
01 Jan 2023

Impact Of Composition And Salinity On Swelling And Gel Strength Of Poly (acrylamide-co-acrylic Acid) Preformed Particle Gel

Ahmed Ben Ali


Reem Elaf

Mohammed Saad

Ibnelwaleed A. Hussein

et. al. For a complete list of authors, see https://scholarsmine.mst.edu/geosci_geo_peteng_facwork/2175

Follow this and additional works at: https://scholarsmine.mst.edu/geosci_geo_peteng_facwork

 Part of the [Biochemical and Biomolecular Engineering Commons](#), [Geological Engineering Commons](#), and the [Petroleum Engineering Commons](#)

Recommended Citation

A. Ben Ali et al., "Impact Of Composition And Salinity On Swelling And Gel Strength Of Poly (acrylamide-co-acrylic Acid) Preformed Particle Gel," *Emergent Materials*, Springer, Jan 2023.

The definitive version is available at <https://doi.org/10.1007/s42247-023-00510-2>

This Article - Journal is brought to you for free and open access by Scholars' Mine. It has been accepted for inclusion in Geosciences and Geological and Petroleum Engineering Faculty Research & Creative Works by an authorized administrator of Scholars' Mine. This work is protected by U. S. Copyright Law. Unauthorized use including reproduction for redistribution requires the permission of the copyright holder. For more information, please contact scholarsmine@mst.edu.



Impact of composition and salinity on swelling and gel strength of poly (acrylamide-co-acrylic acid) preformed particle gel

Ahmed Ben Ali¹ · Reem Elaf¹ · Mohammed Saad^{1,2} · Ibnelwaleed A. Hussein^{1,2} · Baojun Bai³

Received: 25 November 2022 / Accepted: 17 May 2023
© The Author(s) 2023

Abstract

The effects of various material compositions and reservoir environments on the ultimate strength and swelling kinetics of a commercial preformed particle gel (PPG) have been investigated. This study used different ratios of acrylamide and acrylic acid copolymers with a specific crosslinker concentration. Results have indicated that increasing the acrylic acid proportion enhances the PPGs' ability to swell but weakens their network structure. In contrast, increasing the crosslinker content decreases the swelling ratio and increases the gel strength. The highest equilibrium swelling capacity among the six preformed particle gel samples was obtained for PPG2, which has the highest acrylic acid amount and the lowest crosslinker content, with a swelling ratio of 2400 g/g in deionized water and 59.8 g/g in brine 1 (67535.8 mg/l). On the contrary, PPG5, with the lowest acrylic acid and highest crosslinker content, has a swelling capacity of 239 g/g and more than 17 g/g in distilled and brine 1, respectively. Yet, PPG5 has the highest swollen gel strength of 615.5 Pa in deionized water and 3344 Pa in brine 1. The PPGs' swelling ratios showed stepwise improvements along with increasing temperature, notably after 50 °C, yet, the storage modulus (G') was negatively affected. The PPGs revealed the highest swelling behavior in pH 6–8, decreasing dramatically in more acidic and basic conditions. The swelling ratios of the PPGs in brine 1 at 50 °C were between 12 and 32 g/g, having strengths in the range of 566–5508 Pa, depending on the crosslinker ratio. The PPGs also demonstrated the ability to compete with other commercial PPGs as they have shown physical and thermal stability when aging at 50 °C, specifically those with high crosslinker content (PPG5).

Keywords Conformance control · Preformed particle gel · Acrylamide and acrylic acid copolymers · Swelling capacity · Storage modulus · Crosslinker

1 Introduction

Water production is a prominent issue for most mature oil reservoirs worldwide. Excess water production is a concerning issue because it increases the operating costs for

oil–water separation processes, causes high levels of corrosion and scale depositions, and shortens the well's production life. For these reasons, controlling water production has been one of the prime intents of most hydrocarbon producers.

The concept of conformance control refers to the methods used to correct the heterogeneity of reservoirs, which has the potential to improve sweep efficiency while cutting water production. One of the most popular methods for conformance control is the in situ gel technology; it is the injection of chemicals to form a 3D network structure under the reservoir conditions (temperature, salinity, and pH) that block water flow and reduce permeability of channels [1, 2]. In the 1970s, Philips Co. (now Conoco Philips) developed the first in situ polymer gel system using aluminum citrate and partially hydrolyzed polyacrylamides (HPAM) [3]. Since then, various materials have been proposed and used as alternate injection methods or co-injections of polymer and

✉ Mohammed Saad
m.saleh@qu.edu.qa

✉ Ibnelwaleed A. Hussein
ihussein@qu.edu.qa

¹ Gas Processing Center, College of Engineering, Qatar University, P.O. Box 2713, Doha, Qatar

² Department of Chemical Engineering, College of Engineering, Qatar University, P.O. Box 2713, Doha, Qatar

³ Department of Geosciences and Geological and Petroleum Engineering, Missouri University of Science and Technology, Rolla, MO 65409, USA

a crosslinker to fully or partially seal the formation [4–9]. Our research group reported these polymer-based formulations in two different reviews [4–9].

In situ polymer gel systems are cost-effective and efficient in reducing reservoir heterogeneity, consequently reducing water production [10]. Nevertheless, this technology has several drawbacks that restrict its applications for conventional reservoirs, such as a lack of management of the gelation time and difficulties in controlling the stability and strength of the formed gel due to shear degradation. In addition, the limited control of material uptake on the surface of the rocks leads to increased damage to low permeability un-swept oil zone. Furthermore, in situ gels not only have the problem of chromatographic separation between polymer and crosslinker and dilution by the formation water and minerals, but their application is limited to near-wellbore plugging. Therefore, to avoid such limitations, it is preferable to incorporate suitable preformed gel materials at surface facilities in the form of particles before injection into the reservoir.

The injected particles form crosslinked three-dimensional network structures of hydrophilic polymers and act as super-absorbent polymers (SAP) with an ability to absorb and retain water more than 100 times their weight. In addition, these SAP could plug or divert water in the fracture channels and void space conduits in high permeability zones, reducing the water effluents and enhancing the oil sweep efficiency [11]. This technology is known as preformed particle gels (PPGs) and could be used for near wellbore or deep profile applications.

PPG was introduced in 1996 by RIPED, Petro China, and since its inception, PPGs have attracted the interests of many researchers, where various PPGs have been developed for conformance control [12, 13]. The existing scope of preformed gels includes bulk gels, partially preformed gels, and particle gels [14–17]. Most investigations have utilized materials based on polyacrylamide or one of its derivatives [18], along with an organic crosslinker, such as N, N'-methylenebisacrylamide [19] and polyethyleneimine (PEI) [20], or an inorganic crosslinker, such as zirconium lactate [15], aluminum nitrate [21], and others [22]. In some cases, clay [23], silica [24], or graphene oxide [25] are added to the composition to enhance the material's mechanical strength. The success of the PPG treatment mainly depends on how effectively it can reduce the permeability of the channels to a certain level [19]. According to Esfahlan et al. [13], particle size, swelling capacity, swollen particle strength, and thermal stability are the main parameters significantly affecting the PPG's performance.

The ability to adjust the PPG's size is a significant advantage, as dry gels could be crushed and sieved to produce micro-to-millimeter-sized PPGs. Therefore, the sieve diameter determines their initial size [26, 27]. However, the swelling capacity is more critical because it defines the final

size of PPGs, which controls the blocking efficiency in fluid channels. The mechanical properties of the particles, including elasticity and mechanical strength, influence the gel resistance to water flow during the injection. Such properties provide a thorough understanding of the transport mechanism and the deformation of the materials in porous media [17]. While core flooding or filtration tests are commonly used to assess the performance of PPGs, it is also crucial to examine the swelling ratio and strength of PPGs prior to subjecting them to such tests. By doing so, it becomes possible to select the most suitable PPGs based on the specific characteristics of the well, gain a deeper understanding of how these PPGs will act in the reservoir, and make informed decisions regarding how best to optimize their use to achieve maximum oil recovery.

The current study provides a comprehensive investigation of the swelling kinetics and the mechanical properties of commercial PPG samples, including different crosslinking degrees of poly (acrylamide-co-acrylic acid), under different conditions to evaluate their applicability in conformance control. Accordingly, the study investigates the impact of varying two monomers' ratios and various crosslinker contents and assesses the PPG performance under different temperatures, pH, and salinity conditions. Additionally, it describes the long-term effects of high salinity and thermal environments on overall PPGs' performance.

2 Experimental

2.1 Materials

The materials used in this study are poly(acrylamide-co-acrylic acid) with different amounts of monomers and crosslinkers (Fig. 1). The PPG samples were provided by SNF Floerger, France, in the form of powder with a particle size of 300–500 μm . By the disclosed content, the information on materials has been specified in Table 1.

2.2 Methods

2.2.1 Swelling behavior

The purpose of swelling kinetics measurements is to ascertain the time needed for a PPG to reach the maximum swelling capacity to evaluate its ability to swell and plug reservoir fractures and high permeability matrices. We used the gravimetric method to measure the swelling rate where 0.5 g of dry PPG was soaked in 500 ml of DI water or 300 ml of brine 1 (67,535.8 mg/l) or brine 2 (33,867.8 mg/l), for the desired time. Then, the residual solution is separated from the swollen PPG using a mesh of 125 μm or a filter paper, depending on the size of

Fig. 1 Schematic representation of the proposed structure of commercial PPG

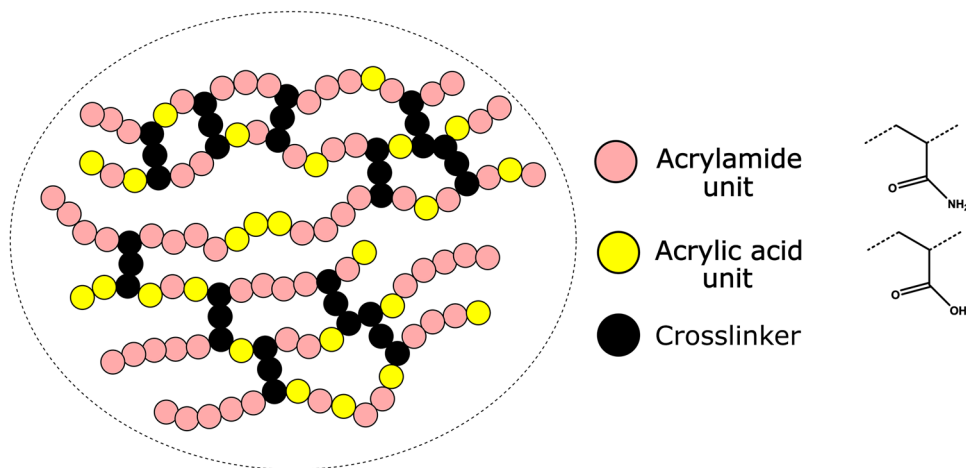


Table 1 The compositions of commercial PPG

Sample	PPG ₁	PPG ₂	PPG ₃	PPG ₄	PPG ₅	PPG ₆
Crosslinker content	Low (1–20 ppm)		Medium (20–75 ppm)		High (75–300 ppm)	
Anionicity/acrylic acid mol%	5	20	5	20	5	20

Table 2 Composition of brine 1 and brine 2 [28, 29]

	Brine 1	Brine 2
Salts	Concentration (g/L)	Concentration (g/L)
NaHCO ₃	0.2382	0.1191
Na ₂ SO ₄	6.5754	3.2877
CaCl ₂ ·H ₂ O	2.3945	1.1972
MgCl ₂ ·6H ₂ O	18.0539	9.1269
NaCl	40.2738	20.1369
TDS	67.5358	33.8678

swollen particles. The net weight of the swollen PPG is measured, and the swelling ratio is determined using the following equation:

$$SR = \frac{W_s - W_d}{W_d}$$

where W_s is the weight after swelling and W_d is the dry PPG weight

The brine samples were prepared in the laboratory by dissolving pure salts in deionized water. The composition of brine 1 and brine 2 is given in Table 2, with the total dissolved salinity (TDS) of 67.5 g/l and 33.9 g/l, respectively, representing the condition found in oil reservoirs in Gulf countries [28, 29]. For conformance control, it is significant to know the effect of different conditions on the behavior of PPGs. The swelling behavior of the PPGs was investigated at different temperatures and varied pH. For

each experiment, 0.5 g was placed in 500 ml of solution and left for 24 h under the studied condition.

2.2.2 Rheology measurements

An Anton Paar MCR 302 rheometer was used to investigate the rheological behavior of the commercial PPGs, specifically, the storage modulus (G'). A frequency sweep test from 0.1 to 100 Hz with a fixed strain of 10%, within the linear viscoelastic region (LVR) region, was conducted to test the storage modulus (G') for the swollen PPGs using parallel plate geometry with a gap of 2 mm and a diameter of 25 mm. The storage modulus (G') measures the resistance of the swollen PPGs to deformation, which indicates the PPGs' ultimate strengths. The PPGs were prepared at a predetermined temperature of 25 to 100 °C. Then, allow enough time to reach their ultimate swelling ratio at that temperature before undergoing the rheological test.

3 Results and discussion

3.1 Salinity effect

Measuring the swelling ratio of PPG is essential as it identifies its ability to plug high permeable streaks and fractures [30]. The amount of liquid absorbed by the material was measured as a function of time until saturation to determine the swelling of PPG samples. The swelling kinetics of the

PPG samples is shown in Fig. 2 for swelling in DI water and Fig. 3 for swelling in brine 1.

The water absorption sharply increased with extended contact time at the initial stage, and then the increasing trend becomes flattened, reaching swelling equilibrium. Most PPGs come to complete swelling in half an hour, and only PPG₂ took more time to reach to its maximum capacity. According to Bai et al., 95% of field applications in China injected fully swelled particles into the formation [12]. Thus, the rapid swelling of PPGs is significant for their practical applications. The nature of the polymer and the crosslinking degree are crucial factors determining the swelling ratio. Acrylamide displays a very high capacity to absorb water; they are permeable to oxygen and possess good biocompatibility. However, acrylic acid has an anionic group, making it highly hydrophilic and absorbing more water than acrylamide. Using the same crosslinker ratio, the PPG with a high amount of acrylic acid has swelled more than those of a low amount [(PPG₂ ≥ PPG₁); (PPG₄ ≥ PPG₃); (PPG₆ ≥ PPG₅)].

This fact makes researchers include acrylic acid in the synthesis of superabsorbent materials to enhance the swelling ratio of the material [31]. On the other hand, the crosslinker builds a complex 3D network by forming bridges between polymer chains, allowing the materials to trap water in cages. The PPGs with low crosslinker content show a better swelling capacity reaching 1530 g/g for PPG₁ and 2400 g/g in the case of PPG₂; then the swelling ratio starts to decrease with increasing the crosslinking content (PPG₅ ≤ PPG₃ ≤ PPG₁) and (PPG₆ ≤ PPG₄ ≤ PPG₂) reaching 232 g/g for PPG₅ and 395 g/g in the case of PPG₆. Both physical [22, 32, 33] and chemical [34–36] crosslinkers have been used to prepare crosslinked PAM and its derivatives. Physical crosslinking refers to the assembly that can be crosslinked by hydrogen or ionic bonds, and chemical crosslinking is mainly attributed to the mechanism, including covalent

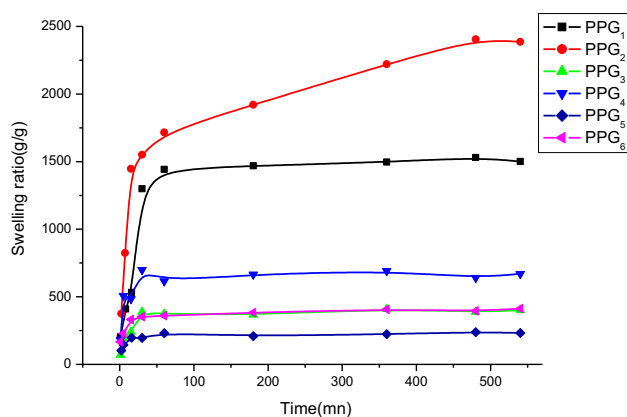


Fig. 2 The effect of PPG composition on the swelling kinetics in DI water

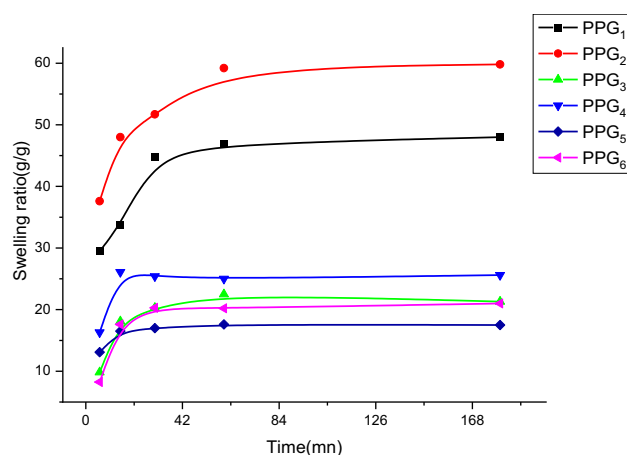


Fig. 3 The effect of PPG composition on the swelling kinetics in brine 1 (salinity = 67,535.8 mg/l)

bonds. Still, in most cases, the chemical crosslinkers show better stability and water absorbency.

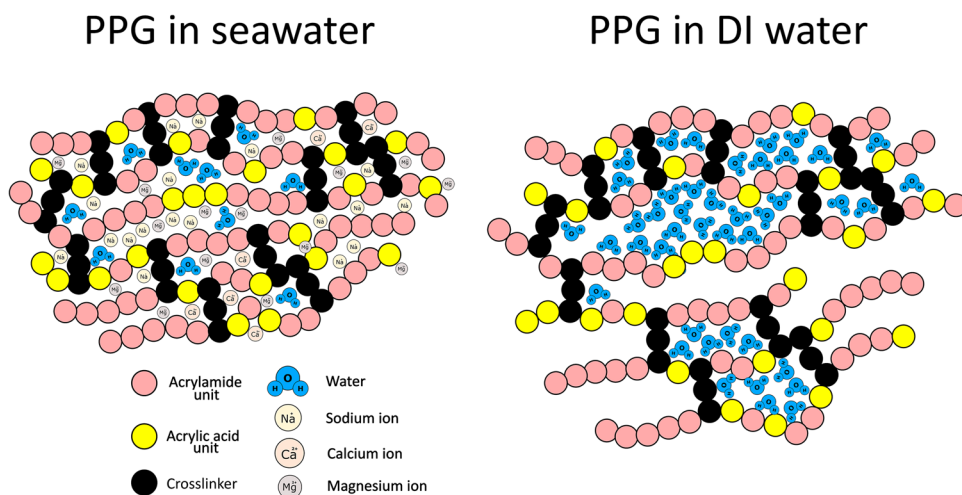
Salt resistance is an important indicator for measuring the effectiveness of this commercial material in conformance control; therefore, PPGs are prepared using field water containing salts. As seen in Table 3, the highest swelling capacity was detected in PPG₂ (59.8 g/g) and PPG₁ (48 g/g) and the lowest for PPG₅ (17 g/g) and PPG₆ (21 g/g). Therefore, these values are one of the highest swelling capacities reported for PPGs [19, 21, 22, 37] in saline water. The swelling of PPG is significantly affected by the presence of salts, and water uptake is decreased dramatically compared to swelling in deionized water. This phenomenon results from the concentrated counter ion effect of Na⁺, Ca²⁺, and Mg²⁺ in seawater that reduces the osmotic pressure difference, the driving force for swelling between the PPG and the solution.

In addition, multivalent cations can form a complex with amide (-CONH₂) and carboxylic (-COOH) groups leading to an increase in the crosslinking degree, also replacing polymer-water interaction by polymer-salt interaction, consequently, poor swelling capacity (see Fig. 4). Decreasing the ionic strength of the brine solution may increase the swelling ratio. Many literature reports tested the effect of

Table 3 The difference in the swelling capacity of PPGs between brine 1 (salinity = 67,535.8 mg/l) and brine 2 (salinity = 33,867.8 mg/l)

Code	SR in brine 1 (g/g)	SR in brine 2 (g/g)
PPG1	48	48.2
PPG2	59.8	65.4
PPG3	22.5	22.1
PPG4	25.6	25.1
PPG5	17.5	18.1
PPG6	21	21.2

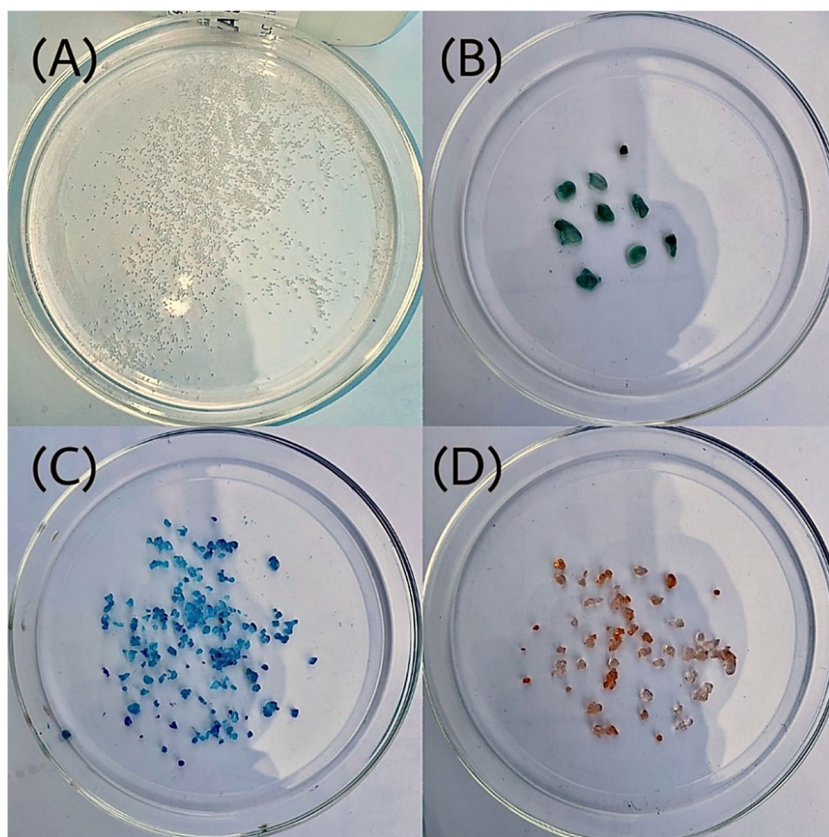
Fig. 4 Schematic representation of the proposed PPG structure and mechanism of swelling in DI water and brine solution



salts concentration of NaCl and CaCl₂ on superabsorbent and PPG's swelling behavior, indicating how these materials react and interact with each salt separately [11, 38–40]. We tested the PPGs in brine 2 (salinity = 33,867.8 mg/l), and the results were similar to brine 1. The swelling did not improve, indicating that a concentration of brine that causes the maximum material shrinking is reached. Likely, the PPGs will not undergo more shrinking in higher salinities.

The effect of salinity on particle swelling was investigated by Qiu et al. [41] at 125 °C and with salt concentrations ranging from 0 to 20%. They concluded that the swelling ratio decreases as salinity increases until a 10% salt concentration is reached. After that, it almost becomes stable, indicating that the particle can have high salinity resistance. Figure 5 illustrates the variations in PPG₁, PPG₃, and PPG₅ swelling ratios in seawater.

Fig. 5 Commercial PPGs swelled in brine 1 for 24 h after coloring with food dyes. **A** Dry PPG before being swelled, **B** swelled PPG₁, **C** swelled PPG₅, **D** swelled PPG₃



The rheological behavior is an essential aspect of PPG characteristics that evaluate the mechanical resistance of the PPG network structure to deformation, especially under several effects such as temperature, salinity, pH, and shear stress. The study aims to mimic the PPGs' behavior inside the reservoir, where they undergo deformation in the porous media and are exposed to different reservoir conditions, such as high temperature, acidity, and salinity. Storage modulus (G'), which characterizes the strength and elasticity, was measured for different swollen and filtered PPG samples using a rheometer apparatus. Figure 6 illustrates the G' of three commercial PPGs (PPG₁, PPG₃, and PPG₅) swelled in DI water and brine 1. The ultimate strength of PPG₅ was the highest, having a value of 615.5 Pa in DI water, followed by PPG₃, which has a value of ~262.3 Pa, and PPG₁, which has the lowest strength of 94.4 Pa in DI water. These results are because PPG₅ has the highest crosslinker content, followed by PPG₃ and PPG₁.

Higher crosslinker content provides a higher degree of crosslinking between the polymer chains. Thus, a stronger network structure is generated. Moreover, PPG₁ has the lowest storage modulus due to the super capability of swelling, reaching a swelling ratio of 1530 g/g, as a higher swelling capacity between the three PPGs weakened the materials. Comparing the G' in both seawater and DI water, one can notice that the G' are much higher in seawater, rounding up to values of 3344 Pa and 1945 Pa for PPG₅ and PPG₃, respectively. The reason could be attributed to the presence of amide ($-\text{CONH}_2$) and carboxyl ($-\text{COOH}$) functional groups in the polymer backbone structure that interact with different multivalent cations (Ca^{+2} , Mg^{+2}) when immersed in seawater, generating complexes that stiffened the network structure [42, 43]. Therefore, the strain applied to the gel samples increased the mechanical resistance. When comparing the storage modulus of these commercial PPGs in seawater to those described in the literature [42], it becomes

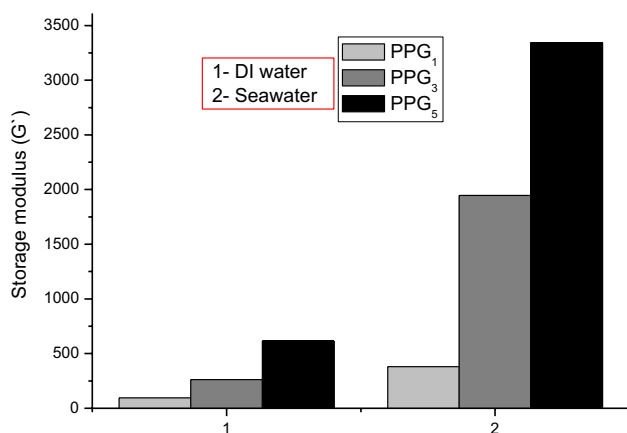


Fig. 6 Salinity effect on the final PPG strength

clear that they have considerable strength, measuring up to 3343.6 Pa with a roughly equivalent swelling capacity value of ~18 g/g.

3.2 Effect of pH

The swelling behavior of the commercial PPGs was studied at various pH values between 2 and 12; at room temperature, the desired acidic or basic pH was adjusted by adding diluted droplets of NaOH or HCl to DI water. Figure 7 shows that the amount of acrylic acid in the material increases the sensitivity of PPGs to pH; when going from pH 4 to 2, the swelling decreased by only 33.04% for PPG₂, while PPG₁ dropped by 81.43%. Protonation of sodium carboxylate groups in the polymer network reduces swelling capacity [32] at low pH by lowering the polymer expansion; swelling capacity is also reduced at high pH, shielding the carboxylate groups to prevent effective anion-anion repulsion. In the pH range from pH = 4 to pH = 8, some carboxylic acid groups are ionized, and electrostatic repulsion between COO^- groups cause an enhancement of the swelling capacity.

The behavior of the PPGs under different pH values is considered according to the variation in reservoir acidity conditions, as G' varies due to many interacting species in the pH-dependent swelling medium. The mechanical properties of PPG samples were taken after exposing the materials to the desired pH for 24 h. The results showed a decrease in the storage modulus of the PPGs when the pH was increased from 4 to 7. Then, a slight change in G' between pH 7 and 9 and a rapid increase in pH 9 to 11 was observed (Fig. 8). The fact that G' is high at a pH of less than 7 could be attributed to the conversion of $-\text{COO}^-$ groups to $-\text{COOH}$ groups, which in turn reduces the negative charge repulsion and enhances the bonding between the $-\text{COOH}$

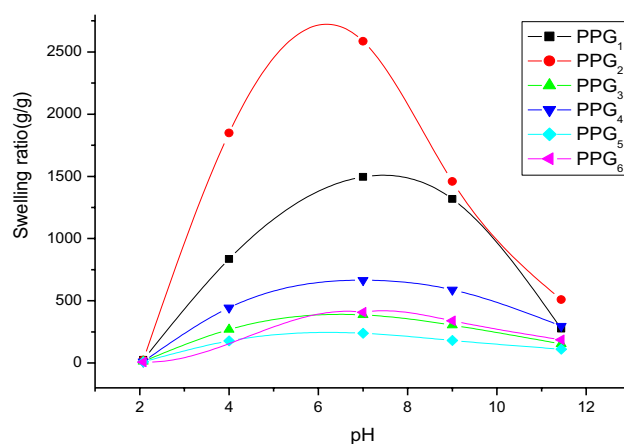


Fig. 7 The effect of pH on the swelling ratio of PPGs in DI water for 24 h

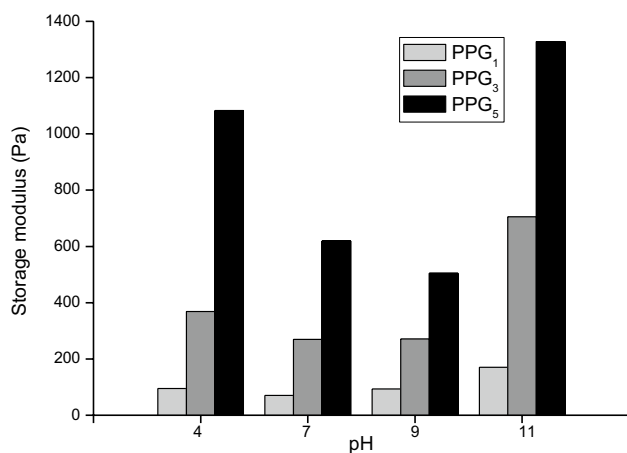


Fig. 8 PH effect on the final gel strength

groups due to the creation of a hydrogen bond, resulting in a higher crosslinking density, thus, higher ultimate strength. Meanwhile, the $-\text{COOH}$ groups turn into $-\text{COO}^-$ groups when the pH exceeds 9, which raises the ionic strength and causes an immediate reduction in osmotic pressure inside the gel particles, shrinking the PPGs and increasing their final strength. The reduction of G' in the pH range of 7–9 implies the buffering effect of $-\text{COOH}$ and $-\text{COO}^-$ groups with weak acids or bases, which enhances the osmotic pressure and water absorbency. Such behavior explains the cooperative relationship between the carboxylic acid ($-\text{COOH}$) and carboxylate ($-\text{COO}^-$) groups, according to earlier investigations [39, 44].

3.3 Effect of temperature

Temperature is an important factor affecting the absorbance capacity and strength of PPGs. The effect of temperature on the PPG strength and swelling was investigated at different temperatures (25 °C, 50 °C, 75 °C, and 100 °C). PPG samples were prepared in screw cap bottles with DI water, immersed in an oil bath at a predetermined temperature, and swollen for 24 h to reach maximum swelling capacity. Then, the PPG samples were filtered, weighed, and tested for swelling kinetics and rheology measurement. As seen in Fig. 9, the PPGs exhibit a slight increase in their swelling ratio at 50 °C compared to room temperature. The swelling of PPG₃ and PPG₄ continued at 75 °C; however, PPG₁ and PPG₂ experienced a gradual decrease in absorbency due to the collapse of the polymer network and the release of water. At a high temperature of 100 °C, PPG₁ and PPG₂ have degraded to highly viscous material, whereas the other PPGs with high crosslinker content have resisted the effect of high temperature, having only a slight decrease in swelling ratios. Bai et al. [17] proposed that the increase in swelling of PPG-based polyacrylamide at temperatures of

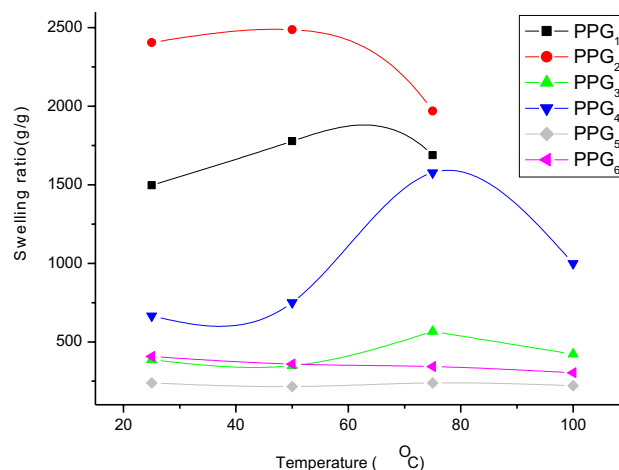


Fig. 9 The effect of temperature on the swelling ratio of PPGs in DI water for 24 h

60 °C or higher can be attributed to the hydrolysis of amino groups ($-\text{CONH}_2$) present in the polymer chains to carboxylate groups ($-\text{COO}^-$). The experimental results of Lenji et al. [21] showed that the network structure of PPG-based sulfonated polyacrylamide crosslinked with aluminum nitrate nanohydrate is weakened at 100 °C. The PPG absorbed heat with increasing temperature until it reached 100 °C; beyond this point, its structure could not absorb any more heat to be subsequently released for breaking, which causes the 3D network structure to collapse. Hence, the swelling ratio dramatically decreases by raising the temperature from 80 to 100 °C.

The energy absorption caused by temperature increment leads to an expansion of the PPGs structure and results in enhanced water uptake while weakening the material. At 75 °C, PPGs with a low amount of crosslinker, such as PPG₁ and PPG₂, lose some of the water and decrease the swellability; the PPG with medium amount of crosslinkers, such as PPG₃ and PPG₄, continue swelling. At 100 °C, the amount of crosslinker in PPG₁ and PPG₂ cannot handle more expansion with the thermal increase, where holding the PPG's material together become unattainable, resulting in a collapse of the network structure and thus a viscous material. At this temperature, PPG₃ and PPG₄ start experiencing what happened to PPG₁ and PPG₂ at 50 °C, losing some of the absorbed water. In contrast, PPG₅ and PPG₆ can resist the increase in temperature up to 100 °C, as they keep the swelling almost steady because of the high crosslinker amount they have that limits any further expansion.

The above explanations could be supported by the graphs shown in Fig. 10. The frequency sweep test depicts the storage modulus (G') of PPG₁, PPG₃, and PPG₅ versus temperature, ranging from 25 to 75 °C. The trend of all PPGs showed a gradual decline in G' when the

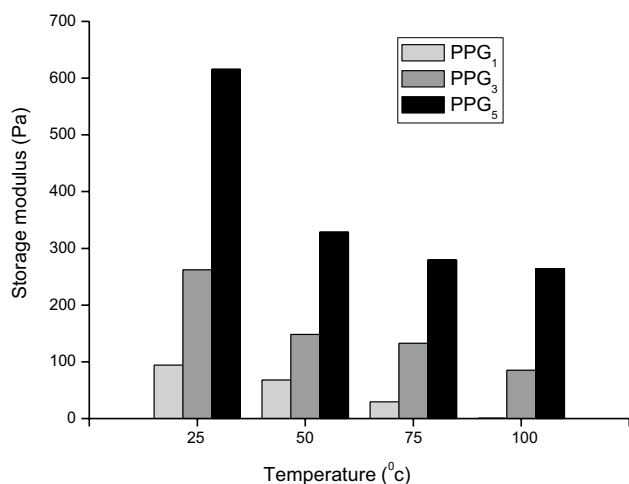


Fig. 10 The effect of temperature on the swelling ratio of PPGs in DI water for 24 h

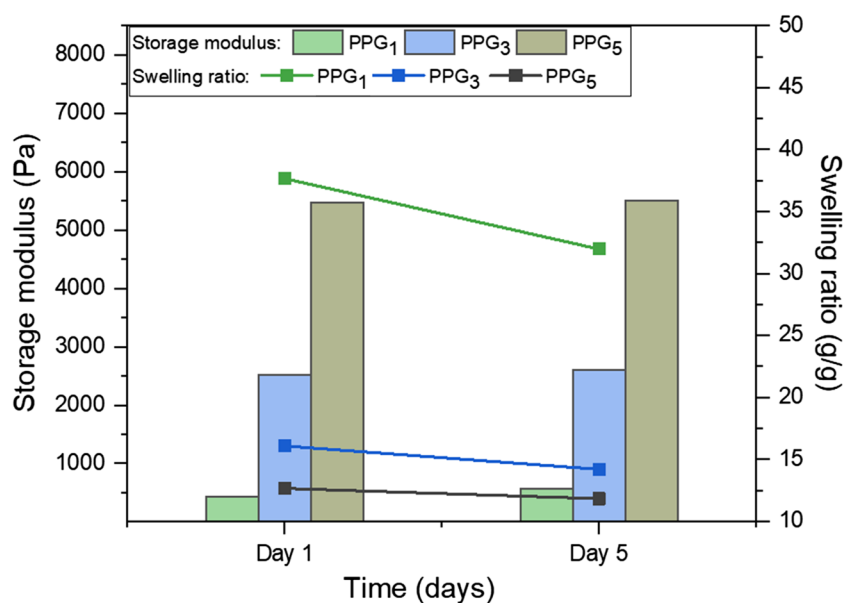
temperature is increased from 25 °C to 100 °C. The G' of PPG₅ has decreased from 615 Pa at room temperature to 264.07 Pa at 100 °C, while PPG₃ decreased from 262.27 to 85.055 Pa, respectively. These results point out the thermal stability of PPG₃ and PPG₅, indicating the stability of the network structure up to 75–100 °C. PPG₁ has the weakest network structure among others, has a G' of 94.40 Pa at 25 °C and 29.40 Pa at 75 °C, while has collapsed and disrupted at 100 °C, limiting its application to low-temperature reservoirs.

3.4 Short- and long-term thermal stability

The thermal stability of the produced PPGs was tested for 5 days in seawater at a temperature of 50 °C to mimic the reservoir's condition and better approximate the PPGs' long-term behavior under temperature and salinity effect. The swelling ratio and the storage modulus were noted on day 5 and were compared to day 1, as shown in Fig. 11. The swelling ratio of PPG₅ on day 5 witnessed a slight change with less than 7% compared to day 1, while PPG₃ and PPG₁ experienced more drop of 11% and 15%, respectively. This drop could be justified by the syneresis behavior, which describes the separation of a liquid from the particle gels due to excess brine or high temperature over a prolonged time [4]. According to the results, PPG₅ exhibited lesser syneresis than PPG₃ and PPG₁, which could be due to the higher bonding density and a stronger network structure, making it more thermally and hydrolytically stable in thermal and ionic environments. The results also reveal that the storage modulus of the three particle gels increased slightly on day 5 compared to day 1, which is usually related to water loss and particle shrinkage. These PPGs, especially PPG₅ and PPG₃, exhibited a slight change in swelling behavior in high salinity and temperature environment. Therefore, these gels could be used for conformance control in reservoirs because of their enhanced mechanical strength of 2500–5500 Pa and a swelling ratio of 12–16 g/g.

The study of the aging factor of the preformed gels is significant in defining their long-term thermal stability in the reservoir's environments. Since PPG₅ exhibited less change in its swelling and strength characteristics in short-term aging at 50 °C and in brine 1 due to its higher crosslinking

Fig. 11 The effect of aging on the strength and swelling ratio of PPGs in brine 2 for 1 day and 5 days



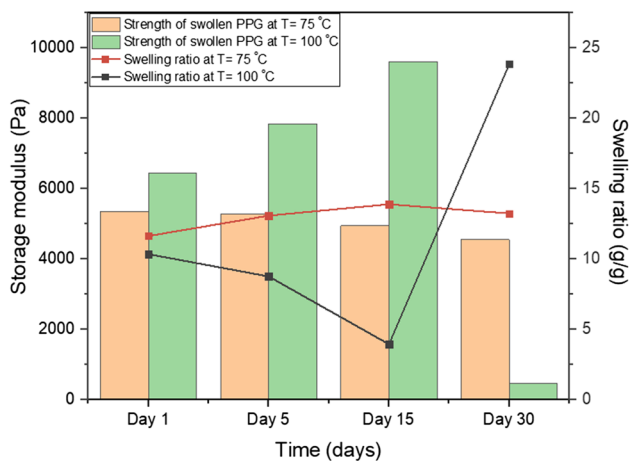


Fig. 12 The aging factor effect on the swelling ratio and storage modulus for PPG₅ at T=75 °C and T=100 °C and in brine 2 in the long term

density and more robust network, we intended to evaluate its long-term thermal performance at higher temperatures in this part of the investigation. Figure 12 shows the swelling ratio and the mechanical strength of PPG₅ at different temperatures of 75 °C and 100 °C in brine 1 on a timescale of one day, 5 days, 15 days, and 30 days. The trend of the swelling ratio at 75 °C (black line) showed a slight gradual increase with time, while the strength (red bar) remained almost stable with a slight gradual decrease, which related to the increased water uptake. A further apparent finding of aging at 100 °C showed that the swelling ratio decreased significantly from day 1 to day 15 (red line), followed by a considerable increase in the strength (green bar). This behavior could be due to the syneresis phenomenon, which causes the dehydration of the particle gels at high temperatures, where the water inside the particles evaporates and separates. A sudden increase in the absorbency to up to 23.00 g/g with a related decrease in the mechanical strength to 464 Pa was observed after one month of aging at 100 °C, which may be due to reswelling with continued high thermal exposure that allows more water to enter the network structure, thus, higher swelling ratio and lower strength. Overall, PPG₅ is recommended to be used at low to moderate reservoir temperatures (< 75 °C), as it was more thermally and hydrolytically.

4 Conclusion

Different tests were conducted on commercial preformed particle gels based on a crosslinked copolymer of poly (acrylamide-co-acrylic acid) with different compositions of acrylamide, acrylic acid, and crosslinker to determine

their performance in preventing and controlling water in hydrocarbon reservoirs; the results of which are summarized below:

- The PPGs showed rapid swelling kinetics and a good swelling capacity in deionized water, equivalent to 232–2400 its dry weight. In addition, they exhibited the highest swelling ratios in literature when swelled in brine 1 with TDS of 67,535.8 mg/l, having values between 17 and 59.8 g/g.
- PPG swelling increases with increasing acrylic acid fraction and decreases with the crosslinker content in the material, whereas based on rheological tests, crosslinker concentrations led to enhanced PPG strength to a value of 3344 Pa.
- The salinity of produced water (33,867.8 mg/l) causes the maximum shrinkage of the PPGs, and their swelling ratio will not be affected by a higher increase in the salinity of the solution.
- The PPGs were stronger in brine 1 than in DI water, where the storage modules were 380–3344 Pa in brine 1 and 94.4–615.5 Pa in DI water.
- The presence of acrylic acid ratios in the PPG materials increases its sensitivity toward acidic and basic environments. At a pH range of 4–9, the swelling capacities of the PPGs were very high, especially for those with high acrylic acid ratios; while at pH=2 and pH=11, the swelling capacities were very low, making the PPG unsuitable at highly acidic and basic conditions. The G' values were reasonable in the pH range of 4–9 and increased significantly in highly acidic and basic conditions.
- The increase in temperature enhances the swelling capacity of the PPG but weakens its 3D network structure, where the commercial PPG is durable at a temperature range of 50 to 75 °C. At temperatures of 100 °C, the structure of PPG with low crosslinker content collapsed and degraded to a viscous solution, while PPG with high crosslinker content remained stable with a slight decrease in G'.

Acknowledgements The findings achieved herein are solely the responsibility of the authors. The authors would also like to thank SNF Floerger Company for supplying the PPG samples. The authors would also like to acknowledge Qatar University for providing Graduate Assistantship to Ms. Reem Elaf in her graduate studies.

Funding Open Access funding provided by the Qatar National Library. The authors would like to acknowledge the Qatar National Research Fund (a member of the Qatar Foundation) for funding through Grant # NPRP13S-1231-190009. Al-Salam Petroleum Services Company, Qatar, is also acknowledged for co-funding this project.

Declarations

Conflict of interest The authors declare no competing interests.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

- R.S. Seright, Impact of dispersion on gel placement for profile control. *SPE Reserv. Eng.* **6**(3), 343–352 (1991). <https://doi.org/10.2118/20127-PA>
- R.B. Needham, C.B. Threlkeld, J.W. Gall, Control of water mobility using polymers and multivalent cations. *SPE Improv. Oil Recover. Symp.* (1974). <https://doi.org/10.2118/4747-MS>
- B. Bai, J. Zhou, M. Yin, A comprehensive review of polyacrylamide polymer gels for conformance control. *Pet. Explor. Dev.* **42**(4), 525–532 (2015). [https://doi.org/10.1016/S1876-3804\(15\)30045-8](https://doi.org/10.1016/S1876-3804(15)30045-8)
- M. Shamlooh, R. Elaf, I.A. Hussein, M. Saad, B. Bai, Chitosan/polyacrylamide green gels for water control in high-temperature reservoirs. *Energy Fuels*. **36**(7), 3816–3824 (2022). <https://doi.org/10.1021/acs.energyfuels.2c00242>
- A. Hamza, M. Shamlooh, I.A. Hussein, M.S. Nasser, S. Salehi, Rheology of triamine functionalized silica reinforced polymeric gels developed for conformance control applications. *Energy Fuels*. **34**(1), 1093–1098 (2020). <https://doi.org/10.1021/acs.energyfuels.9b03625>
- M. Shamlooh, I.A. Hussein, M.S. Nasser, M. Magzoub, S. Salehi, Development of pH-controlled aluminum-based polymeric gel for conformance control in sour gas reservoirs. *ACS Omega*. **5**(38), 24504–24512 (2020). <https://doi.org/10.1021/acsomega.0c02967>
- M. Shamlooh, A. Hamza, I.A. Hussein, M.S. Nasser, M. Magzoub, S. Salehi, Investigation of the rheological properties of nanosilica-reinforced polyacrylamide/polyethyleneimine gels for wellbore strengthening at high reservoir temperatures. *Energy Fuels*. **33**(7), 6829–6836 (2019). <https://doi.org/10.1021/acs.energyfuels.9b00974>
- A. Hamza, M. Shamlooh, I.A. Hussein, M. Nasser, S. Salehi, Polymeric formulations used for loss circulation materials and wellbore strengthening applications in oil and gas wells: A review. *J. Pet. Sci. Eng.* **180**, 197–214 (2019). <https://doi.org/10.1016/j.petrol.2019.05.022>
- K.S.M. El-Karsani, G.A. Al-Muntasheri, I.A. Hussein, Polymer systems for water shutoff and profile modification: a review over the last decade. *SPE J.* (2014). <https://doi.org/10.2118/163100-PA>
- R. S. Seright and J. Liang, “A survey of field applications of gel treatments for water shutoff,” in *SPE Latin America/Caribbean Petroleum Engineering Conference*. 221–231 (1994). <https://doi.org/10.2118/26991-MS>
- M.O. Elsharafi, B. Bai, Influence of strong preformed particle gels on low permeable formations in mature reservoirs. *Pet. Sci.* **13**(1), 77–90 (2016). <https://doi.org/10.1007/s12182-015-0072-3>
- B. Bai, M. Wei, and Y. Liu, “Field and lab experience with a successful preformed particle gel conformance control technology,” in *SPE Production and Operations Symposium, Proceedings*. 506–522 (2013). <https://doi.org/10.2118/164511-ms>
- M. Seidy Esfahlan, E. Khodapanah, and S. A. Tabatabaei-Nezhad, “Comprehensive review on the research and field application of preformed particle gel conformance control technology,” *J. Pet. Sci. Eng.* (2021). <https://doi.org/10.1016/j.petrol.2021.108440>
- G. Chauveteau, A. Omari, R. Tabary, M. Renard, and J. Rose, “Controlling gelation time and microgel size for water shutoff”. (2000). <https://doi.org/10.2118/59317-MS>
- G. Chauveteau, A. Omari, R. Tabary, M. Renard, J. Veerapen, and J. Rose, “New size-controlled microgels for oil production,” *Proc. SPE. Int. Symp. Oilfield. Chem.* 111–118 (2001). <https://doi.org/10.2523/64988-MS>
- B. Bai, U. Of Missouri-Rolla, Y. Liu, J.-P. Coste, and L. Li, “Preformed particle gel for conformance control: transport mechanism through porous media,” (2007).
- B. Bai, L. Li, Y. Liu, H. Liu, Z. Wang, C. You, Preformed particle gel for conformance control: factors affecting its properties and applications. *SPE Reserv. Eval. Eng.* **10**(4), 415–422 (2007). <https://doi.org/10.2118/89389-pa>
- B. Bai, H. Reyes, R. Fajardo-lo, F. Barraga, and C. Dura, “Development of enhanced nanocomposite preformed particle gels for conformance control in high-temperature and high-salinity oil reservoirs,” no. September 2013. 277–284 (2014). <https://doi.org/10.1038/pj.2013.99>.
- A. Imqam, B. Bai, Optimizing the strength and size of preformed particle gels for better conformance control treatment. *Fuel* (2015). <https://doi.org/10.1016/j.fuel.2015.01.022>
- C.N.R. Amaral, P.F. Oliveira, I.O. Roman, C.R.E. Mansur, Preformed particle gels with potential applicability for conformance control of oil reservoirs. *J. Appl. Polym. Sci.* **137**(15), 1–10 (2020). <https://doi.org/10.1002/app.48554>
- M.A. Lenji, M. Haghshenasfard, M.V. Sefti, M.B. Salehi, A. Heidari, Experimental study of swelling and rheological behavior of preformed particle gel used in water shutoff treatment. *J. Pet. Sci. Eng.* **169**, 739–747 (2018). <https://doi.org/10.1016/j.petrol.2018.06.029>
- A. Heidari, E. Vashghani-Farahani, M. Vafaie-Sefti, Preformed particle gels of sulfonated polyacrylamide: preparation, characterization, and application as permeability modifier. *Iran. Polym. J.* **28**(12), 1001–1013 (2019). <https://doi.org/10.1007/s13726-019-00759-7>
- P. Tongwa, B. Baojun, A more superior preformed particle gel with potential application for conformance control in mature oilfields. *J. Pet. Explor. Prod. Technol.* **5**(2), 201–210 (2015). <https://doi.org/10.1007/s13202-014-0136-8>
- X. Tang et al., Characteristics of composite microspheres for in-depth profile control in oilfields and the effects of polymerizable silica nanoparticles. *Powder Technol.* **359**, 205–215 (2020). <https://doi.org/10.1016/j.powtec.2019.09.070>
- F. yang Jin, L. yue Yang, X. Li, S. yu Song, D. jun Du, Migration and plugging characteristics of polymer microsphere and EOR potential in produced-water reinjection of offshore heavy oil reservoirs. *Chem Eng Res Des* **172**, 291–301 (2021). <https://doi.org/10.1016/j.cherd.2021.06.018>
- J.-P. Coste et al., “In-depth fluid diversion by pre-gelled particles. Laboratory study and pilot testing.” (2000). <https://doi.org/10.2118/59362-MS>

27. Y. Liu, B. Bai, Y. Wang, Applied technologies and prospects of conformance control treatments in China. *Oil. Gas. Sci. Technol. Rev. d'IFP Energ. Nouv.* **65**(6), 859–878 (2010). <https://doi.org/10.2516/ogst/2009057>
28. M.A. Mahmoud, Evaluating the damage caused by calcium sulfate scale precipitation during low- and high-salinity-water injection. *J. Can. Pet. Technol.* **53**(3), 141–150 (2014). <https://doi.org/10.2118/164634-PA>
29. A. Abdulazeem, M. Mahmoud, S. Elkatatny, A. Barri, A. Muhamadain, “Development of new seawater-based formulation to stimulate sandstone formations”. *Soc. Pet. Eng. SPE Kingdom Saudi Arab. Annu. Tech. Symp. Exhib.* **2017**, 460–468 (2017). <https://doi.org/10.2118/188004-ms>
30. A. Kumar, V. Mahto, V.P. Sharma, Development of fly ash reinforced nanocomposite preformed particle gel for the control of excessive water production in the mature oil fields. *Oil Gas Sci. Technol. Rev. d'IFP Energ. Nouv.* **74**, 8 (2019). <https://doi.org/10.2516/ogst/2018083>
31. S. Nesrinne, A. Djamel, Synthesis, characterization and rheological behavior of pH sensitive poly(acrylamide-co-acrylic acid) hydrogels. *Arab. J. Chem.* **10**(4), 539–547 (2017). <https://doi.org/10.1016/j.arabjc.2013.11.027>
32. Q. Lv, M. Wu, Y. Shen, Enhanced swelling ratio and water retention capacity for novel super-absorbent hydrogel. *Colloids Surf. A Physicochem. Eng. Asp.* **583**, 123972 (2019). <https://doi.org/10.1016/j.colsurfa.2019.123972>
33. D. Gao et al., Preparation of TiO₂-P(AM-AA) organic-inorganic composite water-retaining agent based on photocatalytic surface-initiated polymerization. *J. Dispers. Sci. Technol.* **42**(4), 537–545 (2021). <https://doi.org/10.1080/01932691.2019.1702555>
34. S. Zhao, D. Zhu, B. Bai, Experimental study of degradable preformed particle gel (DPPG) as temporary plugging agent for carbonate reservoir matrix acidizing to improve oil recovery. *J. Pet. Sci. Eng.* **205**(January), 108760 (2021). <https://doi.org/10.1016/j.petrol.2021.108760>
35. A. Farasat, H. Younesian-Farid, S. Sadeghnejad, Conformance control study of preformed particle gels (PPGs) in mature water-flooded reservoirs: numerical and experimental investigations. *J. Pet. Sci. Eng.* **203**(October 2020), 108575 (2021). <https://doi.org/10.1016/j.petrol.2021.108575>
36. J. Xie, X. Liu, J. Liang, Y. Luo, Swelling properties of superabsorbent poly(acrylic acid-co-saylinide) with different crosslinkers. *J. Appl. Polym. Sci.* **112**(2), 602–608 (2009). <https://doi.org/10.1002/app.29463>
37. M.B. Salehi, A.M. Moghadam, K. Jarraghan, Effect of network parameters of preformed particle gel on structural strength for water management. *SPE Prod. Oper.* **35**(2), 362–372 (2020). <https://doi.org/10.2118/193631-PA>
38. A. Mousavi Moghadam, M. Vafaie Sefti, M. Baghban Salehi, and A. Dadvand Koohi, “Preformed particle gel: evaluation and optimization of salinity and pH on equilibrium swelling ratio,” *J. Pet. Explor. Prod. Technol.* (2012). <https://doi.org/10.1007/s13202-012-0024-z>
39. X. Zhang, X. Wang, L. Li, S. Zhang, R. Wu, Preparation and swelling behaviors of a high temperature resistant superabsorbent using tetraallylammonium chloride as crosslinking agent. *React. Funct. Polym.* **87**, 15–21 (2015). <https://doi.org/10.1016/j.reactfunctpolym.2014.12.006>
40. A. Olad, H. Zebhi, D. Salari, A. Mirmohseni, A. Reyhani-tabar, Synthesis, characterization, and swelling kinetic study of porous superabsorbent hydrogel nanocomposite based on sulfonated carboxymethylcellulose and silica nanoparticles. *J. Porous Mater.* **25**(5), 1325–1335 (2018). <https://doi.org/10.1007/s10934-017-0543-6>
41. Y. Qiu, M. Wei, J. Geng, and F. Wu, “Successful field application of microgel treatment in high temperature high salinity reservoir in China,” in *All Days*. **2016-Janua**, (2016). <https://doi.org/10.2118/179693-MS>
42. S. Baloochestanzadeh, S. Hassanajili, M. Escrochi, Rheological properties and swelling behavior of nanocomposite preformed particle gels based on starch-graft-polyacrylamide loaded with nanosilica. *Rheol. Acta* **60**(10), 571–585 (2021). <https://doi.org/10.1007/s00397-021-01287-z>
43. D. Castel, A. Ricard, R. Audebert, Swelling of anionic and cationic starch-based superabsorbents in water and saline solution. *J. Appl. Polym. Sci.* **39**(1), 11–29 (1990). <https://doi.org/10.1002/app.1990.070390102>
44. Y. Wang, X. Shi, W. Wang, A. Wang, Synthesis, characterization, and swelling behaviors of a pH-responsive CMC-g-poly(AA-co-AMPS) superabsorbent hydrogel. *Turkish J. Chem.* **37**(1), 149–159 (2013). <https://doi.org/10.3906/Kim-1204-52>