

Gelation of an Organically Crosslinked PHPA Polymer Gel System: An Experimental Study

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Abstract

Excessive water production in the oil field is the major difficulty in production for the petroleum industry. Remedial techniques need to be applied to control this excess water production considering the health, safety, and environmental issues and improve the reservoir's economic and productive life. In this study polymer gel system comprising the polymer partially hydrolyzed polyacrylamide (PHPA) and organic cross-linkers (Hydroquinone and Hexamethylene tetramine) were prepared as a water shut-off system to control the excessive production of water in the oil field. The effect of various parameters such as temperature, pH, cross-linker concentration, degree of hydrolysis, and divalent cations on gelation time was investigated using the bottle testing method. The importance of retarders at high temperatures was also evaluated. The gelation temperature was varied from 90 °C to 120 °C to study the effect of different parameters on the gelation time and gel behavior. This study suggests that Partially Hydrolyzed Polyacrylamide (PHPA) with organic cross-linkers can be an effective polymer gel system for water shut-off operations, and with the addition of retarders at high temperature to control gelation time, the performance of the gel can be improved.

Keywords: Water shut-off; Polymer gel; Partially hydrolyzed polyacrylamide.

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1. Introduction

The present state of modern industrial development is characterized by the consumption of enormous quantities of petroleum which includes the manufacture of synthetic rubber, synthetic fibers, plastics, drugs, and thousands of other products. (According to United States Energy Information Administration, the total consumption of crude oil in 2010 was 87,135 barrels of oil/day). Water production in oil reservoirs is one of the most serious problems in the oil industry, and it is increasing worldwide. On average, about 210 million barrels of water are accompanied by 75 million barrels of oil worldwide [1]. Remediation techniques need to be applied to control unwanted water production and to improve the reservoir's economic and productive life. Produced water is defined as water

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brought up from the hydrocarbon-bearing formation strata during the extraction of oil & gas and can include formation water, injection water, and any chemicals added during the downhole or during the oil/water separation process. As reservoir pressure depletes, water production increases as oil and gas reservoirs approach maturity. Although this is more pronounced in aging fields, it could occur early in new fields as a result of poor completion and bad production practices [2].

Costs of lifting, handling, separation, and disposal of large amounts of produced water, environmental concerns about this water, coming due to bottom water drive, large amounts of produced water from high permeability layers, increased corrosion rates, the higher tendency for emulsion and scale formation are among the main problems due to water production which often decreases the economic life of a well. Therefore, there is a need to reduce excessive water production [3].

The source of water production is the formation of water, injected water during secondary oil recovery, and aquifers that sweep oil from the reservoir. There are two types of produced water, i.e., good water and bad water. The water produced at the producing well is said to be good when it produces oil below the economic limit of water to oil ratio (WOR). Usually, the economic limit of WOR is about 50: 1 for individual wells [4]. Good water cannot be shut off without shutting off oil. The water produced at a production well without oil or a very low amount of oil above the economic limit of the water-to-oil ratio is called bad (excessive) water. Water has higher mobility relative to oil; hence lower API gravity oil reservoir has a greater chance of water production by viscous fingering [5].

Today gel polymer treatment is the most useful chemical method to reduce water production. Some kind of polymer solution is injected into the reservoir and is allowed to gel under certain conditions. The gel viscosity is much higher than the displacing fluid, which could impede the flow of displacing fluid through the already flooded regions. Thus, the displacing fluid finds new paths, which means additional oil can be displaced. Gel polymer systems are typically composed of a water-soluble polymer and a crosslinking agent, which are dissolved in water to form a gelant. After allowing sufficient time, the gelant sets into a semisolid mass and behaves as a flow diverting or blocking agent. The selection of a gel polymer system strongly depends on the reservoir conditions, such as temperature, salinity, hardness, and pH of water used for the preparation of the gelant. Other parameters for the proper selection of a given polymer gel system include the salinity of the formation water, the target zone's permeability, and the formation's lithology [6,7].

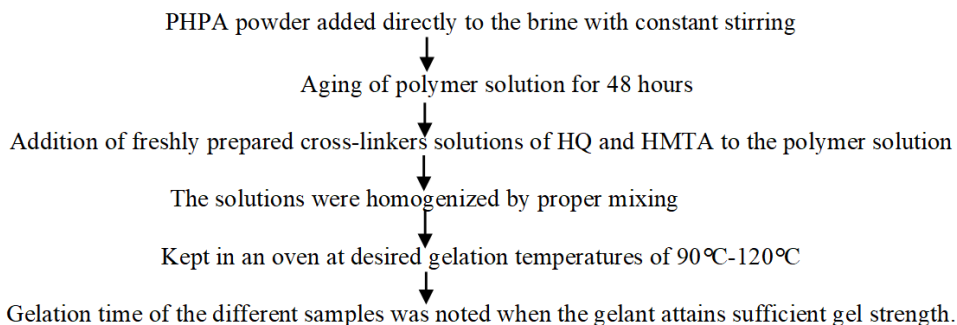
In the present work polymer gel system using partially hydrolyzed polyacrylamide (PHPA) with organic cross-linkers hydroquinone (HQ) and Hexamethylene tetramine (HMTA) was prepared, and its characteristics were investigated with the help of a bottle testing method. The objective of this study was to experimentally evaluate the effectiveness of this organically crosslinked polymer system used to shut off water production in petroleum reservoirs up to temperatures as high as 120 °C. The objectives of this study include investigations of the various parameters independently of the physical and chemical properties of polymer gel using the bottle testing method.

2. Experimental Work

2.1. Materials

Partially hydrolyzed polyacrylamide (PHPA) obtained from M/S Himedia Laboratories Pvt. Ltd. Mumbai was used as the water-soluble polymer. The organic cross-linkers HQ and HMTA, as well as potassium chloride used for the preparation of brine, were obtained from M/S Merck, Mumbai. Sodium carbonate (Na_2CO_3) and Sodium acetate (CH_3COONa) used as gelation time retarders were procured from M/S Ranbaxy Fine Chemicals Ltd., New Delhi. Calcium chloride and Magnesium chloride used as a source of divalent cations were obtained from M/S Qualigens Fine Chemicals Divisions, Mumbai.

2.2. Methodology



2.3. Preparation of gelant solution

The polymer gelant was prepared by mixing a pre-determined amount of PHPA and cross-linkers at room temperature. A stock solution of 1 wt % polymer was prepared in brine with constant stirring in a magnetic stirrer at a shear rate of 20-25 rpm for 1-1.5 h till a uniform viscous solution was obtained (High-speed stirrers are not recommended since it may break the polymer chains). The polymer solution was then aged at normal temperature for almost 48 h to ensure proper hydration of the polymer in brine. After that, cross-linker solutions were prepared by the addition of weighed samples of Hydroquinone and Hexamethylene tetramine. The concentration of the cross-linkers varied from 0.2 – 0.5 wt% each. This is an optimum range of concentration because values lesser than this would result in longer gelation times, and higher values would result in lower gelation time which would be insufficient for the flow of gelants into the reservoirs to fulfill the purpose of water shut-off.

The gelant was prepared by mixing the freshly prepared cross-linker solution with the polymer solution with constant stirring. The pH of the solution was adjusted by using 1N NaOH and 1N HCl as per requirement. The pH of the gelants was maintained from 7.5-

9.5, depending on the alkaline nature of most reservoirs. The different gelants were then placed in small glass bottles sealed with Teflon tape and kept in a hot air oven at the desired temperature ranging from 90–120 °C. The increase in temperature and crosslinking reaction led to gel formation, which was monitored at a regular time interval to study the gel's behavior change. In order to examine the effect of retarders on the gelation time, a pre-determined amount of sodium carbonate and sodium acetate were added to the gelant solution [8].

2.4. Measurement of gelation time

One of the most important characteristics of a gel polymer system is gelation time which could be considered a fundamental parameter in oil field applications. The gelation time will determine the injection period and how deep into the formation the gelant can be placed. Bottle testing provides a semi-quantitative measurement of gelation rate and gel strength. This is a cost-effective and straightforward technique to measure gelation rate and gel strength, and it allows for screening a large number of samples faster than rheological techniques [9]. In the present study, for each test, gelant solution was formulated and placed in the bottle at specific temperatures ranging from 90 °C to 120 °C. The bottle was inverted during each reading at different intervals, and if it was found that there was a significant change in the behavior of the gelant solution, then it was assumed that the gel was formed, and the time required for that period was recorded as the gelation time

3. Results and Discussion

Different sets of gel samples were prepared to keep the polymer (PHPA) concentration constant at 1 wt% and vary the concentration of HQ and HMTA from 0.2 wt% to 0.5 wt% to study the effect of gelation temperature, pH, and the cross-linker concentration on gelation time. The salinity of KCl brine was kept constant at 1 wt%.

3.1. Effect of temperature on gelation time

Temperature is an important factor that plays a significant role in determining gelation time. There is a decrease in gelation time with an increase in temperature for all pH values, as can be observed in Figs. 1 and 2.

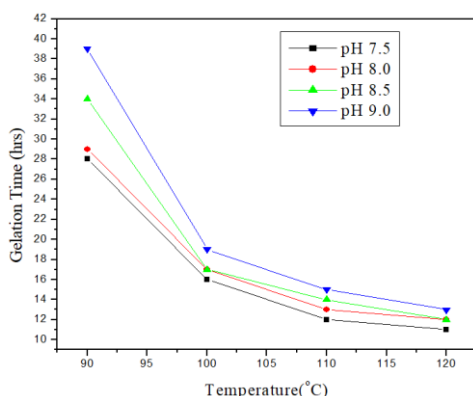


Fig. 1. Gelation time for gelants comprised of 1 wt % PHPA, 0.3 wt% HQ and 0.4 wt% HMTA.

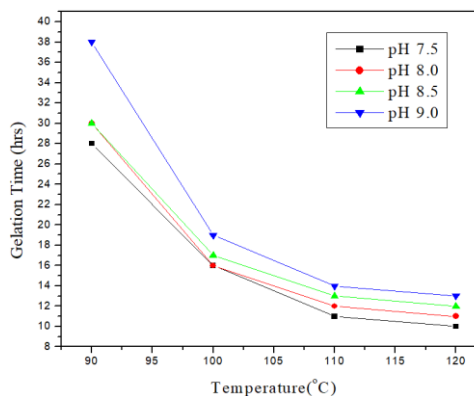


Fig. 2. Gelation time for gelants comprised of 1 wt % PHPA, 0.4 wt% HQ and 0.4 wt% HMTA.

The reason for decreased gelation time is due to the availability of more crosslinking sites at a higher temperature, which increases the rate of gelation reaction, and hence the gelation time decreases [10]. A possible explanation for rapid crosslinking is either due to an increase in molecular mobility or the formation of new crosslinking sites due to gelation reaction. It is a known fact that the degree of hydrolysis of the polymer increases at elevated temperatures, which in turn increases the number of crosslinking sites [11,12]. As is observed from Tables 1 and 2, the gelation time at each value ranging from 7.5-9.0 the gelation time decreases with an increase in temperature, e.g., the gelation time for polymer gelant comprised of 1 wt% PHPA, 0.2 wt% HQ, and 0.3 wt% HMTA is 35 h at 90 °C which decreases to 12 h at 120 °C at pH 7.5. The graph shown in Fig. 1 too depicts the decreasing trend for gelation time for increasing temperature.

3.2. Effect of pH on gelation time

The pH range for different gel systems varied depending on the nature of the gelation reaction. It was observed that it took a long time to form a gel at higher pH values (Fig. 3). Fig. 3 represents the gelation time of the polymer gelant comprised of 1 wt% PHPA, 0.4 wt% HQ and 0.5 wt% HMTA for each gel formed between pH 7.5-9.0. The results showed that this gel system is effective for use in high-temperature reservoirs with lower polymer and cross-linkers concentrations at high pH values.

At pH 9.0 and above, proper gelation does not take place, and syneresis also occurs due to excess crosslinking. Moreover, it was also observed during this study that for high cross-linker concentrations at higher gelation temperatures pH of gelant is not an important factor in determining gelation time, i.e., the gelation time is almost the same. The gelant showed almost the same gelation time at all pH values. Good quality stable gels were found in the pH range 7.5-8.5; above it, proper gelation does not occur [13].

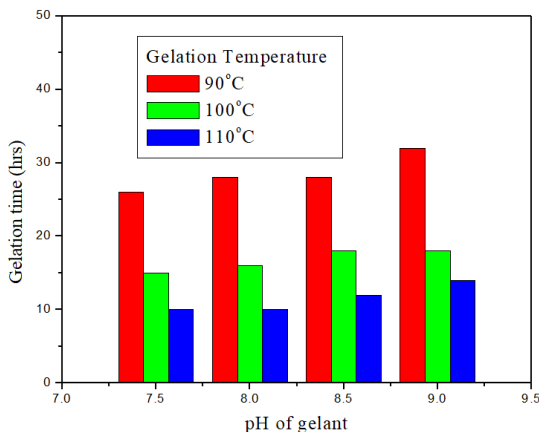


Fig. 3. Gelation time for gelants prepared with 1 wt% PHPA, 0.4 wt% HQ and 0.5 wt% HMTA.

3.3. *Effect of cross-linker concentration on gelation time*

The effect of cross-linker concentration on gelation time was studied in this work with a constant concentration of polymer at 1 wt %, and cross-linker concentration varied from 0.2 wt % to 0.5 wt %. Fig. 4 and Table 3 concluded that gelation time decreases with an increase in cross-linker concentration.

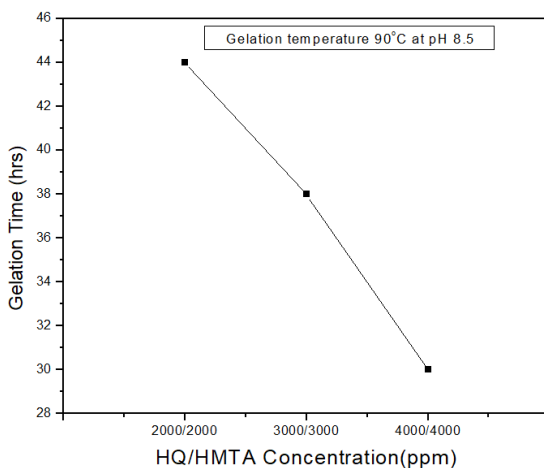


Fig. 4. Change in gelation time with same cross-linker concentration.

The study was carried out with HQ/HMTA ratio 1:1, and observations showed that there is a decrease in gelation time with an increase in cross-linker concentration. Table 3 shows that similar results were obtained when cross-linkers were not taken in the ratio of 1:1. As the concentration increases, the extent of crosslinking on the polyacrylamide chain also increases due to which gel formation takes place in the lesser time interval [14,15].

Table 1. Change in gelation time for gelants prepared at pH 8.5 and temperature 90 °C.

HQ/HMTA concentration (ppm)	Gelation time (h)
2000/2000	48
2000/3000	40
3000/3000	38
3000/4000	34
4000/4000	30
4000/5000	29

3.4. Effect of degree of hydrolysis on gelation time

The effect of the change in the degree of hydrolysis on gelation time was also studied for the same cross-linker concentration (HQ 0.3 wt% and HMTA 0.3 wt%), keeping the polymer concentration of both PHPA and polyacrylamide (PAM) constant at 1 wt% and the temperature was 110 °C. The data from Table 4 indicate that gelation time decreases with an increase in the degree of hydrolysis.

Table 2. Change in gelation time for PAM and PHPA (HQ 0.3 wt% and HMTA 0.3 wt%) at 110 °C.

pH	Gelation time for PAM (h)	Gelation time for PHPA (h)
7.5	20	14
8.0	18	16
8.5	19	16

When the gel was prepared with PAM, the gelation time at pH 8.0 was 18 h, and for the same composition of gel with PHPA instead of PAM, the time was 16 h. An explanation for this could be that the acrylamide-based polymers, upon hydrolysis under alkaline conditions, produce carboxylate groups and ammonia, and negative carboxylate charges on the hydrolyzed acrylamide cause stretching of the polymer network in distilled water. Hence, more crosslinking sites were exposed, which ultimately resulted in an increased gelation rate and decreased gelation time. This fact shows that the gelation time can be reduced by using PHPA instead of PAM. In other words, PAM can be used as the polymer to avail longer gelation times compared to PHPA [16].

3.5. Effect of retarders on gelation time

The effect of retarders on gelation time was also studied using sodium carbonate and sodium acetate. Fresh solutions of retarders were prepared in distilled water and added with different sets of polymer gelants to study the effect on gelation time.

Table 3. Gelation time for gelants comprised of PHPA 1 wt%, HMTA 0.4 wt%, HQ 0.3 wt% and 0.1 wt% Sodium carbonate at pH 8.0.

Sr. No.	Temperature	Gelation time (h) (without retarder)	Gelation time (h) (with sodium carbonate)
1	90°C	29	35
2	100°C	17	22
3	110°C	13	17
4	120°C	12	15

Table 4. Gelation time for gelants comprised of PHPA 1 wt%, HMTA 0.2 wt% HQ 0.2 wt% and 0.1 wt% Sodium acetate at pH 7.5.

Sr. No.	Temperature (°C)	Gelation time (h) (without retarder)	Gelation time (h) (with sodium acetate)
1	90	35	42
2	100	24	36
3	110	16	22
4	120	12	19

Tables 3 and 4 shows that there is a significant increase in gelation time using the retarders' sodium carbonate and sodium acetate. The results are also represented graphically in Figs. 5 and 6.

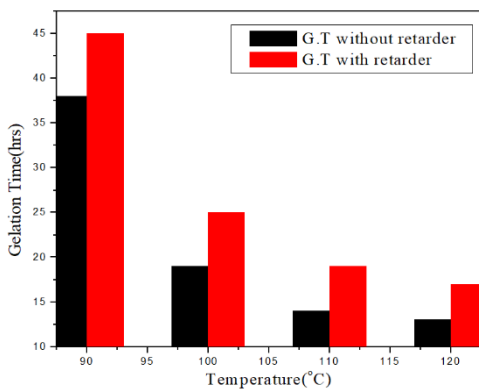
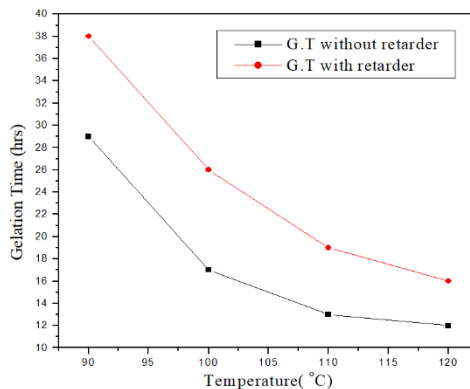
Fig. 5. Gelation time for gelants comprised of PHPA 1 wt%, HMTA 0.4 wt%, HQ 0.4 wt% and 0.1 wt % Na₂CO₃ at pH 9.0.

Fig. 6. Gelation time for gelants comprised of PHPA 1 wt%, HMTA 0.4 wt% and HQ 0.3 wt% and 0.1 wt% sodium acetate at pH 8.0.

This delay in gelation time is due to the effect of sodium cations which shield the amide groups resulting in shrinkage of the polymer chains or masking the crosslinking sites. Consequently, the number of active crosslinking sites decreases, and thus the intensity of crosslinks is lowered; hence, the gel formation takes a much longer time. Sodium acetate solves the problem of incompatibility that sodium carbonate faces in some reservoirs and provides good results in high-temperature reservoirs [17-19].

3.6. Effect of divalent cations

Table 5. Gelation time for gelants comprised of 1 wt% PHPA, 0.2 wt% HMTA and 0.2 wt% HQ at 110 °C and pH 8.5.

Sr. No.	Concentration (ppm)	Gelation Time (h) (With K ⁺)	Gelation Time (h) (With Ca ²⁺)
1	1000	24	27
2	2000	26	28
3	3000	28	30
4	4000	31	33

The effect of divalent cations on gelation time was also examined. Brine was prepared with CaCl₂, and MgCl₂ was added to it as a source of divalent cations along with KCl, which contains monovalent K⁺ ions, and the polymer and cross-linkers solutions were prepared in it. Then the gelation time was studied, keeping the solution at different temperatures ranging from 90 to 120 °C.

Table 6. Gelant Solution comprised of 1 wt % PHPA, 0.2 wt % HMTA and 0.2 wt % HQ at 110°C and pH 8.5.

Sr. No.	Concentration (ppm)	Gelation Time (h) (With K ⁺)	Gelation Time (h) (With Mg ²⁺)
1	1000	24	30
2	2000	26	32
3	3000	28	32
4	4000	31	36

The observations from Tables 7 and 8 and from Fig. 7 revealed that with increasing concentration of divalent cations, gelation time was delayed for both Mg²⁺ and Ca²⁺ cations. Mg²⁺ ion causes much more delay in gelation time as compared to K⁺ and Ca²⁺ ions (comparison of data from Tables 7 and 8).

This increased gelation time is due to the higher charge size ratio of divalent cations as compared to monovalent ions. Hydrolyzed polyacrylamide at temperatures above 110 °C precipitate in brine containing divalent cations such as Ca²⁺ and Mg²⁺. The reason for this is the conversion of the amide group present in the polyacrylamide into the carboxylic group. The newly formed carboxylic group reacts with divalent ions such as Ca²⁺ and Mg²⁺, resulting in the formation of salts of lower solubility in water [20]. The higher the temperature, the faster the carboxylate groups are formed by hydrolysis, and the higher the concentration of divalent cation, the more carboxylate salt is formed. The gelation time can be controlled from a few hours to several days depending upon the gel composition and environmental condition [21]. The crosslinked polymer gel system are most widely used as injection fluids [22]

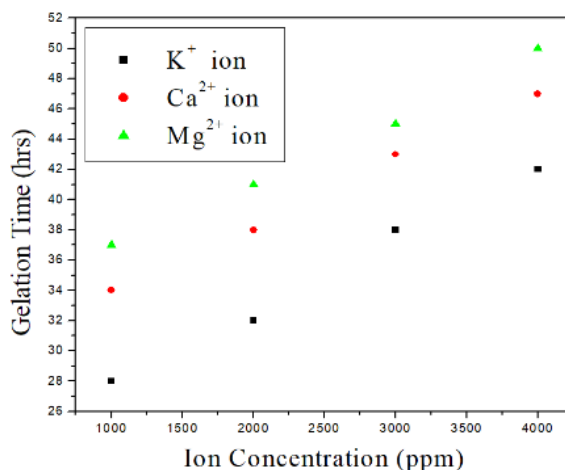


Fig. 7. Comparative graph on the effect of monovalent and divalent cations on gelation time.

4. Conclusion

Gelation time decreases with an increase in the temperature; hence at high temperatures, to control the gelation time, some retarders will be useful for the efficient performance of the gel. Gelation time increases with an increase in pH, and the best results for this gel system comprised PHPA/HQ/HMTA were obtained in the pH range of 7.5-8.5. It decreases with increased concentration of cross-linkers, and stable gels were obtained at a higher concentration of cross-linkers. It is also found that the gelation time decreases with increases in the degree of hydrolysis. The results showed that the gelation time for the same concentration of polymer and cross-linkers was longer compared to PHPA under the same temperature and pH conditions. The addition of retarders can enhance gelation time in high-temperature reservoirs to allow proper flow of gelants in due time to the target zones. Divalent cations cause a delay in gelation time with increasing concentration of the ions.

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