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Optimization Analysis and Performance Study of Amphiphilic Polymer Hydrogel Gelation

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Abstract

Due to the widespread heterogeneity in oil reservoirs and severe water channeling, hydrogel-based agents are employed for profile control and water plugging. Amphiphilic polymers exhibit superior temperature and salt tolerance, and gels formed with these polymers as the primary agent demonstrate enhanced stability, showing broad application prospects. The ternary copolymer P(AM-NaA-ODAM) was synthesized via free-radical solution polymerization, with structural characterization of the product and related monomers performed using infrared spectroscopy. Leveraging the excellent properties of the P(AM-NaA-ODAM) solution, it was utilized as the main agent to construct the gel. The crosslinker formulation was optimized via a single-factor method, with gelation time and gel strength serving as key indicators to determine the optimal composition: hexamethylenetetramine (0.3%), resorcinol (0.05%), and citric acid (0.3%). Furthermore, under this optimized formulation, the effects of temperature and salinity on the amphiphilic polymer gel system were investigated, identifying suitable conditions for stable gel performance and providing a theoretical basis for oilfield profile control and water plugging operations.

Keywords

Amphiphilic polymer; temperature and salt resistance; gel system; optimization.

1. Introduction

Most mature oilfields face challenges of high water cut and low recovery efficiency, with reservoir heterogeneity being a widespread issue. Due to the presence of high-permeability zones and preferential flow paths within heterogeneous reservoirs, injected water tends to channel through these paths and return to the surface during water flooding. This results in high water cut in produced oil, low recovery efficiency, and high residual oil saturation[1]. Consequently, there is an urgent need for water shutoff and profile control agents to address these problems.

Amphiphilic polymers[2], also known as hydrophobically modified copolymers, refer to water-soluble polymers whose molecules simultaneously possess both hydrophilic and hydrophobic groups[3,4]. To modify polyacrylamide (PAM), hydrophobic groups are often copolymerized onto the main PAM chain, resulting in hydrophobically modified PAM polymers. Relying on their unique amphiphilic structure, these modified copolymer solutions exhibit significant advantages in properties like viscosity enhancement and shear resistance. Compared to partially hydrolyzed polyacrylamide (HPAM), amphiphilic polymers hold distinct advantages for oilfield applications.

Sarsenbekuly et al[5]. synthesized the polymer RH-4 via hydrophobic modification and investigated the effects of salt and temperature on its performance. Experiments revealed that while HPAM solution viscosity decreased with increasing salt concentration, RH-4 solution

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viscosity significantly increased. At the same salt concentration, the viscosity of the RH-4 solution was several times higher than that of HPAM. The modified polymer RH-4 demonstrated superior salt tolerance compared to HPAM.

Leveraging the excellent properties of amphiphilic polymers and selecting suitable crosslinkers, researchers have synthesized a series of hydrophobically modified amphiphilic polymer gels. Investigations into their temperature resistance, salt tolerance, and other properties provide theoretical support for water shutoff agents in oilfields.

Yang et al[6]. synthesized the amphiphilic polymer AP-P4 in the laboratory. Gels constructed using AP-P4 and Cr^{3+} were compared to those made with HPAM. Experiments showed that at 85°C, the AP-P4 polymer gel strength remained at 0.036 MPa. As salt concentration increased, gel strength was maintained between 0.03–0.037 MPa. Compared to the HPAM gel, the amphiphilic polymer gel exhibited stronger stability[7].

Building on the excellent properties of modified amphiphilic polymers, selecting suitable crosslinkers to construct gel systems and determining their optimal formulations and applicable conditions ensures that the gels maintain good performance during pumping operations in field applications, thereby effectively improving plugging effectiveness.

2. Experimental

2.1. Principles of Synthesis Methods

A series of ternary copolymer amphiphilic polymers were synthesized via free radical micellar polymerization, using the KPS-SHS redox system as the initiator and sodium dodecyl sulfate as the surfactant. The reaction mechanism is illustrated in Figure 1.

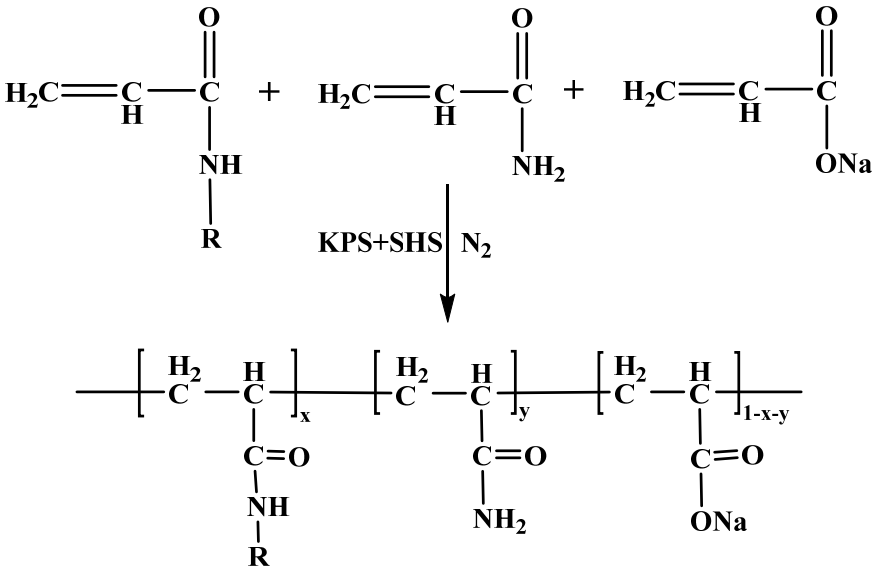

Figure 1. Synthesis Mechanism of Ternary Copolymer Amphiphilic Polymers

2.2. Construction of Gel Systems

The gel was constructed using the N-octadecylacrylamide ternary copolymer P(AM-NaA-ODAM) and phenolic resin crosslinker, with the reaction mechanism illustrated in Figure 2.

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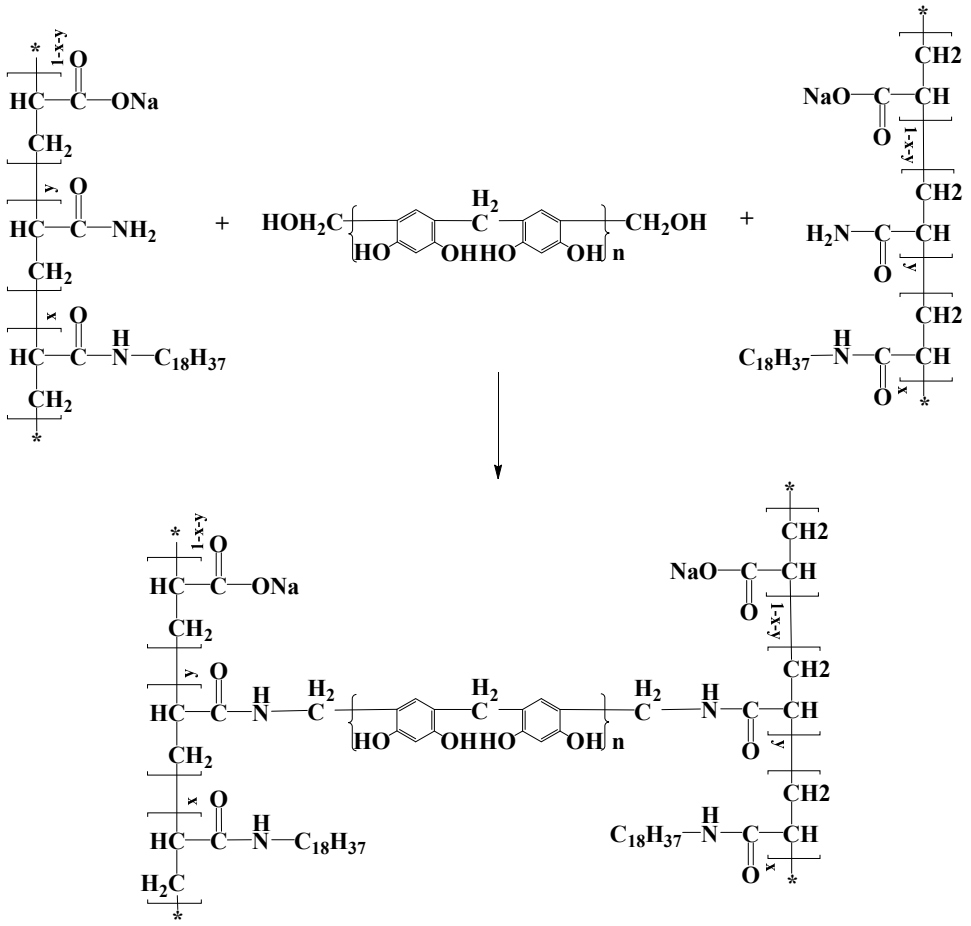

Figure 2. Gelation Mechanism

2.3. Characterization of Amphiphilic Polymers

The sample to be characterized was mixed with KBr and pressed into pellets, then analyzed by Fourier transform infrared spectroscopy (FTIR) to characterize the molecular structures of both the copolymer and monomers. The P(AM-NaA-ODAM) copolymer was specifically characterized

2.4. Optimization of Gel System Formulation

The study employed 1500 mg/L P(AM-NaA-ODAM) as the primary agent. Using a single-factor experimental approach with gelation time and gel strength as evaluation metrics, the effects of varying crosslinker concentrations on gelation performance were investigated to optimize the gel system formulation. The experiments were conducted at a gelation temperature of 45℃, utilizing hexamethylenetetramine (HMTA), citric acid, and resorcinol as crosslinkers.

2.4.1. Effect of Hexamethylenetetramine on Gel System Performance

Hexamethylenetetramine (HMTA) can slowly release formaldehyde under acidic conditions, and using HMTA instead of formaldehyde to participate in crosslinking reactions can reduce the toxicity of the gel system. Additionally, when the formaldehyde concentration is high, reactive resorcinol readily undergoes polycondensation with it to produce trimethylolresorcinol, whose steric hindrance significantly affects gel formation; whereas the reaction of HMTA generating formaldehyde is a slower reversible process that only proceeds forward when formaldehyde is consumed, thus substituting HMTA for formaldehyde can avoid such drawbacks.

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2.4.2. Effect of Resorcinol on Gel System Performance

Resorcinol is highly reactive and readily undergoes polycondensation with formaldehyde released from hexamethylenetetramine (HMTA) decomposition to form phenolic resin-type crosslinkers, which then construct a three-dimensional network gel system with amphiphilic polymers.

2.4.3. Effect of Citric Acid on Gel System Performance

Citric acid provides an acidic environment for the formation of the gel system. The reaction between NH_3 and formaldehyde produced by the decomposition of hexamethylenetetramine (HMTA) is reversible, and a suitable acidic environment favors the forward progression of the reversible reaction, promoting the hydrolysis of HMTA to release formaldehyde. Additionally, under acidic conditions, formaldehyde and resorcinol undergo polycondensation to form phenolic resin crosslinkers, which then construct a phenolic resin gel system with amphiphilic polymers.

2.5. Research on Gel System Performance

Based on single-factor experiments, the optimal ratio of crosslinkers was determined as 0.3% hexamethylenetetramine (HMTA), 0.05% resorcinol, and 0.3% citric acid. Using this optimal ratio, gelation was conducted under different conditions with a primary agent concentration of 1500 mg/L. The study investigated the effects of temperature and salinity on the gelation process, specifically examining their impacts on gelation time and gel strength.

2.5.1. Effect of Temperature on Gel System Performance

To determine the effect of temperature on gel performance, the crosslinkers were added to the amphiphilic polymer solution according to the optimal formulation, and after thorough mixing, the mixtures were allowed to gel at 35°C, 45°C, and 55°C, respectively, to investigate the influence of temperature on the viscosity evolution during the gelation process.

2.5.2. Effect of Salinity on Gel System Performance

Taking NaCl and $CaCl_2$ as examples, this study investigates the influence of salt content on gel system performance under the optimal crosslinker formulation.

3. Result and Discussion

3.1. FTIR Spectroscopy Results

To confirm whether the hydrophobically modified P(AM-NaA-ODAM) ternary copolymer sample was the target product, the synthesized P(AM-NaA-ODAM) was characterized by FTIR spectroscopy, and its spectrum was compared with that of the monomer N-octadecylacrylamide to determine the synthesis success. As shown in Figure 3, the peaks at 2927 cm^{-1} correspond to C-H stretching vibrations in $-CH_3$ and $-CH_2-$, the peak at 1604 cm^{-1} represents C=O stretching vibration in $-CONH_2$, and the peak at 1224 cm^{-1} is attributed to -COO-. By comparing these with the characteristic absorptions of N-octadecylacrylamide, it can be confirmed that the synthesized material is indeed the target product P(AM-NaA-ODAM).

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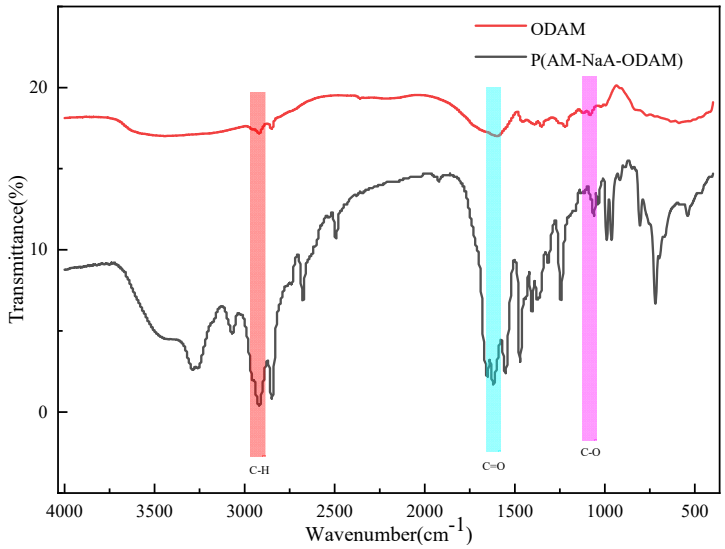

Figure 3. FTIR Spectroscopic Analysis of ODAM and P(AM-NaA-ODAM)

3.2. Optimization Analysis of Hexamethylenetetramine (HMTA)

The effect of hexamethylenetetramine (HMTA) content on gelation viscosity is shown in Figure 4(a), while the variations in gelation time and strength with HMTA content are presented in Figure 4(b). As seen from Figures 4(a) and 4(b), when the HMTA content increased from 0.2% to 0.3%, the gel strength significantly improved and the gelation time decreased from 32 h to 24 h; during the increase from 0.3% to 0.4% HMTA content, the gel strength slightly decreased while the gelation time remained at 24 h. Throughout the HMTA content variation from 0.2% to 0.4%, the gel viscosity first increased and then decreased, with the maximum gel strength of 35,648 mPa·s achieved at 0.3% HMTA content. Considering both gelation time and strength parameters, the optimal HMTA content was determined to be 0.3%.

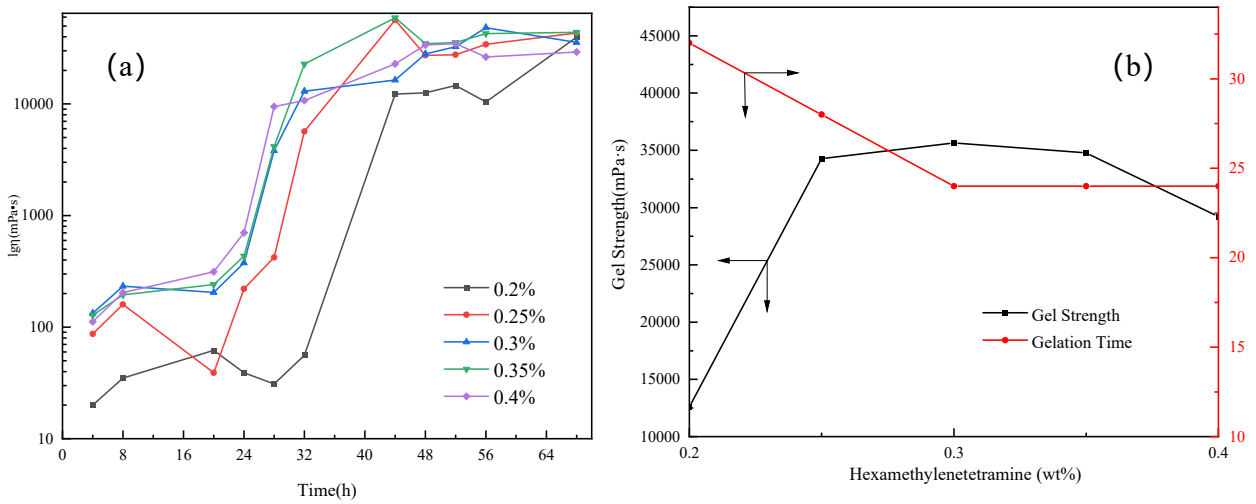

Figure 4. (a) Effect of Hexamethylenetetramine (HMTA) Content on Gelation Viscosity(b) Variation Curves of Gelation Time and Strength with HMTA Content

3.3. Effect of Resorcinol on Gel System Performance

As shown in Figures 5(a) and 5(b), when the resorcinol content increased from 0.01% to 0.09%, the gel strength first increased and then decreased, reaching its maximum value of 42,733 mPa·s at 0.05% resorcinol content. During the increase from 0.01% to 0.05% resorcinol content, the gelation time decreased from 32 h to 20 h, while beyond 0.05%, the gelation time remained constant at 20 h with no further change; the gel strength initially declined rapidly and then

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decreased more gradually. Considering both gelation time and strength parameters, the optimal resorcinol content was determined to be 0.05%.

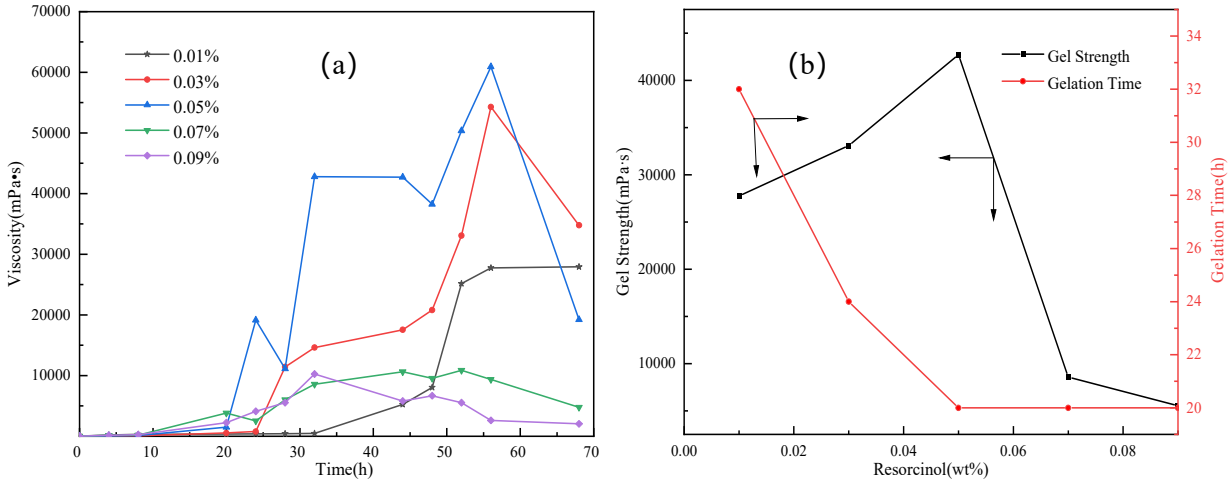

Figure 5. (a) Effect of Resorcinol Content on Gelation Viscosity (b) Variation Curves of Gelation Time and Strength with Resorcinol Content

3.4. Effect of Citric Acid on Gel System Performance

As shown in Figures 6(a) and 6(b), when the citric acid content increased from 0.1% to 0.3%, the gel strength increased rapidly, followed by a sharp decline between 0.3% and 0.4%, and then a gradual decrease beyond 0.4%. The maximum gel strength of 16,730 mPa·s was achieved at 0.3% citric acid content. During the increase from 0.1% to 0.4% citric acid, the gelation time decreased from 24 h to 20 h, remaining constant at 20 h when the content exceeded 0.4%. Considering both gelation time and strength parameters, the optimal citric acid content was determined to be 0.3%.

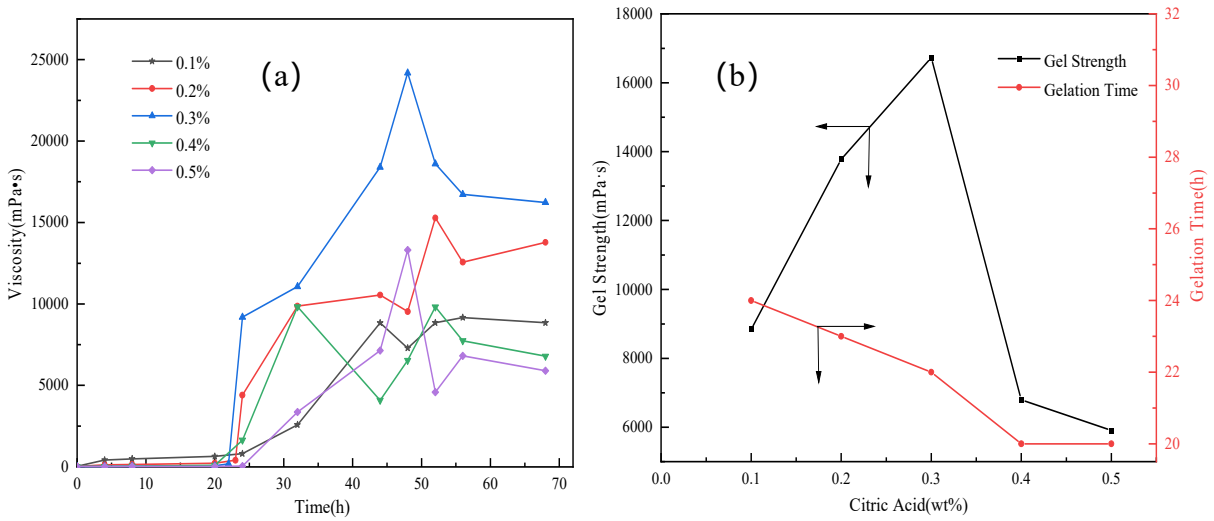

Figure 6. (a) Effect of Citric Acid Content on Gelation Viscosity (b) Variation Curves of Gelation Time and Strength with Citric Acid Content

3.5. Effect of Temperature on Gel System Performance

As shown in Figures 7(a) and 7(b), when the temperature increased from 35°C to 45°C, the gel strength increased, but beyond 45°C, further temperature rise led to a decrease in gel strength, peaking at 45°C with a maximum value of 42,733 mPa·s. The gelation time decreased with increasing temperature, dropping from 68 h at 35°C to 8 h at 45°C. This occurs because the

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thermal motion of amphiphilic polymer molecules intensifies with rising temperature, accelerating molecular diffusion and collision frequency, thereby increasing reaction rates and reducing gelation time. Additionally, in the lower temperature range (35–45°C), enhanced molecular thermal motion increases intermolecular collision frequency, promoting more vigorous crosslinking reactions between molecules and crosslinkers, which facilitates the formation of a three-dimensional network structure. Furthermore, the physical association between P(AM-NaA-ODAM) molecular chains strengthens with temperature [21], explaining why gel strength increases at moderately elevated temperatures. However, if the temperature becomes excessively high, the gel system may undergo over-crosslinking and dehydration, resulting in reduced gel strength.

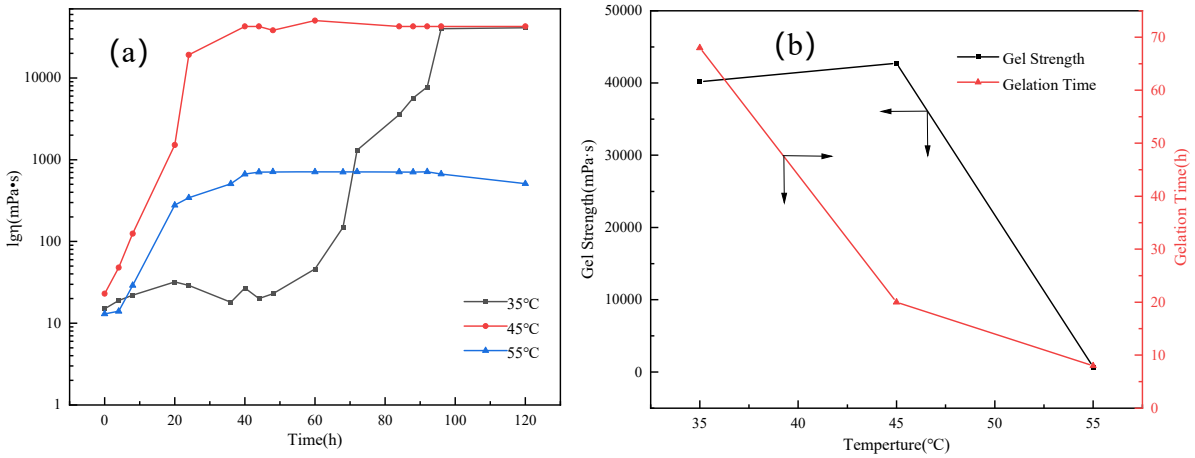

Figure 7. (a) Effect of Temperature on Gelation Viscosity (b) Variation Curves of Gelation Time and Strength with Temperature

3.6. Effect of Salinity on Gel System Performance

3.6.1. Effect of NaCl Concentration on Gelation Performance

As shown in Figures 8(a) and 8(b), when the NaCl concentration increased from 0 to 5,000 mg/L, the gel strength decreased sharply, while the gelation time was reduced from 24 h to 20 h. During the increase from 5000 mg/L to 20000 mg/L NaCl, the gel strength showed a slight decline, and the gelation time remained unchanged at 20 h. Even at 20000 mg/L NaCl, the gel system maintained a viscosity retention value of 3037 mPa·s.

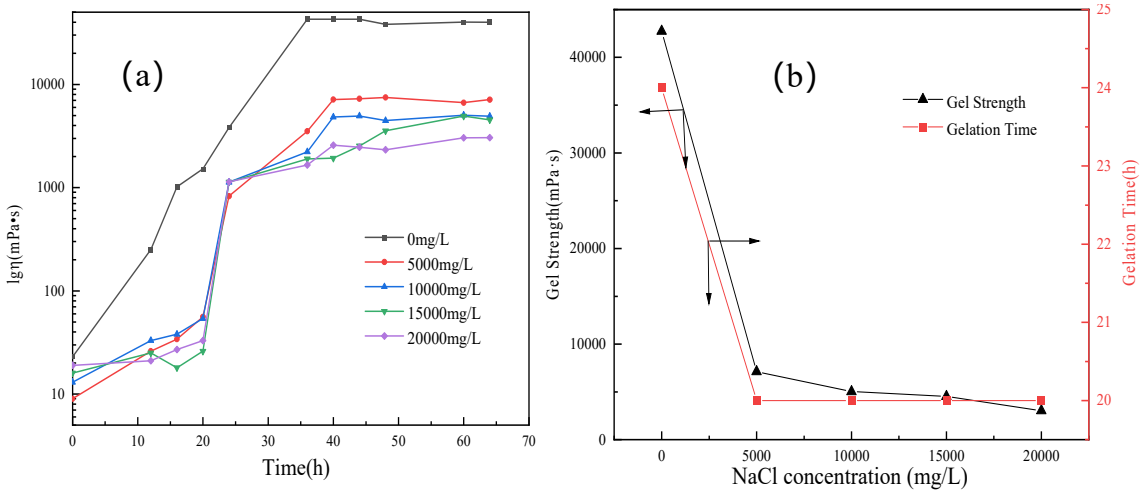

Figure 8. (a) Effect of NaCl Content on Gelation Viscosity (b) Variation Curves of Gelation Time and Strength with NaCl Content

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3.6.2. Effect of CaCl2 Concentration on Gelation Performance

As shown in Figures 9(a) and 9(b), when the $CaCl_2$ concentration increased from 0 to 400 mg/L, the gel strength decreased sharply. As the $CaCl_2$ concentration rose from 400 mg/L to 1000 mg/L, the rate of gel strength decline slowed, and at 1000 mg/L $CaCl_2$, the gel system still maintained a viscosity retention value of 1766 mPa·s. During the increase from 0 to 600 mg/L $CaCl_2$, the gelation time decreased from 24 h to 16 h, remained constant at 16 h from 600 mg/L to 800 mg/L, and then further decreased to 14 h with additional $CaCl_2$.

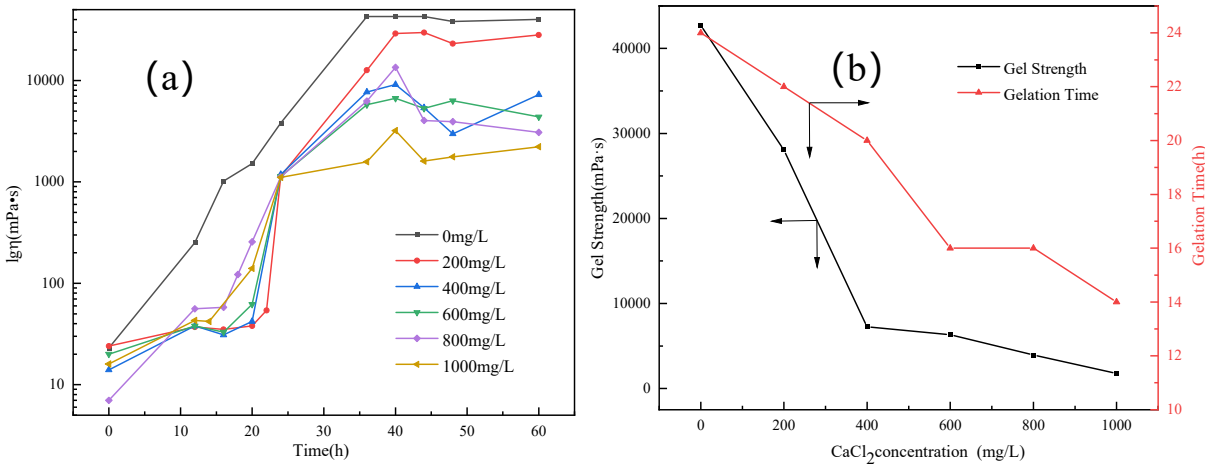

Figure 9. (a) Effect of $CaCl_2$ Content on Gelation Viscosity(b) Variation Curves of Gelation Time and Strength with CaC_2 Content

The observed trends indicate that divalent Ca^{2+} ions, with their higher charge density, exert significantly greater influence on gel performance than monovalent Na^+ ions, resulting in a consistent decrease in gel strength upon salt addition. This phenomenon occurs because metal ions form counterion pairs with carboxylate groups, shielding the negative charges on polymer chains and reducing electrostatic repulsion between polymer coils, leading to excessive coiling of polymer molecules and a decrease in their hydrodynamic volume. Moreover, higher salt concentrations intensify these effects, causing tighter intermolecular structures, reduced gel network space, limited water entrapment capacity, and increased free water content, ultimately diminishing the strength of the constructed gel.

4. Conclusions

(1) The copolymer P(AM-NaA-ODAM) was synthesized via free radical solution polymerization and characterized by FTIR spectroscopy to verify the successful copolymerization of hydrophobic monomers.

(2) As the concentrations of hexamethylenetetramine (HMTA), resorcinol, and citric acid increased, the gelation time initially decreased and then stabilized, while the gel strength first increased and subsequently decreased, exhibiting a maximum strength value. Through single-factor experiments, the optimal crosslinker formulation was determined to be 0.3% HMTA + 0.05% resorcinol + 0.3% citric acid. This system achieved a gel strength of 42733 mPa·s, meeting the requirements for oilfield water shutoff applications.

(3) As temperature increased from 35℃ to 55℃, the gel strength first rose and then declined, peaking at 45℃ with a maximum value of 42733 mPa·s, while the gelation time consistently decreased from 68 h to 8 h during this process. With increasing salinity, both gelation time and strength decreased, yet the gel strength could still reach 3037 mPa·s at 2000 mg/L Na^+ concentration and 1766 mPa·s at 1000 mg/L Ca^{2+} concentration.

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