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Stabilization Mechanism and Rheological Behavior of Temperature- and Salinity-Resistant Gels Based on AM/AMPS Polymers

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Abstract: Gel treatment represents a significant technical method for addressing the issue of excessive water production in oilfields. The stability and plugging properties of the gel are pivotal factors in determining the effectiveness of the treatment. In this study, two acrylamide/2-acrylamide-2-methylpropanesulfonic acid (AM/AMPS) copolymers with different AMPS content were crosslinked with hydroquinone (HQ) and hexamethylenetetramine (HMTA) to prepare gels adapted for high-temperature and high-salinity reservoirs at 110 °C in brine with a salinity of 250 000 mg/L. The comparison of the performance of the two gels showed that with the same polymer and crosslinker concentrations in the gel, the gelation time of the AM/AMPS copolymer with 60% AMPS content (CP60) was longer than that of the copolymer with 30% AMPS content (CP30). The gel strength was also lower but the thermal stability was better. A water-flooding experiment was conducted to compare the plugging capabilities of the two gels in a porous medium. The results indicated that, under identical conditions, the plugging pressure difference of the CP30 gel in the porous medium was greater than that of the CP60 gel. However, when the cross-linking agent concentration was 0.4%, there was a significant difference in gel strength between the two gels, whilst their residual resistivity coefficients in the porous medium were relatively similar. Rheological analysis indicated that this phenomenon was attributable to differences in the rheological properties of the two gels. As gel strength increased, the CP30 gel became more brittle, whilst the CP60 gel became more ductile. Analysis of the gels' rheological behavior elucidated the mechanism by which gel rheology influences

plugging performance. Finally, Fourier transform infrared spectroscopy was employed to elucidate the stabilization mechanisms of the two gels. Based on the insights gained from this study into gel plugging and stabilization mechanisms, methods can be developed to modulate gel properties, thereby providing better guidance for the application of gels in water shutoff in oilfields.

Keywords: Temperature-resistant and salinity-resistant gel; AM/AMPS; Conformance control； Stabilization mechanism; Rheological properties

1. Introduction

Oil fields in western China are rich in oil resources but the reservoirs are very deep with harsh environments. Reservoir temperatures and water salinity in these fields often exceed 100 °C and 200,000 mg/L, respectively. With the development of long-term water injection in oil fields, excessive water production has become an increasingly serious problem that requires an effective solution. Polymer gels are commonly used for reservoir conformance control and the prevention of excessive water production. (Amir et al., 2019; Bai et al., 2015; El-Karsani et al., 2013; Norman et al., 2006) Because gel properties can be controlled by adjusting the gel components, they have a wide range of applications.

In high-temperature and high-salinity reservoirs, acrylamide (AM)-based polymers, such as partially hydrolyzed polyacrylamides (HPAM), often encounter hydrolysis and oxidative degradation problems. (Jouenne et al., 2016; Moradi-Araghi and Doe, 1987; Ryles, 1988; Seright and Skjevrak, 2015； Unomah et al., 2018) Normally, at temperatures above 60 °C, the amide groups on the polymer chains gradually hydrolyze to carboxylate groups, with the hydrolysis rate sharply increasing with the temperature. Moreover, the carboxylate produced by amide hydrolysis chelates with divalent cations in the brine, leading to polymer precipitation and syneresis of the gel (Moradi-Araghi and Doe, 1987; Ryles, 1988). Therefore, to improve the stability and inhibit the degradation and precipitation of polymers in high-temperature and high-salinity environments, polymers have been synthesized using more stable monomers (e.g., 2-acrylamide-2-methylpropanesulfonic acid (AMPS) and N-vinylpyrrolidone (NVP)) copolymerized with AM (Doe et al., 1987; Dupuis et al., 2017; Gaillard et al.,

2010; 2014; 2015; Moradi-Araghi and Doe, 1987; Rodriguez et al., 2018; Sandengen et al., 2018; Seright et al., 2021). Among them, the AM/AMPS copolymer and AM/AMPS/NVP terpolymer have exhibited good temperature and salinity resistance. Sandengen et al. (Sandengen et al., 2017; Sandengen et al., 2018) reported that the stability of AM/AMPS copolymers at high temperatures increased with increasing AMPS monomer content. The viscosity half-life of the AM/AMPS copolymer containing 70% AMPS was approximately 50 days at 120 °C in synthetic seawater. The polymer stability further increased with an AMPS content of 80% (Sandengen et al., 2018). Vermolen et al. (Vermolen et al., 2011) and Gaillard et al. (Gaillard et al., 2014) reported that AM/AMPS/NVP terpolymers containing more than 35% NVP remained stable at 120 °C for one year. Therefore, AM/AMPS copolymers and AM/AMPS/NVP terpolymers have become the most widely used primary agents for preparing temperature- and salinity-resistant gels.

In practical applications, in addition to the gel's inherent properties, its plugging performance in porous media is also a major focus of attention. The gel's plugging performance is influenced not only by its strength but is also closely related to its complex rheological behavior. Therefore, characterising the rheological behavior of gels is crucial for elucidating the mechanisms underlying gel plugging and for establishing methods to control the performance of gel plugging. A gel is a viscoelastic material whose rheological behavior is significantly influenced by the structure and proportions of its components. The rheological properties of gels can be characterised using methods such as large-amplitude oscillatory shear tests, creep and creep recovery tests, and others. (Hyun K, et al., 2002; Ewoldt R H et al., 2010; Wathier M et al., 2010) However, there remains a lack of research into the mechanisms by which rheological behavior influences plugging effectiveness. Consequently, research is required to elucidate the patterns by which gel rheological behavior influences plugging performance, thereby establishing methods to control gel plugging performance by regulating the gel's composition and structure.

In this study, two AM/AMPS copolymers with different AMPS content were selected and prepared by crosslinking with HQ and HMTA in 250 098 mg/L of brine at 110 °C. The differences in the gelation time, strength, thermal stability, and plugging ability of the prepared gels were evaluated. Subsequently, rheological testing methods were employed to analyse the differences in the rheological properties of the two gels. An analysis of the gels' rheological behavior explained the differences in their plugging

performance within porous media, elucidating the mechanism by which gel rheology influences plugging performance. Finally, Fourier transform infrared spectroscopy and Beer's law were utilised to analyse the stability mechanism of the gels at high temperatures. Based on the insights gained from this study into the mechanisms of gel plugging and stability, methods can be developed to regulate the plugging performance and stability of gels by controlling the proportions of gel components and the polymer structure. This will facilitate the improved application of gels in high-temperature, high-salinity reservoirs.

2. Experimental

2.1 Materials

The polymers used in this study were AM/AMPS copolymers CP30 and CP60 with molecular weights ranging from 6×10^6 to 8×10^6 g/mol and AMPS contents of 30% and 60%, respectively. They were supplied by Qingdao Qucheng Technology Co., Ltd. The HQ and HMTA were analytical purity-grade reagents from Aladdin. Thiourea (TH), sodium chloride, anhydrous calcium chloride, magnesium chloride hexahydrate, sodium bicarbonate, and sodium sulfate from Sinopharm Chemical Reagent Co. were used for oxygen removal and to prepare the synthetic brine.

All gelants were prepared from synthetic brine with a total salinity of 250098 mg/L. The composition of synthetic brine is listed in Table 1.

Table 1 Composition of synthetic brine

Ion content (mg/L)						Total dissolved solids
Cl^-	SO_4^{2-}	HCO_3^-	Na^+	Ca^{2+}	Mg^{2+}	(mg/L)
153 642	500	43	79 129	14 756	2 028	250 098

2.2 Methods

2.2.1 Preparation of gels

Following the predetermined gel formulation, mix HQ, HMTA, TH, and synthetic saline until fully dissolved. Then, stir the solution at 400 rpm while slowly adding the polymer powder. Finally, stir the solution at 120 rpm for 2 hours to produce a uniform gel solution. Every 20 g of gel solution is sealed in an ampoule and placed in an oven at 110 ℃ for aging to evaluate gel performance. In this study, multiple samples of each gel were prepared for comparison and observation.

2.2.2 Evaluation of gels

The evaluation of a gel's basic performance characteristics primarily focuses on gelation time, gel strength, and gel stability. The gelation time was determined by visual observation of the gel strength (Sydansk's gel-strength codes (Sydansk, 1990)). The time required for the gel strength to reach the F-level was defined as the gelation time.

The gel strength was characterized by the storage modulus in the linear viscoelastic region (LVER) of the gel. The storage modulus of the gel was measured at 25 °C using an Anton Paar MCR92 rheometer equipped with a 25 mm diameter parallel-plate module system. Tests were conducted using the Large-Amplitude Oscillatory Shear (LAOS) mode, with the following test conditions: a measurement gap of 1.00 mm, a shear amplitude range of 1%~1000%, and a fixed oscillation frequency of 10 rad/s.

The gel stability at different stages was characterized by the dehydration ratio, which is the ratio of the mass of water removed from the gel after aging and the mass of the initial gelant.

2.2.3 Gel dehydration and drying

The gels prepared in this study contain a large amount of brine that needed to be dehydrated and desalted prior to the analyses by FTIR spectroscopy. The following procedure was used to dehydrate and desalt the gels and minimize their structural changes. The gel was first soaked in distilled water 8–10 times, followed by soaking in anhydrous ethanol 5–7 times. Each soaking time was 4–5 h. The volume ratio of the distilled water or anhydrous ethanol and the gel was 10:1. Next, the gels were dried in a vacuum drying oven at 50 °C for 10 h. Finally, the dried gel was ground into a powder for further testing.

2.2.4 FTIR analysis

All the samples for FTIR measurements were pretreated by the press method. The dried gel powder was thoroughly mixed with potassium bromide at a mass ratio of 1:100. Then, the mixed powder was ground and pressed into a mold to form translucent sheets. The FTIR spectra of the gels were measured in the spectral range of 400–4000 cm^{-1} with a NEXUS FTIR spectrometer (Thermo Nicolet Corp., USA) at 25 °C and a spectral resolution of 4 cm^{-1}.

2.2.5 NMR analysis

The liquid NMR carbon spectra of the polymers were determined with a Bruker

AVANCE III™ 400 M NMR spectrometer. A 3% polymer solution was prepared using D_2O and loaded into the NMR tube prior to testing. The polymer carbon spectrum was then determined at 298 K via distortionless enhancement by polarization transfer, including the detection of the quaternary nuclei pulse sequence (DEPTQSP) with 10496 repetitions.

2.2.6 Cryo-SEM analysis

The morphological analysis of the gels was performed by SEM (Hitachi SU8010, Japan). Water was removed from the gel by rapid freezing at −160 °C with liquid nitrogen and vacuum sublimation to maintain the gel structure. The dried lyophilized gel was then coated with nanogold and imaged by SEM.

2.2.7 Rheology tests

The LAOS test method was described in section 2.2.2 .

The creep and creep recovery tests of the gels and the viscosity testing of the polymer solutions were performed using an Anton Paar MCR92 rheometer at 25 °C. The creep and creep recovery tests were performed using the same parallel-plate module system and sample preparation methods in the LAOS test. In the creep test, a fixed shear stress was applied to the gel and held for 300 s. This was followed by the creep recovery test, in which the shear stress was instantaneously reduced to 0 Pa and held for 600 s.

The viscosity of the polymer solution was determined using a concentric cylinder module system with a rotor diameter of 39 mm. The prepared polymer solution of approximately 40 mL was added to the circular cylinder and subjected to a rotary shear test. The shear rate ranged from 0.05 to 50 s^{-1}.

2.2.8 Flooding experiments

The plugging ability of the gel in porous media was characterized by the maximum plugging pressure difference and residual resistance factor (F_{RR}), which were determined by flooding experiments. First, a sand-packed model with a length of 15 cm, inner diameter of 1 cm, and permeability of approximately 1–2 μm^2 was prepared, and the brine permeability (k_{wi}) was measured. Then, 1 pore volume (PV) of gelant was injected into the sand-packed model at a flow rate of 0.4 mL/min. Next, the sand-packed model was sealed and heat-treated in an oven at 110 °C for seven days to solidify the gel. Finally, the excess gel was cleaned from both ends of the model and pipelines, and the water-flooding experiment was conducted at a water injection rate of 0.4 mL/min.

The pressure at both ends of the sand-packed model was recorded. The pressure difference at 50 PV of water injection was used to calculate the brine permeability (k_{wa}) of the sand-packed model after gel plugging. The F_{RR} is defined as the ratio of the sand-packed model permeability before and after gel plugging (i.e., k_{wi}/k_{wa}). The entire experiment was conducted at 110 °C. The test system pressure was set at 0.5 MPa to maintain the water in a liquid state at high temperatures.

3. Results and Discussion

In this study, gels were prepared by crosslinking two AM/AMPS copolymers (CP30 and CP60) of varying AMPS content with HQ and HMTA. Fig. 1 shows the liquid NMR carbon spectra of the CP30 and CP60 polymers. The resonance peaks at the chemical shifts 176.02 ppm and 179.60 ppm correspond to the carbonyl carbons of AMPS and AM, respectively (Parker and Lezzi, 1993; Sandengen et al., 2017). The AMPS contents of CP30 and CP60, estimated from the integration of the peak areas, were 30.1% and 57.3%, respectively. First, the differences in gelation time, gel strength, thermal stability and plugging ability of the gels formed by the two polymers at 110 °C were compared.

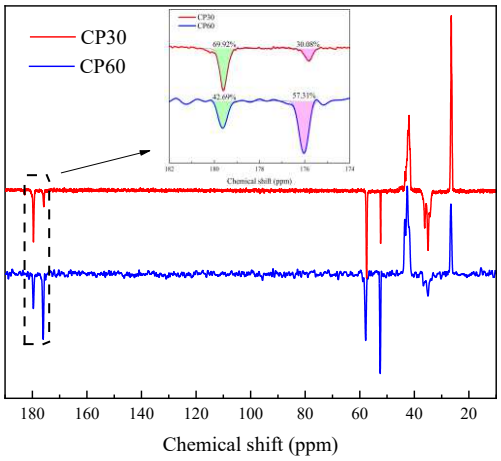


Fig. 1 C-NMR of AM/AMPS copolymers with different AMPS content

3.1 Evaluation of gel properties

3.1.1 Gelation time

The gelation time of the gels with different polymer and crosslinker concentrations at 110 °C were measured for both polymers, as shown in Fig. 2. The gelation times of the gels formed by both polymers with different AMPS content decreased with increasing crosslinker and polymer concentrations. The contour trend of the gelation times showed that the crosslinker had a more significant effect on the gelation time.

Comparing the gelation times of the two gels with the same polymer and crosslinker concentrations showed that the gelation process was faster when the gels were prepared with the CP30 polymer. In particular, when the crosslinker concentration in the gel was low (0.1%), it took more than two days for the CP60 to form a gel, whereas the CP30 could form a gel in less than 15 h.

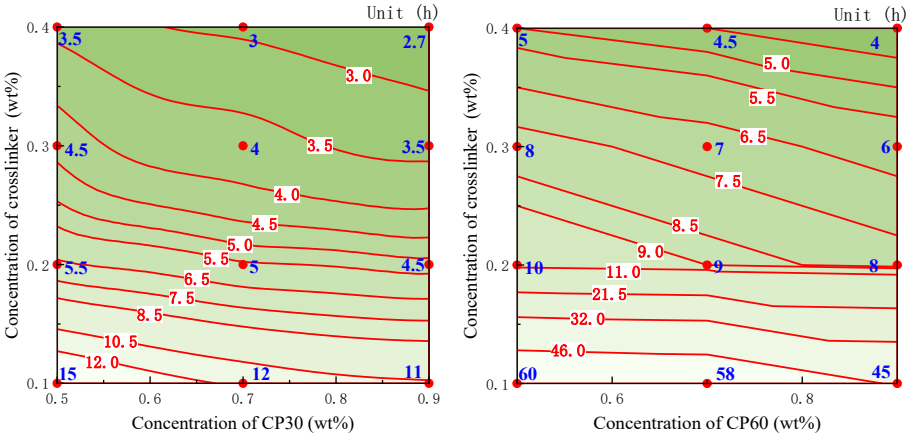


Fig. 2 Gelation time at 110 °C for gels with different crosslinker and polymer concentrations

This result confirms that the high AMPS content in the polymer is unfavorable for gel formation, which may be related to the crosslinking mechanism of the gel. Fig. 3 shows the crosslinking reaction of the AM/AMPS copolymer with HQ and HMTA. The crosslinking agent must react with the amide groups on the polymer to form the gel grid (Juárez et al., 2020). More AMPS means that less AM can participate in the reaction; hence, a longer gelation time was required. Both the spatial site resistance and electrostatic force of the AMPS group inhibited the crosslinker from approaching the amide group near the AMPS group. This is one of the main reasons why polymers with a high AMPS content form gels more slowly.

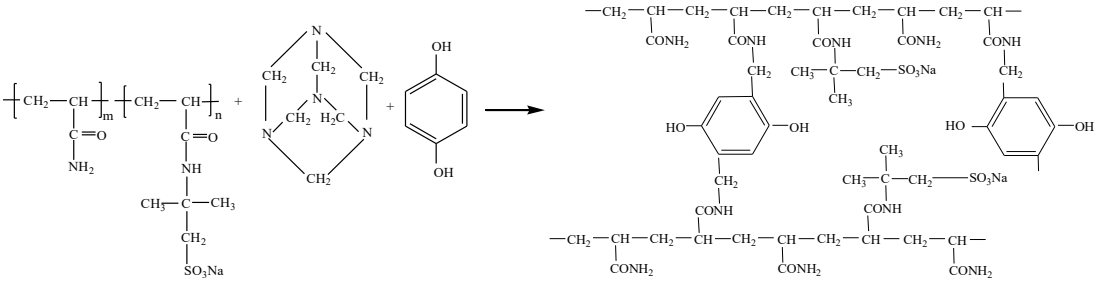


Fig. 3 Crosslinking reaction of AM/AMPS with HQ and HMTA

3.1.2 Gel strength

The storage modulus of the gel within the LVER is a key parameter for characterizing the gel strength. Fig. 4 shows the storage moduli of the two gels with different polymer and crosslinker concentrations.The storage modulus of the gel

increased with increasing polymer and crosslinker concentrations. For the same crosslinker and polymer concentration, the storage modulus of the CP30 gels was higher than that of the CP60 gels. This is attributed to the higher number of amide groups in the CP30 gel. Under identical conditions, a higher number of amide groups results in a gel with higher cross-linking density and a more compact network structure. As shown in Fig. 5, the polymer grid gaps of the CP30 gel is approximately 5~7 μm, which is significantly smaller than the approximately 15~20 μm grid gaps of the CP60 gel.

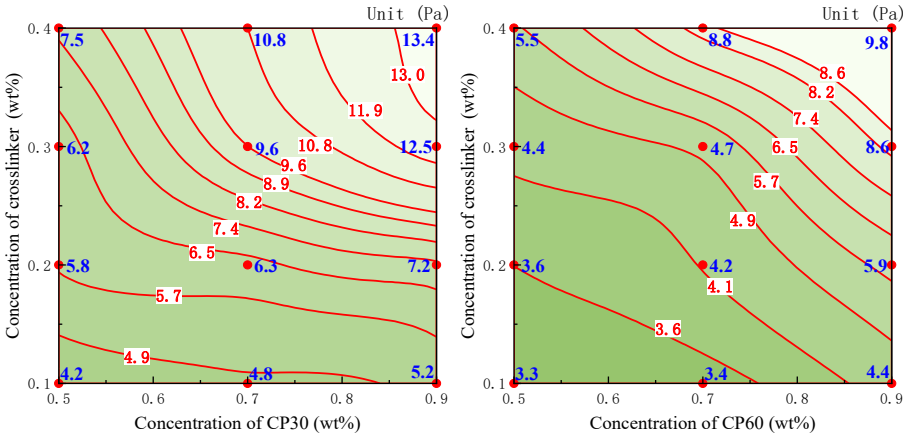
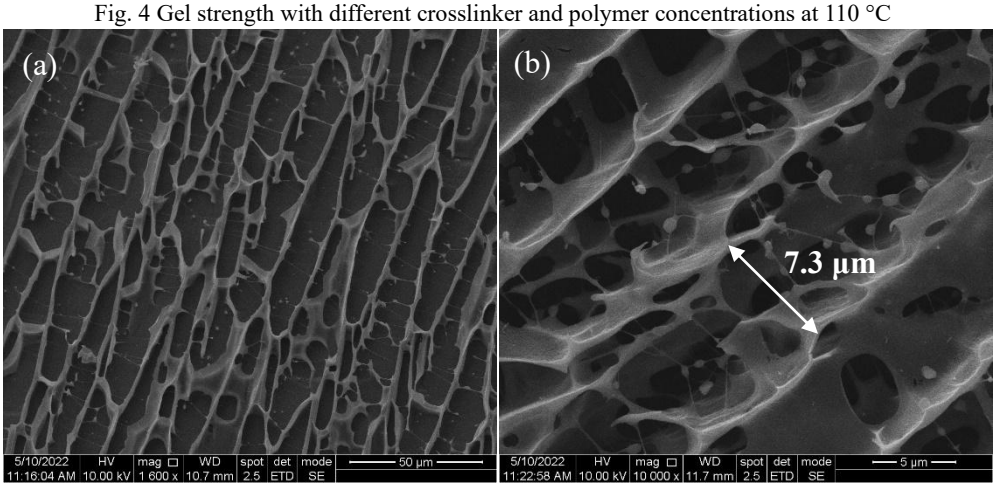
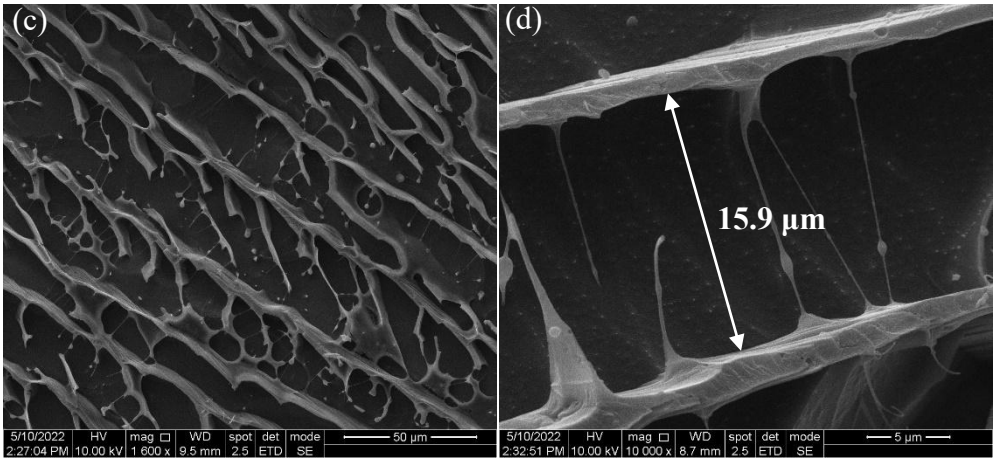


Fig. 4 Gel strength with different crosslinker and polymer concentrations at 110 °C





(a), (b) Images of gels consisting of 0.5 wt% CP30 and 0.1 wt% crosslinker after 1600x and 10000x magnification, respectively.
(c), (d) Images of gels consisting of 0.5 wt% CP60, and 0.1 wt% crosslinker after 1600x and 10000x magnification, respectively.

Fig. 5 Microscopic images of CP30 and CP60 gels

As the crosslinker concentration in the gel increased, the increasing trend of the storage modulus of the CP30 gels became more significant, while that of the CP60 gels was much flatter. This is attributed to the fact that gel strength is primarily determined by the crosslinking density of the gel, which is controlled jointly by the amount of crosslinking agent and the number of amide groups in the polymer.In the case of CP30 gel, there are sufficient amide groups present during polymerization for the cross-linking agent to react with. The increasing crosslinker concentration could significantly increase the crosslinking density of the gels. However, since the number of amide groups in the CP60 gel is limited, increasing the crosslinking agent concentration may exceed the carrying capacity of these amide groups, and thus does not significantly increase the gel crosslinking density. Furthermore, the inhibitory effect of additional AMPS in CP60 on the crosslinking reaction also causes the rate of increase in gel strength to slow down as the crosslinking agent concentration rises.

3.1.3 Gel stability

Stability is the most critical factor for gels under reservoir conditions as it determines their lifetime as a plugging agent. However, the high-temperature and high-salinity reservoir environment poses a great challenge to the gel stability. Moreover, aging in a high-temperature and high-salinity environment changes the performance of the gel, affecting its effectiveness. The stabilities of the two gels at 110 °C were evaluated. Fig. 6 shows the dehydration ratios and images of the two gels with different polymer and crosslinker concentrations aged at 110 °C for different times.

The CP30 gels with a polymer concentration of 0.5% and crosslinker concentration of 0.1% had dehydration ratios of over 20% and 83% after 60 and 180

days of aging, respectively. The gels with a polymer concentration of 0.5% and a crosslinker concentration of 0.4% exhibited significant syneresis when aged for 180 days. The CP30 gels with a polymer concentration of 0.9% exhibited good thermal stability with no more than 8% dehydration after aging for up to 180 days. Compared with the CP30 gels, the CP60 gels exhibited better thermal stability, with dehydration ratios of less than 5% for different polymer concentrations and after aging for up to 180 days. In fact, the gel with a polymer concentration of 0.9% was hardly dehydrated.

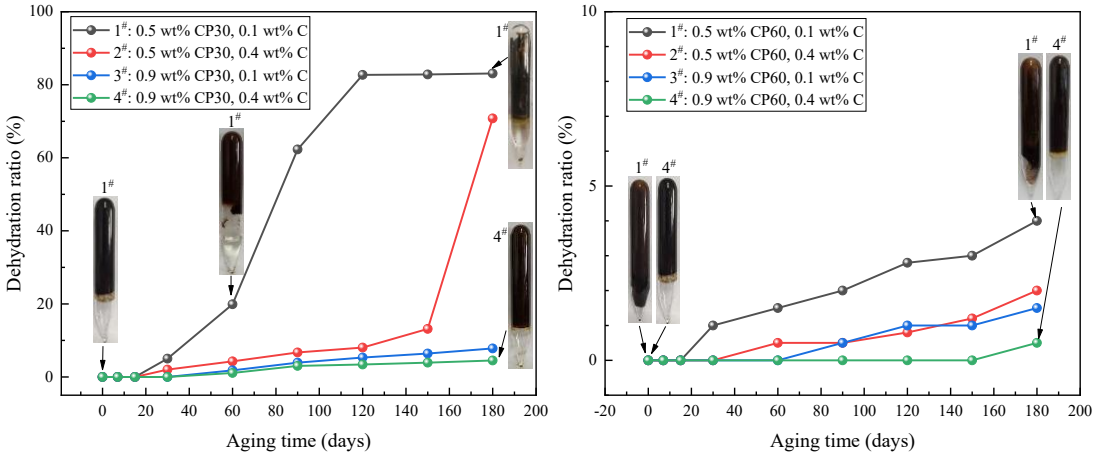


Fig. 6 Dehydration ratio of gels after aging for different times at 110 °C (C in the legend represents crosslinker)

Differences in gel stability lead to different dehydration ratios and variations in gel strength. The changes in gel strength at different aging times were further investigated. Four gel samples were selected, and their storage moduli were measured after aging at 110 °C for 7, 30, 60, and 120 days, as shown in Fig. 7. The storage modulus of CP30 gels increased with the aging time, especially when the crosslinker concentrations were 0.1% and 0.2%. The storage modulus of the gel appeared to increase with the aging time. This was attributed to the large portion of the CP30 gel that was dehydrated after aging at a high temperature to form a concentrated gel, as shown in Fig. 7. The CP60 gel exhibits superior thermal stability at 110 ℃. The gel storage modulus remained constant or increased slightly with as the aging time increased.

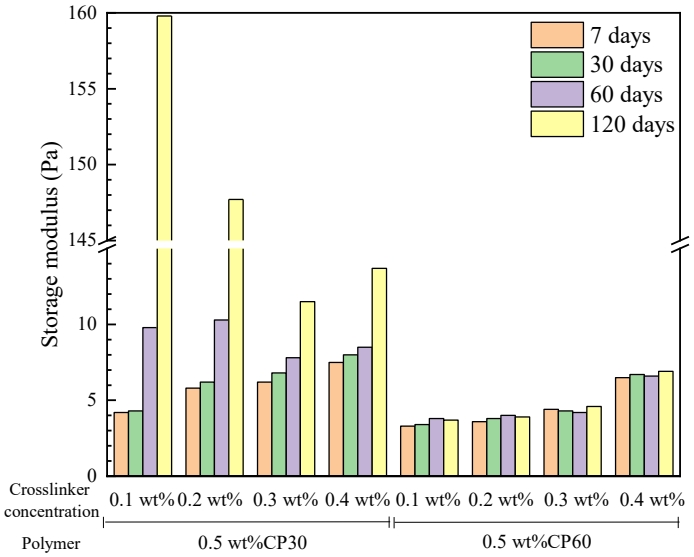


Fig. 7 Storage modulus of the gel after aging at 110 °C for different times

3.1.4 Plugging ability of the gel

The plugging ability of gels in porous media is a factor of great interest, as it provides a more direct representation of the value of the gel. The plugging ability of the gels was determined using a sand-packed model with a permeability of approximately 1–2 μm^2. The gel composition, sand-packed model data, and results of the sand-packed model water-flooding experiments are shown in Table 2 and Fig. 8.

Table 2 Parameters and results of the sand-packed model water-flooding experiments

Number	Gel composition	k_{wi} (10^{-3}μm^2)	Maximum plugging pressure (MPa)	k_{wa} (10^{-3} μm^2)	F_{RR}
1	0.5 wt% CP30, 0.1 wt% crosslinker	1674	21.5	10.7	156.4
2	0.5 wt% CP30, 0.4 wt% crosslinker	2123	38.9	5.5	386
3	0.5 wt% CP60, 0.1 wt% crosslinker	1769	11.2	28.3	62.5
4	0.5 wt% CP60, 0.4 wt% crosslinker	1676	23.8	4.5	372.4

Note: All the above gels were added with 0.3 wt% TH.

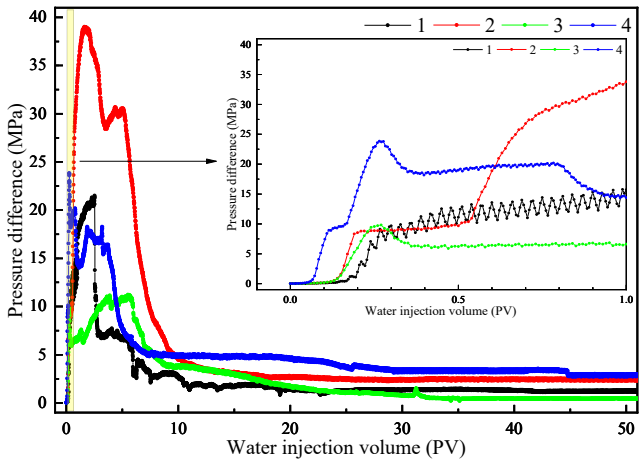


Fig. 8 Pressure difference curves of four gels during water-flooding experiments.

The results of the water-flooding experiments showed that the pressure differences began fluctuating at approximately 8~10 MPa during the water-flooding process. The trend in the water-injection pressure differential changes. This indicates that the gel plug has been partially breached. Subsequent increases or decreases in the pressure difference indicate that the gel may be migrating through the porous medium. As the gel migrates through the porous medium, it may form a more robust plug, causing the pressure differential to continue rising. Alternatively, the gel may be completely breached and displaced from the porous medium, causing the pressure differential to gradually decrease. We compared the plugging strength of the gel with the maximum gel plugging pressure in the sand-packed model. The plugging strength of the CP30 gel was significantly greater than that of the CP60 gel, which can be attributed to the higher strength of CP30.

As the amount of water flooding increased, the gel in the sand-packed model was continuously broken and squeezed out of the model, and the pressure difference generated by gel plugging continuously decreased and eventually stabilized. We used the pressure difference at 50 PV of water flooding to calculate the post-seal permeability and residual resistance factor (F_{RR}) of the gel in the sand-packed model. The results showed that the F_{RR} of CP60 gels with a crosslinker concentration of 0.1% was significantly lower than that of CP30 gels. However, the F_{RR} of CP60 gels with a crosslinker concentration of 0.4% was similar to that of CP30 gels. This phenomenon may be caused by the different rheological behaviors of the two gels.

3.2 Gel Rheological Behavior

3.2.1 Gel viscosity

The viscosity of the gel is a key factor determining its injection performance and warrants particular attention during application. The gel viscosity before gelling affects its injection speed and pressure, which indirectly affect the operating costs. Hence, the viscosities of different concentrations of polymer solutions were measured to compare their injectability. In Fig. 9, the viscosity curves for different concentrations of CP30 and CP60 polymer solutions formulated with synthetic saline show that the CP30 polymer solution has better injectability. At the same concentration and a lower shear rate, the viscosity of the CP60 polymer solution was more than twice that of the CP30 polymer solution. Although the CP60 polymer solution had a more significant shear

dilution effect, its viscosity was still higher than that of the CP30 polymer solution at high shear rates. In fact, achieving high shear rates during gel injection is a challenge. At the same injection pressure, the higher the gel viscosity, the slower the injection speed. Overall, CP30 gel has lower viscosity and offers greater advantages during actual injection.

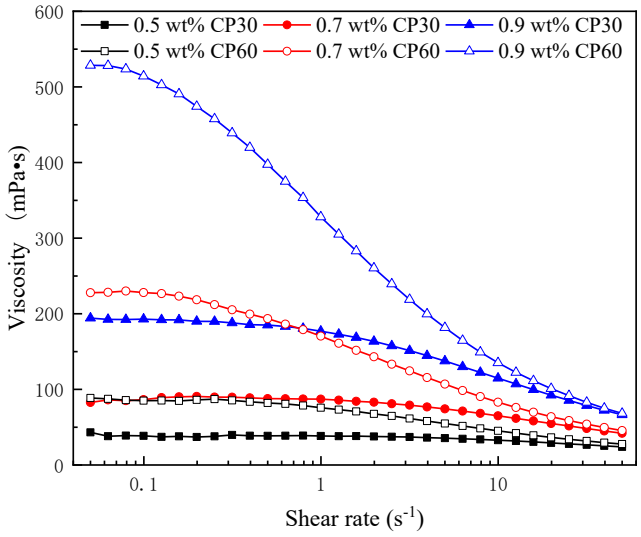


Fig. 9 Viscosity curves of polymer solutions with different polymer concentrations

3.2.2 Gel viscoelasticity

The storage modulus of the gel reflects its strength but does not its rheological and mechanical properties. Other rheological properties of the gel, such as viscoelasticity and toughness, are also important. Therefore, the viscoelastic properties of the two gels were compared using the LAOS test. Four samples of each gel type with different polymer and crosslinker concentrations were selected for comparison. Their compositions and processing conditions are listed in Table 3.

Table 3 Composition and processing conditions of gel samples for rheological tests

Gels	Composition of gel samples	Aging time, Days	Temperature, °C
1#	0.5 wt% CP30, 0.1wt% HQ, 0.1wt%HMTA, 0.3 wt% TH	7	110
2#	0.5 wt% CP30, 0.4wt% HQ, 0.4wt%HMTA, 0.3 wt% TH	7	110
3#	0.9 wt% CP30, 0.1wt% HQ, 0.1wt%HMTA, 0.3 wt% TH	7	110
4#	0.9 wt% CP30, 0.4wt% HQ, 0.4wt%HMTA, 0.3 wt% TH	7	110
5#	0.5 wt% CP60, 0.1wt% HQ, 0.1wt%HMTA, 0.3 wt% TH	7	110
6#	0.5 wt% CP60, 0.4wt% HQ, 0.4wt%HMTA, 0.3 wt% TH	7	110
7#	0.9 wt% CP60, 0.1wt%HQ, 0.1wt%HMTA, 0.3 wt% TH	7	110
8#	0.9 wt% CP60, 0.4wt%HQ, 0.4wt%HMTA, 0.3 wt% TH	7	110

First, the samples were subjected to LAOS tests to compare the moduli of the CP30 and CP60 gels with the same component concentrations. At small shear strains, the storage modulus (G') and loss modulus (G") of the gel are constant. The modulus values

in this strain range characterize the gel strength. This shear strain region where the modulus is constant is also referred to as the LVER. As shown in Fig. 10, the moduli of the CP30 and CP60 gels increased with increasing polymer and crosslinker concentrations, whereas their LVER gradually decreased. This is because as the polymer and crosslinker concentrations increased, the mesh density of the gel increased, which in turn increased the gel strength and gradually changed the mechanical properties of the gel from a viscoelastic liquid to a viscoelastic solid that was more sensitive to strain. CP30 and CP60 gels exhibited the same trends described above, but the variation in the LVER range was more pronounced for the CP30 gel, indicating that the CP30 gel is more susceptible to changes in component concentration and network structure.

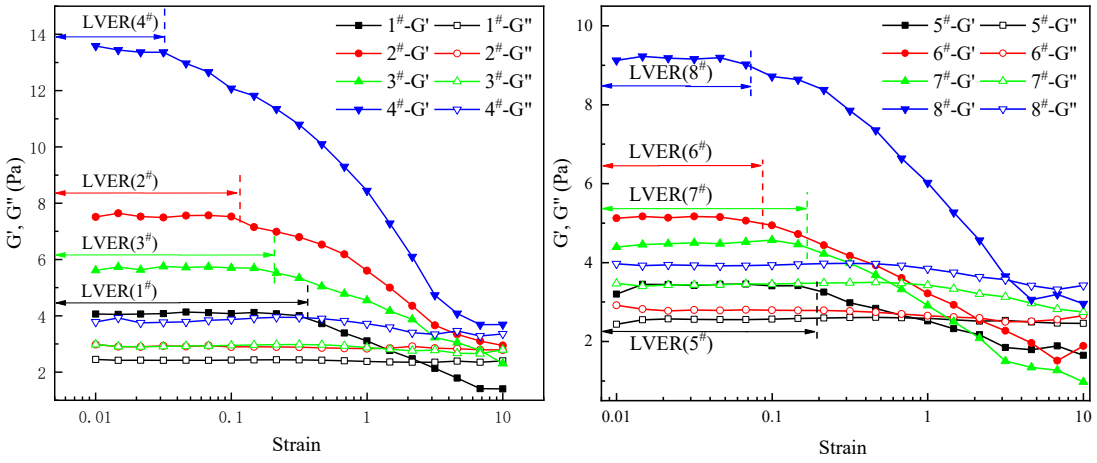


Fig. 10 LAOS tests on CP30 and CP60 gels

3.2.3 Creep and Creep Recovery

The gel in the reservoir gradually deformed or was penetrated after being subjected to a certain degree of pressure difference. Most deformation processes occurred in the nonlinear viscoelastic region of the gels. Therefore, creep and creep recovery tests were used to determine the state of the gel after stress and unloading. The gel deformation under a shear stress of 5 Pa and the recovery ratio of the deformation after unloading were evaluated. The creep and creep recovery test results of the gel samples are shown in Fig. 11.

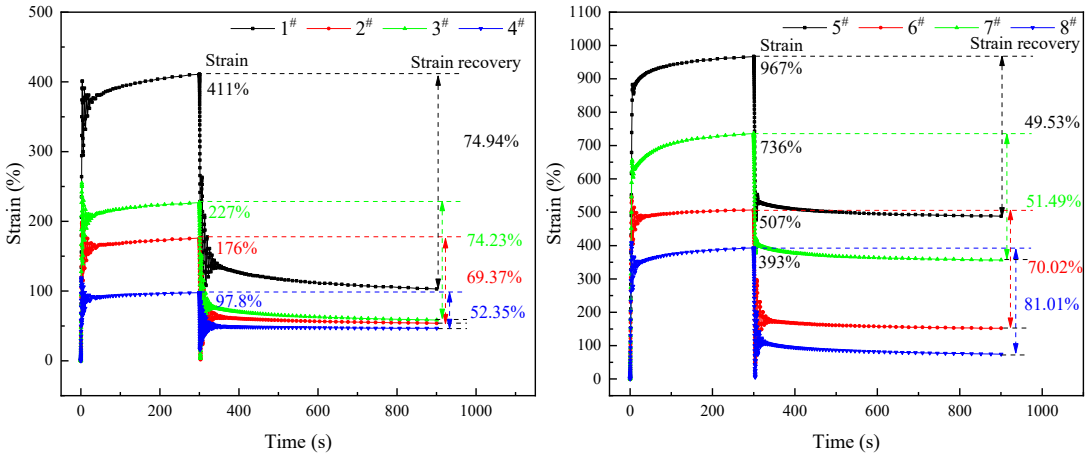


Fig. 11 Creep and creep recovery tests on CP30 and CP60 gels

The comparison of the gels showed that the higher the strength of the gel prepared from the same polymer, the lower the strain. However, as the gel strength increased, the CP30 gel strain recovery gradually decreased, whereas that of the CP60 gel gradually increased. In other words, as the gel strength increased, plastic and elastic deformation gradually dominated the deformation of the CP30 and CP60 gels, respectively. This indicates that as the gel strength increased, the brittleness of the CP30 gels was increased, whereas the toughness of the CP60 gels was increased.

3.2.4 Gel plugging mechanism

The rheological properties of the gels can effectively reveal the plugging performance of the two gels and the characteristics of the breakthrough pressure difference curve. The creep amplitude of the gel under stress is negatively correlated with the storage modulus of the gel in the LVER. The greater the gel storage modulus (i.e., the gel strength), the smaller the creep amplitude of the gel. This indicates that the greater the gel strength, the greater the stress required to cause the gel to deform and migrate. This rule can be well correlated with the maximum plugging pressure produced by different gel strengths. The plugging strength of the gel is directly influenced by the structural strength of the gel. The higher the structural strength of the gel (the storage modulus within the LVER of the gel), the higher the plugging pressure produced.

Furthermore, the plugging performance tests revealed significant differences in the gel storage modulus (as shown in Table 2, items 2 and 4), yet the F_{RR} of the two after plugging the rock cores was similar. This phenomenon is also worthy of discussion. This study suggests that the F_{RR} of the gel after being extensively flushed with water is influenced by the viscoelasticity and toughness of the gel. The viscoelastic testing results show that compared with the CP60 gel, the LVER of the CP30 gel is smaller,

and the irreversible structural damage caused by the transport shear stress is more severe. The creep recovery results also show that the CP30 gel has greater brittleness, while the CP60 gel has greater toughness.This resulted in the fact that after the CP30 gel was breached, it was prone to being sheared into gel fragments and being displaced from the model, which was not conducive to the retention of F_{RR}. In contrast, the CP60 gel was more tougher and thus better able to stay in the porous medium.

In conclusion, in order to enhance the gel water-plugging effect, it is necessary to increase the gel strength as much as possible through reasonable methods, which will help to increase the maximum gel plugging pressure and F_{RR}. Furthermore, enhancing the toughness of the gel can also improve its erosion resistance, thereby enhancing the water-plugging effect of the gel. The strength and toughness of the gel can both be controlled by optimizing the molecular structure of the polymer and the concentration of the gel components.

3.3 Gel stabilization mechanism

The AM/AMPS copolymer is a typical temperature- and salinity-resistant polymer whose temperature and salinity resistance have been widely reported. Although AMPS has good temperature resistance, it can hydrolyze on the polymer chain when the temperature exceeds 110 °C. (Moradi-Araghi et al., 1987; Parker and Lezzi, 1993). In addition, the hydrolysis of AMPS is accelerated by adjacent carboxylic acid groups. This phenomenon is known as the intramolecular catalytic hydrolysis of AMPS. (Guo et al., 2022; Parker and Lezzi, 1993; Sandengen et al., 2017)

In this study, the gels containing two different amounts of AMPS polymer exhibited different thermal stabilities at 110 °C. The CP60 gels exhibited better thermal stability than the CP30 gels. Moreover, the CP30 gels with high concentrations of polymers and crosslinkers exhibited good thermal stability. Therefore, we analyzed the stabilization mechanism of both gels using FTIR. We prepared eight gel samples (Table 4) and analyzed their stabilization mechanism by FTIR.

Table 4 Composition and processing conditions of gel samples

	Composition of gel samples	Processing conditions		
		Aging time, Days	Temperature, ℃	Dehydration ratio, %
1#	0.5 wt% CP30, 0.1wt% HQ, 0.1wt%HMTA, 0.3wt% TH	5	110	0
2#	0.5 wt% CP30, 0.1wt% HQ, 0.1wt%HMTA, 0.3wt% TH	60	110	19.9
3#	0.5 wt% CP30, 0.4wt% HQ, 0.4wt%HMTA, 0.3wt% TH	5	110	0

4#	0.5 wt% CP30, 0.4wt% HQ, 0.4wt%HMTA, 0.3wt% TH	60	110	4.3
5#	0.5 wt% CP60, 0.1wt% HQ, 0.1wt%HMTA, 0.3wt% TH	5	110	0
6#	0.5 wt% CP60, 0.1wt% HQ, 0.1wt%HMTA, 0.3wt% TH	60	110	0
7#	0.5 wt% CP60, 0.4wt%HQ, 0.4wt%HMTA, 0.3wt% TH	5	110	0
8#	0.5 wt% CP60, 0.4wt%HQ, 0.4wt%HMTA, 0.3wt% TH	60	110	0

The FTIR spectra of the gels are shown in Fig. 12. The absorbance at approximately 1650 cm^{-1} was caused by the C=O stretching of the primary and secondary amides. The absorbance at approximately 1560 cm^{-1} was caused by the N-H bending and C-N stretching of the secondary amide (McCormick et al., 1982), and the antisymmetric stretching vibrations of C=O bonds of carboxylates. The transmittance peaks near 1200 and 1046 cm^{-1} were caused by the S=O stretching of AMPS, which is a common characteristic of AMPS groups. (McCormick et al., 1982) The absorbance at approximately 1390–1420 cm^{-1} was attributed to the symmetric stretching of the C=O bond of the carboxylate. According to Beer's law, the absorbance A can be related to the concentration c as follows:

$$A = atc \tag{1}$$

where a is the molar absorptivity of the characteristic frequency, and t is the film thickness. The total contribution of the primary and secondary amides to the absorbance at approximately 1650 cm^{-1} is given in Eq. (2), where a_1, a_2 represent the absorptivity and c_1, c_2 represent the concentration of each unit.

$$A_{1650} = a_1 t c_1 + a_2 t c_2 \tag{2}$$

At approximately 1560 cm^{-1}, the contributions of secondary amides and carboxylates to the absorbance are given in Eq. (3), where a_3, a_4 represent the absorptivity and c_3 represents the concentration of carboxylates.

$$A_{1560} = a_3 t c_2 + a_4 t c_3 \tag{3}$$

The contributions of carboxylate and AMPS to the absorbance at approximately 1410 cm^{-1} and 1046 cm^{-1} are given by Eqs. (4) and (5), respectively; where a_5, a_6 represent the absorptivity and c_4 represents the carboxylate concentration.

$$A_{1410} = a_5 t c_3 \tag{4}$$

$$A_{1046} = a_6 t c_4 \tag{5}$$

The ratio of absorbances at 1650 cm^{-1} and 1560 cm^{-1} is given by

$$\begin{aligned} A_{1650}/A_{1560} &= (a_1 t c_1 + a_2 t c_2)/(a_3 t c_2 + a_4 t c_3) \\ &= (a_1 c_1 + a_2 c_2)/(a_3 c_2 + a_4 c_3) \end{aligned} \tag{6}$$

The ratio of absorbances at 1410 cm^{-1} and 1046 cm^{-1} is given by

$$A_{1410}/A_{1040} = a_5 tc_3/a_6 tc_4 = a_5 c_3/a_6 c_4 \quad (7)$$

A semi-quantitative analysis of the concentration variation of each unit in the gel was performed according to Eqs. (6) and (7), and the infrared spectra of the gel (13). During the aging of the gel, the primary amide and AMPS were hydrolyzed to form carboxylates; hence, the concentration of primary and secondary amides in the gel decreased, and the carboxylate concentration increased as the aging time increased. As a result, the value of A_{1650}/A_{1560} decreased and that of A_{1410}/A_{1040} increased. From the data in Fig. 12, the gel formed by 0.5% CP30 and 0.1% crosslinker showed the greatest decrease in A_{1650}/A_{1560} values after 60 days of aging compared with 5 days of aging. Increasing the crosslinker and AMPS monomer contents in the polymer could suppress these changes. Thus, the A_{1650}/A_{1560} values of the gels formed by 0.5% CP60 and 0.4% crosslinker remained almost unchanged. The A_{1410}/A_{1040} values exhibited a similar trend. The variation of the A_{1410}/A_{1040} values of the CP30 gels was much larger than that of the CP60 gels, indicating that polymer hydrolysis was more pronounced in the CP30 gels.

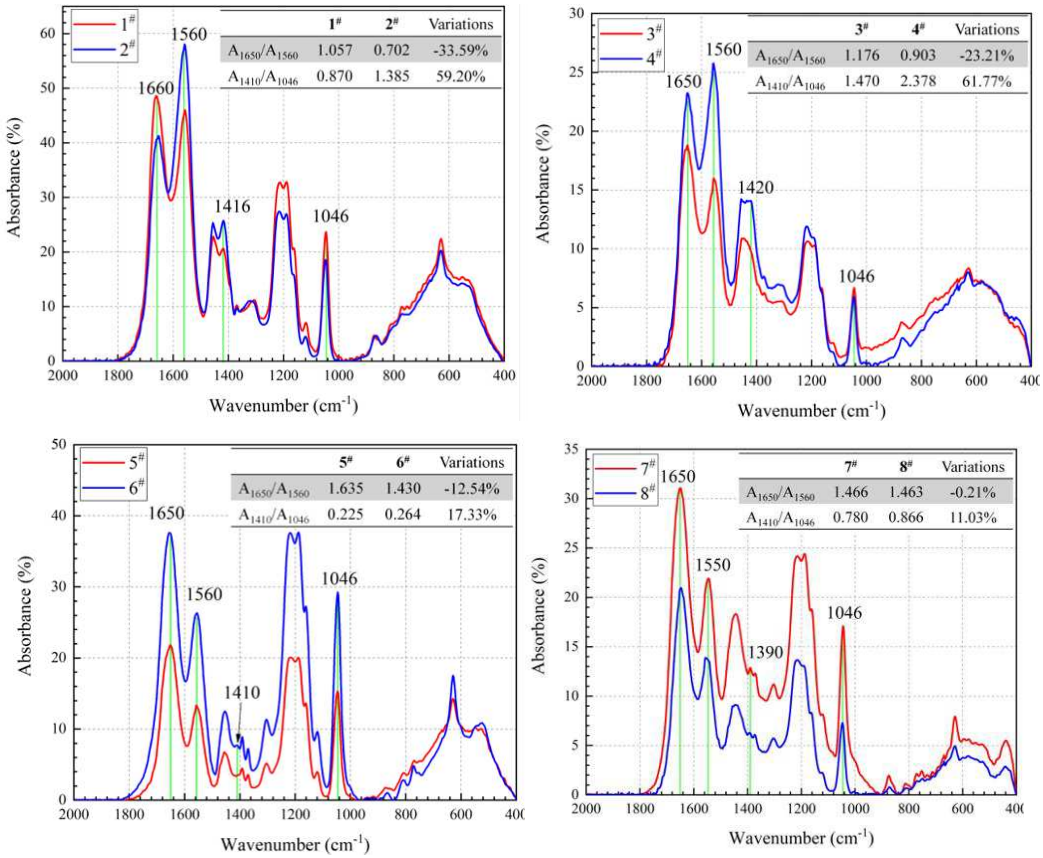


Fig. 12 Infrared spectra of different gel samples

Based on the above results, we propose a deduction for the structural changes that occur during gel aging. Firstly, the syneresis of the gel is caused by the carboxylate ions

formed by the hydrolysis of the amide groups in the polymer chelating with divalent cations in the water (Moradi-Araghi and Doe, 1987; Ryles, 1988). For the CP60 gels, the polymer contains a large amount of AMPS monomer, which significantly improves their thermal stability. Some of the primary amides became more stable secondary amides after the crosslinking reaction. As a result, only a small amount of primary amide remaining in the CP60 gel was converted to carboxylic acid after aging, thus providing good thermal stability. For the CP30 gels, the polymer contains a less AMPS monomer. Many amide groups remain in the gel after the crosslinking reaction that are easily hydrolyzed to produce carboxylic acid roots. In turn, the chelation of carboxylate with divalent cations leads to the syneresis of the CP30 gels. In addition, the crosslinking reaction consumes the amide group of the polymer to prevent its conversion to a carboxylic acid group. As more amides participate in the crosslinking reaction, the hydrolyzable amides remaining in the gel decrease. This also explains the tendency of the CP30 gels to dehydrate at lower crosslinker concentrations and their increased stability at higher crosslinker concentrations. Furthermore, CP60 contains fewer amide groups than CP30 gel, making them more susceptible to depletion during the cross-linking reaction. This is a key reason why CP60 gel exhibits greater stability than CP30 gel.

4. Conclusion

Based on the above research, we have reached the following conclusions.

1. AM/AMPS copolymers containing 30% and 60% AMPS were crosslinked with HQ and HMTA to prepare gels that could be stable for more than 180 days at 110 °C in brine with a salinity of 25×10^4 mg/L.

2. The increase in the AMPS content of the polymers was unfavorable to gel formation but favorable to increasing the stability properties of the gels. At the same polymer and crosslinker concentrations in the gel, the gelation time of the AM/AMPS copolymer containing 60% AMPS was longer than that of the copolymer containing 30% AMPS. The gel strength was also lower but the stability was higher.

3. Rheological tests showed that as the gel strength increased, the CP30 gel became more brittle, whereas the CP60 gel became tougher. A comprehensive analysis combining rheological testing and water-flooding experiments has revealed that the higher the storage modulus of the gel in the LVER, the greater its maximum plugging pressure, the stronger its creep and creep recovery properties, and the better its

resistance to scouring.

4. The number of hydrolysable amide groups in the gel is the primary factor determining its stability. To improve the gel's stability, the hydrolysis of amide groups into carboxylate ions should be avoided as far as possible.

In summary, the gel's temperature and salt resistance, plugging performance, and erosion resistance can all be controlled by modifying the polymer structure within the gel and adjusting the concentrations of the polymers and crosslinking agents. In practice, polymer gels can be customized to meet specific requirements.

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