Development of a High-Strength and Adhesive Polyacrylamide Gel for Well Plugging

Li Cheng,* Yi Qin, Yubin Su, Yuan Pan, Ying Wang, Ruiquan Liao, and Zhen Li

1. INTRODUCTION

Reducing water flow in the void space conduits, fractures, fracture-like features, or other superpermeability channels using in situ gel materials has been previously studied by many researchers. All of the gels were used to plug the channels in the reservoir rather than the tubing or casing. To seal the well effectively, gels are desired to possess a broad range of highly controllable and predictable gelation times, strength, and adhesion. The process is applicable to a broad range of temperatures, salinities, and environments. If the wellbore is desired to return to operation after plugging, the gel can be dissolved with a suitable solvent and the dissolved gel can be pumped to the surface. Alternatively, the gel can be drilled out or mechanically removed with relative ease.

To maintain the pressure from downhole, temporary (remedial) zonal isolation can be achieved either mechanically (using a coiled tubing packer) or chemically (using gel plugs).1,2 During the operation, mechanical zonal isolation must be installed in the well for water or gas shutoff using external casing packers or sliding side doors. However, sometimes, due to deformation, wax precipitation, and scale formation in the tubing, the mechanical packer is unable to effectively seal the pressure from downhole. In these cases, chemical means can be more advantageous than the mechanical isolation.3,4 The design idea of this plugging technology is to use gel slug to plug the open well and the gel to be self-removed in the subsequent oil and gas production processes. Moreover, with the high strength of the gel and adhesion to the inside wall, the gel slug can sustain the high pressure from downhole. In this way, this well can be processed for subsequent workover and completion operations.5–8 The engineering efforts demonstrated that the polymeric materials and composites must meet production requirements for stimulation operations. To meet the requirement for plugging, the gel should have good physical strength and adhesion property, as well as controllable degradation under a variety of bottom-hole conditions.

Chemical treatment has been known as a feasible and practical method in industrial scales for decades. One of the most useful materials in chemical treatment with simple and costless preparation is a system of gel polymers, which comprise of water, a crosslinker, a water-soluble polymer, and some other additives, altogether called a gelling solution. When a polymer reacts with a crosslinker, a gel polymer system is formed. Numerous gels with viscosity and strength are developed in the past decades, especially for the water shutoff and conformance control in the enhanced oil recovery aspect, such as partially hydrolyzed poly(acrylamide) (HPAM)/Cr3+,9–14 HPAM/polyethylenimine (PEI),15–18 HPAM/phenol/formaldehyde,19 HPAM/hydroquinone (HQ)/hexamethylenetetramine (HMTA),20 HPAM/resorcinol/hexamethylenueretamene,21,22 and polyacrylamide/tert-butyl acrylate.
greater materials compared with a mechanical packer may possess well as high static and dynamic contact stress. The degradable controlling the permeability of the formation, etc. 24

2. EXPERIMENTAL STUDIES
2.1. Materials. The commercial materials used in this paper were utilized without further purification. HPAM as the polymer was purchased from Aldrich SNF Company (France). HPAM is a white solid powder with a hydrolysis degree of 10−15 mol % and an average molecular weight of around 5−6 MDa. Melamine (99%) and formaldehyde (37.0 wt % AP) were supplied by Aldrich Chemical Company, USA, and Fine Chemical Tianjin Yong Sheng, China, respectively. The crosslinker MF contains three hydroxymethyls per molecule, which was polymerized in our lab as reported previously, with minor modifications. 23,29 Briefly, MF was polymerized at the formaldehyde/melamine molar ratio of 3:1 at 60 °C for 6 h. Inorganic salts of NH4Cl, NaCl, and NaOH were AR grade and were supplied by Macklin (China). HCl (36.46 wt %, AP) was purchased from Beijing Chemical Works, China. All the solutions were prepared with deionized water.

2.2. Methods and Procedures. 2.2.1. MF-HPAM Gel Preparation. The crosslinker solution was prepared with the desired concentration, then a certain amount of granulated HAPM powder was added, and the mixture was stirred at 500 rpm with a magnetic stirrer until the solution was homogeneous. Then, a certain amount of starch was added into the gelling solution followed by stirring for 10 min. Subsequently, the pH of the solution was adjusted to a certain value using HCl solution or 1 M NaOH solution before being transferred into an oven at the desired temperature.

The mechanical properties of this gel mainly originated from crosslinking interactions by the entanglement of the MF molecule with HPAM (Figure 1). The process can be described as follows: (1) Through the nucleophilic reaction between the active amide group on the side chain of HPAM and the hydroxymethyl group from MF, HPAM and MF can easily crosslink to form a network structure. (2) Due to a large number of aromatic triazine rings in MF being introduced to the gel and a greater number of reactive sites being available, which improved the crosslinking density compared with the other crosslinker of HPAM, the viscosity and adhesion strength were improved significantly. 22,31

2.2.2. Measurement of Gel Viscosity. The gel viscosity was measured through a Brookfield viscometer RVDV-III+ (Brookfield Engineering Laboratories, Inc., USA) at constant temperature.
2.2.3. FTIR Measurements. The FTIR samples were prepared by the pellet method and the spectra were carried out on a Nicolet iS 10 FTIR spectrometer at room temperature.

2.2.4. Morphology Characterization. Scanning electron microscopy (SEM) images were collected on a Quanta FEG 650 microscope to elucidate the microstructures of the gels. All images were captured with the free-drying samples in the nonhydrated state and sputter-coated with Au prior to imaging.

2.2.5. Degradation of the Crosslinked Polymer Gel. Degradation of the crosslinked MF-HPAM gel was performed by adding the same mass of aqueous solution of ammonium persulfate with different concentrations (1.0, 2.0, 5.0, and 7.5 wt %) at the top layer of the gel, and all the samples were sealed and placed in the oven at 80 °C. At different time intervals, the supernatant was withdrawn and the remaining gel was weighed. Then, the supernatant was poured back to the top layer of the gel slowly and the sample was kept in the oven for degradation. The treatment was continued until the mass of the gel was constant for more than 1 h.

2.2.6. Measurement of the Pressure-Bearing Capacity of the Gel. The facility shown in Figure 2 was employed to evaluate the pressure plugging performance of the gel. The specific experimental procedures are as follows: (1) fill the testing tube with the polymer solution and seal the two ends of the tube; (2) turn on the thermostatic water bath at a certain temperature and pump the hot water into the casing to circulate the water bath; (3) after full gelation, begin to load pressure at a rate of about 5 kPa/min through a pressure maintenance pump and monitor the fluid loss and pressure drop. The pressure at which the sharp pressure drop occurred is recorded as the pressure-bearing capacity of the gel.

3. RESULTS AND DISCUSSION

3.1. Effect of NH₄Cl on Gel Performance. To meet the demands of a particular wellbore, the correlation between the independent gelation parameters with the dependent variables such as the gelation rate, gel strength, and stability should be studied. The independent gelation parameters mainly include ionic strength, temperature, pH, polymer concentration, and crosslinker concentration.

To investigate the effect of NH₄Cl on the gel performance, the pH of the solution was fixed at 9 and the reaction temperature was kept at 80 °C. NH₄Cl with a concentration ranging from 0.2 to 1.5 wt % was added to the gel formulation of 3.0 wt % starch + 0.5 wt % MF + 1.0 wt % HPAM. The gelation time and final strength of the gel at different NH₄Cl concentrations are summarized in Figure 3. Without NH₄Cl, the gelation is very slow. Even after gelation at 80 °C for 7 days, the gel is still very weak, indicating little crosslinking. The presence of NH₄Cl could significantly shorten the gelation time, as well as increase the gel strength.

In the presence of 0.8 wt % NH₄Cl, the solution gelled just after 8 h. Figure 3 also demonstrates that an increased NH₄Cl concentration significantly shortens the gelation time and enhances the gel strength, indicating that the gelation is accelerated mainly by ammonium salt. This phenomenon is quite similar with the HPAM/formaldehyde/resorcinol gel described in Jia and Ren’s paper. As is known, ammonium salts have been extensively applied as catalysts in organic synthesis, which can be used as neutral catalysts to substitute the metallic or strongly acidic environment. The crosslink mechanism of the present gel is the nucleophilic substitution reaction between the amino group in the side chain of HPAM and the hydroxyl group in MF. As we know here, MF acts as an amino resin crosslinker and all crosslinking reactions of amino resins are acid-catalyzed reactions. NH₄Cl as a salt consisting of a strong acid and a weak base dissociates into NH₄⁺ and Cl⁻ in aqueous solution. The proton transfer from NH₄⁺ offers a source of H⁺ for the protonation of the hydroxyl group, which increases the positivity of carbon atoms and makes them more active to react with the amino group. Therefore, the presence of NH₄Cl at a sufficient concentration with an optimum of 0.8 wt % significantly reduces the gelation time and elevates the gel strength.

3.2. Effect of the Crosslinker MF on Gelation Time. The viscosity of solution before gelation was determined mainly by the concentration of HPAM. As the concentration of the polymer increases, the viscosity of the solution will increase significantly. The higher initial viscosity means the higher resistant force needed to pump the solution into the wellbore. Therefore, in consideration of the dissolving time, solution viscosity, and easiness in pumping, the polymer HPAM was used at a concentration of 1.0 wt % with a viscosity of less than 300 mPa·s. To evaluate the effect of the crosslinking agent on the polymer gel, the gelation and strength of the gelling solutions with MF concentrations of 0.3, 0.5, and 1.0 wt % were investigated as shown in Figure 4.

The results showed that an increase in MF concentration results in the reduction of gelation time and the enhancement of gel strength. At a low MF concentration of 0.3 wt %, most of polymeric chains remain unreacted. On the contrary, at a higher MF concentration of 0.5 wt %, more HPAM chains react with MF followed by a faster formation of numerous
crosslinked bonds, which decrease the gelation time and enhance the gel strength. By further increasing the MF concentration to 1.0 wt %, the gelation is even faster with a higher strength; however, the gel is a little brittle because of the overcrosslinking. Consequently, the optimal MF concentration is believed to be 0.5 wt % for the proposed polymer gel system with suitable gelation time, better gel strength, and long-term stability.

3.3. Effect of pH on Gel Performance. The mechanical behavior of the gel was studied under different pH values. The polymer gelling solution was prepared with 3.0 wt % starch + 0.5 wt % MF + 1.0 wt % HPAM + 0.8 wt % NH₄Cl. The reaction was performed at 80 °C. Considering that too low or too high pH values are not favorable for the gelation process and gel performance of the plugging agent system, pH was evaluated within the range of 3.0−13.0. The initial pH of this gelling solution is about 8.9−9.2. For the samples prepared here, their pH values were adjusted by dropwise adding 1 M NaOH or 20 wt % HCl to the gelling solution. Gelling conditions at different pH values were compared, and the experimental data are shown in Figure 5.

As can be seen from Figure 5, the gelation time and gel viscosity highly depend on the pH of the gelling solution. Under the strong acid (pH = 3.0) and strong alkali (pH = 11.0 and 13.0) conditions, the viscosity of the gelling solution increases slowly, indicating weak gelation and an adverse effect of the strong acid and alkali on the gelation reaction. We found that, when the pH increased, the gelation time was extended and the gel viscosity significantly strengthened in the neutral condition with a pH of around 7.0 as shown in Figure 3. However, the gel viscosity of the phenol/formaldehyde/HPAM system decreased rapidly above pH of 7.0. Therefore, our covalent crosslinked gel has good resistance against alkaline conditions, which allows its use inside the wellbore for plugging of the gel for the acidity may cause corrosion and affect its sealing ability. The primary reasons for this phenomenon can be classified as follows: (1) Too low or too high pH can cause the polymer molecular chain to shrink and coil; especially, a high initial pH can also promote further hydrolysis of amide group to carboxyl groups, which are not favorable for crosslinking reaction. (2) The increase in pH might inhibit the protonation of the hydroxymethyl and make it unavailable to initiate a nucleophilic attack on an amide carbonyl group of HPAM, which makes the mass fraction of the crosslinker too low to form a tight crosslinking network structure with the polymer. The gelation time and gel strength could be controlled by the pH based on the requirement and condition of the well. For a fast gelation, the pH of 5.0−9.0 is desirable to form a stable and high-strength gel to plug the pressure from downhole for a long time. Since the acidic environment is detrimental due to the corrosion to the internal wall of the wellbore, the pH of 8.0−9.0 is desirable for field application.

3.4. Effect of Temperature on Gel Performance. The temperature is an important factor influencing the gelation performance and practical application. To investigate the impact of temperature, gel strength was evaluated at temperatures ranging from 60 to 100 °C. Figure 6 shows the viscosity evolution of the gelling solution at different temperatures for the polymer gelling solution prepared with 3.0 wt % starch + 0.5 wt % MF + 1.0 wt % HPAM + 0.8 wt % NH₄Cl at pH = 9.0.

As can be seen from Figure 6, at all temperatures tested, the gelling solution could form a stable and high-strength gel; however, the gelation time differs significantly. Obviously, the gelation reaction becomes more rapid with increasing temperature. The gelation time is less than 5 h at 90 °C.
As can be seen from Figure 6, it is evident that a higher temperature resulted in a shorter gelation time and higher complex viscosity. At a higher temperature, the number of activated sites increases, and the irregular Brownian motion for molecular collision becomes more vigorous. The higher temperature also promotes the nucleophilic substitution reaction between HPAM and MF. Therefore, the gelation is much faster. The initial gel strength becomes stronger and the gelation time decreases at a higher temperature. It also can be seen from the curves that the gelation time of this gel can be controlled between 1 and 20 h under temperatures ranging from 60 to 100 °C.

Fang et al. and Sun et al. have derived a relationship between viscosity and temperature in multicomponent liquids known as the McAllister equation:

\[ \ln(\eta/\eta_0) = \ln A + \Delta G^*/RT \]

(1)

where \( \eta = \eta/\rho \) and \( \eta_0 = \eta_0/\rho_0 \) are the kinematic viscosities of the solution and solvent, respectively, with \( \eta \) and \( \eta_0 \) being the viscosities of the solution and solvent, respectively, and \( \rho \) and \( \rho_0 \) being the densities of the solution and solvent, respectively. \( \Delta G^* \) is the Gibbs free energy of activation for viscous flow.

In this study, eq 1 was employed to calculate \( \Delta G^* \) to study the effect of temperature on different gel formulas. For small temperature changes, the influence of temperature on gel density can be ignored, and eq 1 can be approximately converted into:

\[ \ln(\eta/\eta_0) = \ln B + +\Delta G^*/RT \]

\( B = A\rho/\rho_0 \) maintains approximately a constant value and the rest of the symbols have the same meaning aforementioned. To study the effect of temperature on viscosity, three other different gel systems were selected, namely, HPAM/Cr\(^{3+}\), HPAM/resorcinol/HMTA, and HPAM/PEI, which are crosslinked by the formation of a coordinate bond, chemical bond, and covalent bond, respectively. According to eq 2, if the curve of \( \ln(\eta/\eta_0) \) against \( T^{-1} \) is a straight line, the relationship between the viscosity and the temperature of the gel system follows the McAllister equation. Therefore, according to eq 2, the curves of \( \ln(\eta/\eta_0) \) against \( T^{-1} \) for three kinds of gel formulas were linearly regressed using the least square method as shown in Figure 7. \( \Delta G^* \) is calculated from the slope of the linear line and listed in Table 1.

The correlation coefficients of the linear fitting with values close to 1 indicate the linear relationship and the agreement of gelation reactions to the McAllister equation. From this equation, the relationship between \( \eta \) and the temperature is obtained easily through \( \Delta G^* \), regardless of the crosslinking mechanisms (covalent bond, coordinate bond, and chemical bond).

### 3.5. Morphology under SEM

The gel made from the formula of 0.5% MF + 1% HPAM + 0.8% NH\(_4\)Cl, at pH = 8.0 and 80 °C, is rigid, and it cannot flow even when the bottle with the gel is inverted; moreover, this gel has very good adhesion. There was no dehydration shrinkage occurring from the observation of the gel stability for more than 30 days. It could not be peeled off from the inner surface of the beaker even if it has been left there for a long time, which is quite different from the HPAM gel system crosslinked with the metal ion crosslinkers, such as Cr\(^{3+}\), Zr\(^{4+}\), Ti\(^{4+}\), Al\(^{3+}\), etc., which are susceptible to syneresis. Therefore, crosslinking done by a covalent bond has great advantage for gel stability. Microstructures of the in situ gel under the hydrated state control its bulk properties in a subterranean reservoir environment. To clarify this phenomenon, the observation analysis of the microstructure by SEM was conducted (Figure 8).

As shown in Figure 8, the MF crosslinked gel showed a dense three-dimensional porous microstructure with a pore size of ~0.1–1 μm while corresponding to a previous report that the HPAM-Cr\(^{3+}\) gel showed a typical porous continuous network with a pore size of ~100–150 μm, which is, through the nucleophilic attack of hydroxymethyl (–CH\(_2\)OH) moieties on MF to the amide group along the HPAM backbone, generating the ester bridges as shown in Figure 1 within the polymeric network. As observed in Figure 8, the dense porous and hook-like microstructures were scattered in the crosslinked gel, might contribute to the good rigid and mechanical integrity of the MF bridged gel, and decreased the water retention capacity and increased the adhesive force of the gel upon the wall.

Closer inspection of the micromorphology of this gel shows that it is filled with hook-like dendritic-shaped structures just like Velcro, and the branched chain diffuses in an arbitrary direction, which is quite different from other HPAM gels, such as PEI/HAPM, Cr\(^{3+}\)/HPAM, resorcinol/phenol-formaldehyde/HPAM, and resorcinol/formaldehyde/HPAM gel systems. These structures suggested that the gel was sufficiently crosslinked by a chemical reaction. Thus, the viscosity and strength are very high, which is beneficial for the gel sealing the wellbore entirely under high pressure. Moreover, this kind of micromorphology guarantees the firm connection to the wellbore surface. Before gelation, the adhesive polymer solution penetrates into the internal surface of the wellbore wall, and the hook-like structure of the gel after gelation adds greatly to the potential strength of the joint through physical interlocking.
3.6. FTIR Analysis. Furthermore, the formation of organic crosslinks during gelation was demonstrated by the FTIR spectra of HPAM and MF before and after thermal treatments shown in Figure 9, and the corresponding peaks of different functional groups are listed in Table 2.

![Figure 8. Photograph (inset picture) and micromorphology image of the gel (left: 200 nm; right: 1 μm).](image)

![Figure 9. FTIR spectra of HPAM, MF, and the gel.](image)

Both in HPAM and the final gel, 3436 cm\(^{-1}\) related to the N–H stretching vibration is observed.\(^{43}\) In HPAM, the band at 725 cm\(^{-1}\) corresponding to the N–H bending vibration from the primary amide group disappears in the gel; this indicates the formation of the gel accompanied by the destruction of the N–H band. In contrast, in MF and the gel, the C–N–H bending vibration at 585 cm\(^{-1}\) is observed; meanwhile, the peaks at 1168 and 998 cm\(^{-1}\) are respectively ascribed to the stretching vibration of the C–O band and the O–H bending vibration in –CH\(_2\)OH that disappeared in the gel. It can be theorized that the nucleophilic substitution reaction between the C–O band in –CH\(_2\)OH and the N–H band in the amide group is the reason why the new material is produced. Meanwhile, the band at 1106 cm\(^{-1}\) corresponding to the stretching vibration of N–C–O is shifted to a lower wavenumber of 1016 cm\(^{-1}\), and 1641 cm\(^{-1}\) is the absorption peak in the presence of trans secondary amide NH–C═O as well. This phenomenon also indicates that the chemical reaction occurred between the amide groups of HPAM and –CH\(_2\)OH in MF.

3.7. Pressure-Bearing Capacity. The high physical strength and adhesive strength of the MF-HPAM gel can enhance its pressure-bearing capacity. The breakthrough pressure of the gel slug could show the sealing properties of the gel. Breakthrough pressure may be measured using a self-designed plugging apparatus shown in Figure 2. After the gelling polymer solution is prepared, it is poured into the casing tube with the length of 60 cm. After both ends are sealed, the casing is placed in a constant temperature water bath. By allowing the gels to age for a sufficient period of time in the casing, the pipeline is connected between the casing and the water pump followed by testing the application of pressure to the substrate containing the gel therein. With the increase in pressure, the gel deforms slightly first due to its well elasticity and high strength. With increasing pressure, the gel begins to experience greater deformation; however, because of the gel’s good adhesion, there was no tear between the gel and the inside wall of the casing. When the pressure gradually

### Table 2. Analysis Results of the FTIR Spectra of Functional Groups in HPAM, MF, and the Gel

| wavenumber (cm\(^{-1}\)) | characteristic peak          | wavenumber (cm\(^{-1}\)) | characteristic peak          | wavenumber (cm\(^{-1}\)) | characteristic peak          |
|-------------------------|-----------------------------|-------------------------|-----------------------------|-------------------------|-----------------------------|
| 3436                    | N–H stretching vibration    | 3436                    | N–H stretching vibration    | 1106                    | N–C–O stretching vibration |
| 1106                    | N–C–O stretching vibration | 1016                    | N–C–O stretching vibration | 725                     | N–H bending vibration      |
| 1371                    | CH\(_2\) bending vibration | 1397                    | CH\(_3\) bending vibration |
| 1168                    | C–O stretching vibration   | 1641                    | absorption peak in the presence of trans secondary amide NH–C═O |
| 998                     | O–H bending vibration of hydroxymethyl | 585                     | C–N–H bending vibration |
| 585                     | C–N–H bending vibration    | 1641                    | absorption peak in the presence of trans secondary amide NH–C═O |

ACS Omega http://pubs.acs.org/journal/acsodf

https://doi.org/10.1021/acsomega.1c06626

ACS Omega 2022, 7, 6151−6159

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increased, the gel was broken through. The pressure-bearing capacity curves measured by taking water as a pressure medium after gelation at temperatures of 60, 80, and 100 °C were plotted as displayed in Figure 10.

Excellent placement was observed and the gel plugs were well packed. Compared with the HPAM/Cr³⁺ gel, the MF-HPAM gel showed more excellent physical strength and adhesive strength by forming chemical bonds with HPAM, which simultaneously enhanced its physical strength. The pressure-bearing value becomes higher as the temperature increases since the gel strength is greatly improved at a higher temperature. The adhesion forces between the steel surface and the MF-HPAM gel film are mostly in the form of secondary bonds (i.e., hydrogen bonding and van der Waals forces). The adhesive strength of MF-HPAM is controlled by the degree of crosslinking and secondary bonds because the force of chemical bonds is far greater than that of the hydrogen bonds and van der Waals forces. Chemical crosslinking also enhances the force between HPAM chains. When the degree of crosslinking and the number of secondary bonds increase, the adhesive strength of MF-HPAM becomes stronger. When the temperature increases, the degree of MF-HPAM crosslinking increases. Therefore, adhesive strength increases. When fluid was injected into the wellbore to test the resistance of the plug, it did not enter through the plug at first. As the pressure becomes higher, the gel will deform and form a round protuberance at the top. Then, water is pumped out between the plug and the wellbore, which is probably caused by the interface between the wellbore and the gel being destroyed for the secondary bonds are relatively weaker than the chemical bonds. These tests were repeated for this gel-plug system; the integrity of the gels was not damaged, which verified that, compared with strength, adhesion finally defined the pressure-bearing capacity value.

3.8. Degradation of MF-HPAM Gels. To simulate the downhole environment, the degradation of the crosslinked HPAM gels by ammonium persulfate solution with different concentrations of 1.0, 2.0, 5.0, and 7.5 wt % was examined (Figure 11). In this experiment, a breaker of the same mass was added on the top layer of the gel and the sample was sealed and placed in the oven at 80 °C. It was found that the interface of the gel and breaker became blurry, and the HPAM gel gradually dissolved. The gel added with a high concentration of ammonium persulfate solution degraded at a higher rate than that with a low concentration, which is possibly due to increased interactions of the gel and breaker, and more inner bonds were broken by oxidation. At about 3.5 h, the samples with 5.0 and 7.5 wt % ammonium persulfate solution were completely dissolved; however, the other two samples still had a certain amount of elastic gel at the bottom. After the observation for 6 h, they cannot be broken totally, which is because once the SO₄²⁻ ions produced by the S₂O₈²⁻ supply are depleted, the degradation of the HPAM gel will stop.

Figure 10. Pressure-bearing capacity curves measured by taking water as the pressure medium after gelation at different temperatures: (A) 60 °C, (B) 80 °C, and (C) 100 °C. (D) Appearance of the gel gelated in the casing tube.
crosslinks showed robust mechanical behaviors upon mechanical performance. The formed gel with covalent a relatively regular and dense spatial three-dimensional strength and good adhesion for the HPAM gel. This gel has the crosslinker trimethylol melamine guarantees a high guarantee for embodiment of high strength and good adhesion and provides pressure in the wellbore, which is the comprehensive embodiment demonstrated that the gel could e thermal treatment, and the pressure-bearing capacity experi- ciently plug the different concentrations.

4. CONCLUSIONS
A gel-plug system for temporary zonal isolation used in the open well has been developed for certain reservoir conditions. The basic gelling polymer solutions were formulated with a combination of 3.0 wt % starch, 0.5 wt % MF, 1.0 wt % HPAM, and 0.8 wt % NH₄Cl. NH₄Cl could act as an effective accelerator for this gel. The gelation mechanism can be described by the notion that the generation of covalent crosslinking through the nucleophilic attack by hydroxymethyl from MF tethered to the amide group from the HPAM backbone formed a large amount of stable junctions within the gel after thermal treatment, which was demonstrated by the corresponding spectrum analysis of FTIR. The gelation between MF and HPAM occurred over a broad range of temperature from 60 to 100°C with controllable gelation time. The crosslinker trimethylol melamine guarantees a high strength and good adhesion for the HPAM gel. This gel has a relatively regular and dense spatial three-dimensional microscopic network, which makes it have an excellent mechanical performance. The formed gel with covalent crosslinks showed robust mechanical behaviors upon in situ thermal treatment, and the pressure-bearing capacity experiment demonstrated that the gel could efficiently plug the pressure in the wellbore, which is the comprehensive embodiment of high strength and good adhesion and provides guarantee for field application as well.

AUTHOR INFORMATION

Corresponding Author
Li Cheng – Hubei Cooperative Innovation Center of Unconventional Oil and Gas and Key Laboratory of Drilling and Production Engineering for Oil and Gas, Yangtze University, Wuhan, Hubei 430100, P. R. China; orcid.org/0000-0003-4770-781S; Email: chengli_whu@163.com

Authors
Yi Qin – Petroleum Engineering Technology Research Institute, SINOPEC Zhongyuan Oilfield Company, Payang, Henan 457001, P. R. China
Yubin Su – Oil & Gas Technology Research Institute, Changqing Oilfield Branch Company, PetroChina, Xi’an, Shanxi 710021, P. R. China

Yuan Pan – Hubei Cooperative Innovation Center of Unconventional Oil and Gas and Key Laboratory of Drilling and Production Engineering for Oil and Gas, Yangtze University, Wuhan, Hubei 430100, P. R. China
Ying Wang – Hubei Cooperative Innovation Center of Unconventional Oil and Gas and Key Laboratory of Drilling and Production Engineering for Oil and Gas, Yangtze University, Wuhan, Hubei 430100, P. R. China
Ruiquan Liao – Hubei Cooperative Innovation Center of Unconventional Oil and Gas and Key Laboratory of Drilling and Production Engineering for Oil and Gas, Yangtze University, Wuhan, Hubei 430100, P. R. China
Zhen Li – Hubei Cooperative Innovation Center of Unconventional Oil and Gas and Key Laboratory of Drilling and Production Engineering for Oil and Gas, Yangtze University, Wuhan, Hubei 430100, P. R. China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c06626

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
The authors gratefully acknowledge the Cooperative Innovation Center of Unconventional Oil and Gas (Ministry of Education & Hubei Province) (no. UOG2020-15) and Hubei Province Department of Education (nos. Q20201304 and Q20201308) for the financial support. The authors express their appreciation to technical reviewers for their constructive comments.

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Figure 11. Degradation of the HPAM/MF gel broken by the same mass of ammonium persulfate solution with different concentrations.
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