

Synthesis and Performance Evaluation of an Organic/Inorganic Composite Gel Plugging System for Offshore Oilfields

Kun Xie, Cheng Su, Changlong Liu, Weijia Cao,* Xin He, Hongna Ding, Jie Mei, Kun Yan, Qian Cheng, and Xiangguo Lu



Cite This: *ACS Omega* 2022, 7, 12870–12878



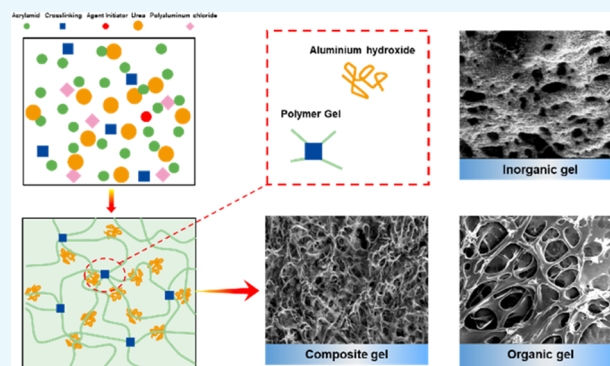
Read Online

ACCESS |

Metrics & More

Article Recommendations

ABSTRACT: In this article, we developed a new composite gel for plugging dominant fluid flow channels in offshore oilfields. The composite gel was synthesized by organic and inorganic gel networks interpenetrating into a compact three-dimensional spatial network structure, resulting in a good plugging effect. The performance of the composite gel was evaluated from the aspects of gelling characteristics and gel microstructure, while the plugging effect was evaluated through core experiments. The results showed that the influencing order of each component on gelling was acrylamide > cross-linking agent > urea > initiator > polyaluminum chloride. The initial viscosity of the composite gel was about 5–6 mPa·s, and it had good plugging abilities in different permeability cores. In comparison with inorganic gels (plugging ratio of 77.2%) or organic gels (84.8%), the composite gel system has a plugging ratio of up to 99.5% using a core with water permeability of 4300 mD. Besides, the reservoir applicability of the composite gel was studied, and the results suggested that the composite gel system had good resistance to dilution, mechanical shear, oil corrosion, and aging and could be quickly removed after plugging.



1. INTRODUCTION

Bohai oilfield is the largest offshore oilfield in China, and it has been developed by chemical flooding for tens of years.^{1–3} In recent years, it has been found that oil production in the medium- and low-permeability reservoir layers is unsatisfactory due to the existence of large fluid flow channels after the long-term scouring process of the oil displacement agent.^{4–6} To enhance the oil recovery in Bohai oilfield, it is important to find effective plugging agents to plug the dominant fluid flow channels to improve the swept volume of the oil displacement agent.^{7–11} The commonly used plugging agents for offshore reservoirs can be classified into organic gels or inorganic gels. The organic plugging agents include chromium(III) polymer gel,^{12,13} phenolic gel,¹⁴ starch-acrylamide gel,^{15,16} thermoresponsive polymer gel,¹⁷ amphiphilic copolymers,¹⁸ and so on. Inorganic gels primarily refer to the gels formed by the reaction between cations and various inorganic salts.^{19–21} In general, organic gels can form a three-dimensional network structure by the gelling reaction in the porous medium, thus plugging the dominant fluid flow channels and improving the reservoir heterogeneity,^{22–25} while the inorganic gel normally has stronger rigidity and retention in the reservoir, thus effectively reducing the reservoir permeability after its utilization.

As for organic gels, their good deformation ability can contribute to maintaining a complete structure, but this

deformation cannot resist the scouring of the oil displacement agent injected after the plugging. Besides, organic gel agents commonly have problems of quick gelling and higher initial viscosity decided by polymer concentration, which definitely influences the injectivity. Inorganic gels often use the injected water or the low-viscosity polymer solution as the carrier fluid. Although they have the ability to selectively enter large pores and have better stiffness to resist scouring, it is difficult to achieve high plugging strength and their gel structure quickly collapses when the scouring pressure is high.²⁶ A simple mixture of the organic and inorganic gels can treat the dominant fluid flow channels well, but the mixing operation requires complex operation equipment to meet high-production requirements in the oilfield, which is unfavorable for the offshore platform with limited construction space.

It is thus necessary to develop a plugging agent that has characteristics of low initial viscosity, good injectivity, controllable gelling time, and good plugging strength. Since the

Received: January 7, 2022

Accepted: March 22, 2022

Published: April 5, 2022

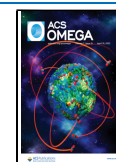


Table 1. Ion Composition of Formation Water in Bohai LD10-1 Oilfield

parameter	ion						total dissolved solids (TDS) (mg/L)	
	Ca ²⁺	Mg ²⁺	Na ⁺	CO ₃ ²⁻	HCO ₃ ⁻	Cl ⁻		SO ₄ ²⁻
concentration (mg/L)	826.7	60.8	2968.8	0	208.7	6051.6	60.0	10,176.6

evolution degree of dominant fluid flow channels in offshore oilfields is serious, it is difficult to achieve a stronger plugging effect using single organic plugging agents; hence, improving the performance of organic gel is an effective way to meet the plugging need in offshore oilfields from the aspect of material property.^{27–29} In this article, we synthesize a composite gel system composed of both organic and inorganic gel plugging agents, which has low initial viscosity and good gelling strength for a small molecular initial reactant and composite structure compared with the existing plugging agent used in Bohai oilfield. The properties of this synthesized gel plugging agent, such as gelling time, gel microstructure, plugging ratio, and reservoir applicability, are evaluated using a viscometer, a Fourier transform infrared (FTIR) spectrometer, scanning electron microscopy (SEM), and a core plugging ratio test using an artificial core.

2. EXPERIMENTAL SECTION

2.1. Experimental Materials. Polyaluminum chloride (>90%), urea (>99%), ammonium persulfate (98%), acrylamide (>99%), and *N,N'*-methylene bisacrylamide (98%) were used.

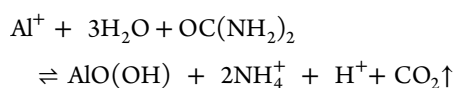
A simulated oil was used in the core plugging ratio test, which was made up of the degassed crude oil from the Bohai LD10-1 oilfield and kerosene. The viscosity of this simulated oil was measured to be 17 mPa·s at 65 °C. The injection water was formation water from the LD10-1 oilfield, and its ion composition is shown in Table 1.

Artificial homogeneous cores cemented by quartz sands (4.5 cm × 4.5 cm × 30 cm) were used in this study to investigate the plugging ratio of the composite gel.^{30,31} The permeabilities of these cores were approximately 9000, 5000, and 2000 mD, respectively, and their pore structures and permeabilities were similar to those of reservoir cores in the Bohai oilfield. The procedures to prepare the artificial cores can be found in the Chinese patent “Quartz sand epoxy resin cementation heterogeneity model making method”,^{32,33} and the picture of the entire core coated with epoxy resin is shown in Figure 1.



Figure 1. Example picture of the artificial core sample used in this study.

2.2. Experiments. **2.2.1. Gelling Reaction of the Composite Gel.** The gelling reaction of the composite gel can be divided into two parts, that is, the gelling reaction of inorganic gel,³⁴ which involves Al³⁺ hydrolysis in the urea solution,



and the gelling reaction of organic gels (Figure 2), which is achieved by the polymerization of acrylamide monomers, followed by the cross-linking of polyacrylamide with *N,N'*-methylene bisacrylamide.^{35–39}

Based on the reaction of organic gelling and inorganic gelling, the gelling reaction of the composite gel can be explained as shown in Figure 3.

2.2.2. Conversion Ratio Testing of the Composite Gel. To test the conversion ratio of the composite gel, polyaluminum chloride, acrylamide, urea, the cross-linking agent (*N,N'*-methylene bisacrylamide), and the initiator (ammonium persulfate) were added to the formation water and then mixed by magnetic stirring for 48 h. After the gelling of the composite gel, the unreacted chemicals were washed off with excess pure ethanol and then the composite gel was collected. The mass ratio between the composite gel and the acrylamide is termed the unreacted ratio of acrylamide. It was found that the unreacted ratio of acrylamide was lower than 2.0% in this study, which indicates that the conversion ratio of acrylamide monomers could reach up to 99.5%. Thus, the composite gel can be used directly without further purification.

2.2.3. Viscosity. A DV-II Brookfield viscometer equipped with a Brookfield water bath was used to test the apparent viscosity of the composite gel. As the viscosity range of the composite gel may vary greatly, the rotor type (Rotor 1–6) was selected according to the specific viscosity of the composite gel in the test.

2.2.4. Evaluation of Gelling Time. The gelling time was measured using the Sydansk (1988) gel strength code method, which is a semiquantitative measurement. During the experiment, we defined the gelling time as the moment when the gel strength reached Grade G. Gels of Grade G have moderately deformable and nonflowing characteristics and can only flow approximately halfway down the bottle upon inversion.

2.2.5. Infrared Spectrum. A Nexus 870 Fourier transform infrared (FTIR) spectrometer was used to obtain the infrared spectra to determine the chemical structure of the composite gel.

2.2.6. Gel Micromorphology. An FEI Quanta 450 field emission scanning electron microscope was used to observe the morphology of the composite gel. When using the scanning electron microscope to observe the gel aggregates, no coating was required. The sample preparation temperature was –196 °C.

2.2.7. Plugging Ratio in the Cores. The plugging ratio of the composite gel was evaluated using the homogeneous artificial cores wrapped in epoxy resin. The main devices include an advection pump, a pressure sensor, a coating core, and the container of the plugging agent. All of the equipment, except for the advection pump, was placed in a thermostatically controlled oven at 65 °C (reservoir temperature) to simulate actual reservoir conditions. The diagram of the experimental setup is shown in Figure 4. The experimental procedures for testing the plugging effect can be described as follows.

- (1) The artificial core was saturated with formation water using a vacuum pump, and then the pore volume and

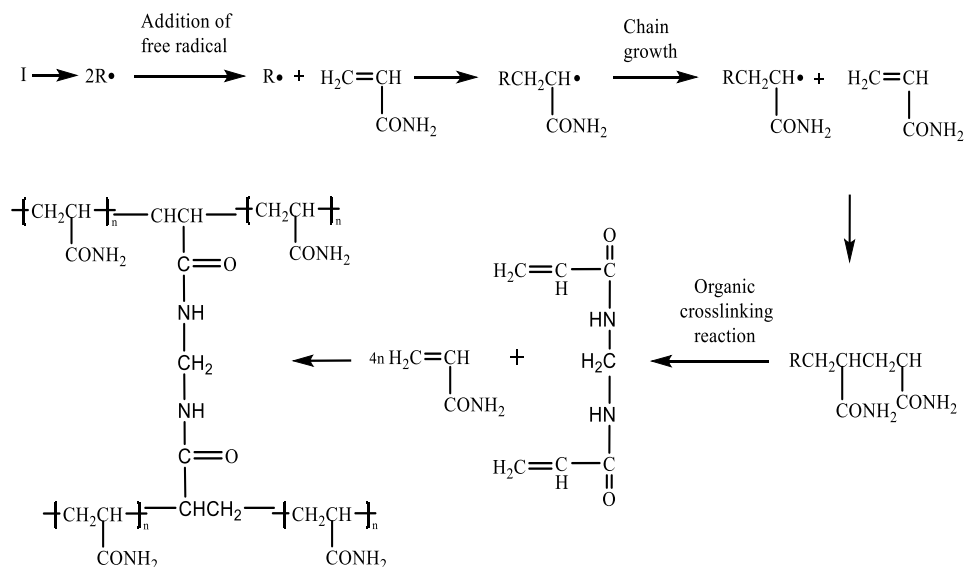


Figure 2. Schematic of the synthesis of organic gels.

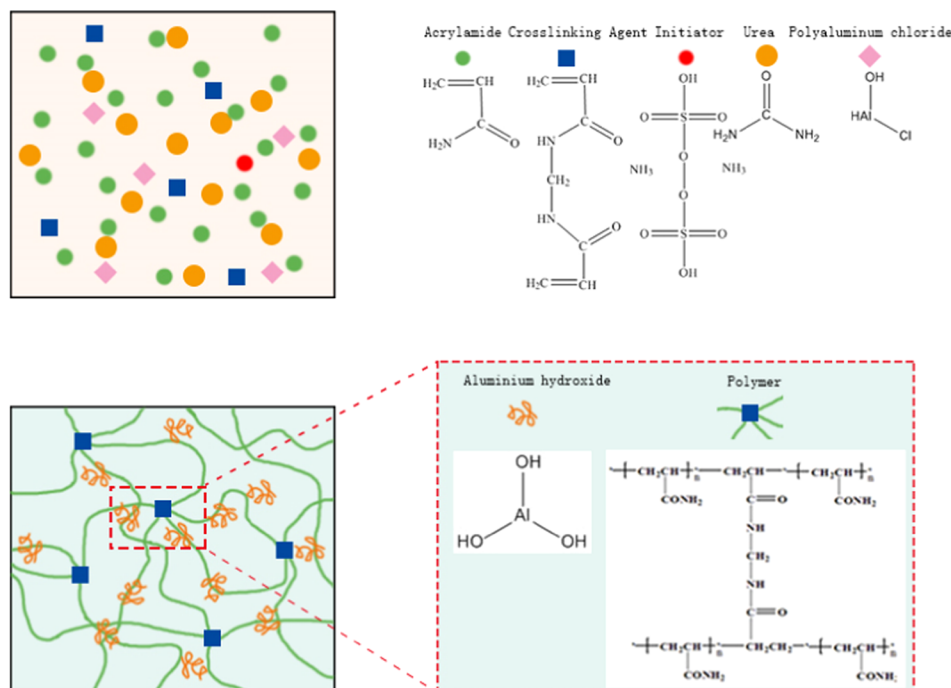


Figure 3. Diagram of the gelling process of the composite gel.

porosity of the core were calculated from the difference between the dry weight and the wet weight of the core.

- (2) The core was flooded by the formation water at flow rates of 0.5, 1.0, and 1.5 mL/min separately to determine the core permeability (denoted as K_1) using the classical Darcy's law.
- (3) The core was flooded by the composite gel at a flow rate of 1.0 mL/min with a 1.5 pore volume (PV), and then the core was stood for 72 h to allow for the gelling of the composite gel at a temperature of 65 °C. To eliminate the ending effect (the gelled composite gel existed in the outlet valve), a valve was placed 2 cm away from the injection end and the production end of the core,

respectively. The core permeability (denoted as K_2) was also determined in this process.

- (4) The plugging ratio of the composite gel can be calculated as $(K_1 - K_2)/K_1$.

3. RESULTS AND DISCUSSION

3.1. Formula Optimization of the Composite Gel. The ingredients of the composite gel included polyaluminum chloride, urea, ammonium persulfate, acrylamide, and N,N' -methylene bisacrylamide. This paper thus varied the mass percent of each component or mass ratio between polyaluminum chloride and urea to prepare composite gels according to the orthogonal design of L16(4^5).⁴⁰ The

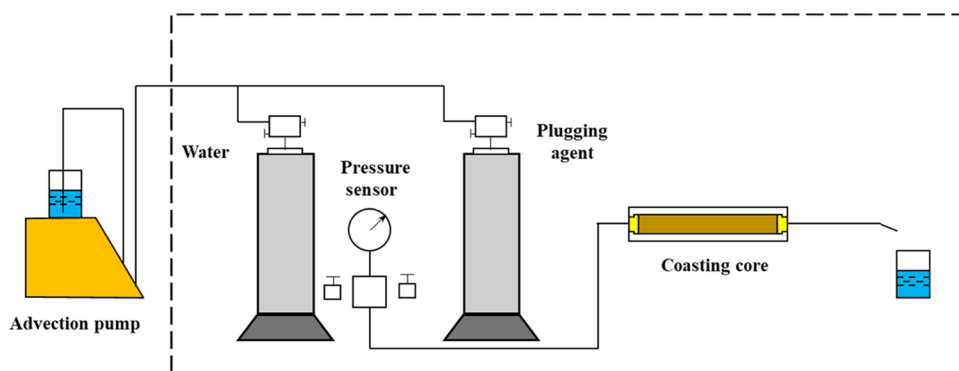


Figure 4. Schematic diagram of the equipment setup in the plugging test.

Table 2. Orthogonal Experimental Results of the Composite Gel^a

system	factors					initial viscosity (mPa·s)	gelling time (h)
	polyaluminum chloride (%)	acrylamide (%)	polyaluminum chloride/urea	Ω (initiator/acrylamide) (%)	Ω (cross-linking agent/acrylamide) (%)		
1	1.0	2.8	1:1.0	0.25	0.2	5.1	28.0
2	1.0	3.0	1:1.2	0.35	0.3	5.7	17.0
3	1.0	3.2	1:1.4	0.45	0.4	6.2	2.5
4	1.0	3.4	1:1.6	0.55	0.5	6.1	1.5
5	1.5	2.8	1:1.2	0.45	0.5	5.3	15.5
6	1.5	3.0	1:1.0	0.55	0.4	6.0	21.5
7	1.5	3.2	1:1.6	0.25	0.3	5.7	7.5
8	1.5	3.4	1:1.4	0.35	0.2	5.6	11.0
9	2.0	2.8	1:1.4	0.55	0.3	6.3	23.0
10	2.0	3.0	1:1.6	0.45	0.2	5.7	13.0
11	2.0	3.2	1:1.0	0.35	0.5	5.9	6.0
12	2.0	3.4	1:1.2	0.25	0.4	6.2	2.5
13	2.5	2.8	1:1.6	0.35	0.4	5.6	13.5
14	2.5	3.0	1:1.4	0.25	0.5	6.1	9.0
15	2.5	3.2	1:1.2	0.55	0.2	5.3	22.0
16	2.5	3.4	1:1.0	0.45	0.3	5.7	18.0

^aThe gelling time refers to the time when the gel strength reached Grade G. Ω is the mass percentage.

Table 3. Range Analysis of Gelling Time^a

factors		polyaluminum chloride (%)	acrylamide (%)	polyaluminum chloride/urea	Ω (initiator/acrylamide) (%)	Ω (cross-linking agent/acrylamide) (%)
gelling time	α	12.25	20.00	18.38	11.75	18.50
	β	13.88	15.13	14.25	11.88	16.38
	γ	11.13	9.50	11.38	12.25	10.00
	δ	15.63	8.25	8.88	17.00	8.00
	R	4.50	11.75	9.50	5.25	10.50

^aParameters α , β , γ , δ , and R are calculated according to the calculation rule of the orthogonal table. α , β , γ , and δ , respectively, represent the gelling time average value under the condition of each type of value of different factors.

orthogonal experiments included five factors, and each factor had four types of values. The results of orthogonal experiments are shown in Table 2. Then, the initial viscosity and gelling time of the composite gels were evaluated to obtain the optimum formula for the composite gel at 65 °C (see Table 3).

It can be seen from Tables 2 and 3 that the content of each component in the composite gel influences the gelling effect, which follows the order acrylamide > cross-linking agent > urea > initiator > polymeric aluminum chloride. It is also found that the organic gels contribute to a greater extent than the inorganic gels to the viscosity of the composite gel. Moreover, the initial viscosity of the composite gel is observed to be low (5.1–6.3 mPa·s), and the gel strength reaches Grade G, suggesting that

the composite gel has good injectivity and plugging performance. It is worth noticing that the period of gel plugging in an offshore oilfield at present is approximately 20 days,⁴¹ and the dosage of the plugging agent in a single plugging period may reach 5000 m³, which also requires the plugging agent to have good injectivity to smoothly enter the target plugging layers containing dominant fluid flow channels to avoid pollution in the middle- and low-permeability layers under a specific pressure range. Therefore, a gelling time of over 24 h for the plugging agent is favorable to ensure both construction safety and the plugging effect in offshore oilfields. In regard to this time threshold, the optimum formula of the composite gel is supposed to be 1.5–2.5% polyaluminum chloride, polyalumi-

num chloride/urea ratio of 1:1.0–1:1.4, 2.8–3.0% acrylamide, and Ω (initiator/acrylamide) of 0.45–0.55% and Ω (cross-linking agent/acrylamide) of 0.2–0.3%. In the following discussions, we select the formula of 1.5–2.5% polyaluminum chloride, 1.5–3.5% urea, 2.8–3.0% acrylamide, 0.005–0.009% cross-linking agent, and 0.012–0.017% initiator to investigate the performance of the composite gel.

3.2. Performance Evaluation of the Composite Gel. In this section, the composite gel made of 3.0% acrylamide, 0.008% cross-linking agent, 0.015% initiator, 2.0% polyaluminum chloride, and 2.6% urea; the organic gel made of 3.0% acrylamide, 0.008% cross-linking agent, and 0.015% initiator; and the inorganic gel made of 2.0% polyaluminum chloride and 2.6% urea were tested with respect to the three aspects of infrared spectra, gel morphology, and plugging effect.

3.3. Infrared Spectra. The infrared (IR) spectra of the inorganic gel, organic gel, and composite gel are shown in Figure 5. In the IR spectrum of the inorganic gel, we clearly observe the

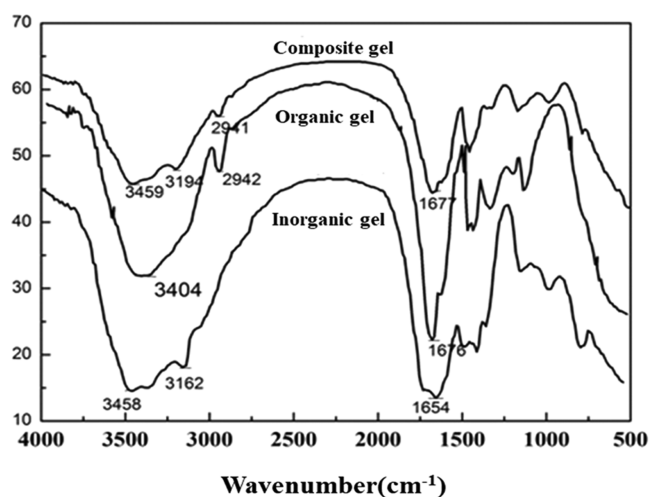


Figure 5. IR spectra of different kinds of gels.

absorption peaks of the amino group (3458 cm^{-1}), an associative hydroxyl group (3162 cm^{-1}), and carbonyl group (1654 cm^{-1}), suggesting that the inorganic gel was formed by the reaction of urea with the amide group and polyaluminum chloride. In the IR spectrum of the organic gels, the absorption peaks of the amino groups (3404 cm^{-1}), saturated hydrocarbon bonds (2942 cm^{-1}), and the carbonyl groups (1676 cm^{-1}) were observed, which indicated that the acrylamide monomer

completely reacted in an organic gel. In comparison with the organic gel spectrum, it was found that in the IR spectrum there was no change in the shift of the absorption peak and the peak pattern of the amino group, the saturated hydrocarbon bond, and the carbonyl group, whereas the absorption peak of the associative hydroxyl group (3194 cm^{-1}) was added to the molecular chain of the polymeric aluminum chloride, implying that the composite gel was formed by the physical interpenetration of the organic gel with the inorganic gel.

3.4. Gel Morphology. The SEM images of the inorganic gel, organic gel, and composite gel are shown in Figure 6. We clearly observed that the inorganic gel was unable to form a continuous three-dimensional network; hence, its morphology displayed a dense packing structure with holes. In direct contrast, the organic gel was polymerized and cross-linked by an acrylamide monomer; thus, it presented a three-dimensional network structure with a typical “hole-network” morphology. The morphology of the composite gel, however, lies in between the “hole-network” and the dense packing structures, which may be attributed to the physical interpenetration between the organic gel and the inorganic gel, and consequently, the overall morphology of the composite gel showed a spatial configuration.

3.5. Influence of Gel Types on the Core Plugging Ratio. The core plugging ratio is usually quantified by the reduction of permeability after the injection of gels. It can be seen from Table 4 that the gel plugging ratio of each gel type was different, and

Table 4. Experimental Results of Core Plugging Effect ($K = 4300\text{ mD}$)

parameter		gel type		
		inorganic gel	organic gel	composite gel
water permeability (mD)	before plugging	4326.5	4387.2	4352.8
	after plugging	985.8	665.7	20.4
plugging rate (%)		77.2	84.8	99.5

the core plugging ratio followed the order composite gel > organic gel > inorganic gel. As discussed previously, the inorganic gel encountered structural damage when it was transported in the pore throat, resulting in an unsatisfactory plugging ratio. Although the elasticity of the organic gel was better compared to that of the inorganic gel, the scouring effect of subsequent water caused gel deformation; its plugging ratio was still not effective. Whereas the composite gel had the strongest scouring resistance and the highest plugging ratio due

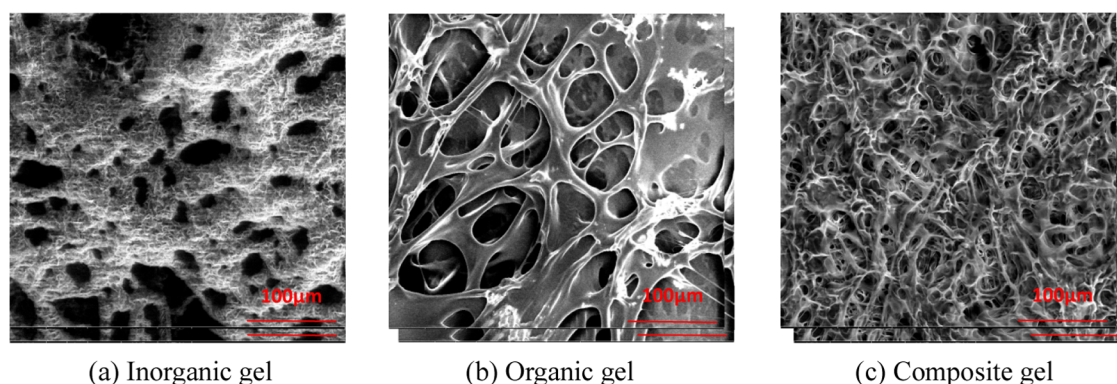


Figure 6. SEM images of gel morphology.

to its good mechanical strength and deformation ability owing to its composite network.

3.6. Influence of Core Permeability on the Plugging Ratio.

Table 5 shows the influences of core permeability on the

Table 5. Influence of Core Permeability on Plugging Ratio

parameter	core permeability permeability K (mD)		
	2000	5000	9000
plugging ratio (%)	97.1	98.3	99.5

plugging ratio of the composite gel. In general, with the increase of core permeability, the pore-throat size also increased, and the larger pore throat thus provided a more continuous and abundant space for the gelling reaction.⁴² With respect to the plugging ratio, it can be seen from Table 4 that the plugging ratio of each core was higher than 97%, indicating that the composite gel had a significant plugging ability for different permeability reservoirs, which can effectively improve the reservoir heterogeneity and enhance the displacement efficiency of subsequent fluid after plugging.

3.7. Applicability of the Composite Gel in Reservoirs.

During the process of injecting the plugging agent, it undergoes the shearing of pipeline and pore throat, the dilution by formation water, and the influences of crude oil in the reservoir. Considering the influences of operation technology and reservoir conditions, the applicability of the composite gel in the reservoir was comprehensively evaluated from five aspects, including dilution resistance, shear resistance, oil resistance, acid resistance, and aging resistance. In regard to the requirement of the gelling time of the plugging agent being more than 24 h in offshore oilfields, we designed two systems of the composite gel according to the orthogonal experimental results: system I of 2.0% polyaluminum chloride, 2.6% urea, 0.015% initiator, 0.008% cross-linking agent, and 3.4% acrylamide (gelling time of 26.5 h) and system II of 2.0% polyaluminum chloride, 2.6% urea, 0.015% initiator, 0.011% cross-linker, and 3.0% acrylamide (gelling time 31.0 h). The composite gel is prepared with the formation water and then placed in a glass jar in an incubator at 65 °C.

3.8. Dilution Resistance. It can be seen from Table 6 that with the decrease of the $V_{\text{gel}}/V_{\text{water}}$ ratio (10:1, 7:1, 5:1, 3:1, and 1:1), the mass percent of each component in the composite gel decreased, the speed of cross-linking reaction decreased, and the gelling time increased. Only when the $V_{\text{gel}}/V_{\text{water}}$ ratio was higher than 7:1 was the viscosity of the composite gel larger than 10×10^4 mPa·s after the gelling, suggesting that the composite gel had good dilution resistance, which could facilitate the gel system to achieve a good plugging effect on the dominant fluid flow channels in deep reservoirs.

3.9. Shear Resistance. The composite gel was sheared at 30, 70, 100, 150, and 200 s using a WARING laboratory blender

at a shearing ratio of 7000 rpm, as Table 7 shows the gelling time of the composite gel. Apparently, the gelling time of the

Table 7. Effect of Shearing on the Gelling Time

parameter		shearing time (s)					
		0	30	70	100	150	200
time (h)	system I	26.5	26.0	26.5	27.0	26.0	26.0
	system II	31.0	30.5	31.5	31.0	31.0	30.5

composite gel was not influenced by the shear indicating that the components of the composite gel were made by small molecules that were insensitive to the shearing. In other words, the composite gel had good shear resistance, and its gelling effect was affected by the shearing of the injection equipment, wellbore, and pore throats.

3.10. Oil Resistance. The reservoir oil was mixed with the composite gel at 5, 8, 12, 16, and 20%. It can be seen from Table 8 that the crude oil did not influence the gelling time of the

Table 8. Effect of Crude Oil on Gelling Time

parameter		percent of oil (%)					
		0	5	8	12	16	20
time (h)	system I	26.5	25.0	25.5	27.0	27.5.0	27.0
	system II	31.0	30.0	31.5	32.0	30.5	32.0

composite gel, indicating that the composite gel had good oil resistance, and moreover, the gelling effect after the gel entered the reservoir was not affected by the remaining oil in the pore throats of the rock.

3.11. Acid Resistance. A mixture solution of 10% HCl and 5% HF was added to the gelled composite gel at a ratio of $V_{\text{acid}}/V_{\text{gel}} = 1:9$. The weight changes of the gelled composite gel are shown in Table 9. The dissolution process of the composite gel is shown in Figure 7, and the weight loss ratio was defined as (gel initial weight – residual weight)/initial weight.

Table 9. Results of Weight Loss Experiments

parameter		soaking time (min)				
		10	30	60	90	130
weight loss ratio (%)	system I	19.97	43.96	70.59	85.85	94.52
	system II	24.13	49.51	72.94	88.92	97.35

The results showed that the weight loss ratio increased gradually with the increase in soaking time. In general, it is supposed that once the inorganic gel was degraded, the main structure of the composite gel was also degraded, and the composite gel may decompose within 2 h. The results indicated that if the composite gel was injected into the medium- and low-permeability layers, a designated acidizing can be carried out to

Table 6. Effect of Dilution on the Gelling Time and Viscosity

parameter		$V_{\text{gel}}/V_{\text{water}}$					
		undiluted	10:1	7:1	5:1	3:1	1:1
time (h)	system I	26.5	32.0	35.5	40.5	44.0	53.5
	system II	31.0	35.0	38.5	42.0	48.0	59.5
viscosity (mPa·s)	system I	$>10 \times 10^4$	$>10 \times 10^4$	$>10 \times 10^4$	89,324	65,324	13,657
	system II	$>10 \times 10^4$	$>10 \times 10^4$	$>10 \times 10^4$	72,314	48,324	7963

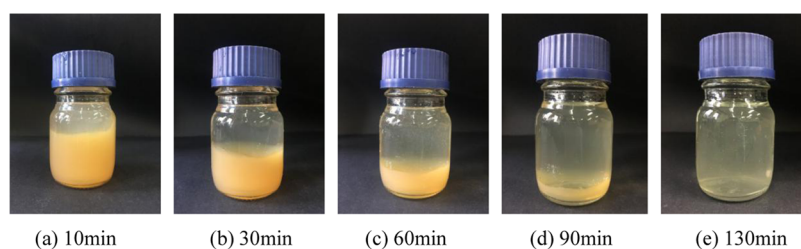


Figure 7. Dissolution process of the composite gel.

Table 10. Effect of Aging Time on Gel Viscosity

parameter		storage time (days)						
		1	2	5	10	30	60	90
viscosity (mPa·s)	system I	$>10 \times 10^4$	$>10 \times 10^4$	$>10 \times 10^4$	$>10 \times 10^4$	$>10 \times 10^4$	95,236	88,523
	system II	66,978	$>10 \times 10^4$	$>10 \times 10^4$	$>10 \times 10^4$	98,754	83,542	78,632

achieve rapid removal of the plugging gel to prevent reservoir contamination.

3.12. Aging Resistance. The gelled viscosities of the composite gel are shown in Table 10. It seems that the viscosity of each gel system remained at a higher level with the prolongation of the aging time. However, the viscosity of system II began to decrease after 30 days but remained at a high level, suggesting that the composite gel had good aging resistance.

4. CONCLUSIONS

- (1) The initial viscosity of the composite gel is low, which is good for transport and migration in different permeabilities cores. Different from the inorganic gel or the organic gel, the composite gel is formed by a complex interpenetration of the organic gel network with the inorganic gel network, forming a compact three-dimensional spatial network structure that has great strength and good deformation, resulting in a high plugging ratio.
- (2) The orthogonal testing showed that the mass percent of each component in the composite gel influenced the gelling effect, following the order acrylamide > cross-linking agent > urea > initiator > polyaluminum chloride.
- (3) The organic gel contributed more to the gel viscosity of the composite gel than the inorganic gel. The optimized formulation of the composite gel was 1.5–2.5% polyaluminum chloride, 1.5–3.5% urea, 2.8–3.0% acrylamide, 0.005–0.009% cross-linking agent, and 0.012–0.017% initiator to ensure the gel-forming effect in the offshore reservoir.
- (4) The composite gel had good dilution resistance, shear resistance, oil resistance, and aging resistance, and it was easy and quick to be removed after plugging.

AUTHOR INFORMATION

Corresponding Author

Weijia Cao – Laboratory of Enhanced Oil Recovery of Education Ministry, Northeast Petroleum University College of Petroleum Engineering, Daqing 163318, P. R. China;
 orcid.org/0000-0002-3399-6591;
 Email: caoweijia131466@163.com

Authors

Kun Xie – Laboratory of Enhanced Oil Recovery of Education Ministry, Northeast Petroleum University College of Petroleum Engineering, Daqing 163318, P. R. China

Cheng Su – Laboratory of Enhanced Oil Recovery of Education Ministry, Northeast Petroleum University College of Petroleum Engineering, Daqing 163318, P. R. China

Changlong Liu – Bohai Oilfield Research Institute, Tianjin Branch of CNOOC (China) Co., Ltd., Tianjin 300459, P. R. China

Xin He – Laboratory of Enhanced Oil Recovery of Education Ministry, Northeast Petroleum University College of Petroleum Engineering, Daqing 163318, P. R. China; orcid.org/0000-0001-9524-9420

Hongna Ding – Laboratory of Enhanced Oil Recovery of Education Ministry, Northeast Petroleum University College of Petroleum Engineering, Daqing 163318, P. R. China; orcid.org/0000-0003-4526-5507

Jie Mei – Laboratory of Enhanced Oil Recovery of Education Ministry, Northeast Petroleum University College of Petroleum Engineering, Daqing 163318, P. R. China

Kun Yan – Laboratory of Enhanced Oil Recovery of Education Ministry, Northeast Petroleum University College of Petroleum Engineering, Daqing 163318, P. R. China

Qian Cheng – Laboratory of Enhanced Oil Recovery of Education Ministry, Northeast Petroleum University College of Petroleum Engineering, Daqing 163318, P. R. China

Xiangguo Lu – Laboratory of Enhanced Oil Recovery of Education Ministry, Northeast Petroleum University College of Petroleum Engineering, Daqing 163318, P. R. China

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acsomega.2c00133>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Postdoctoral Innovative Talents Support Program of China (BX20190065), Natural Science Foundation of China (No. 51834005), and National Science and Technology Major Projects (2016 ZX05058-003-010).

NOMENCLATURE

K_g core permeability measured by gas (mD)

K_1	core permeability measured by water before plugging (mD)
K_2	core permeability measured by water after plugging (mD)
V_{gel}	volume of composite gel (mL)
V_{water}	volume of dilution (mL)

REFERENCES

- (1) Cao, W. J.; Xie, K.; Lu, X. G.; Liu, Y.; Zhang, Y. Effect of profile-control oil-displacement agent on increasing oil recovery and its mechanism. *Fuel* **2019**, *237*, 1151–1160.
- (2) Zhou, Y. X.; Lu, X. G.; Wang, R. J.; Liu, Y. G. Numerical Simulation for Optimizing Injection – Production Parameters When Using Cyclic Steam Injection Plus Polymer Gel Flooding in An Offshore Heavy-Oil Field. *Chem. Technol. Fuels Oils* **2017**, *53*, 621–631.
- (3) Xie, K.; Lu, X. G.; Li, Q.; Jiang, W.; Yu, Q. Analysis of reservoir applicability of hydrophobically associating polymer. *SPE J.* **2016**, *21*, 1–9.
- (4) Dai, C. L.; Yang, S.; Wu, X. P.; Liu, Y. F.; Peng, D. X.; Wang, K.; Wu, Y. N. Investigation on Polymer Reutilization Mechanism of Salt-Tolerant Modified Starch on Offshore Oilfield. *Energy Fuels* **2016**, *30*, 5585–5592.
- (5) Xie, K.; Cao, W. J.; Lu, X. G.; Song, K. P.; Liu, Y. G.; Zhang, Y. B.; Liu, J. X.; Lv, J. L.; Wang, W.; Na, R. Influence of water dilution on performance of chromium polymer weak gel in porous medium. *J. Dispersion Sci. Technol.* **2020**, *41*, 1549–1558.
- (6) Wang, J.; Liu, H. Q. A novel model and sensitivity analysis for viscoelastic polymer flooding in offshore oilfield. *J. Ind. Eng. Chem.* **2014**, *20*, 656–667.
- (7) Liu, R.; Du, D. J.; Pu, W. F.; Peng, Q.; Tao, Z. W.; Pang, Y. Viscoelastic displacement and anomalously enhanced oil recovery of a novel star-like amphiphilic polyacrylamide. *Chem. Eng. Res. Des.* **2019**, *142*, 369–385.
- (8) Zhou, Y. Z.; Wang, D. M.; Wang, Z. P.; Cao, R. The formation and viscoelasticity of pore-throat scale emulsion in porous media. *Pet. Explor. Dev.* **2017**, *44*, 111–118.
- (9) Li, Y. B.; Chen, Y. F.; Pu, W. F.; Gao, H.; Bai, B. J. Experimental investigation into the oxidative characteristics of Tahe heavy crude oil. *Fuel* **2017**, *209*, 194–202.
- (10) He, Y. W.; Chen, S. Q.; Li, L.; Mu, G.; Zhang, T.; Xu, H.; et al. Waterflood Direction and Front Characterization With Four-Step Work Flow: A Case Study in Changqing Oil field, China. *SPE Reservoir Eval. Eng.* **2017**, *20*, 708–725.
- (11) Lin, W.; Yang, Z. M.; Li, X. Z.; Wang, J.; He, Y.; Wu, G. M.; Xiong, S. C.; Wei, Y. Y. A method to select representative rock samples for digital core modeling. *Fractals* **2017**, *25*, No. 1740013.
- (12) Sun, Z.; Lu, X. G.; Xu, G. R.; Kang, X. D.; Li, Q.; Jiang, W. D. Effects of core structure and clay mineral on gel-forming performance of chromium polymer. *Colloids Surf., A* **2018**, *540*, 256–264.
- (13) Jia, H.; Chen, H. The potential of using Cr^{3+} / salt-tolerant polymer gel for well workover in low-temperature reservoir: laboratory investigation and pilot test. *SPE Prod. Oper.* **2018**, *33*, 569–582.
- (14) Gu, C. L.; Lv, Y. H.; Fan, X. Q.; Zhao, C. X.; Dai, C. L.; Zhao, G. Study on rheology and microstructure of phenolic resin cross-linked nonionic polyacrylamide (NPAM) gel for profile control and water shutoff treatments. *J. Pet. Sci. Eng.* **2018**, *169*, 546–552.
- (15) Zhiyu, W.; Zuoxin, L. The optimization of synthesizing graft copolymer of starch with vinyl monomers. *J. Wuhan Univ. Technol., Mater. Sci. Ed.* **2006**, *21*, 83–87.
- (16) Li, X. H.; Fu, H.; Li, Y. X.; Li, N. Corrosion inhibition of cassava starch graft copolymer for Al in HCl solution. *Corros. Sci. Prot. Technol.* **2016**, *28*, 525–530.
- (17) Ngeue, R.; Omondi, B. A.; Yamasaki, S.; Mandai, S.; Sugai, V.; Sasaki, K. Evaluation of CO_2 -triggered and thermo-responsive gels for heterogeneous oil formations-scienced direct. *Colloids Surf., A* **2021**, *622*, No. 126688.
- (18) Raffa, P.; Broekhuis, A. A.; Picchioni, F. Amphiphilic copolymers based on PEG-acrylate as surface active water viscosifiers: towards new potential systems for enhanced oil recovery. *J. Appl. Polym. Sci.* **2016**, *133*, No. 44100.
- (19) Pham, L. T.; Hatzignatiou, D. G. Rheological Evaluation of A Sodium Silicate Gel System for Water Management in Mature. *J. Pet. Sci. Eng.* **2016**, *138*, 218–233.
- (20) Zhao, J.; Zhang, J. Research and Advances of Silicate Plugging Agent in the Oilfields. *J. Mater. Sci. Chem. Eng.* **2019**, *07*, 1–10.
- (21) Hatzignatiou, D. G.; Askarinezhad, R.; Giske, N. H.; Stavland, A. Laboratory Testing of Environmentally Friendly Sodium Silicate Systems for Water Management Through Conformance Control. *SPE Prod. Oper.* **2016**, *31*, 337–350.
- (22) Aldhaheer, M.; Wei, M. Z.; Zhang, N.; Bai, B. A Review of Field Oil-Production Response of Injection-Well Gel Treatments. *SPE Reservoir Eval. Eng.* **2019**, *22*, 597–611.
- (23) Liu, Y. F.; Dai, C. L.; Wang, K.; Zhao, M. W.; Gao, M. W.; Yang, Z.; Fang, J. C.; Wu, Y. N. Investigation on Preparation and Profile Control Mechanisms of the Dispersed Particle Gels (DPG) Formed from Phenol-Formaldehyde Cross-linked Polymer. *Ind. Eng. Chem. Res.* **2016**, *55*, 6284–6292.
- (24) Bai, B. J.; Zhou, J.; Yin, M. F. A comprehensive review of polyacrylamide polymer gels for conformance control. *Pet. Explor. Dev.* **2015**, *42*, 525–532.
- (25) Seright, R.; Brattekas, B. Water shutoff and conformance improvement: an introduction. *Pet. Sci.* **2021**, *18*, 450–478.
- (26) Niu, L. W.; Lu, X. G.; Xiong, C. M.; Tang, X. F.; Wu, X. C.; Jia, X.; Zhang, S. Experimental study on gelling property and plugging effect of inorganic gel system (OMGL). *Pet. Explor. Dev.* **2013**, *40*, 780–784.
- (27) Jia, H.; Pu, W. F.; Zhao, J. Z.; Liao, R. Experimental investigation of the novel phenol–formaldehyde cross-linking HPAM gel system: based on the secondary cross-linking method of organic cross-linkers and its gelation performance study after flowing through porous media. *Energy Fuels* **2011**, *25*, 727–736.
- (28) Farizal, H.; Damian, D. S.; Achmad, A.; Nuraeni, S.; Aditya, W.; Siregar, S. In *SPE/IATMI Asia Pacific Oil & Gas Conference and Exhibition, Is Epoxy-Based Polymer Suitable for Water Shut-Off Application?*, Nusa Dua, Bali, Indonesia, 2015.
- (29) He, H.; Wang, Y. F.; Sun, X. J.; Zhang, P.; Li, D. D. Development and evaluation of organic/inorganic combined gel for conformance control in high temperature and high salinity reservoirs. *J. Pet. Explor. Prod. Technol.* **2015**, *5*, 211–217.
- (30) Xie, K.; Lu, X. G.; Pan, H.; Han, D.; Hu, G.; Zhang, J.; Zhang, B.; Cao, B. Analysis of dynamic imbibition effect of surfactant in micro cracks in reservoir with high temperature and low permeability. *SPE Prod. Oper.* **2018**, *33*, 596–606.
- (31) Cao, W. J.; Xie, K.; Wang, X. Y.; Lu, X. G.; He, X.; Xu, G. R.; Li, X. Starch graft copolymer and polymer gel applied in Bohai oilfield for water plugging and profile control and their mechanisms. *Geosyst. Eng.* **2020**, *23*, 197–204.
- (32) Xie, K.; Cao, B.; Lu, X. G.; Jiang, W. D.; Zhang, Y. B.; Li, Q.; Song, K. P.; Liu, J. X.; Wang, W.; Lv, J. L.; Na, R. Matching Between the Diameter of the Aggregates of Hydrophobically Associating Polymers and Reservoir Pore-Throat Size during Polymer Flooding in an Offshore Oilfield. *J. Pet. Sci. Eng.* **2019**, *177*, 558–569.
- (33) Cao, W. J.; Xie, K.; Lu, X. G.; Chen, Q.; Tian, Z. Y.; Lin, W. Self-suspending proppant manufacturing method and its property evaluation. *J. Pet. Sci. Eng.* **2020**, *192*, No. 107251.
- (34) Wang, P.; Dai, C. L.; You, Q. Experimental study on shearing and salt tolerant deep profile control agents composed of inorganic aluminum gel. *Pet. Geol. Recovery Effic.* **2013**, *20*, 100–103.
- (35) Liang, H.; Lu, J. *Fundamentals of Polymer Science*; Chemical Industry Press: Bei Jing, 2006; Vol. 54, pp 81–94.
- (36) Chen, W. J.; Wang, X. J.; Hu, K.; Zhu, Y.; Zhang, J.; Wang, H. Synthesis and properties of polyacrylamide polymer flooding agent with high shear resistance. *J. Xi'an Shiyou Univ., Nat. Sci. Ed.* **2018**, *33*, 105–111.

(37) Xue, D.; Yang, Q.; Xie, Q. J.; Yang, P. H.; Wang, Z. F. Synthesis of hydrophobic associated terpolymer based on acrylamide. *Appl. Chem. Ind.* **2018**, *47*, 312–314.

(38) Lai, A. K.; Liu, M.; Zhang, Z. M.; Qin, G.; Wang, Y.; Gou, S. Synthesis and performance of a novel amphiphilic acrylamide copolymers. *Pet. Ind. Appl.* **2018**, *38*, 114–119.

(39) Ma, Y. X. Experimentation research of acrylamide polymerizing technology. *J. China Univ. Pet., Ed. Nat. Sci.* **2002**, *15*, 32–34.

(40) Lu, X. G.; Xie, K.; Cao, B.; Chen, X. Study on gelling effect of Cr^{3+} polymer gel and its influence factors. *J. China Univ. Pet., Ed. Nat. Sci.* **2015**, *39*, 170–176.

(41) Lu, X. G.; Liu, Y. G. *Study on Comprehensive Treatment Technology of High Water Cut Oilfield in Bohai Sea*; Chemical Industry Press: Bei Jing, 2011; pp 57–62.

(42) Liu, J. X.; Lu, X. G.; Liu, J. F.; Hu, S. Q.; Xue, B. Q. Mechanism and gelling effects of linked polymer solution in the core. *Pet. Explor. Dev.* **2013**, *40*, 507–513.