Preparation of high-temperature gels for enhanced oil recovery using methyl etherized melamine-formaldehyde resin

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Abstract. Polymer gels are the most commonly used materials in the petroleum industry for reservoir conformance control and resolving excessive water production problems. In this study, high-temperature gels were prepared with HPAM or AM/AMPS as the gel-forming agent, methyl etherified melamine-formaldehyde resin (MEMFR) as the crosslinker, and nano-silica as the stabilizer, and their properties were evaluated. The results showed that HPAM-MEMFR gels were unstable at 110°C in a brine of 20665 mg/L. AM/AMPS-MEMFR gels are stable at 110°C, with gelation time ranging from 15 h to 92 h and storage modulus ranging from 3.6 Pa to 50 Pa. AM/AMPS-MEMFR gel has less than 10% dehydration after aging at 110°C for 90 days, almost no shrinkage in volume, and a significant increase in strength, making it suitable as a gel material for enhanced oil recovery.

Keywords: High-temperature gel; gel evaluation; conformance control; enhanced oil recovery.

1. Introduction

Due to the existence of fractures and high permeability areas in the formation, oil fields developed by water injection always have the problem of excessive water production [1]. The injection of plugging agents from oil recovery wells or water injection wells to seal high permeability layers or fractures is an important measure to improve the effectiveness of water injection development. A key to this technology is the development of high-performance plugging agents [2,3]. Gels are one of the most commonly used plugging agents and are formed by the reaction of a polymer and a crosslinker [4]. Gels used at high temperatures are generally prepared from organic crosslinkers. These crosslinkers include polyethyleneimine (PEI), water-soluble phenolic resins (WSPR), and combined systems of hydroquinone (HQ) and hexamethylenetetramine (HMTA).

PEI gel is friendly to the environment but has a high price, which is mainly used in offshore oil fields at present [5]. Although WSPR crosslinker is inexpensive, its application is more restricted, with disadvantages such as short storage time (less than 3 months) and high residual formaldehyde content in the product (greater than 5%). HQ and HMTA can react at high temperature to form a phenolic resin intermediate, which can play a crosslinking role similar to that of WSPR. These crosslinkers are currently used in high-temperature formations [6], but there are problems such as increasing HQ prices and restrictions on the purchase, transportation, and use of HMTA because it is a hazardous chemical.

In addition to the above-mentioned crosslinkers, methyl-etherified melamine-formaldehyde resin (MEMFR) can also crosslink with polymers containing hydroxyl and amide groups to produce gels. MEMFR is often used as an adhesive for rubber, wood, and paper in the industry, with formaldehyde content below 1% and a storage time up to one year. It was used as a gel crosslinker, but the application in the oil field did not attract attention. In this study, high-temperature gels were prepared using partially hydrolyzed polyacrylamide (HPAM) and acrylamide/2-acrylamide-2-methylpropanesulfonic acid (AM/AMPS) crosslinked with MEMFR, respectively. The performance of the gel was evaluated in terms of gel formation time, strength, and stability in a brine of 20 665 mg/L salinity at 110°C. The prepared gel can be used as an alternative system for reservoir conformance control.

2. Experimental

2.1 Materials

The HPAM used in the experiment was purchased from the product of Anhui Jucheng Fine Chemical Co., Ltd. with a hydrolysis degree of 12-14% and a relative molecular weight of 1.4×10^7-1.5×10^7 g/mol. The AM-AMPS was supplied by Qingdao Qucheng Technology Co., Ltd. with an AMPS content of 10% and a relative molecular weight of 6×10^6-8×10^6 g/mol. The crosslinker MEMFR for gel preparation was provided by Shandong Baomao Biochemical Co. In addition, nano-silica was

added to the gel as a stabilizer with a particle size of 10-20 nm, which was obtained from Qingdao Jinfangge Technology Co.

The gelants in this study were prepared using synthetic brine with a salinity of 20665 mg/L. The ionic composition of the brine is shown in Table 1. Synthetic brine was prepared from potassium chloride, sodium chloride, sodium bicarbonate, anhydrous sodium sulfate, magnesium chloride hexahydrate, and calcium chloride anhydrous, supplied by Sinopharm Chemical Reagent Co.

Table 1 Composition of synthetic brine

Ions (mg/L)						TDS (mg/L)
Na^+/K^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	HCO_3^-	Cl^-	
6359	632	196	68.5	140.5	13269	20665

2.2 Methods.

2.2.1 Preparation of gels

Synthetic saline, MEMFR, and nano-silica were weighed according to the composition of the gelant and mixed well by stirring them. Then, HPAM or AM/AMPS were slowly added to the mixture while stirring. Next, the mixture was stirred at 120 r/min for 2 hours to obtain a homogeneous gelant. Finally, the gelant was dispensed into ampoules using a syringe and sealed using an alcohol torch for performance evaluation.

2.2.2 Evaluation of gels

The gels were evaluated in terms of gelation time, strength, and stability. The gelation time of the gels was determined visually using Syndansk's gel strength code [7] as a standard. The time required for the gel to reach the F level of strength at 110°C was recorded as the gelation time.

The strength of the gel was characterized by strength code and storage modulus. The energy storage modulus of the gels was measured by an Anton paar MCR92 rheometer equipped with a parallel plate system at 25°C. The test was conducted in amplitude sweep mode with a measurement gap of 1 mm, a fixed oscillation frequency of 10 rad/s, and an amplitude range of 0.1% to 1000%.

The stability of the gels was characterized by the dehydration ratio of the gels after aging for different times at 110°C. The dehydration rate was defined as the ratio of the mass of water removed from the gel after aging to the mass of the initial gelant.

3. Results and Discussion

3.1 HPAM-MEMFR gel

HPAM is the most commonly used water-soluble polymer in the oilfield. Therefore, HPAM was first used as a gel-forming agent crosslinked with MEMFR to prepare the gel. The methyl ether group in MEMDR will hydrolyze

under acidic conditions to form hydroxymethyl, as shown in Fig. 1. These hydroxymethyl groups can crosslink with the amide groups on the polymer to form a gel, and the crosslinking reaction is shown in Fig. 2. We made up 16 gel formulations by orthogonal design, in which polymer concentration range of 0.4%-1.0%, cross-linker concentration range of 0.2%-0.8%, and stabilizer concentration fixed at 1%, and their gelation time and strength are shown in Table 2.
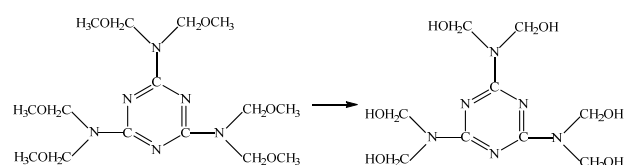

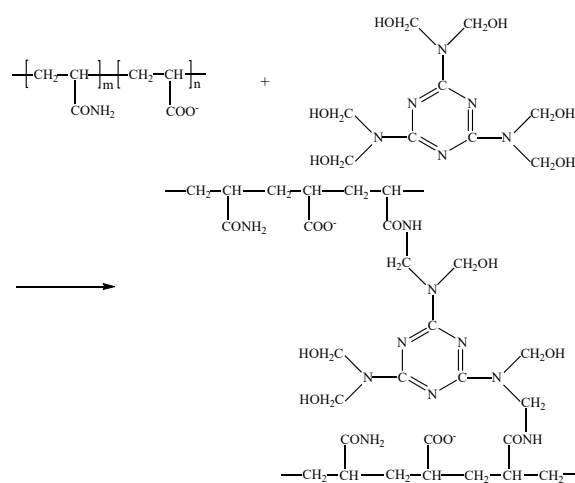Fig. 1 Hydrolysis of methyl ether groups.

Fig. 2. Crosslinking reaction of HPAM with MEMFR.

Table 2. Composition, gelation time, and strength of gels.

No.	$w(HPAM)/\%$	$w(MEMFR)/\%$	$w(SiO_2)/\%$	Gelation time/h	Strength code
1	0.4	0.2	1	86h-E	E
2	0.4	0.4	1	50h	G
3	0.4	0.6	1	47h	G
4	0.4	0.8	1	41h	G
5	0.6	0.2	1	50h	G
6	0.6	0.4	1	47h	G
7	0.6	0.6	1	23h	H
8	0.6	0.8	1	18h	H
9	0.8	0.2	1	25h	G
10	0.8	0.4	1	10h	H
11	0.8	0.6	1	7h	H
12	0.8	0.8	1	6h	H(I)
13	1.0	0.2	1	23h	G
14	1.0	0.4	1	9h	H
15	1.0	0.6	1	6h	H(I)
16	1.0	0.8	1	5h	H(I)

It can be seen that the reaction of HPAM with MEMFR can form gels with high strength. The gelation

time of the gels at 110°C was in the range of 5-50 h, and the gel strength was between G-I level. However, these gels were not stable at high temperatures, and most of them showed significant syneresis when aged at 110°C up to 8 days, as shown in Fig. 3.
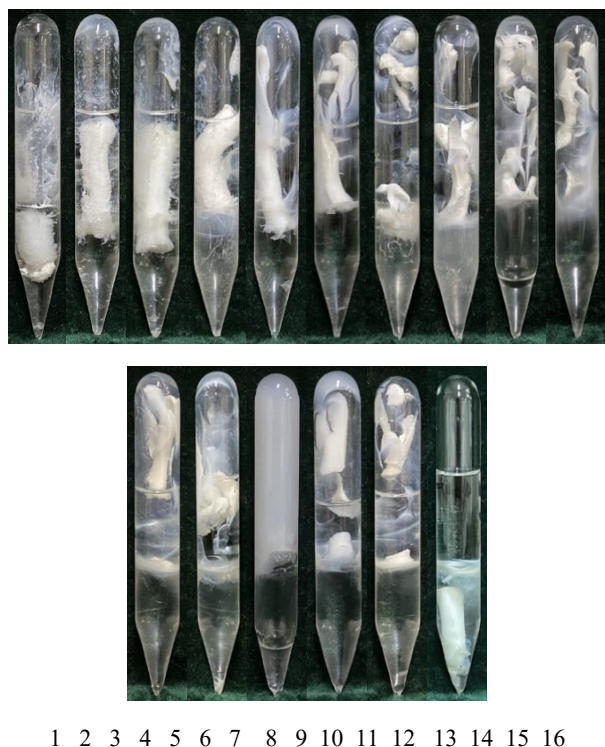

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16

Fig. 3. The state of HPAM-MEMFR gel after aging at 110°C for 8 days.

3.2 AM/AMPS-MEMFR gel

Considering the instability of HPAM-MEMFR gels, the gels were considered to be prepared by crosslinking AM/AMPS with MEMFR for better thermal stability. Sixteen gels were prepared following the gel composition in Table 2 after replacing HPAM with AM/AMPS. The gelation time, strength, and stability of these gels were investigated.

3.2.1 Gelation time

The gelation times of gels formed by crosslinking AM/AMPS with MEMFR are given in Figure 4 and compared with the gelation times of HPAM-MEMFR gels.
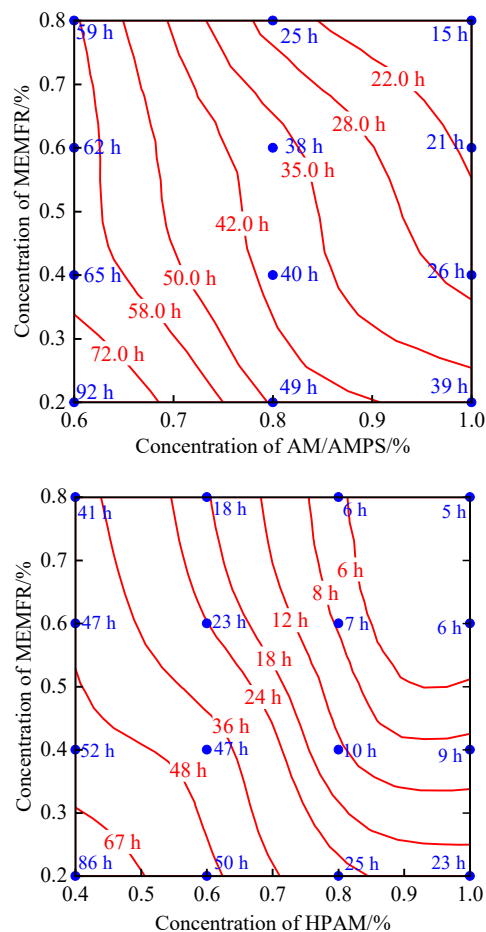
(a) AM/AMPS-MEMFR   (b) HPAM-MEMFR

Fig. 4. Gel formation time of AM/AMPS-MEMFR gels and HPAM-MEMFR gels.

By comparison, although the molecular weight of AM-AMPS is slightly lower than that of HPAM, the gel formation of AM/AMPS is significantly slower than that of HPAM for the same polymer and cross-linker concentrations, which is related to the electrostatic repulsion of the cross-linker and polymer in water. The sulfonic acids on AM/AMPS molecules are strongly ionized groups, and their charged nature is less affected by electrolytes in water than the carboxylic acids on HPAM molecules. Therefore, the electrostatic repulsion between AM/AMPS and MEMFR is higher than that of HPAM, which hinders the crosslinking reaction between the crosslinker and the polymer.

3.2.2 Gel strength

The storage moduli of the gels prepared from AM/AMPS and MEMFR were determined after aging at 110°C for 5 and 90 days, respectively, as shown in Fig. 5.

The storage modulus of the gels aged for 5 days ranged from 3.6 Pa to 50.0 Pa. Except for the gels with polymer concentrations of 0.6% and 0.8% and MEMFR concentrations of 0.2%, the storage modulus of all the gels could be more than 10 Pa, which belongs to strong gels. The gel strength gradually increased with the increase of

aging time. The gel storage modulus after aging at 110°C for 90 days ranged from 42.5 Pa to 645.4 Pa, showing a substantial increase in strength. This is because the primary amide on the polymer will hydrolyze under high-temperature conditions, and the carboxylate generated by hydrolysis will chelate with Ca^{2+} and Mg^{2+} in the brine, enhancing the crosslink density of the gel.
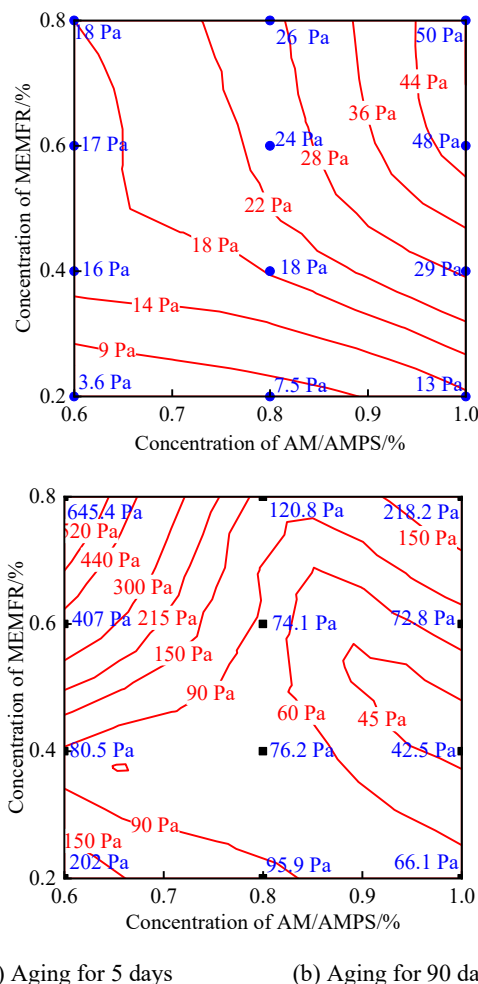

(a) Aging for 5 days   (b) Aging for 90 days

Fig. 5. Storage moduli of AM/AMPS-MEMRF gels aged at 110°C for different times.

(a) Aging for 15 days   (b) Aging for 90 days

Fig. 6. Dehydration ratios of AM/AMPS-MEMRF gels aged at 110°C for different times.

3.2.3 Gel stability

To evaluate the gel stability formed by AM/AMPS and MEMFR, their dehydration ratios after aging at 110°C for 15 and 90 days were measured, as shown in Fig. 6.
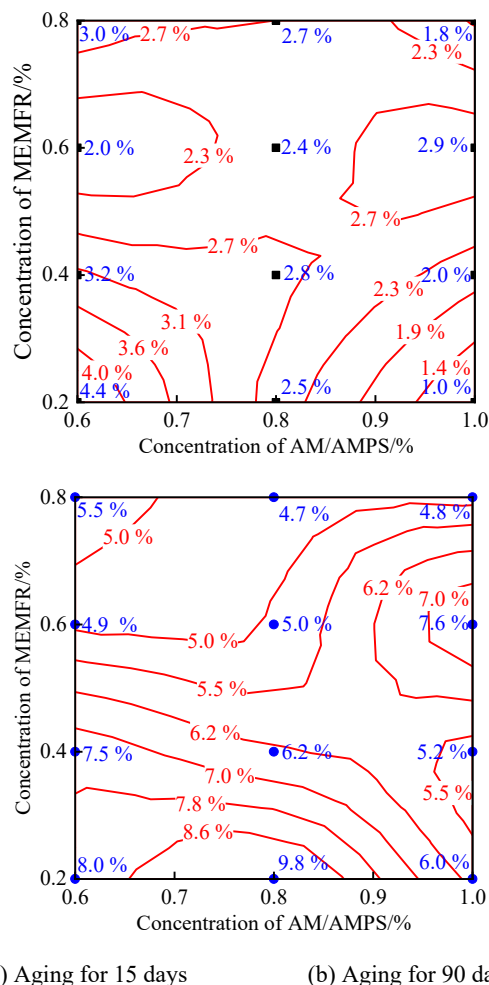
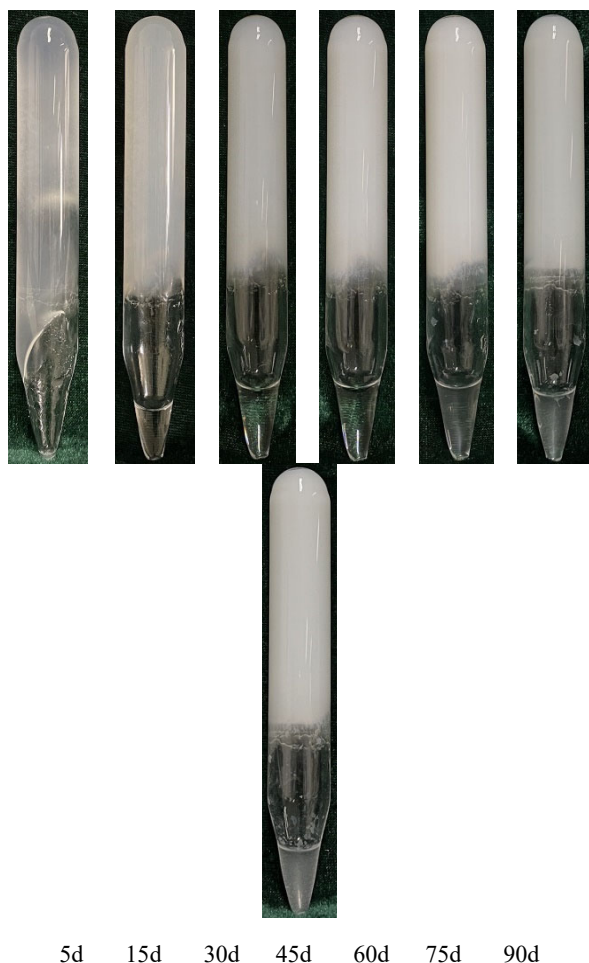5d   15d   30d   45d   60d   75d   90d

Fig. 7. The state of gel aged at 110°C for different times.

The dehydration rate of the gel formed by AM/AMPS and MEMFR was less than 5% after aging at 110°C for 15 days and less than 10% after aging for 90 days. Their stability was significantly better than the gels formed by HPAM and MEMFR. Figure 7 shows the states of the gels composed of 0.6% AM/AMPS, 0.2% MEMFR, and 1.0% SiO2 aged at 110°C for different times. The overall volume of the gel remained unchanged and the strength increased, although small dehydration occurred. Therefore, we believe that the stability of AM/AMPS-MEMFR gels is sufficient to support their application for enhanced oil recovery.

4. Summary

Based on the above results and discussions, the following conclusions were obtained：

(1) Gels can be prepared by using HPAM as the gel-forming agent and MEMFR as the cross-linking agent. However, HPAM-MEMFR gels are unstable under high-temperature conditions and exhibit severe syneresis after aging at 110°C for 8 days.

(2) High-temperature stable gels can be prepared by crosslinking AM/AMPS with MEMFR. AM/AMPS-MEMFR gels have a gelation time range of 15 h-92 h, a storage modulus range of 3.6 Pa-50 Pa, and a dehydration ratio of less than 10% after 90 days of aging at 110 °C.

(3) AM/AMPS-MEMFR gels showed almost no volume shrinkage and a significant increase in gel strength after aging at 110°C, making them suitable as a gel system for enhanced oil recovery.

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