



Original Paper

Development of re-crosslinkable dispersed particle gels for conformance improvement in extremely high-temperature reservoirs



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ABSTRACT

Micro-scale and nano-scale dispersed gel particles (DPG) are capable of deep migration in oil reservoirs due to their deformability, viscoelasticity, and suitable particle size. Therefore, it has been widely studied and applied in reservoir conformance control in recent years. However, for highly permeable channels, their plugging performance is still limited. In addition, conventional *in situ* cross-linked polymer gels (ISCPGs) have fast gelation time under extremely high-temperature conditions, which often causes problems such as difficulty in pumping. Therefore, a re-crosslinkable dispersed particle gel (RDPG) system applied for conformance control in highly permeable channels of extremely high-temperature petroleum reservoirs was investigated. The particle size distribution, gelation time, gel strength, injection performance, and performance strength in porous media were investigated using a laser particle size meter, the Sydansk bottle test method, rheometer, and core displacement experiments, respectively. Results show that the RDPG suspension can be stable for more than 6 months at room temperature with storage modulus G' much lower than 10 Pa. It can pass through the pore throat by elastic deformation effect and does not cause strong blockage. Moreover, it can undergo re-crosslinking reaction at 150 °C to form a strong bulk gel. The gel strength G' of re-crosslinked RDPG can be as high as 69.3 Pa, which meets the strength requirement of conformance control. The RDPG suspension has the properties of easy injection, and it also has strong plugging, and high-temperature resistance after re-crosslinked in the core, which can be a very promising material for conformance improvement in extremely high-temperature reservoirs.

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1. Introduction

As the international conventional petroleum resources gradually decay due to continuous exploration and development, the increasing human demand for oil makes the development of high-temperature (higher than 80 °C) petroleum reservoirs gradually increased (Sotomayor et al., 2021; Jin et al., 2021; Zhang et al., 2021). However, high-temperature petroleum reservoirs usually have deeper burial depths, stronger formation heterogeneity, and higher crude oil viscosity, making the conformance problems more obvious and challenging to deal with when developed with water injection (Wang et al., 2018; Salunkhe et al., 2021; Hadia et al., 2021). Therefore, there has been an upsurge of research on

conformance improvement techniques and methods for high-temperature reservoirs in recent years (Yu et al., 2022; Amir et al., 2019; Zhu et al., 2019a). The method of using chemical plugging materials for conformance improvement has the characteristics of relatively simple procedures, low cost, and selective plugging. Therefore, it is given priority in the operation of reservoir profile modification and water shutoff in the major oil fields worldwide (Zhu et al., 2017; Liu and Seright, 2001; Seright and Brattekas, 2021). In addition, with the continuous research and development of high-temperature-resistant polymers, low biological toxicity adhesives, and nano-reinforced materials, the development of polymer gel systems for high-temperature reservoirs has gradually become a hot spot (Ma et al., 2017; Zhu et al., 2017). In addition, in recent years, re-crosslinkable particle gel has been widely used in fractured reservoirs due to its easy injection and high plugging strength (Ahdaya et al., 2022; Yang et al., 2022).

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However, these particles are usually pre-formed gel particles (PPG), and there are few studies of the re-crosslinking effect of dispersed particle gel (DPG).

Polymer gels for high-temperature reservoirs usually include *in situ* cross-linked polymer gels (ISCPGs), monomer polymerized gels, particle polymer gels, and gel foams (Kang et al., 2021; Bai et al., 2015; Zhu et al., 2017). Among these, *in situ* cross-linked polymer gels (ISCPGs) are the most widely used. ISCPGs are usually classified according to either the type of polymer used in the system or the type of cross-linker (Bai et al. 2015, 2021). The classification method based on the type of crosslinker is more common. Therefore, ISCPGs for high-temperature reservoirs can generally be divided into *in situ* metal cross-linked polymer gels and *in situ* organic cross-linked polymer gels (Zhu et al. 2017, 2021). Due to the disadvantages of metal (e.g., chromium, zirconium, aluminum, etc.) crosslinking in high-temperature conditions, such as the rapid rate of complexation reaction formed and the ease of dehydration of the gel under high-temperature conditions, its suitable reservoir temperature usually does not exceed 90 °C (Zhu et al., 2019a). Organic crosslinkers mainly include aldehydes, phenolic resins, and low biological toxicity crosslinkers (e.g., polypropylene imide, etc.) studied more in recent years (Bai et al., 2015). Since they can form covalent bonds through dehydration condensation reactions or nitrogen transfer reactions as cross-linking points, they are more suitable for high-temperature reservoirs since their cross-linking strength is stronger than that of metal cross-linking compared to ligand bonds (Jia et al., 2020; Bai et al., 2015). However, when the reservoir temperature is higher than 120 °C (i.e., extremely high-temperature reservoir), the rate of organic cross-linking reaction also increases significantly, leading to the possible formation of high-strength bulk gels during the pumping of ISCPGs into the wellbore or formation (Zhu et al., 2017, 2019b). After gelation, the significant increase in gel viscosity can make the pumping of the gel system sharply more difficult. Hence, its deep propagation in the deep reservoir is very limited. Therefore, it is necessary to study a new type of plugging agent for high-temperature reservoirs, which has good injection performance as well as excellent plugging strength and thermal stability.

To improve the injection and deep propagation performance of *in situ* cross-linked polymer gels (ISCPGs), on the idea of conventional particle-based polymer gels, Dai et al., (2012) developed a dispersed particle gel (DPG). DPG is based on the system formulation of conventional ISCPGs, and the cross-linking reaction is carried out in advance in the ground equipment. Then, it is dispersed into a suspension of very small particles using ground equipment such as a colloid mill. Since the DPG can reach micron and even nanometer sizes, it can be easily pumped into the deep formation. Dai et al. (2012) used a ground colloid mill device to crush the ISCPG system consisting of polyacrylamide (PAM) and phenolic resin pre-crosslinked to DPG at room temperature. The DPG is spherical and has an average size of up to 2.5 μm. Liu et al. (2016) investigated the conformance improvement performance of this DPG using a repulsion model and microscopic visualization experiments. The DPG can aggregate in high permeability layers and seal or plug them, thus improving the sweep efficiency and improving oil recovery. In addition, this DPG has good elastic deformation and can propagate in porous media. Dai et al. (2017) also investigated the matching relationship between DPG particle size and pore throat using a core model to optimize the particle size of the system so that it can be used as an agent for in-depth profile control. In addition, Zhao et al. (2013) prepared DPG particles using bulk polymer gels after crosslinking PAM and zirconium in a ground crushing device (e.g., the colloid mill) for 2.5 h. The higher the shear force during milling, the smaller the size of DPG particles and the lower the zeta potential (absolute value) of the particles. Zhao et al.

(2014) also investigated the injection performance of DPG in reservoir porous media using core displacement experiments and glass visualization simulation experiments. DPG particles can pass directly through the pore throat of porous media by deformation and then be transported deep in the formation. Then, the permeability of the formation is reduced by retention and adsorption, which improves the injection profile.

To improve the temperature and salt resistance of DPG, Dai et al. (2016) added nanomaterials (i.e., 0.2 wt% nano-sized silica) to the DPG system prepared from PAM and phenolic resin to obtain the strengthened dispersed particle gel (SDPG). In addition, to improve the oil displacement ability of the DPG system, Liu et al. (2019) employed surfactant (i.e., dodecyl dimethyl sulfo-propyl betaine, DDSB) to the conventional DPG system. This composite system can combine the advantages of the above two systems and has a high EOR effect in core oil displacement experiments. However, studies on re-crosslinkable DPG have not been reported, and few DPG systems applicable to reservoir temperatures above 130 °C have been reported. Therefore, based on the above problems, the existing DPG system should be optimized, a high-performance conformance control agent can be developed, and the mechanism of its profile improvement should be systematically studied. Therefore, it will help to improve the sweep efficiency of ultra-high temperature reservoirs and crude oil recovery.

In this paper, we have developed a re-crosslinkable dispersed particle gel (RDPG), which has the effect of re-crosslinking compared with conventional DPGs and can plug high-permeability channels with high strength. Compared with ISCPG, it has the advantages of easy injection, high strength, etc. The system is based on an *in situ* cross-linked polymer gels (ISCPGs) composed of PAM and a cross-linking agent with low biological toxicity PEI. When it was gelled on the ground, different particle sizes of DPG could be prepared by adjusting the mixing time. Using a laser particle size meter, the particle size of the un-re-crosslinked RDPG suspension was determined, and the relationship between particle size and grinding time was investigated. The gelation time, gel strength after being crosslinked, and high-temperature stability of RDPG prepared by mixing different contents of bulk gels under high-temperature conditions were determined using the Sydansk bottle test method. In addition, the rheological properties (i.e., storage modulus G') of different RDPG systems before being re-crosslinked were tested. Then, the dynamic injection performance and plugging strength of the RDPG system in porous media were investigated using a core displacement experimental model. Finally, the re-crosslinking mechanism of the RDPG system was explained by integrating the above experimental results. The research in this paper enables the development of a conformance improvement agent with good injectivity, in-depth propagation performance, and strong plugging performance under extremely high-temperature petroleum reservoir conditions. This novel RDPG system can effectively solve the problems of injectability and chromatographic separation caused by the rapid gelation of the conventional ISCPGs under extremely high-temperature conditions.

2. Experimental materials and methods

2.1. Experimental materials

The terpolymer (ZP-4, made by the polymerization of acrylamide and two different temperature and salt-resistant monomers, etc., molecular weight 2 to 3 million Daltons) was supplied by Beijing Yuanyang Huanyu Petroleum Technology Co. Polyethyleneimine (PEI, molecular weight 10,000 Daltons, 30% aqueous solution) and inorganic salts such as NaCl (AR, 99.5%) and Na₂CO₃

(AR, 99.5%) were purchased from Shanghai Macklin Biochemical Technology Co. The river sand (40–60 mesh) was supplied by Beijing Yuanyang Huanyu Petroleum Technology Co.

2.2. Preparation of RDPGs and determination of re-crosslinking time

First, the polymer bulk gels were prepared at 65 °C in advance from 1.2% terpolymer and 0.6% polyethyleneimine, etc. (Zhu et al., 2019a), as shown in Fig. 1a. The chemical structure of ZP-4 and the preparation method of ISCPG have been described in previous research work (Zhu et al., 2019b). Converted, the molar ratio of the amide group in the polymer to the imino group in PEI is about 1:10–1:15, so PEI is excessive. Then, the above-mentioned bulk gels were mixed with different proportions of 0.1% Na₂CO₃ solution. It was placed in a Warning high-speed mixer and crushed at a speed of 600 r/min at room temperature. Samples were taken at grinding times of 1, 2, 5, 10, 20, and 30 min, respectively. Different concentrations of RDPG suspensions were obtained, as shown in Fig. 1b. Finally, after grinding for 30 min, the RDPG suspension was measured and placed in a high-temperature resistant test tube and then placed in an oven at 150 °C. The gel code evaluation grade in the Sydansk bottle test method (Zhu et al., 2019a) was used every half-hour to evaluate the re-crosslinking time and gel strength of the RDPG system. The strength of the gel was enhanced step by step from grade A to I. The gelation time was defined as the time when the gel strength reached grade D in this study.

2.3. Particle size measurement of RDPG suspension

A particle size analyzer (LA-950S2, Horiba, Japan) was used to measure the RDPG particle size distribution in the un-re-crosslinked DPG suspension system at different grinding times.

2.4. Microstructural and SEM observation of RDPG suspensions

The prepared RDPG suspension was pipetted with a rubber-tipped dropper and added dropwise to a slide. Then, the slide was placed on a carrier table, where it was observed and photographed using an Axio Vept AI-type light microscope (Carl Zeiss, USA). Moreover, the re-crosslinked polymer gel was frozen in liquid nitrogen and dried in a vacuum. After being completely dried, the microstructures were observed using an environmental scanning electron microscope (ESEM, Quanta 200F, FEI Co., USA).

2.5. Rheological testing of RDPG systems before and after re-crosslinking

For bulk gels of the re-crosslinked RDPG in high-temperature resistant test tubes, to quantitatively evaluate the gel strength, the storage modulus G' and loss modulus G'' were tested using a Haake MAKES III rheometer (Haake Technik GmbH, Germany). The test temperature was room temperature (25 °C), the shear stress during the test was 1 Pa, and the shear frequency was 1 Hz. The curves of the relationship between the gel strength (G' and G'') with time could be measured.

2.6. Injection and plugging experiments of RDPG in porous media

In order to simulate the injection and plugging performance of the RDPG system in the reservoir, this paper used a sandpack model with three pressure measurement taps for experiments. The sandpack with a length of 50 cm was wholly filled with 40–60 mesh of slightly moist river sand and then vacuumed for 8 h. The experimental equipment was assembled according to the experimental flow chart shown in Fig. 2. The experimental temperature was 150 °C. The experimental steps were as follows. First, the 1% NaCl solution was injected into the sandpack at a flow rate of 1 mL/min, and the pressure at each pressure measurement point was recorded in real-time, and the permeability was calculated to be nearly $3000 \times 10^{-3} \mu\text{m}^2$ according to Darcy's law. Then, the RDPG suspension of one pore volume (PV) was injected into the sandpack at a flow rate of 1 mL/min, and the pressure change out of each pressure measurement tap was recorded in real-time. The sandpack was aged in a constant temperature oven at 150 °C for 3 days (to simulate the gel-forming state) and 30 days (to simulate the stability of the gel under high-temperature conditions), respectively. Then, 1% NaCl solution was injected into the sandpack again at a flow rate of 1 mL/min, and the pressure changes at each pressure measurement tap were recorded in real-time.

3. Experimental results and discussion

3.1. Preparation of RDPG and its particle size distribution

According to the preparation method of the RDPG system in Fig. 1, the pre-formed terpolymer gels were mixed with an aqueous solution. In order to investigate the effect of different gel (i.e., solid-phase particles) concentrations on the re-crosslinking time and gel strength of the formed RDPG, the mixing ratios of terpolymer gel

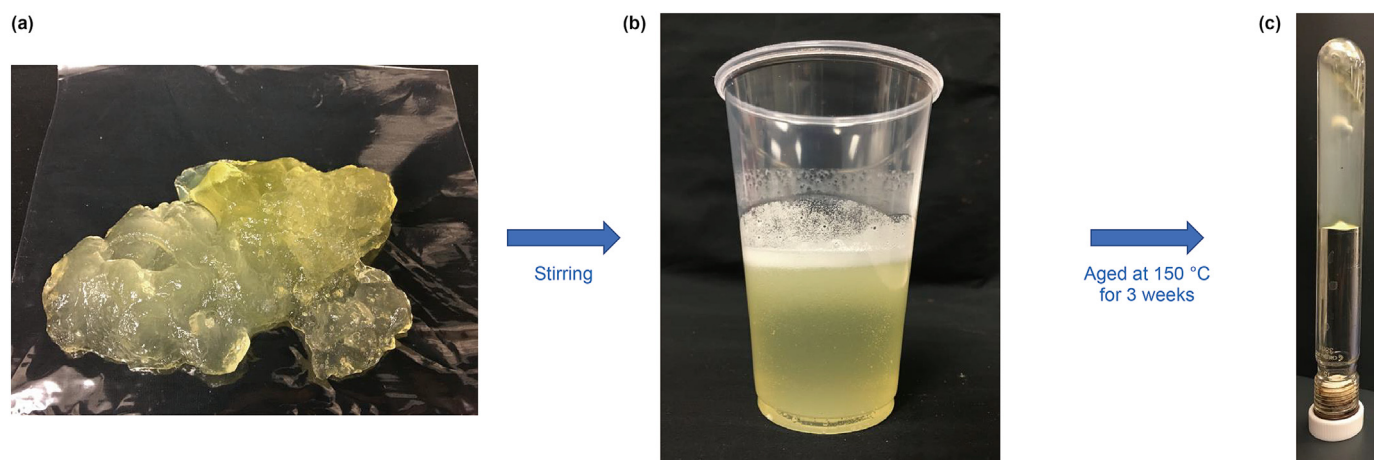


Fig. 1. Schematic diagram of the preparation and re-crosslinking reaction of RDPG system.

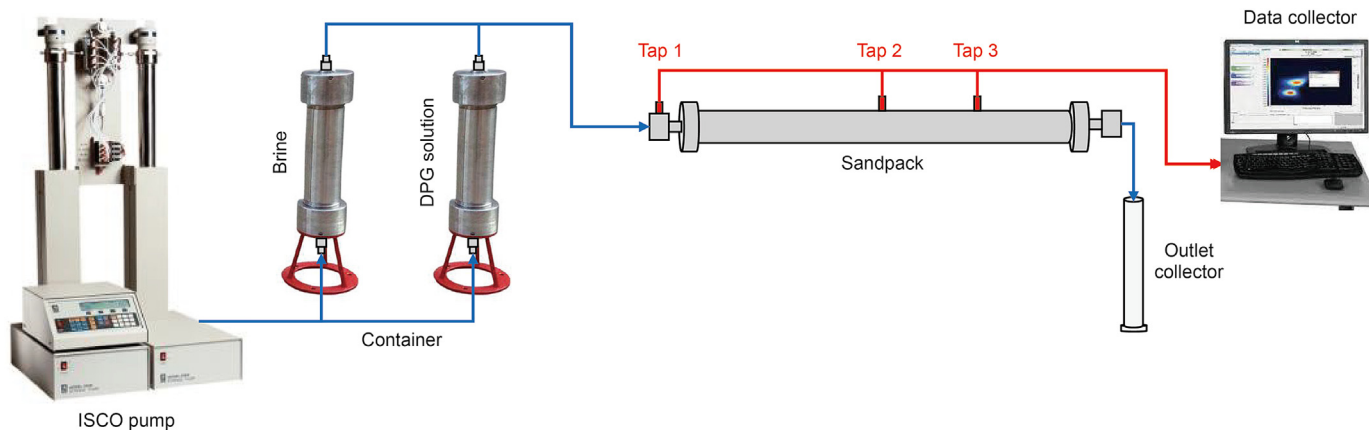


Fig. 2. Schematic diagram of the displacement experiment flow.

and water were 2:8, 3:7, 4:6, 5:5, and 6:4, respectively. The above mixes were ground using a Warning mixer. Samples of the suspension at different grinding moments were retained for particle size testing and then analyzed. They were numbered from RDPG-1 to RDPG-5 in order. The RDPG-5 system with a gel to water ratio of 6:4 was used as an example. The particle size test was conducted on the RDPG suspension after being grounded in the Warning stirrer for 30 min, and the experimental results are shown in Fig. 3.

As shown in Fig. 3, the particle size of RDPG-5 after 30 min of grinding was mainly distributed between 7 and 30 μm, and the particle size distribution was uniform in general. In addition, RDPG-5 has the largest particle size distribution around 10 μm, with an average particle size M_z of 29.41 μm, a number average particle size M_N of 16.43 μm, and a diameter of 13.57 μm at the peak position. Thus, the particle size of the RDPG mixture after comminution is basically on the micron scale, which is theoretically capable of deep transport in medium to high permeability formations due to its deformability (Zhao et al., 2014). It is worth noting that to obtain DPG with smaller particle size, ground equipment such as colloidal mills can be used (Dai et al., 2012), which will not be analyzed in-depth in this paper.

To analyze the effect of grinding time on the average particle size of the gel in suspension during the preparation of the RDPG suspension system, the RDPG-5 sample was used as an example.

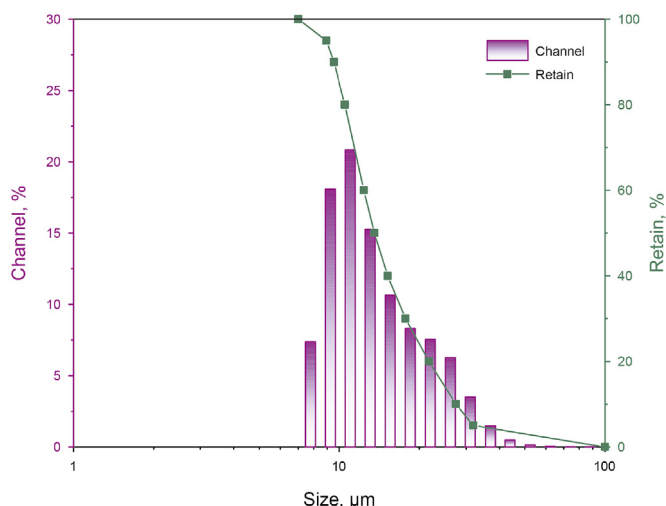


Fig. 3. Particle size distribution curve of RDPG-5 mixture after 30 min of grinding.

RDPG-5 system was mixed with gel and water at the gel content of 60%. The relationship between the average particle size of the mixed system RDPG-5 and grinding time at room temperature was investigated. The experimental results are shown in Fig. 4.

As can be seen from Fig. 4, the average particle size of the RDPG-5 mixture decreased with the increase in the grinding time. The average particle size decreased from 4239 to 2894 μm from 1 to 2 min, then decreased to 1502 μm in the middle of the 5th min, then decreased to 132 μm, and decreased to 30 μm in the 20th min. After that, the average particle size did not change significantly with the increase in the grinding time and was almost stable at 30 μm. It can be seen that the average particle size of DPG colloidal particles is about 30 μm after the grinding time of 20 min for the RDPG-5 mixture. Due to the excellent deformability of DPG, it can enter the medium to high permeability formations and transport them to the deeper part of the formation (Dai et al., 2017). In addition, it is also clear from Fig. 4 that micron-sized particles can be obtained when the grinding time of the RDPG mixture exceeds 10 min, i.e., after a certain time of sufficient grinding. In summary, the dispersed gel particles with different particle sizes can be obtained by changing the grinding time during RDPG preparation. Moreover, the average particle size of the dispersed gel particle

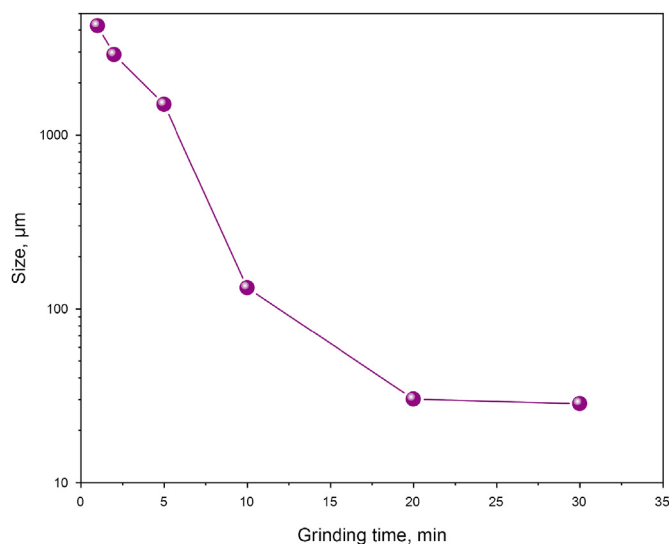


Fig. 4. The relationship curve between average particle size and grinding time of RDPG-5 mixture.

solution decreases and finally stabilizes as the grinding time increases.

The microscopic morphology of the RDPG-5 suspension at 30 min of grinding was observed and photographed using an optical microscope. Fig. 5 shows the photos of the RDPG-5 suspension at different magnification. It can be seen that the particle distribution of the RDPG-5 suspension at 30 min of grinding becomes relatively uniform, and the particles have an irregular stereotypic shape with a relatively uniform particle size ranging from 10 to 30 μm . Thus, very homogeneous samples of RDPG particle suspensions could be obtained when the grinding time reached 30 min. The viscosity of the RDPG-5 suspension at room temperature was measured by a Brinell viscometer to be 10.3 mPa s. In addition, the RDPG-5 suspension remained very stable at room temperature for 3 months without re-crosslinking, and the viscosity remained at 10.3 ± 0.5 mPa s. It means that the RDPG system has excellent stability at room temperature and can be stored and transported at room temperature for a short period.

3.2. Gelation time and strength of RDPG under high-temperature conditions

To investigate the injection performance and plugging strength of the RDPG system in the subsurface formation, it is necessary to determine the gelation time and gel strength of the system under high-temperature conditions. Sydansk bottle test method was used to test the gelation time (i.e., the time required for the gel strength to reach the D level) at 150 °C after crushing the mixture of bulk gel and water in the ratio of 2:8, 3:7, 4:6, 5:5, and 6:4 for 30 min, respectively. Strength D indicates that the gel at this time is moderately liquidity, i.e., a small fraction (<15%) of gels cannot flow to the other end of the bottle when the ampoule is turned over. They were numbered in order from RDPG-1 to RDPG-5. The experimental results are shown in Fig. 6.

As can be seen in Fig. 6, the RDPG-1 (i.e., 20% gel content) suspension required 49 h to reach gel strength D, and it was unable to reach gel strength G and could only reach gel strength E at most. When the gel content was increased to 30%, the gelation time required for RDPG-2 to reach gel strength D was significantly reduced to 24 h. In addition, it was able to reach gel strength G, but it took 60 h to do so. After that, the gel content was increased to 40%, and the gelation time for RDPG-3 to reach the gel strength D was slightly reduced to 18 h, while the gelation time to reach the gel strength G was significantly reduced to 26 h. With the gel content further increases to 60%, the gelation time required to reach gel strength D remains unchanged at 10 h. However, the time to reach the gel strength G did not change significantly, which was 18 h. It can be seen that with the increase in gel content in the RDPG

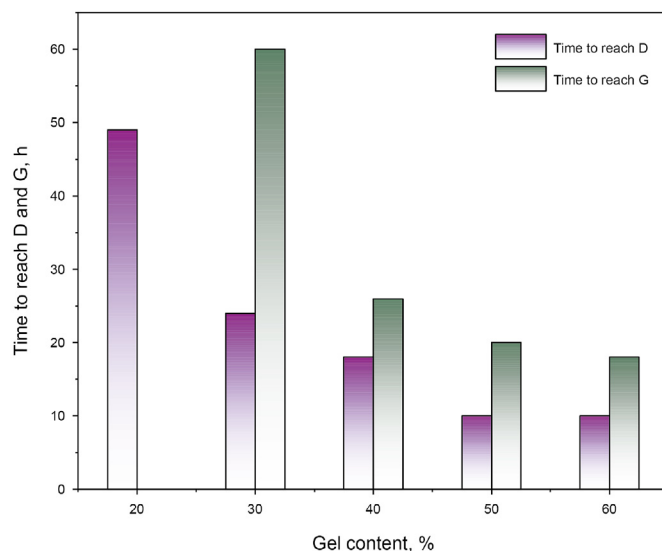


Fig. 6. Gelation time of RDPG suspensions composed of different gel contents at 150 °C (Sydansk bottle test method).

system, the gel strength under extremely high-temperature conditions also increases, and the gelation time required to reach both the gel strength D and G decreases.

When the gel content exceeds 40%, the change in gelation time and gel strength of the RDPG system was no longer noticeable. The above experimental results show that the RDPG system has a long (suitable) gelation time under high-temperature conditions, which is favorable for the system to be pumped deep into the formation. Therefore, when preparing the RDPG system, the content of gel in the system should exceed a certain amount (e.g., 30% in this study) to obtain a bulk gel with appropriate strength after re-crosslinking.

Fig. 7 gives a picture of the gelation state of different RDPG systems consisting of different contents (i.e., 20%–50% gel content) of bulk gels when aged at high temperature for 3 days at 150 °C. When the tubes were turned over, all of the re-crosslinked RDPG systems were almost immobile and showed a colloidal appearance. Among them, the gel strength of RDPG-1 is weakest, and a part of it can still flow to the bottom of the bottle. However, as the amount of gel added to the RDPG system increased, the strength of gel formed gradually increased. Among them, the strength of RDPG-3 to RDPG-5 reaches G with less dehydration. It is noteworthy that after the gel content exceeds 40%, the gel strength reaches H level, and the gel remains almost unchanged when turned over.

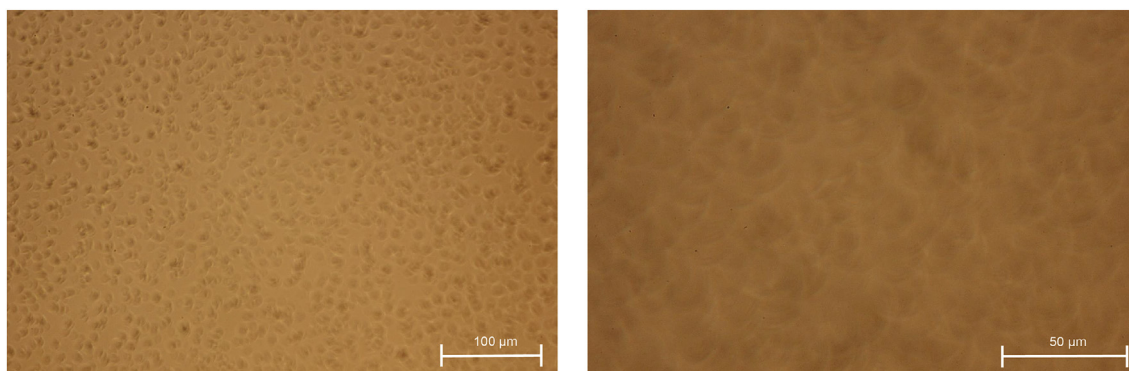


Fig. 5. Optical micrographs of the RDPG-5 suspension at 30 min of grinding.

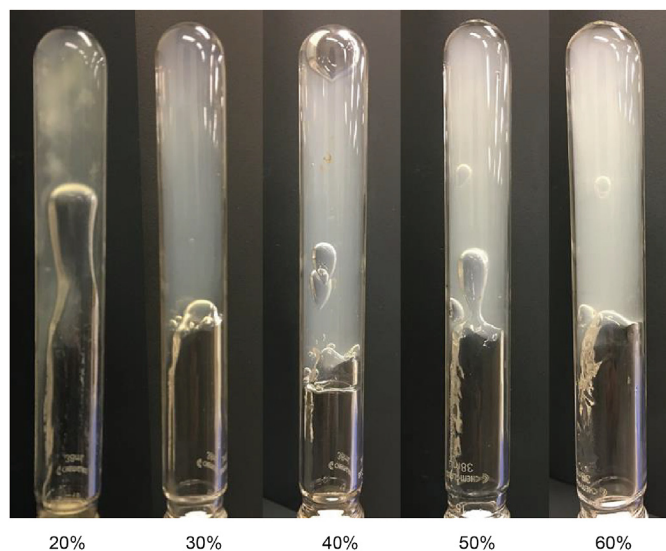


Fig. 7. The state of the RDPG system composed of different gel contents at a high temperature of 150 °C for 3 days.

3.3. Rheological measurement of RDPG before and after re-crosslinking

3.3.1. Rheology of RDPG mixtures prepared at different gel concentrations

The rheological parameters of the RDPG suspension samples before re-crosslinking were measured using a rheometer. The test temperature was room temperature (25 °C), the shear stress was 1 Pa, the shear frequency was 1 Hz, and the plate-plate test system was used. The test results are shown in Fig. 8.

As can be seen from Fig. 8, the storage modulus (G') of RDPG-1 before re-crosslinking gradually and smoothly increases slightly after 130 s. The energy storage modulus (G') reaches 2.38 Pa, and the loss modulus is 0.94 Pa. The energy storage modulus is higher than the loss modulus, showing the nature of a solid. The particle gel is dispersed in an aqueous solution and has a certain elasticity. Therefore, in the process of injection into the formation, the gel

particles in DPGR can pass through the pore throat by elastic deformation, and the G' at this time is much less than 10 Pa, which will not cause obvious plugging (Zhu et al., 2019b). The energy storage modulus (G') and loss modulus (G'') of RDPG-2 increase smoothly and slightly at the beginning, with the G' increasing slowly from 2.15 to 2.84 Pa and the G'' increasing slightly from 1.07 to 1.33 Pa. The G' of RDPG-3 increases significantly, and after that, the G' of RDPG-3 to RDPG-5 remains almost the same. Among them, the G' of the RDPG-5 system after re-crosslinking is slightly lower than that of the RDPG-4 system, which is 4.82 Pa, and its G'' is also slightly lower than that of RDPG-5. Therefore, the higher the content of the particle gel in the RDPG system, the higher the G' and G'' . When a certain content is reached, its viscoelasticity does not change significantly with the gel content.

To show more clearly the effect of different contents of gel in the RDPG system on the rheological properties, the comparison bar was presented in Fig. 9. As the gel content in the RDPG system keeps increasing, the G' of the system first increases rapidly and then gradually stabilizes, with an increase and then a slightly decrease in G' . It is worth pointing out that G' in the rheology test refers to the energy storage modulus, the elastic part of the viscoelastic behavior of the fluid during variable shear action, which describes the solid-state properties of the fluid. In addition, G'' refers to the loss modulus, the viscous part of the viscoelastic behavior of the fluid during variable shear action, which describes the liquid state properties of the fluid. Therefore, with the increasing gel content in the RDPG system, the increase in gel particles in the system will significantly increase the strength of the RDPG after re-crosslinking (Fig. 7). In addition, the G' of all RDPG mixtures is much less than 10 Pa, which will not result in noticeable plugging of the reservoir. Therefore, the RDPG system with a higher gel content should be selected to ensure stronger elasticity (representing deformation passage ability) and gel strength (representing plugging strength) under the guarantee of suitable gelation time and gel strength.

3.3.2. Rheology of RDPG at different aging times

The strength change of the gel under high-temperature conditions and the thermal stability are essential parts of the analysis of the gel system. If the strength of the system keeps increasing with aging time, it means that the re-crosslinking reaction of the gel is still going on, the microstructure of the gel keeps dense, and the

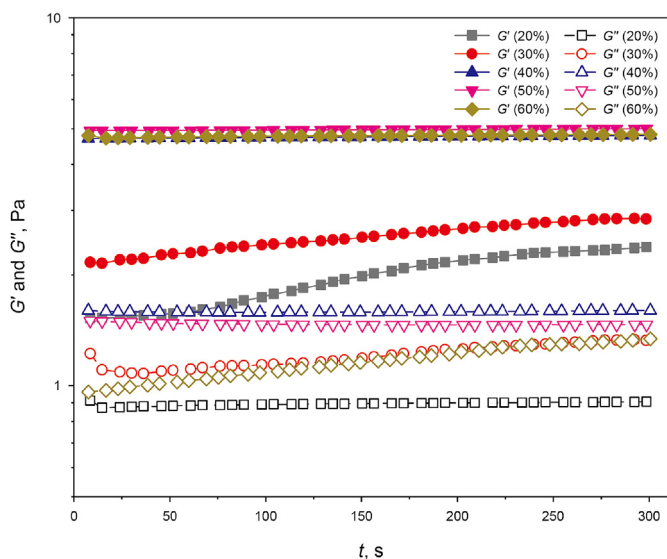


Fig. 8. Energy storage modulus (G') and loss modulus (G'') of RDPG composed of different gel contents at room temperature.

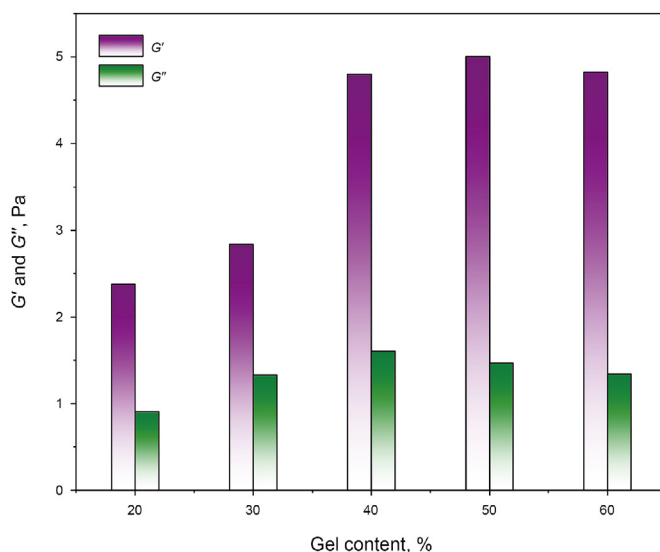


Fig. 9. Energy storage modulus (G') and loss modulus (G'') of RDPG composed of different gel contents at room temperature (bar graph).

shear resistance is stronger and it is less deformable. After the RDPG suspension was prepared, it was placed at 150 °C at different times to test its rheology to investigate the system strength change and rheological properties. The RDPG suspension was placed in a constant temperature oven at 150 °C and heated continuously. The samples were taken at two to 6 days of heating to test the energy storage modulus (G') and loss modulus (G''), and the experimental results are shown in Fig. 10.

As can be seen in Fig. 10, the energy storage modulus (G') of RDPG-5 at a high temperature of 150 °C increases substantially in the first two days, i.e., from 4.82 to 35.04 Pa dramatically. It is followed by a smooth slight increase from 36.35 Pa on day 3–37.81 Pa on day 4, with little differences between the G' on day 3 and day 4. Then, the G' continues to increase to 44.27 Pa on day 5 and 69.31 Pa on day 6, remaining approximately constant. In addition, the loss modulus increases from 1.34 to approximately 7.26 Pa in the first two days, and then it continues to increase, and the difference between the loss modulus on days 4 and 5 remains at approximately 10.5 Pa. The loss modulus continues to increase to a maximum of 28 Pa on day 6, and overall, it is significantly higher than the strength on day 0 (at the beginning of aging). It can be seen that the gel strength of RDPG keeps increasing after a few days of aging. In addition, G' further increases and is almost stable above 30 Pa, which further proves that this RDPG system will gradually undergo re-crosslinking reactions and form a highly viscoelastic gel under high-temperature conditions. For a more clear comparison, a comparison bar of the values of the plateau period in Fig. 10 is given in Fig. 11.

As can be seen from Fig. 11, the energy storage modulus (G') of the RDPG-5 suspensions at a high temperature of 150 °C increases significantly in the first three days of aging, from 4.82 to 35.04 Pa, and after that, the energy storage modulus reaches a maximum value of about 69.31 Pa on the sixth day. In addition, the loss modulus increases from 1.34 to 7.26 Pa in the first three days, and the difference between the loss modulus on day 4 and day 3 is not significant, which remains at 7.75 Pa. After that, the loss modulus increases sharply from 10.31 to 27.58 Pa on day 6. It can be seen that with the increase in aging time of RDPG suspension at 150 °C, both the energy storage modulus (G') and the loss modulus (G'') will increase significantly and can almost reach the maximum value on the sixth day. Among them, G' can be as high as 69.31 Pa, which

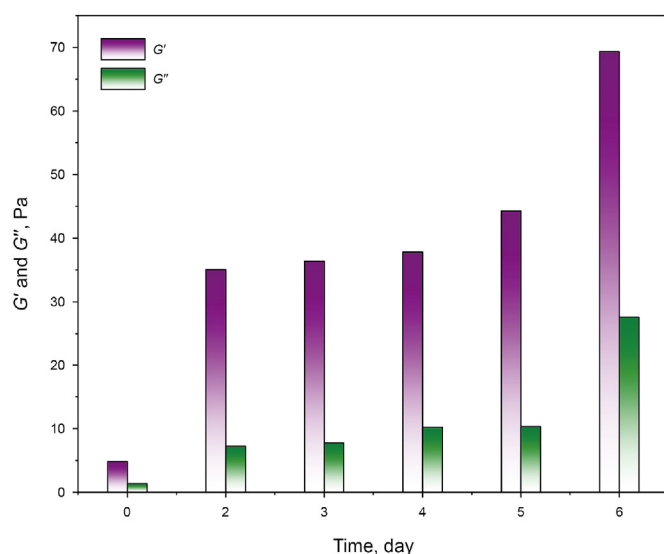


Fig. 11. Energy storage modulus (G') and loss modulus (G'') of RDPG-5 at a high temperature of 150 °C when reaching the maximum gel strength (bar graph).

meets the requirements of on-site conformance improvement construction (Zhu et al., 2019b).

3.4. Injection performance and plugging effect of RDPG system

The particle size of RDPG suspension was about 30 μm as analyzed by a laser particle size analyzer, and the static evaluation experiment results show that the gelation time of the RDPG system was higher than 20 h at 150 °C, and it had a strong gelation strength. Therefore, the RDPG system should theoretically have good deep propagation and plugging ability in the reservoir. A sandpack displacement experimental setup with three pressure measurement taps was used to investigate the injection and plugging performance of the RDPG system in the sandpack under high-temperature conditions. The matching relationship between DPG and reservoir pore structure has been introduced in detail in the literature published by Dai et al. (2017). Therefore, sandpack was used for the experiment, and the experiments in the core were not repeated in this study. Experimental results in sandpack are shown in Fig. 12.

As can be seen from Fig. 12, the pressure at the three taps of the primary water injection stage did not exceed 10 kPa, the pressure distribution in the sandpack could be uniformly distributed. The pore volume was 73.36 mL (i.e., the porosity was 29.89%) and the water permeability of the sandpack was calculated to be $2894 \times 10^{-3} \mu\text{m}^2$ at this time. Then, the RDPG suspension was injected into the sandpack. When the injection amount reached to 1.0 PV (i.e., 73.36 mL), the pressure at all three taps only started to rise. At this time the pressure reached 36.9 at Tap 1, 10.2 kPa at Tap 2, and reached a maximum of 24.3 kPa at Tap 3, respectively. Subsequently, the pressures in the sandpack almost stabilized, and the RDPG suspension was produced at the outlet. And then, the sample was taken, retained, and aged simultaneously in a high-temperature resistance test tube (as shown in Fig. 13). It can be seen that the differential pressure of this RDPG remained almost constant during the injection process, indicating that the system has good injection performance in porous media and can be propagated deep in the reservoir.

The outlet of the sandpack was closed, and the sandpack was placed in the oven at 150 °C for 3 days, followed by a subsequent water injection to test the plugging strength of RDPG in porous

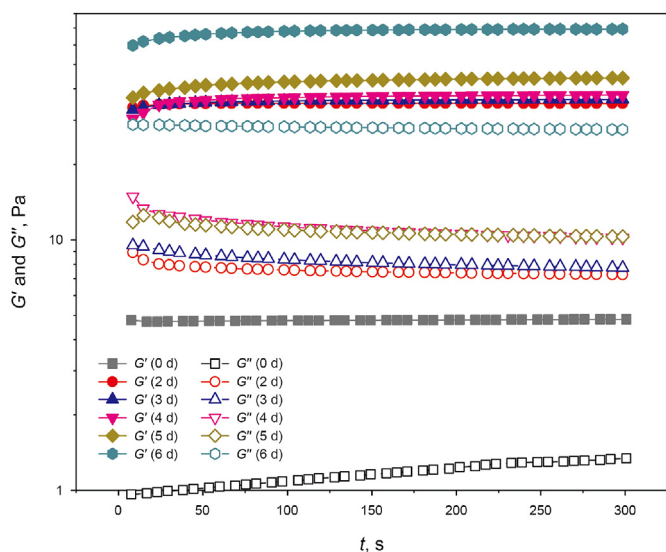


Fig. 10. Energy storage modulus (G') and loss modulus (G'') of RDPG-5 at a high temperature of 150 °C when reaching the maximum gel strength.

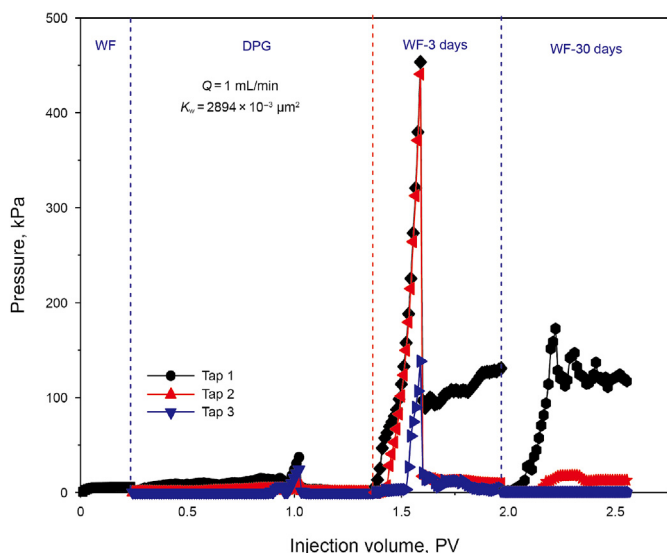


Fig. 12. Injection and plugging performance of RDPG-5 system in sandpack model (WF: water flood).

media after gelation. It can be found that when the water injection commenced, the pressure at Tap 1 rose sharply to 453.4 kPa, and the pressure at Taps 2 and 3 also rises sharply to 440.74 and 138.4 kPa, respectively. It means that the sandpack is in a state of holding pressure at this time. With the continuous injection of water, the pressure at the inlet of sandpack reaches 460 kPa (i.e., the permeability value is reduced by a factor of 78.36), and the water then break through the gel due to the effect of pressure, and the pressure at each point drops sharply. However, the pressure at Tap 1 remains at about 110 kPa (i.e., the permeability value is reduced by a factor of 18.74). It indicates that the RDPG system has strong plugging strength in porous media with high breakthrough pressure and decreased flow mobility in porous media after breakthrough. That is, it had excellent ability to improve reservoir conformance.

Then the sandpack was placed in the oven at 150 °C and aged for 30 days before secondary water injection. At this time, the pressure at Tap 1 rises to 160 kPa (i.e., the permeability value is reduced by a factor of 27.26) and remains stable after the breakthrough, while the pressure at Taps 2 and 3 does not change much. It indicates that after the injection breakthrough and stopping the aging for a while, RDPG is still undergoing re-crosslinking to form a certain plugging strength. Therefore, the RDPG suspension has excellent injectability

in porous media, and the sandpack has high plugging strength when it is aged at a high temperature of 150 °C for 3 days after injection of 1 PV. Moreover, it can still have an excellent plugging effect after aging at a high temperature of 150 °C for 30 days. In practical application, if the waterflood breaks through in the oil well, periodic water injection can be used to make full use of the re-crosslinking effect of RDPG.

The RDPG suspension collected at the outlet was placed in a high-temperature test tube and heated in an oven at 150 °C for three weeks, and the experimental results are shown in Fig. 13a. A small number of sand particles washed out from the sandpack dispersed in the RDPG suspension, but it could still be cross-linked to form a non-fluid gel at this time. After turning over the high-temperature resistant test tube, the gel was almost unable to flow, and the surface of the gel system was slightly deformed. Fig. 13b shows the microstructure of the gel obtained by microscopy, and it can be seen that the microstructure of RDPG is smaller in size and has a clearer dense network-like spatial structure after re-crosslinking at a high temperature of 150 °C. The networks are intertwined and interwoven with each other to form a grid close to 5–20 μm, and the grid is approximately circular or polygonal in shape. In addition, the RDPG molecules are woven and cross-linked together to form a thicker main backbone as well as thin branches, with a hierarchy of reticulated spatial structures and the presence of obvious connections between branches. The presence of these dense structures allows RDPG to macroscopically exhibit excellent stability, injectivity, and high-strength plugging at high temperatures of 150 °C. In addition, RDPG also has excellent elastic deformation and can form high-strength plugging in porous media, which is consistent with what has been observed on a macroscopic scale.

3.5. Mechanistic analysis of RDPG re-crosslinking

Combining the above-mentioned preparation of RDPG, the static re-crosslinking performance evaluation, and the dynamic injection and plugging effect in porous media, a schematic diagram of the preparation of RDPG and its re-crosslinking mechanism is given in Fig. 14. First, the polyacrylamide polymer, polyethyleneimine (PEI), and other additives are mixed and cross-linked to form a bulk gel in a ground facility. Then, it is mixed with water at a certain ratio and ground into micron or even nano-scale particles using a grinder or colloid mill (Dai et al., 2016), respectively. These micro- and nano-scale particles can pass through the pores of the reservoir rocks by deformation and then can be transported to the deeper zones of the reservoir. Then, the remaining imine groups on the PEI that have not been fully reacted under high-temperature conditions can be re-crosslinked with the amide groups on the polyacrylamide polymer to form a bulk gel again. The bulk gel has strong strength and thermal stability and is suitable for conformance improvement operations in extremely high-temperature (150 °C) reservoirs.

Therefore, firstly, compared with the conventional ISCPG system, the RDPG suspension developed in this paper can effectively overcome the problems of injectability and chromatographic separation of components in the formation caused by rapid gelation reaction at high temperature (Zhu et al., 2018). In addition, RDPG can undergo a re-crosslinking reaction under formation conditions, and its strength is similar to that of conventional ISCPG (Zhu et al., 2017), so it can effectively overcome the current injectability problem of ISCPG. Second, the conventional DPG system has good injection performance (Dai et al., 2012), but it is mainly used as a displacement agent with excellent injection performance but weak plugging strength. Based on the conventional DPG system, the RDPG developed in this paper can re-crosslink between the gel

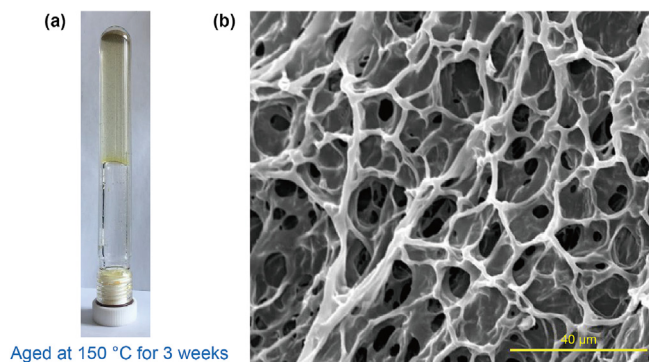


Fig. 13. RDPG effluent at the outlet of the sandpack and its state and microstructure when aged at a high temperature of 150 °C for 3 weeks.

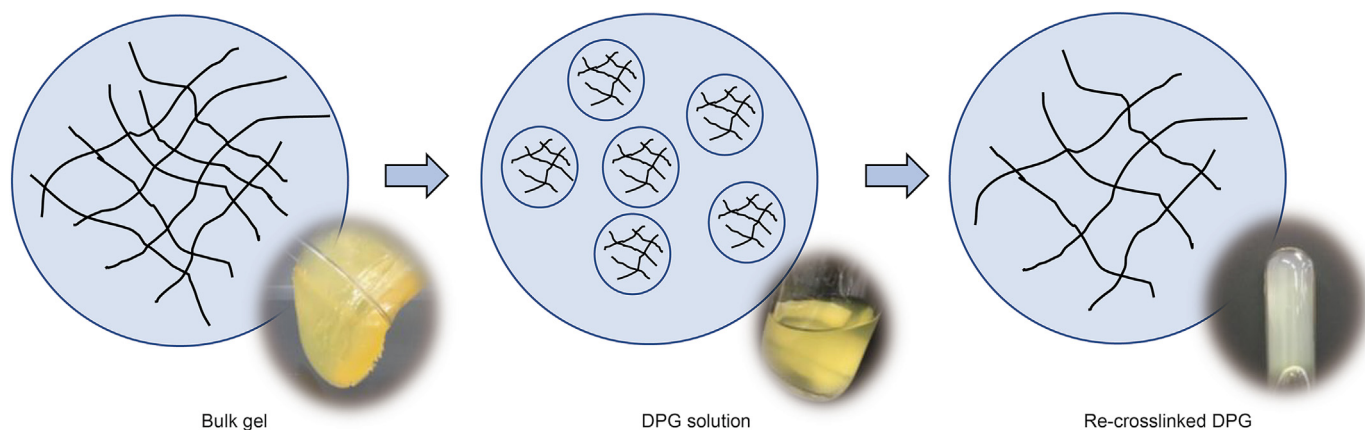


Fig. 14. Preparation of DPG and its re-crosslinking mechanism.

particles, which can expand the application range of DPG and make it a strong in-depth plugging material. In addition, the polymers used in RDPG herein are terpolymers, which are particularly temperature resistant, making them suitable for use in extremely high-temperature reservoirs.

4. Conclusions

- (1) A micron-scale RDPG suspension can be obtained by a bulky polyacrylamide–PEI gel system mixed with water in a certain ratio and then ground. The suspension can be stable for 6 months at room temperature, and the viscosity is almost maintained at 10 mPa s.
- (2) By changing the grinding time, RDPG suspensions with different particle sizes can be obtained, and with the increase in the grinding time, the particle size in the RDPG suspension decreases continuously and finally stabilizes at 30 μm .
- (3) The RDPG suspension has a suitable elasticity at room temperature, G' is much lower than 10 Pa. Therefore, it can pass through the pore throat by elastic deformation and does not cause plugging in the process of injection into the formation.
- (4) The RDPG suspension can be cross-linked at high temperature and form a bulk gel with high strength again. With the increase in aging time of RDPG suspension at high temperatures, the strength of the system (G' as well as G'') will increase significantly, and the G' at 150 $^{\circ}\text{C}$ can be as high as 69 Pa, which meets the strength requirement of water conditioning and plugging construction.
- (5) The RDPG suspension has excellent injectability in porous media and can reach high plugging strength in sandpack when it is aged at a high temperature of 150 $^{\circ}\text{C}$ for 3 days after injection of 1 PV. In addition, it can cross-link again at high temperatures and still has an excellent plugging effect after being aged for 30 days.
- (6) Unlike conventional DPGs, the RDPG system not only has excellent injectability but also can undergo re-crosslinking at high-temperature formation conditions and has strong plugging strength. The developed RDPG system can avoid the problems of short cross-linking time (i.e., the problem of injectability during construction) and the deterioration of gelation performance of each component in the formation due to adsorption and chromatographic separation under the conventional *in situ* cross-linked polymer gel in high-temperature conditions. Therefore, the RDPG system can be a promising material for conformance improvement in ultra-high temperature reservoirs.

- (7) Many factors, such as reservoir temperature, the ionic composition of formation water, etc., may have an impact on the gelation properties of RDPG, and their influence mechanisms will be carried out in the follow-up work.

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