Self-Lubricating Supramolecular Hydrogel for In-Depth Profile Control in Fractured Reservoirs

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ABSTRACT: In-depth profile control is a great challenge for high-efficiency oil displacement by water flooding. In this work, a shear-responsive self-lubricating hydrogel FPP-0.5, by combining the thixotropic FT (N-fluorenylmethoxy carbonyl-l-tryptophan) supramolecular network with high-strength PAM–PAANa (PAM: polyacrylamide, PAANa: sodium polyacrylate) polymer network, was synthesized and applied for in-depth profile control in water flooding. The disassembly of the FT supramolecular network induced by shear force, accompanied by the formation of a lubricating layer on the gel surface, gives FPP-0.5 gel self-lubricating function. Meanwhile, the PAM–PAANa polymer network, as a protective scaffold for the FT network, endows FPP-0.5 with high strength, making it difficult to be broken by water flow. Moreover, the shear responsiveness enables FPP-0.5 to adjust its own strength and self-lubricating performance according to the different stages of the profile control process, so as to realize dynamic profile control. From oil displacement results, in comparison to the PAM–PAANa gel, the plugging rate, water flooding volume sweep efficiency, and oil recovery of FPP-0.5 were improved by 83.1, 155.4, and 34.0%, respectively, up to 86.6, 83.5, and 71.3%, indicating its better in-depth profile control ability.

1. INTRODUCTION

Channeling is one of the main problems reducing water flooding performance. With increasing water flooding rounds as well as fracturing or acidizing implementation, amounts of crude oil were displaced in shallow formation, forming a high-permeability layer with largely increased fractures, thus significantly enhancing the in-layer and interlayer heterogeneity of reservoirs. The subsequent water flow generally passes through a high-permeability layer by water channeling, or leaks through formation fractures, rather than entering into deep formation with high oil saturation, leading to a decrease of subsequent water flooding performance. To solve this problem, many inorganic (e.g., cement, clay, etc.) and organic materials (e.g., hydrogel, chemical-modified starch, etc.) were developed to plug formation channels. Herein, gel is one of the most popular and effective profile control agents in organic materials. At present, the commonly used gel profile control agents are composed of hydrophilic polymers by chemical cross-linking, such as polyacrylamide–hexamethylene netetramine–hydroquinone (PAM–HMTA–HQ), gels with asphalt particles (GAP), and PAM–poly(acrylic acid) (PAA). As for these gel systems, gel mechanical property and plugging performance were improved by adding reinforcing fillers (e.g., HMTA–HQ, DDSB, asphalt nanoparticles, etc.) to generate and strengthen covalent bonds, hydrogen bonds, and van der Waals force between polymer chains and additive molecules.

However, due to the strong adhesion between the traditional polymer gel and the formation rock surface, their friction is also great, thus causing some deficiencies of gel in-depth profile control. These problems are as follows: (1) High frictional resistance results in a poor macroscopic in-depth profile control ability of gel. With the prolongation of water flooding, part of crude oil in deep formation is driven out, and a new “high permeable intermediate layer” in low-permeability zones is formed. Because of the high friction force, the gel, mainly concentrated in the large channels of the high-permeability layer, is difficult to migrate in formation and freely access the low-permeability layer and in-layer microchannels (Figure 1a), resulting in a poor plugging performance for the high permeable intermediate layer and low subsequent water flooding effect. (2) High friction force brings about a low microscopic sweep efficiency of water flooding. It also causes inferior injectivity and migration ability of gel, not only making water leakage from some large channels not being blocked by gel, but also the gel is hard to migrate into microchannels and
slits to displace oil in them. Meanwhile, owing to the high viscosity and strong adhesion, a polymer gel is easy to be broken through to produce viscous fingering and channeling (Figure 1a), hence reducing the oil displacement efficiency.13,17

To solve the above-mentioned problems, in this work, a novel self-lubricating hydrogel FT$-$PAM$-$PAANa (FPP), by introducing a shear-responsive supramolecular FT network into a chemically cross-linked polymer gel PAM$-$PAANa (FT: N-fluorenlymethoxycarbonyl-L-tryptophan, PAM: polyacrylamide, PAANa: sodium polyacrylate), was synthesized to efficiently decrease the friction between the gel and rock surface in formation. To be specific, the thixotropic FT supramolecular network ruptures, degrades into a lubricating fluid, triggered by external shear force, and then weeps out to the gel surface to form a lubricating layer with an ultralow friction coefficient between the gel and rock surface.18,19 As a result, FPP gel is endowed with self-lubricating ability and displays a piston-like movement driven by water flow in the formation channel, so as to increase the oil displacement efficiency (Figure 1b). Compared to traditional polymer gels, low-friction FPP gels have the following advantages in reservoir profile control. (1) FPP, easy to migrate in formation channels, can quickly enter into deep formation and effectively plug the high permeable intermediate layer, thus to improve gel in-depth profile control performance. (2) FPP can be facilely pushed into formation slits and microchannels by water flow to drive out the residual oil, largely enhancing water flooding sweep efficiency (Figure 1b). (3) The shear responsiveness of FPP enables it to dynamically adjust its strength and self-lubricating property according to profile control requirements from different displacement stages and reservoir areas, thus realizing dynamic profile control.

2. RESULTS AND DISCUSSION

2.1. FPP Gel Characterization. The shear-responsive self-lubricating composite gel FPP, with FT and PAM$-$PAANa forming a parallel staggered network, was prepared by a one-pot reaction. To be specific, benzene proton resonances (FPP: 7.17$-$7.83 ppm, FT: 7.19$-$7.74 ppm; Figure 2a), its skeleton vibration band (FPP: 1562 cm$^{-1}$, FT: 1526 cm$^{-1}$; Figure 2b), and out-of-plane vibration band (FPP: 782 cm$^{-1}$, FT: 762 cm$^{-1}$; Figure 2b) simultaneously appeared in 1H nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectra as for FT and FPP gel, respectively. However, methylene protons (1.07 ppm, Figure 2a), carbon (36.07 ppm, Figure 2c) resonances, and methine carbon resonance (45.51 ppm, Figure 2c) of PAM$-$PAANa only appeared in the NMR spectra of FPP gel, without FT gel, indicating the existence of PAM$-$PAANa polymer chain and benzene structure from FT in FPP. Meanwhile, the appearance of fluorenlymethoxycarbonyl (Fmoc) methylene proton resonance (FPP: 4.27 ppm, Figure 2c) of PAM$-$PAANa only appeared in the NMR spectra of FPP gel, without FT gel, indicating the existence of PAM$-$PAANa polymer chain and benzene structure from FT in FPP. Meanwhile, the appearance of fluorenlymethoxycarbonyl (Fmoc) methylene proton resonance (FPP: 4.27 ppm, Figure 2c) of PAM$-$PAANa only appeared in the NMR spectra of FPP gel, without FT gel, indicating the existence of PAM$-$PAANa polymer chain and benzene structure from FT in FPP. Meanwhile, the appearance of fluorenlymethoxycarbonyl (Fmoc) methylene proton resonance (FPP: 4.27 ppm, Figure 2c) of PAM$-$PAANa only appeared in the NMR spectra of FPP gel, without FT gel, indicating the existence of PAM$-$PAANa polymer chain and benzene structure from FT in FPP. Meanwhile, the appearance of fluorenlymethoxycarbonyl (Fmoc) methylene proton resonance (FPP: 4.27 ppm, Figure 2c) of PAM$-$PAANa only appeared in the NMR spectra of FPP gel, without FT gel, indicating the existence of PAM$-$PAANa polymer chain and benzene structure from FT in FPP. Meanwhile, the appearance of fluorenlymethoxycarbonyl (Fmoc) methylene proton resonance (FPP: 4.27 ppm, Figure 2c) of PAM$-$PAANa only appeared in the NMR spectra of FPP gel, without FT gel, indicating the existence of PAM$-$PAANa polymer chain and benzene structure from FT in FPP. Meanwhile, the appearance of fluorenlymethoxycarbonyl (Fmoc) methylene proton resonance (FPP: 4.27 ppm, Figure 2c) of PAM$-$PAANa only appeared in the NMR spectra of FPP gel, without FT gel, indicating the existence of PAM$-$PAANa polymer chain and benzene structure from FT in FPP. Meanwhile, the appearance of fluorenlymethoxycarbonyl (Fmoc) methylene proton resonance (FPP: 4.27 ppm, Figure 2c) of PAM$-$PAANa only appeared in the NMR spectra of FPP gel, without FT gel, indicating the existence of PAM$-$PAANa polymer chain and benzene structure from FT in FPP. Meanwhile, the appearance of fluorenlymethoxycarbonyl (Fmoc) methylene proton resonance (FPP: 4.27 ppm, Figure 2c) of PAM$-$PAANa only appeared in the NMR spectra of FPP gel, without FT gel, indicating the existence of PAM$-$PAANa polymer chain and benzene structure from FT in FPP.

Figure 1. Schematic diagram of the gel profile control mechanism: (a) polymer gel and (b) FPP supramolecular gel.
FT: 4.32 ppm, Figure 2a), tryptophan methylene proton (FPP: 3.53 ppm, FT: 3.24 ppm, Figure 2a), carbon (FPP: 18.67 ppm, FT: 16.82 ppm, Figure 2c) resonance, and methine carbon resonance (FPP: 53.27 ppm, FT: 57.40 ppm, Figure 2c) in the 1H NMR and 13C NMR spectra of FPP evidence the successful introduction of FT into the FPP gel. Furthermore, the emergence of diffraction peaks in the X-ray diffraction (XRD) pattern of FPP (Figure 2d), corresponding to π−π stacking (FPP: 20.8°, FT: 21.6°) and hydrogen-bond (FPP: 16.7°, FT: 16.1°) interactions from the FT network, indicates FT self-assembly into the supramolecular network in the FPP gel. In a word, the results of 1H NMR, 13C NMR, FTIR, and XRD analyses showed that the one-pot reaction had completed

Figure 2. Gel samples' characterization: (a) 1H NMR, (c) 13C NMR spectra, and (d) XRD patterns of FT and FPP gels; (b) FTIR spectra of FT, PAM–PAANa, and FPP gels.

Figure 3. Gel self-lubricating property analysis: (a, b) gel friction force and coefficient versus FT concentration and (c) schematic diagram of gel supramolecular network thixotropy.
to obtain the FPP gel, with the FT supramolecular network being successfully introduced into the PAM−PAANa network.

2.2. Effect of FT Concentration on FPP Friction Property. From Figure 3a,b, the FT addition in PAM−PAANa gel can significantly reduce the friction force and friction coefficient between the gel and solid surfaces. With FT concentration increasing, surface friction of the FPP gel first decreased and then became stable. Accordingly, the optimum FPP was chosen to be FPP-0.5, corresponding to the smallest friction force, friction coefficient, and FT concentration. Its friction force and friction coefficient were, respectively, reduced by 52.13 and 51.85% (from 1.80 mN and 0.026) compared to the PAM−PAANa gel, indicating that the FPP-0.5 gel has better self-lubricating properties. Because of the FT supramolecular network with strong thixotropy, it can break into fragments and monomers (Figure 3c) under external shear, which transforms the FT gel structure into sol (Figure 4a(i)). Then, removing shear force and leaving the FT sol standing for a period of time (15−30 min), the FT supramolecular network can recover itself (Figure 4a(i)) and regenerate gel. Therefore, the strong friction between the FPP gel and solid surfaces makes the FT supramolecular network in FPP disassembled into fragments and monomers, which then combines with water molecules to form sol. Thereafter, the sol weeps out on gel surface to produce a lubricating layer (Figure 4a(ii)), largely decreasing the gel surface friction and endowing the self-lubricating function to the FPP gel. In addition, comparing frequency sweep results of gel samples, it shows that: (1) Within the sweep frequency range, gel−sol transition does not occur in PAM−PAANa gel (Figure 4b). (2) With FT concentration increasing, the gel−sol transition frequency of FPP gels, larger than that of the FT gel, first decreased and then tended to be unchanged (Figure 4b,d), proving that a better self-lubricating property and mobility can be acquired by increasing FT concentration appropriately. Meanwhile, the FT supramolecular network displays aggregation-induced emission property in the fluorescence spectrum. Accordingly, its broken network will reduce the fluorescence intensity of the spectral peak. From Figure 4c,d, with the increase of FT concentration, the FT network fluorescence

Figure 4. (a) (i) Schematic diagram of FT gel thixotropy and (ii) shear-responsive self-lubrication, (b) frequency sweep results of FPP, PAM−PAANa, and FT gel in rheological analysis, (c) fluorescence emission spectra of FPP and FT gel, and (d) gel−sol transition frequency and FT network fluorescence peak (at 367 nm) intensity versus FT concentration.
peak (at 367 nm) intensity first increases and then tends to be stable. Hence, an effective reinforcement of the FT supramolecular network and a good self-lubricating performance of FPP can be acquired by properly increasing FT addition.

2.3. Effect of FT Concentration on FPP Mechanical Property. Loss tangent \(\tan \delta (\tan \delta = G''/G')\), an important parameter for judging fluid type, can be used to characterize the solidlike property of a gel. A larger \(\tan \delta\) value represents a weaker solidlike structure and a stronger mobility of a gel.25−27 From Figure 5g–i, due to the addition of FT, the PAM−PAANa gel elastic modulus \((G')\) decreases to some extent with its \(\tan \delta\) increasing obviously. As the FT concentration rises, the FPP gel \(G'\) decreases slowly and then rapidly, and its \(\tan \delta\) enlarges gradually, indicating a reduced strength, while an improved mobility of PAM−PAANa gel induced by FT addition. The reasons for the above results are as follows. (1) FT addition can decrease PAM−PAANa network strength. With the rise of FT addition, the PAM−PAANa gel network became looser (Figure 5a–c), and the connection among gel colloidal particles was weakened (Figure 5d–f). This indicates that supramolecular connections in the PAM−PAANa network were impaired by added FT, thus reducing the gel strength.19,28 (2) FT addition can decrease the cross-linking degree of the PAM−PAANa gel. The average transverse relaxation time \((T_{2,avg})\) of all low-field NMR (LF-NMR) peaks of a gel can be employed to qualitatively analyze its overall cross-linking degree, and a lower \(T_{2,avg}\) value suggests a higher cross-linking degree.29,30 Meanwhile, the relative strength of each peak in the LF-NMR spectra represents the contribution ratio of its corresponding cross-linking interaction to total cross-linking reaction.31 From Figure 5j–l, the increased FT concentration enlarged \(T_{2,avg}\) and reduced the polymer−\(H_2O\) peak relative intensity of the FPP gel (Figure 5j–l), evidencing weakened supramolecular interaction (hydrogen-bond interaction, ion−dipole interaction, etc.) between polymer chain and \(H_2O\) molecules36,37 and the decreased overall cross-linking degree and strength of FPP. According to the influence of FT concentration on the FPP gel self-lubricating property (Figure 3a,b) and strength (Figure 5g–i), FPP-0.5 has good self-lubricating property and high strength, up to 1287 Pa.

2.4. Effect of Shearing on Self-Lubricating Property and Strength of FPP-0.5. From Figure 6b,c, with shear cycle rising, the FPP-0.5 gel \(G'\) and friction coefficient were stable first and then increased gradually, while that of the PAM−PAANa gel remained unchanged, indicating that the FPP-0.5 self-lubricating property was due to shear resistance to some extent—ultralow friction force was kept between FPP gel and solid surfaces within some shear cycles (18 cycles). Then, the friction force and gel strength obviously enlarged with further increasing shear cycle. Meanwhile, the gel−sol transition frequency of FPP-0.5 displayed a first stable and then significant increase trend with shear cycle rise (Figure 6d), demonstrating the shear resistance of gel mobility in certain shear cycles. The reasons are as follows. (1) Shearing lessens
the FT supramolecular network in the FPP gel. From Figure 6a, induced by shear cycle increase, the fluorescence peak intensity of the FT network in the FPP gel reduced gradually with the compressed mesh and thickened wall of the FPP network as well as its enhanced colloidal particles’ aggregation (Figure 6a(i−iii)), showing that excess FT was squeezed out on gel surface with shear force imposed continuously, leading to the decreased self-lubricating property and improved strength of FPP. (2) Shearing increases the cross-linking degree of the FPP gel. From Figure 6e, compared to the unchanged value of PAM−PAANa, the $T_{2,\text{avg}}$ value of FPP-0.5 decreased under multicycle shearing (more than 18 cycles), indicating the effective enhancement of physical cross-linking and gel network (Figure 6a(i−iii)) in FPP-0.5 by continuous shearing, thus efficiently improving gel strength.

### 2.5. Core Flooding Experiments

From Figure 7a,b, in comparison to the PAM−PAANa gel, the larger decrease of water cut and higher differential pressure of subsequent water flooding were obtained induced by the FPP-0.5 gel injection, showing its better profile control performance, namely, displacing water in more formation channels and blocking these channels to effectively increase displacement differential pressure. Meanwhile, compared to the PAM−PAANa gel (Table 1), the plugging rate ($\eta$), water flooding volumetric sweep efficiency ($E_v$), and oil recovery (RE) of FPP-0.5 were increased by 83.1, 155.4, and 34.0%, respectively, up to 86.6, 83.5, and 71.3%, proving its wider plugging scope for core, larger sweep volume, and better oil displacement performance of water flooding. Moreover, the breakthrough pressures ($\Delta P_b$) of PAM−PAANa and FPP-0.5 were almost the same (Table 1), suggesting that the introduction of the FT network in the PAM−PAANa gel did not reduce its plugging strength in core. The above experimental results proved that: (1) FPP-0.5 shows better in-depth profile control ability. FPP-0.5, with good self-lubricating property, can effectively reduce its own surface friction (Figure 3) and more easily enter the low-permeability area, microchannels and slits to displace oil in them, and thus efficiently improve the in-depth profile control performance of gel and sweep efficiency of subsequent water flooding. (2) FPP-0.5 has dynamic profile control ability to some extent. The introduction of the FT supramolecular network in the FPP gel brings about newly presented shear responsiveness as well as reduced strength. In a certain shear time, FPP-0.5 can maintain ultralow friction (Figure 6) with...
solid surfaces. However, its self-lubricating property decreased along with increased strength (Figure 6) under multicycle shear. Therefore, the shear responsiveness of FPP-0.5 enables it to flexibly adjust its own strength and the self-lubricating property according to different stages in the profile control process and the distinct regions of heterogeneous reservoirs, so as to achieve dynamic profile control. To be specific, as for the initial injection stage, FPP-0.5, having good self-lubricating property and low strength, can be easily pushed into the low-permeability layer and microchannels by water flow, thus to realize in-depth profile control and effectively improve water flooding sweep efficiency. With the prolongation of injection and shearing, the decreased self-lubricating property, enlarged surface friction, and strength of FPP-0.5 enable it to effectively block channels and slits, to make water flow divert into a low-permeable area and further improve the in-depth profile control performance of the gel.

3. CONCLUSIONS

In this work, a novel shear-responsive self-lubricating hydrogel FPP was synthesized. And the effects of FT concentration and shear cycle on its strength and friction property were studied with the specific investigation of FPP-0.5 gel plugging and profile control performance. The main conclusions are as follows:

(1) Self-lubricating supramolecular hydrogel FPP was successfully prepared by the one-pot method, and the results of FTIR, NMR, and XRD analyses showed the molecular structure of the synthesized product in agreement with design.

(2) FT supramolecular network endows the FPP gel with the shear-responsive self-lubricating property with reduced strength. The increase of FT addition results in an enhanced self-lubricating property and declined gel–sol transition frequency, surface friction, overall cross-linking degree, and strength of FPP gel. Evidenced by the influence of FT addition amount on the FPP strength and friction property, the optimal gel sample was chosen as FPP-0.5.

(3) Multicycle shearing can enhance FPP-0.5 strength with reduced self-lubricating property. With shear cycle increasing, the FT network in the FPP-0.5 gel was gradually lessened with tightened network and enhanced overall cross-linking degree of gel, leading to its decreased self-lubricating property and enhanced strength.

(4) In comparison to PAM–PAANa, the FPP-0.5 gel shows better in-depth profile control ability. Its plugging rate, water flooding volumetric sweep efficiency, and oil recovery were increased by 83.1, 155.4, and 34.0%, respectively.

4. EXPERIMENTAL SECTION

4.1. Materials. N-fluorenlymethoxycarbonyl-L-tryptophan (FT, purity: 98%), acrylamide (AM, purity: 99.0%), acryloyl acid (AA, purity: >99%), sodium persulfate (Na2S2O8, purity: 99%), sodium bicarbonate (NaHCO3, purity: ≥99.8%), N,N'-methylene-di-acrylamide (MBAA, purity: ≥97%), and glutaraldehyde (GD, 50% in H2O) were all purchased from Macklin (China). The quartz sand used in sand packs, with two average diameters of 355 μm (45 mesh) and 63 μm (230 mesh), was provided by Macklin (China). Crude oil, with a viscosity of 2.74 mPa·s and a density of 0.903 g·cm−3 at 80 °C (reservoir temperature), and formation water, with a salinity of 30 261 mg·L−1 and a density of 1.057 g·cm−3 at 80 °C, were from Shengli Oilfield, China.

4.2. FPP Gel Preparation. The supramolecular hydrogel FT–PAM–PAANa (FPP) was synthesized by a facile one-pot approach (Figure 8) at 80 °C. In detail, designed quantities (0, 0.3, 0.5, 0.7, 0.9 g) of supramolecular monomer FT, 0.04 g of chemical cross-linking agent MBAA, 0.04 g of initiator Na2S2O8, and 0.5 g of amine-reactive cross-linker GD were dissolved in 100 mL of deionized water under room temperature and pH = 8 (solution pH was adjusted by Na2HCO3). Then, 6 g of AM and 6 g of AA as monomers were slowly added into the solution under stirring at 600 rpm, maintaining the solution pH constant (pH = 8) by Na2HCO3. After complete swelling of polymers, the sol was sealed and transported into an oven at 80 °C for 24 h. Then, the FPP gel was obtained. In accordance with the adding amount of FT in FPP, the prepared FPP gels were named as FPP-0, FPP-0.3, FPP-0.5, FPP-0.7, and FPP-0.9. For example, FPP-0.5 refers to FPP-0.5, FPP-0.7, and FPP-0.9. In comparison to PAM–PAANa, the FPP-0.5 gel shows better in-depth profile control ability. Its plugging rate, water flooding volumetric sweep efficiency, and oil recovery were increased by 83.1, 155.4, and 34.0%, respectively.

4.3. Characterization. Fourier transform infrared (FTIR) spectra, using an Antains II FTIR spectrometer (Thermo Fisher) with the KBr pellet method, were analyzed by Omnic software. 1H and 13C NMR spectra were acquired from an AVANCE 600 NMR spectrometer (Bruker, Germany) in D2O with its residual proton signals at δ 4.79 ppm as a reference. Meanwhile, X-ray diffraction (XRD) analysis was carried on by a D8 ADVANCE powder X-ray diffractometer (Bruker, Germany) in the 2θ range of 4–50° with a scanning speed of 0.02° s−1 at a speed of 20° min−1. The gel samples were measured after dried in an oven at 80 °C for 24 h.
of 0.2°-min⁻¹ and a step size of 0.02°. Fluorescence study was performed on an F-7000 fluorescence spectrometer (Hitachi, Japan) in solid mode as for wet gel samples fixed on an accessory, with the excited wavelength of 365 nm and slit width of 1.0 nm. The surface structure and micromorphology of gel were studied by a Zeiss-Supra55 field emission scanning electron microscope (Carl Zeiss, Germany) and a CM 100 transmission electron microscope (Philips, the Netherlands). Herein, the wet gel was treated to be solid block by freeze drying and then ground into powder for morphological observation.

Rheological analysis of gel samples was performed on a DHR-2 rotary rheometer (TA Instruments). To be specific, the storage modulus (\(G'\), Pa), loss modulus (\(G''\), Pa), and loss tangent (\(\tan \delta\)) of the gel samples were determined by frequency and time sweep in the oscillation mode at 25 °C to obtain gel mechanical property, viscoelasticity, and shearing resistance. The scanning range of frequency sweep is 0.01–100 Hz with strain fixed at 0.5%, and the frequency in time sweep is 1 Hz with the same strain and duration of 200 s. In addition, with friction force and friction coefficient as the evaluation index, the self-lubricating property of gel was measured by friction test on a UMT-2 tribometer (Bruker). In detail, a ceramic Al₂O₃ contact ball (diameter, 6 mm) performs a reciprocating rectilinear movement on the gel surface, with a shear velocity of 0.3 mm·s⁻¹, reciprocating frequency of 0.06 Hz, loading force of 70 mN, and shear velocity of 0.3 mm·s⁻¹. One reciprocating rectilinear motion was marked as one shear cycle with a length of 5 mm. Since the friction force and friction coefficient of all gel samples tend to be stable after 10 shear cycles, the data in the 10th shear cycle were selected to analyze the gel friction property. Moreover, as for the influence of shear cycles on gel strength and friction property, after 10 shear cycles, lubricating fluid on the ball surface would be wiped up when each succeeding shear cycle was accomplished. Meanwhile, LF-NMR (low-field nuclear magnetic resonance) analysis on the gel was carried out using a MicroMR-CL-1 NMR cross-linking density instrument with TW 3000.000 ms and eight scans, so as to analyze the gel cross-linking rate.

### 4.4. Core Flooding Experiments

The schematic of the core flooding experimental setup is shown in Figure 9. A double-sublayer heterogeneous core, composed of a high-permeability sublayer (abbreviated as HPL) and a low-permeability sublayer (abbreviated as LPL), was used for core flooding tests to effectively simulate the heterogeneity of fractured reservoirs, and its physical properties (mean value) are shown in Table 2. The experimental procedure was as follows. (1) Sand core saturation. Water and crude oil were separately injected into a sand pack at rates of 1 and 0.5 mL·min⁻¹, respectively, to make it saturated with water and crude oil successively. The saturated core was aged for 72 h in a thermostat at 80 °C and then weighted to calculate saturated oil volume, oil saturation \(S_o\) (Table 2), and irreducible water saturation \(S_{wirr}\). (2) Water flooding. Formation water was injected into the core at a rate of 1 mL·min⁻¹ until injection pressure was stable, and the water cut of produced liquid reached up to 95%. (3) Gel injection. 0.5 PV (pore volume) gel was injected into the core at the same rate, and then the core was kept in a thermostat at 80 °C for 120 h. (4) Subsequent water flooding. Subsequent water flooding was performed (1 mL·min⁻¹) until the water cut reached 95% again. Then, the formation brine injection rate was gradually enhanced to 2 and 4 mL·min⁻¹, while recording water saturation \(S_w\) and residual oil saturation \(S_{or}\) to calculate volumetric sweep efficiency (\(E_v\)). The whole displacement was carried out at 80 °C along with continuously recorded data, including the volume of produced oil and water and differential pressure (\(\Delta P\)). The mechanical strength and plugging performance of gel in formation were evaluated by breakthrough pressure (\(\Delta P_b\)), plugging rate (\(\eta\)), volumetric sweep efficiency (\(E_v\)), and oil recovery (RE). The calculation formulas of \(\eta\) and \(E_v\) are shown in eqs 1 and 2 and 3–5, respectively.

- \(K = \frac{\mu LQ}{\Delta PA}\) (1)
- \(\eta = \frac{K_i - K_f}{K_i} \times 100\%\) (2)
- \(N_{pd} = S_w - S_{wirr}\) (3)
- \(E_v = \frac{N_{pd}}{1 - S_{cor} - S_{wirr}}\) (4)
\[ E_v = \frac{\text{RE} (\%)}{E_D} \]  

(5)

where \( \mu \) is the viscosity of flooding fluid, \( \text{Pa}s; L \) is the core length, \( \text{mm} \); \( Q \) is the flow rate of fluid flooding, \( \text{mL} \cdot \text{s}^{-1} \); \( \Delta P \) is the differential pressure in displacement, \( \text{Pa} \); \( A \) is the cross-sectional area of core, \( \text{m}^2 \); \( K \) is the water permeability, \( \mu \text{m}^2 \); \( N_w \) is the dimensionless cumulative oil production, \( \% \); \( S_w \) is the average water saturation, \( \% \); \( S_\text{res} \) is the irreducible water saturation, \( \% \); \( S_o \) is the residual oil saturation, \( \% \); \( \text{RE} \) is the oil recovery efficiency, \( \% \); and \( E_D \) is the displacement sweep efficiency, \( \% \).

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## Notes
The authors declare no competing financial interest.

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## REFERENCES

(1) Alhuraishawy, A. K.; Bai, B. J.; Imqam, A.; Wei, M. Z. Experimental study of combining low salinity water flooding and preformed particle gel to enhance oil recovery for fractured carbonate reservoirs. Fuel 2018, 214, 342–350.
(2) Alhuraishawy, A. K.; Sun, X. D.; Bai, B. J.; Wei, M. Z.; Imqam, A. Areal sweep efficiency improvement by integrating preformed particle gel and low salinity water flooding in fractured reservoirs. Fuel 2018, 221, 380–392.
(3) Goudarzi, A.; Zhang, H.; Varavei, A.; Takaudeau, P.; Hu, Y. P.; Delshad, M.; Bai, B. J.; Sepetghoori, K. A. Laboratory and simulation study of preformed particle gels for water conformance control. Fuel 2015, 140, 502–513.
(4) Liu, C.; Han, Y. H.; Liu, H. H.; Abousleiman, Y. N. Wellbore-stability analysis by integrating a modified hoek-brown failure criterion with dual-porochoemoelectrostatic theory. SPE J. 2019, 24, 1957–1981.
(5) Al-Zahrani, A. A.; Daous, M. A. Recycling of spent bleaching clay and oil recovery. Process Saf. Environ. Prot. 2000, 78, 224–228.
(6) Alfarge, D. K.; Wei, M. Z.; Bai, B. J. Numerical simulation study of factors affecting relative permeability modification for water-shutoff treatments. Fuel 2017, 207, 226–239.
(7) Chen, L. F.; Zhang, Q.; Fu, M. L.; et al. Experimental investigation on the nanosilica-reinforcing polycrylamide/polyethylenimine hydrogel for water shutoff treatment. Energy Fuels 2018, 32, 6650–6656.
(8) Leslie, T.; Xiao, H.; Dong, M. Z. Tailor-modified starch/cyclodextrin-based polymers for use in tertiary oil recovery. J. Pet. Sci. Eng. 2005, 46, 225–232.
(9) Liu, Y. F.; Zou, C. W.; Zhou, D. Y.; Li, H.; Gao, M. W.; Zhao, G.; Bai, C. L. Novel chemical flooding system based on dispersed particle gel coupling in-depth profile control and high efficient oil displacement. Energy Fuels 2019, 33, 3123–3132.
(10) Liu, Y. F.; Bai, C. L.; Wang, K.; Zhao, M. W.; Zhao, G.; Yang, S.; Liu, Y. H.; You, Q. New insights into the hydroquinone (HQ)–hexamethylenetetramine (HMTA) gel system for water shut-off treatment in high temperature reservoirs. J. Ind. Eng. Chem. 2016, 35, 20–28.
(11) Liu, G. W.; Jiang, H. Q.; Li, J. J.; Wang, M.; Chen, F. Z.; Ding, S. W.; Lu, X. A. Evaluation of the performance of polymer gels mixed with asphalt particle as a novel composite profile control system. J. Ind. Eng. Chem. 2015, 26, 309–314.
(12) Zhao, L.; Zhang, H.; Hu, Y. L.; Duan, Q. Q. Research on testing a prototype of an expandable profile liner in a directional-well section in a high-fidelity laboratory environment. SPE J. 2019, 24, 2047–2063.
(13) Dai, C. L.; Liu, Y. F.; Zou, C. W.; You, Q.; Yang, S.; Zhao, M. W.; Zhao, G.; Wu, Y. N.; Sun, Y. P. Investigation on matching relationship between dispersed particle gel (DPG) and reservoir pore-throats for in-depth profile control. Fuel 2017, 207, 109–120.
(14) Hasanbakhani, G. M.; Madani, M.; Esmaeilzadeh, F.; Motwela, D. Experimental investigation of asphaltene-augmented gel polymer performance for water shut-off and enhancing oil recovery in fractured oil reservoirs. J. Mol. Liq. 2019, 275, 654–666.
(15) Ding, M. C.; Yuan, F. Q.; Wang, Y. F.; Xia, X. R.; Chen, W. H.; Liu, D. X. Oil recovery from a CO2 injection in heterogeneous reservoirs: The influence of permeability heterogeneity, CO2-oil miscibility and injection pattern. J. Nat. Gas Sci. Eng. 2017, 44, 140–149.
(16) 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 gel. Ind. Eng. Chem. Res. 2016, 55, 6284–6292.
(17) Imqam, A.; Bai, B. J. Optimizing the strength and size of preformed particle gels for better conformance control treatment. Fuel 2015, 148, 178–185.
(18) Zhang, X. W.; Wang, J. J.; Jin, H.; Wang, S. T.; Song, W. L. Bioinspired supramolecular lubricating hydrogel induced by shear force. J. Am. Chem. Soc. 2018, 140, 3186–3189.
(19) Chakraborty, P.; Mondal, S.; Khara, S.; Bairi, P.; Nandi, A. K. Integration of poly(ethylene glycol) in N-fluorenylmethoxycarbonyl-L-tryptophan hydrogel influencing mechanical, thixotropic, and release properties. J. Phys. Chem. B 2015, 119, 5933–5944.
(20) Al-Shalabi, E. W.; Sepehrnoori, K.; Pope, G. New mobility ratio definition for estimating volumetric sweep efficiency of low salinity water injection. Fuel 2015, 158, 664−671.

(21) Yousef, A. A.; Al-Saleh, S. H.; Al-Kaabi, A.; Al-Jawfi, M. S. Laboratory investigation of the impact of injection-water salinity and ionic content on oil recovery from carbonate reservoirs. SPE Reservoir Eval. Eng. 2011, 14, No. 137654.

(22) Hu, G. A new method for calculating volumetric sweep efficiency in a water-flooding oilfield. Pet. Explor. Dev. 2013, 40, 111−114.

(23) Mewis, J.; Wagner, N. J. Thixotropy. Adv. Colloid Interface Sci. 2009, 147−148, 214−227.

(24) Bai, P.; Chakraborty, P.; Mondal, S.; Roy, B.; Nandi, A. K. A Thixotropic supramolecular hydrogel of adenine and riboflavin-5′-phosphate sodium salt showing enhanced fluorescence properties. Soft Matter 2014, 10, S114−S120.

(25) Smith, C. S.; Savliwala, S.; Mills, S. C.; Andrew, J. S.; Rinaldi, C.; Arnold, D. P. Electro-infiltrated nickel/iron-oxide and permalloy/iron-oxide nanocomposites for integrated power inductors. J. Magn. Magn. Mater. 2020, 493, No. 165718.

(26) Ying, Z. R.; Wu, D. F.; Wang, Z. F.; Xie, W. Y.; Qiu, Y. X.; Wei, X. Rheological and mechanical properties of polylactide nanocomposites reinforced with the cellulose nanofibers with various surface treatments. Cellulose 2018, 25, 3955−3971.

(27) Wu, D. F.; Yuan, L. J.; Laredo, E.; Zhang, M.; Zhou, W. D. Interfacial properties, viscoelasticity, and thermal behaviors of poly(butylene succinate)/polylactide Blend. Ind. Eng. Chem. Res. 2012, 51, 2290−2298.

(28) Ji, L. J.; Qiao, W.; Zhang, Y. H.; Wu, H. Y.; Miao, S. Y.; Cheng, Z. L.; Gong, Q. M.; Liang, J.; Zhu, A. P. A gelatin composite scaffold strengthened by drug-loaded halloysite nanotubes. Mater. Sci. Eng., C 2017, 78, 362−369.

(29) Patel, J. P.; Hsu, L. S. Development of low field NMR technique for analyzing segmental mobility of crosslinked polymers. J. Polym. Sci., Part B: Polym. Phys. 2018, 56, 639−643.

(30) Zang, X.; Zu, Y. X.; Zhang, T.; Xia, K. X.; Song, Y. K.; Wang, Y.; Dong, X. P.; Tan, M. Q. Dynamic water mobility in sea cucumber (stichopus japonicas) during drying process assessed by LF-NMR and MRI in situ. Int. J. Food Eng. 2017, 13, No. 20160360.

(31) Beck, G.; Thybring, E. E.; Thygesen, L. G.; Hill, C. Characterization of moisture in acetylated and propionylated radiata pine using low-field nuclear magnetic resonance (LFNMR) relaxometry. J. Am. Chem. Soc. 2017, 72, 225−233.

(32) Sang, Q.; Li, Y. J.; Yu, L.; Li, Z. Q.; Dong, M. Z. Enhanced oil recovery by branched-preformed particle gel injection in parallel-sandpack models. Fuel 2014, 136, 295−306.

(33) Goudarzi, A.; Zhang, H.; Varavei, A.; Taksaudom, P.; Hu, Y. P.; Delshad, M.; Bai, B. J.; Sepehrnoori, K. A laboratory and simulation study of preformed particle gels for water conformance control. Fuel 2015, 140, 502−513.

(34) Goudarzi, A.; Almohsin, A.; Varavei, A.; Taksaudom, P.; Hosseini, S. A.; Delshad, M.; Bai, B. J.; Sepehrnoori, K. New laboratory and transport model implementation of microgels for conformance and mobility control purposes. Fuel 2017, 192, 158−168.

(35) Khamees, T. K.; Flori, R. E. A comprehensive evaluation of the parameters that affect the performance of in-situ gelation system. Fuel 2018, 225, 140−160.

(36) Babu, S. S.; Praveen, V. K.; Ajayaghosh, A. Functional π-gelators and their applications. Chem. Rev. 2014, 114, 1973−2129.

(37) Dong, S.; Luo, Y.; Yan, X.; Zheng, B.; Ding, X.; Yu, Y. H.; Ma, Z.; Zhao, Q. L.; Huang, F. H. A dual-responsive supramolecular polymer gel formed by crown ether based molecular recognition. Angew. Chem., Int. Ed. 2011, 50, 1905−1909.

(38) Halim, A. Y.; Nielsen, S. M.; Lantz, A. E.; Suicmez, V. S.; Lindeloff, N.; Shapiro, A. Investigation of spore forming bacterial flooding for enhanced oil recovery in a North Sea chalk Reservoir. J. Pet. Sci.Eng. 2015, 133, 444−454.

(39) Chen, L. F.; Zhu, X. M.; Wang, L.; et al. Experimental study of effective amphiphilic graphene oxide flooding for an ultralow-permeability reservoir. Energy Fuels 2018, 32, 11269−11278.