formula 1: 0.5wt% NPAM + 0.06wt% PEI	50	17.6	57.686	0.9529	51.91
	60	10.5	74.852		
	70	7.2	104.703		
	80	3.2	111.609		
Formula 2: 0.7wt% NPAM + 0.08wt% PEI	50	12.6	155.138	0.8919	49.39
	60	9	204.382		
	70	6.1	239.317		
	80	2.5	267.564		

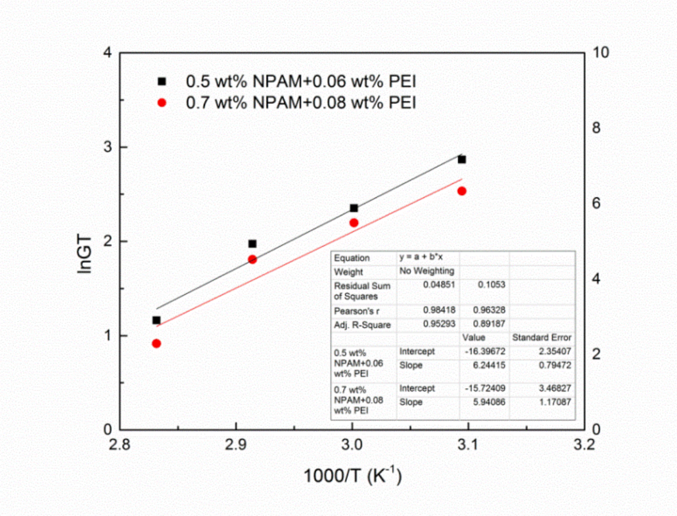
The Arrhenius-type equation can be utilized to predict the gelation time with different temperature [16]:

$$GT = A\exp\left(E/RT\right) \tag{6}$$

where E is the activation energy in kJ/mol, R is the universal gas constant in kJ/(mol•K), T represents the absolute temperature in K, and A is the frequency factor in hour. Logarithmic transformation of **equation (6)** can be expressed as:

$$\ln(GT) = \ln A + E/RT \tag{7}$$

The logarithm data of GT in this study is extracted and fitted to the reciprocal of absolute temperature, and the plot of ln(GT) vs 1/T was given in **Figure 6**. The data of GT are fitted well with **equation (5)**. The activation energies of two formulas are calculated to be 51.91 and 49.39 kJ/mol, respectively. These values are lower than the data obtained by Al-Muntasheri et al. [16], which indicates that NPAM with high molecular weight is easier to react with PEI.



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0.04851	0.1053	
Pearson's r	0.98418	0.96328	
Adj. R-Square	0.95293	0.89187	
		Value	Standard Error
0.5 wt% NPAM+0.06 wt% PEI	Intercept	-16.39672	2.35407
	Slope	6.24415	0.79472
0.7 wt% NPAM+0.08 wt% PEI	Intercept	-15.72409	3.46827
	Slope	5.94086	1.17087

Figure 6. The plot of ln(GT) vs 1000/T

3.5. Effect of retarder

To prolong the gelation time of NPAM/PEI gel system and ensure it migrated into the depth of reservoir, sodium citrate (NaCit) was selected as a retarder. The dosages of NaCit were loading at the range of 0.25 to 1.0 wt%. All samples were prepared with fresh water with the formulation of 0.5 wt% NPAM and 0.06 wt% PEI. The experiments were conducted at 80℃, and the results were given in **Figure 7**. The gelation time of NPAM/PEI gel system is prolonged significantly with the increment of NaCit concentration. Compared to the sample with salt-free (3.2 hour), the gelation time was retarded to 21.3 hour with the addition of 1.0 wt% NaCit, which increased by approximately 6.6 times. The gelation time varies linear with the concentration of NaCit, and the relationship is expressed as follow:

$$\mathrm{GT} = 3.58 + 18.6\mathrm{C}_{NaCit} \tag{8}$$

where C_{NaCit} is the concentration of NaCit in mg/L.

To further discuss the retarding capacity of NaCit on NPAM/PEI gel system, the samples in the present of NaCit, NaCl and NH_4Cl were compared at the same mass fraction in **Figure 8**. It can be observed that the retarding capacity of NaCit is better than that of NaCl. Despite the addition of NH_4Cl results in the longest gelation time, a significant reduction in gel viscosity is also observed. The retarding effect of NaCl is mainly due to the charge shielding effect of Na^+ on carboxyl groups (COO^-) of NPAM chains as shown in **Figure 9(a)**. However, the molar concentration of Na^+ in NaCit is lower than that of NaCl at the same mass fraction. It suggests that the effect of NaCit on the gelation time of NPAM/PEI gel system is not only due to the charge screening of Na^+, the presence of citrate ions also plays a key role on the delaying of the gelation time. Avadiar reported the PEI molecular adsorbed on the surface of silica particles could remove the citric ions in solution acted as a bridging agent [31]. It indicated that the interaction between citric ions and PEI due to the opposite charge of their molecules. Moreover, there are three

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carboxylate groups on citric ion. Two possible scenarios, intramolecular and intermolecular interaction, may occur between the carboxylate groups of citrate ions and the ammonium groups on PEI molecules, as illustrated in **Figure 9(b)**.

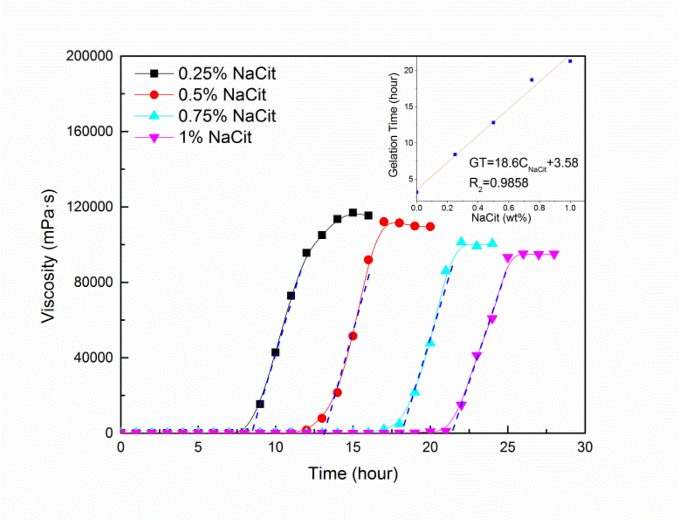


Figure 7. Effect of NaCit on gelation performance of NPAM/PEI gel system

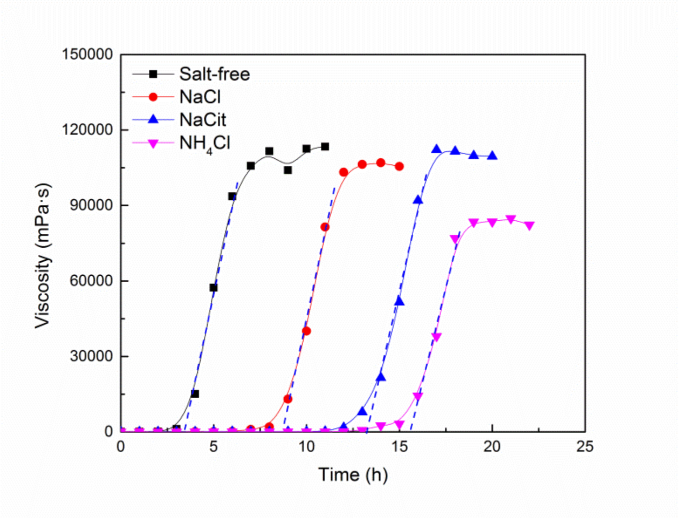
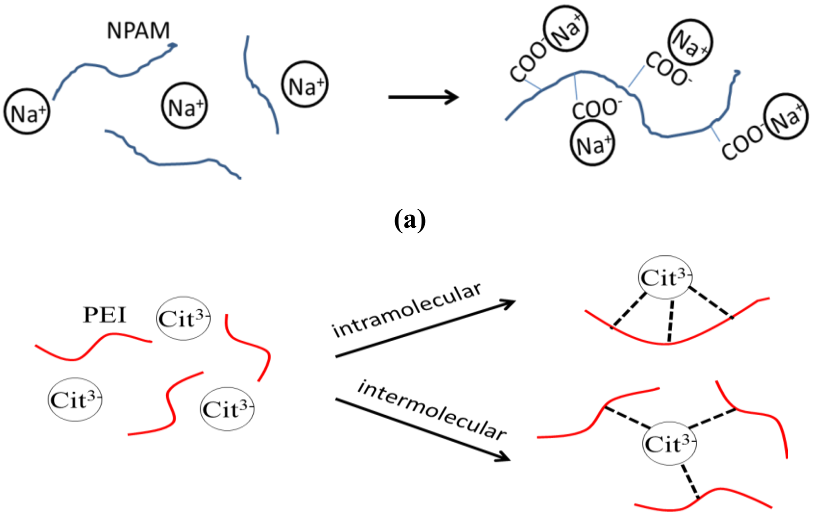


Figure 8. Comparison of different types of retarder



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(b)

Figure 9. Schematic of interaction of sodium ions and citrate ions on NPAM/PEI gel system. (**a**) Charge shielding effect of sodium ions on NPAM; (**b**) complexation of citrate ions and PEI

3.6. Compatibility with formation water

Two gelling solutions were prepared with the injected and formation water, respectively. The gel system was composed of 0.5wt% NPAM, 0.06wt% PEI and 0.5wt% NaCit. The gelation process of these two samples were measured at 80℃, and the results were shown in **Figure 10**. Comparing with the gel prepared with fresh water (Figure 4, pH=9), two gels in these experiments have a longer gelation time, and the equilibrium viscosity of the gel prepared with formation water decreases significantly. That is because the large amount of metal cations in the formation water plays strong charge shielding effect on NPAM molecules, causing the molecular chains of polymer to coil seriously, which reduced the available crosslinking amide groups (-CONH$_2$). Nevertheless, both of two gels are observed to form the bulk gels and show good viscoelasticity property as suggested by the tongue phenomenon. It indicates that the NPAM/PEI/NaCit gel system have a good compatibility with the injected and formation water.

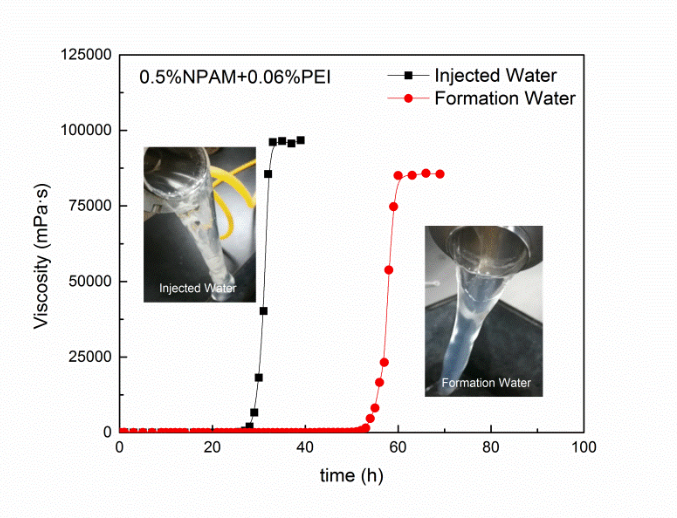

Figure 10. Gelation performance of NPAM/PEI/CitNa gel system in injected and formation water

3.7. Microstructure of the bulk gel

The microstructure of the bulk gel was observed by SEM. The bulk gel sample was composed of 0.5% NPAM, 0.06% PEI, 0.5% CitNa and matured at 80℃. As shown in **Figure 11 (a)**, a remarkable tongue phenomenon of crosslinked polymer gel is observed while gradually inverting the sample adapter containing the gel sample. It indicates that the formed gel possesses a good viscoelasticity, which contributes to bridge across the pore throats and restrict the flow of water in high permeability zone of the formation. **Figure 11 (b) and (c)** shows the microstructure of this gel system. The dense three-dimensional network is built by the transamidation of amide groups of NPAM and amine nitrogen of PEI. Many pores with size of 1-3 μm are distributed in the network structure of the gel. This kind of microstructure is conductive to lock the free water and keep the gel stable.

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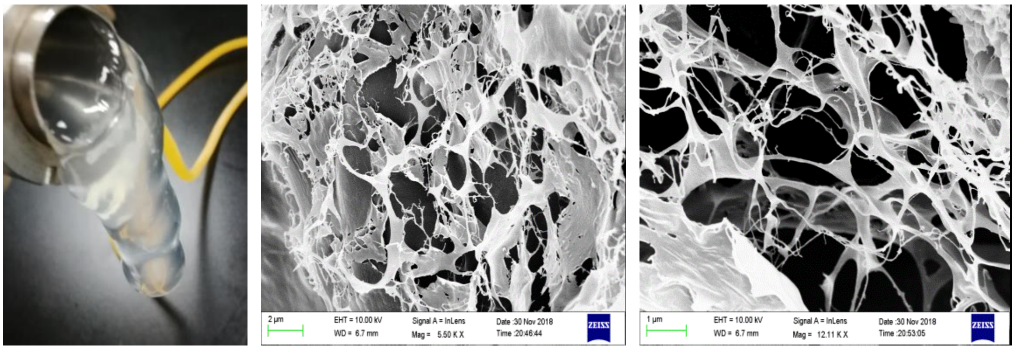

(a) **(b)** **(c)**

Figure 11. Microstructures of gel system composed of 0.5wt% NPAM, 0.06wt% PEI and 0.5wt% CitNa. (**a**) the bulk gel and the microstructure of gel system are magnified up to (**b**) 5500 times, and (**c**) 12110 times, respectively.

3.8. Thermal stability of NPAM/PEI gel system

The thermos-analysis was conducted by DSC. The matured gel system in this experiment was composed of 0.5wt% NPAM, 0.06wt% PEI and 0.5wt% NaCit. **Figure 12** shows the DSC thermosgram of NPAM/PEI gel system. A endothermic peak is observed at 153.09℃, and the onset temperature of this peak is around 150℃. It indicates that the three-dimensional network which formed by the crosslinking of NPAM and PEI is stable below 150℃. The thermal degradation of the gel sample occurs as the temperature exceeds 150℃. When the temperature reaches to 153℃, the chemical bonds of the gel are almost destroyed, and it changes from colloidal to liquid state. Therefore, the gel system should be applied below 150℃.

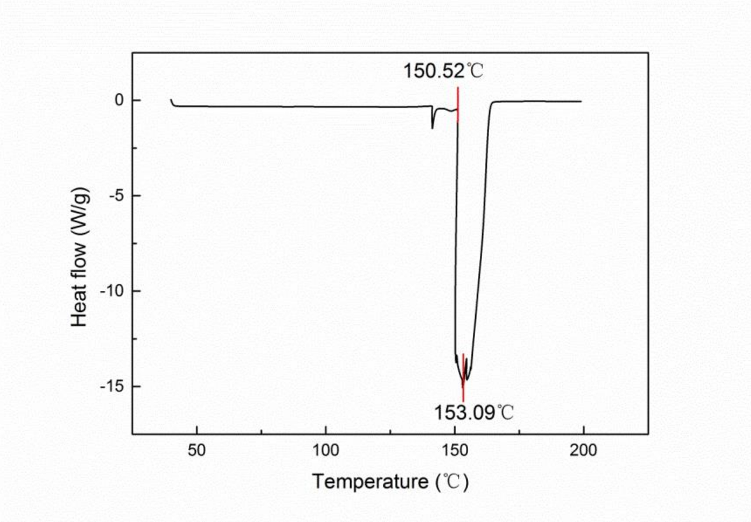

Figure 12. DSC curve of the matured NPAM/PEI gel

3.9. Plugging Capacity of NPAM/PEI Gel System

Two cores with similar permeability were selected and numbered core1 and core2, and the plugging capacity of two gel systems were evaluated by the core flowing experiment, respectively. The injected water was used as the displacement water in these experiments. As shown in **Table 5**, the variation of the permeability before and after gel injection suggests that the gel system effectively blocks the high permeability channels of the cores after matured, and forces the

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subsequent brine water into the low permeability zone. Consequently, a high water flow resistance is obtained. The plugging rates of the two gels are more than 95%, and their residual resistance factors (RRF) are above 25. The results indicate that NPAM/PEI gel system has a good plugging capacity. Moreover, the higher the gel viscosity, the larger the plugging rate. The plugging mechanism of crosslinked polymer gel mainly depends on the retention of gel in high permeability channel and adsorption on the rock surface [18]. The higher residual resistance factor suggested that the stronger gel generally has better blocking effect in porous media.

Table 5. The plugging capacity of NPAM/PEI gel system

Gel System	Core	Size		Porosity %	Permeability ($\times 10^{-3}\mu m^2$)		Plugging rate (%)	RRF
		Length (cm)	Diameter (cm)		Before gel injection	After gel injection		
0.5wt%NPAM+0.06wt% PEI+0.5%NaCit	Core1	4.74	2.54	28.73	66.88	2.35	96.49	28.45
0.7wt%NPAM+0.08wt% PEI+0.5%NaCit	Core2	4.88	2.54	28.50	68.82	1.58	97.70	43.56

4. Conclusions

The gel system composed of NPAM, PEI and NaCit shows low initial viscosity (<75 mPa·s), adjusted gelation time (2.5-21 hour) and gel viscosity (27.02-267.56×10^3 mPa·s). A prediction model of gelation time which reflects the effect of NPAM and PEI and their interaction is developed through the statistical analysis. The mathematical model fit perfectly with the experimental data. The obtained model is highly significance approved by the F-ratio of 175.16, and is capable of explaining 95% of the variability in gelation time (p-value of <0.05). The reliability and accuracy of the model are verified by the high R-square value (0.9788) and high adjusted R-square value (0.9732). The gelation time is elongated as the initial pH value of gelling solution varies from alkaline to acid, whereas the gel viscosity tender to be weaker. Increasing temperature accelerates the gelation process of NPAM/PEI gel system. The addition of NaCit is effectively retarded the gelation time of NPAM/PEI gel system, which is due to the synergy of the charge shielding effect of sodium ions on NPAM molecules and the complexation of citrate ions and PEI. The dense microstructure of the gel with the formulation of 0.5wt% NPAM, 0.06wt% PEI and 0.5wt% NaCit is observed, and it can keep stable below 150℃. Moreover, this gel system showed a good compatibility with the injected and formation water. The permeability of the core is reduced more than 95% and the water flow resistance increases significantly after the NPAM/PEI gel formed in the natural cores. Thus, the delayed crosslinked polymer gel which composed of NPAM, PEI and NaCit has the potential to apply for indepth water control in mature oilfields.

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