07 Apr 2022

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Recommended Citation

M. Shamlooh et al., "Chitosan/Polyacrylamide Green Gels for Water Control in High-Temperature Reservoirs," *Energy and Fuels*, vol. 36, no. 7, pp. 3816 - 3824, American Chemical Society, Apr 2022.
The definitive version is available at https://doi.org/10.1021/acs.energyfuels.2c00242

energy&fuels

pubs.acs.org/EF Article

Chitosan/Polyacrylamide Green Gels for Water Control in High-Temperature Reservoirs

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Cite This: *Energy Fuels* 2022, 36, 3816−3824 Read Online

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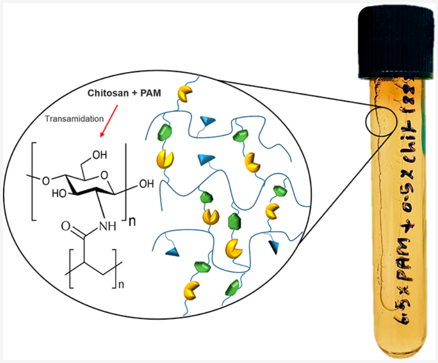
ABSTRACT: The rheology of a gel system composed of polyacrylamide (PAM) and chitosan is studied under typical reservoir conditions. The impacts of the degree of chitosan deacetylation, temperature, and salinity on the gelation behavior are assessed. The said system was prepared under ambient conditions and matured for 24 h at altered temperatures ranging from 50 up to 125 °C. An optimum formulation has been identified considering the rheological response and the initial viscosity constraints. The increase in the degree of syneresis with the degree of deacetylation indicates the long-term thermal stability of the gels. Ammonium chloride was an effective retarder for the PAM/chitosan gelant, which delayed the gelation time from 60 to 210 min when 2 wt % is used; however, it compromised the final gel strength. The chitosan/PAM system showed a good rheological behavior and potential as a green plugging agent in high-temperature oil and gas wells. Chitosan could be an alternative for commercial crosslinkers, such as polyethyleneimine.



1. INTRODUCTION

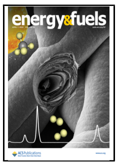
Chitin, which comes after cellulose as the most abundant polymer in nature, produces the chitosan polymer through deacetylation.[1] Chitin is found widely in living creatures as it is the material that strengthens the exoskeletons of many animals, such as crabs, shrimps, insects, insects, eggshells, and mushrooms.[2−5] Chitosan has many advantages being a renewable material, biodegradable, and nontoxic. This broad spectrum of properties gave it popularity among scientists, where it has been implemented in many applications to replace synthetic polymers. The use of chitosan is not particularly new, such as its use for many years in medicine, pharmaceuticals, and the food industry.[6−8] Yet, chitosan applications in engineering have gradually broadened as more methods have been explored for production.[9] Chitosan met with significant successes in many engineering challenges as it has been implemented for water treatment,[3] CO_2 capturing,[10] and agricultural uses.[11] Chitosan has been proposed as a crosslinking agent to prevent and control water production from oil and gas wells.[12]

Chitosan has received extensive attention in petroleum engineering research as its applications extended from the drilling stage up to processing the oil in the midstream facilities.[13] Several researchers suggested using chitosan to formulate a polymer-based mud as a biodegradable material and resolve the environmental issues raised about polymer-based muds.[14] Besides, Raffa et al. (2016) reviewed polymeric surfactants used in EOR applications and suggested chitosan as a potential biopolymer as a green alternative.[15] Moreover, chitosan showed a significant role in flow assurance management in the upstream oil and gas industry because of its ability to create a high-performance and environment-friendly scale inhibitor for calcium carbonate.[16,17] Lately, chitosan has also been proposed as a reducing agent used in lines for pumping heavy crude oil.[18] The wide range of applications of chitosan gave it acceptability in the engineering sector.

Excess water production is a significant challenge facing the oil and gas industry, costing more than $40B annually.[19] A common technique to minimize the water cut is injecting the mixture of crosslinkable polymer and crosslinker into the water production zones. They crosslink and form a gel that blocks the area triggered by the temperature of the reservoir.[20] Polyethyleneimine (PEI) is the most abundantly used crosslinker for high-temperature application due to its ability to produce a stable gel in reservoirs with temperatures between 90 and 130 °C.[12] Yet, due to the environmental issues, PEI was planned to be phased out from some countries such as Norway,[21] creating a need for a greener alternative to be used in high-temperature applications. Chitosan has been nominated as a suitable green replacement for PEI as they share the same functional group responsible for crosslinking with polyacrylamide (PAM).[12]

Chitosan is reported to have good potential to replace PEI as a crosslinker with PAM for high-temperature reservoirs in many

Received: January 24, 2022
Revised: March 9, 2022
Published: March 22, 2022



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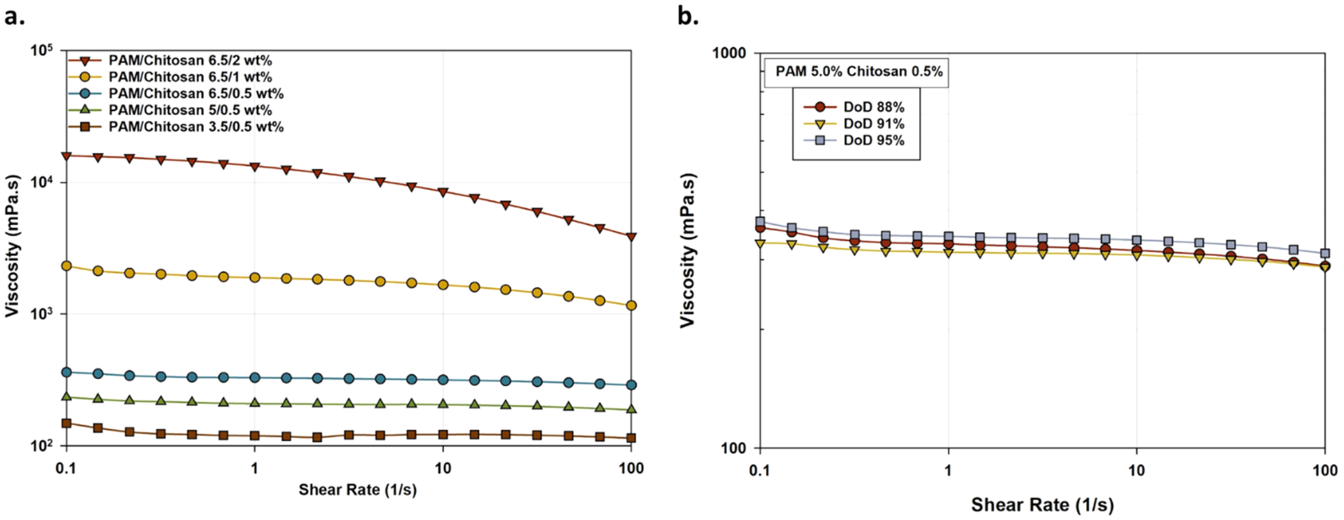

Figure 1. Viscosity vs shear rate behavior for PAM/chitosan systems by varying (a) polymer/crosslinker concentration and (b) DoD.

review articles.[12,13,21−23] Yet, very few studies have investigated this system. Reddy et al. (2003) were the first to introduce chitosan as a crosslinker for PAM. In this study, the temperature application window for chitosan to crosslink was reported to be between 150 °F (65 °C) and 250 °F (121 °C).[24,25] They also concluded that the chitosan-based gel could effectively plug core samples as it crosslinks in a manner similar to PEI. George et al. (2017) reported that the PAM/chitosan gelant is effective in treating wells with low pH conditions, typically below 6.[26] This is attributed to chitosan's poor solubility in neutral conditions because it has a pK_a (dissociation constant) of around 6.5, while it has a good solubility under mild acidic conditions.[27,28] Kamarulizam and Ismail (2020) investigated a Guar Gum/chitosan system for water shut-off applications and reported its ability to achieve a reduced permeability of more than 99%.[29]

A close look at the literature on the gelation of chitosan-based polymers reveals several gaps and shortcomings. The degree of deacetylation (DoD) is an important characteristic that can define the performance of chitosan. Yet, no study, up to date, has investigated the effect of deacetylation on the gel performance. Moreover, the available data in the open literature about the rheological behavior of chitosan-based gels for upstream applications are very little. Therefore, in this study, we intend to perform a broad set of rheological analysis of the PAM/chitosan gelant. The study aims at investigating the main factors affecting gel performance, namely, base-polymer/crosslinker concentrations, temperature, salinity, aging time, and chitosan DoD. The objective of this study is as follows:

(1) To define, through viscosity measurements, the applicable range of concentrations for the base polymer and the crosslinker by conducting a preliminary screening.
(2) To investigate the effect of concentration, temperature, and aging time on the final gel strength of PAM/chitosan gel.
(3) To assess the impact of the degree of deacetylation on the performance of the PAM/chitosan gelation process.
(4) To study the gelation kinetics of PAM/chitosan gel and explore methods for delaying the reaction.

2. MATERIALS AND METHODS

2.1. Materials. Polyacrylamide (PAM) samples, with a molecular weight of 700,000 Da, were provided by SNF Floerger, France. Chitosan with low molecular weight (<50,000 Da), different DoD values (88, 91, and 95%) were purchased from ChitoLytic, Canada. Other additives, namely, acetic acid glacial solution (CH_3CO_2H) and ammonium chloride salt that were used to enhance the gelling properties of the formulations were acquired from Research Lab, India.

2.2. Experimental Procedures. The synthesis of the gelling solution is prepared at room temperature, as several concentrations of PAM (5−9%) and chitosan (0.5−2%) are screened. To overcome the dissolution problem of chitosan, a solution of 1 wt % acetic acid was used to lower the pH to below 6.5. The order of addition is PAM, followed by the acetic acid solution, salts (if any), and finally the chitosan powder. The solutions are left to stir for 10−15 min to have a well-mixed solution and to allow the agglomerated chitosan particles to de-flocculate and dissolve. After that, the solutions were placed into small test tubes and immersed in an oil bath for 24 h at a predetermined temperature (50−125 °C) to allow for curing.

Anton Paar MCR 302 Rheometer was used for conducting the rheological testing. An initial viscosity screening was conducted under ambient conditions using a cop and pop geometry. A frequency sweep test from 0.1 to 100 Hz with a fixed strain of 5% (within the LVR range) is performed on the different gel samples using parallel plates geometry with a diameter of 25 mm and a gap of 2 mm to test the storage modulus (G'). The storage modulus (G') is the solid-like behavior that indicates the strengths of the developed gels. A high-pressure bob and cup cell was used to test the gelation kinetics. The test was conducted in two stages: the first stage was a temperature ramp to increase the temperature from 25 to 100 °C linearly at a rate of 2 °C, followed by an isothermal stage to allow for complete curing until the equilibrium gel strength is reached. This test yields a gelation profile, including the storage modulus (G') and loss modulus (G''), which is essential for providing the crossover point indicating the onset of the gelation time. All experiments were duplicated and ensured an error of less than 5%.

3. RESULTS AND DISCUSSION

3.1. Formulation Optimization. Several factors affect the success of a gelling formulation in sealing the designated zone in a reservoir. While most studies focus on assessing the gelation kinetics and the final gel strength, many of these formulations fail to make it to the industry due to practicality issues.[22] Therefore, we attempt in this study to address all the aspects by conducting extensive rheological testing to simulate the real case scenarios.

A crucial factor that plays a decisive role in favoring one gelling system over another is the initial viscosity of the formulation. Besides the increased pumping cost a highly viscous solution can have, it may fail to properly seal the targeted fractures or zones as the flow through pores depends on the fluid's viscosity.[30] Hence,

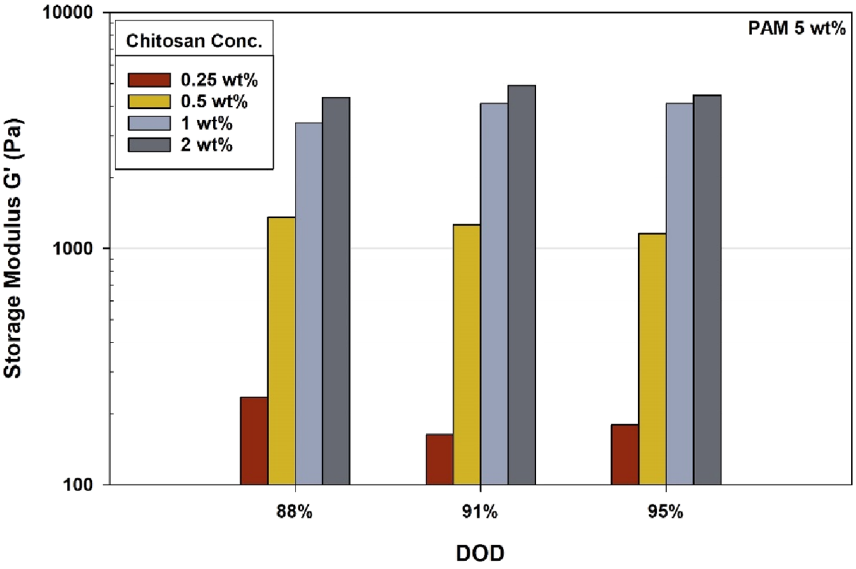

Figure 2. Chitosan concentration effect on the equilibrium storage modulus.

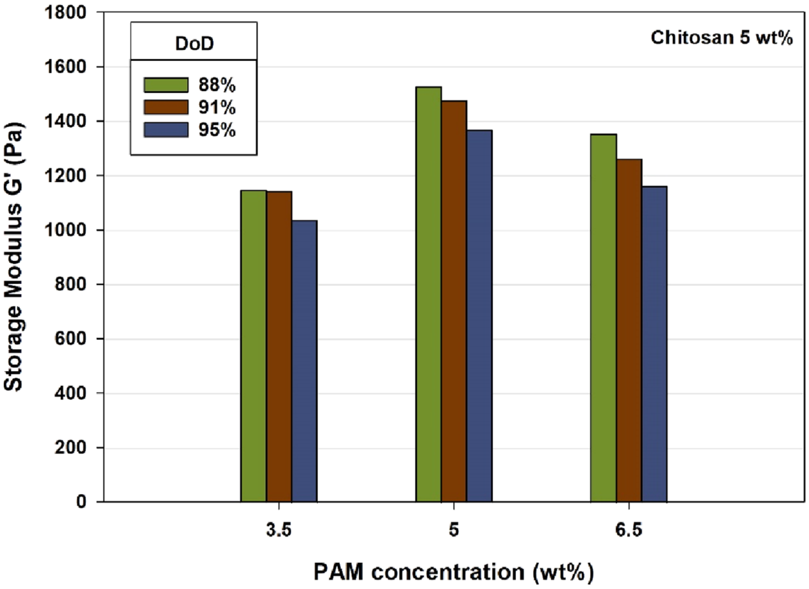

Figure 3. Effect of PAM concentration on the final gel strength.

the lower the viscosity of the gelant, the higher the probability of its success. The viscosity of a polymeric solution is directly proportional to the concentration of polymers due to the increased entanglements, which can be observed in Figure 1a. Although increasing the crosslinker's concentration provides a strong crosslinking network, it results in a high initial viscosity. Figure 1 reveals that the viscosity increases by 1 order of magnitude when the concentration of chitosan is increased from 0.5 to 1.0 wt %. Therefore, it is recommended not to exceed 0.5 wt % to avoid pumpability issues. Moreover, the mixing time is not to exceed 1 h to avoid any potential increase in the initial viscosity. Figure 1b provides a comparison between different systems with different DoD values, which appears to have no significant effect on the viscosity of the PAM/chitosan solution.

While lowering the concentration of polymers reduces the solution's viscosity, it indeed affects the final gel strength. Therefore, a compromise between these two measures is conducted to optimize the formulation. Figure 2 provides a comparison based on storage modulus, between different systems with varying concentrations of chitosan. Although the storage modulus peaked when the chitosan concentration was increased to 1 and 2 wt %, the high apparent viscosity limits the applicability of these formulations as discussed earlier. On the contrary, the gel strength dropped to below 200 Pa when the chitosan concentration was reduced to 0.25 wt %, making a fragile gel that cannot function properly to seal inside a reservoir. Hence, this result demonstrates that a concentration of 0.5 wt % is optimum for a sufficient final gel strength with a suitable initial apparent viscosity. Using the optimum chitosan concentration, the gel strength produced from this formulation, (1160−1350 Pa), ties nicely with the gel strength of the commercial gelant PAM/PEI where the gel produced had a comparable gel strength, making chitosan a competitive green alternative.

The last step toward optimizing the PAM/chitosan formulation is to define the concentration of the base polymer in the system (PAM). PAM concentration was varied from 3.5 to

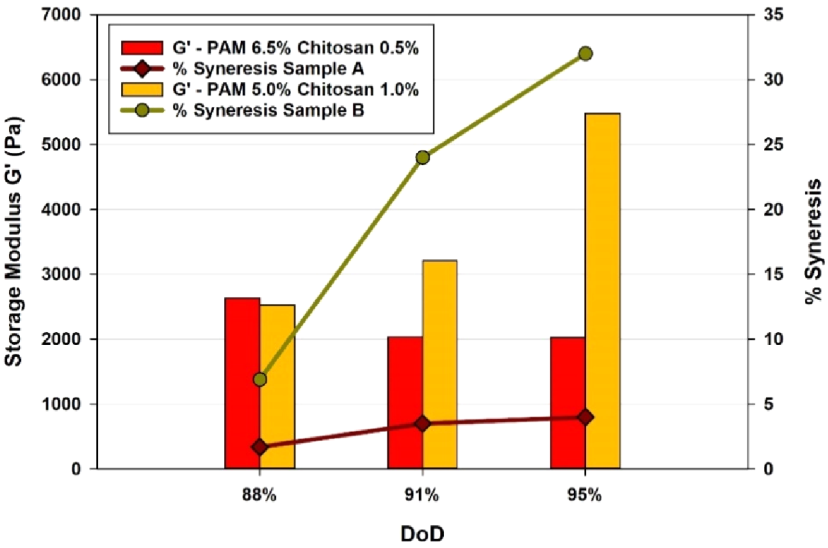

Figure 4. Degree of syneresis of two gelling systems and the corresponding storage modulus.

6.5 wt %, and the storage modulus was found to peak at a concentration of 5 wt % with a storage moduli in the range 1367−1526 Pa. Increasing the concentration beyond 5 wt % reduced the gel strength, which is likely due to the excessive crosslinking in the polymeric matrix, leading to a lower crosslinking density. Albeit the lowest gel strength is achieved at a PAM concentration of 3.5% (which has the advantage of a lower initial viscosity), the recorded storage modulus is still sufficient enough for the sealing applications and is comparable with the commercial gelants.[31] Thus, the range between 3.5 and 5 wt % is considered as the optimum for PAM concentration in the formulation. Another highlight from the results in Figures 2 and 3 is the insignificant effect from the DoD when varying the concentration of the crosslinker at a fixed base polymer concentration. On the contrary, the lowest degree of deacetylation (88%) had a slight advantage of achieving the highest gel strength when varying the PAM concentration at a fixed chitosan concentration.

3.2. Syneresis and Temporal Effect.

The term syneresis refers to the undesirable phenomena of liquid separation from gelling materials. This phenomenon has been widely studied in the food industry to improve the quality of food gels such as jams and dairy products. Several factors affect the liquid repulsion process from gels, such as the crosslinking intensity, polymer concentration, anionic content, and the surrounding temperature.[32] Gel syneresis can be easily detected and monitored by observing the gel sample for leaching liquids. Moreover, several techniques exist to evaluate the syneresis in a gel sample. This study uses a simple approach to compare the weight percentage of the liquid lost from syneresis as in eq 1 below.

$$\% \text{ syneresis} = \frac{\text{mass of lost liquid}}{\text{initial mass of the gel}} \qquad (1)$$

As the crosslinking density is a significant factor affecting the syneresis behavior of gel, two systems representing two extremes have been investigated in this study. Sample A is a solution of 6.5 wt % PAM + 0.5 wt % chitosan, illustrating a system with a low crosslinking density. Sample B is a solution of 5.0 wt % PAM + 1.0 wt % chitosan representing the high crosslinking density to the high crosslinker/base-polymer ratio. The results presented in Figures 4 and 5 aligned with the previous studies, where in

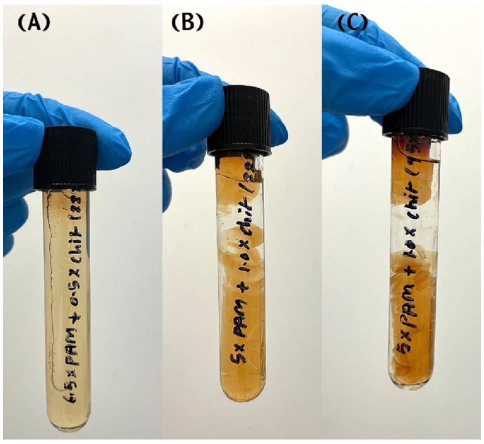

Figure 5. Degree of syneresis of three gel systems, aging for 3 days. (A) PAM 6.5 wt % chitosan 0.5 wt % (88%), (B) PAM 5 wt % chitosan 1.0 wt % (88%), and (c) PAM 5 wt % chitosan 1.0 wt % (95%).

Figure 4 sample B (yellow) had a higher crosslinking density showed a much higher % syneresis than sample A (red). Although the short-term gel strength of sample B is higher, the high syneresis rate makes it less thermally stable. A further novel finding is the apparent effect of DoD on the syneresis in the long run. The % syneresis in sample B rose from around 7% to more than 30% when the DoD was increased from 88 to 95%. The experiment results found a clear support for the theory suggesting that increasing the crosslinking sites boosts the syneresis because the chitosan with higher DoD possesses many amine groups. These results cast a new light on the importance of deacetylation in designing the PAM/chitosan system. The short-term effect on the viscosity and gel strength was shown to be insignificant; it has a pronounced impact on the long-term gel stability.

Besides crosslinking density, anions in the solution affect the thermal stability and degree of syneresis in gels.[32] The results in Figure 6 show that the gel weakens as it undergoes thermal degradation. The degradation effect was observed to be more dominant as the DoD decreases. The gel sustained around 75% of the original strength with 95% DoD compared to less than 45 when 88% DoD was used (Figure 6). This impact of salts on the

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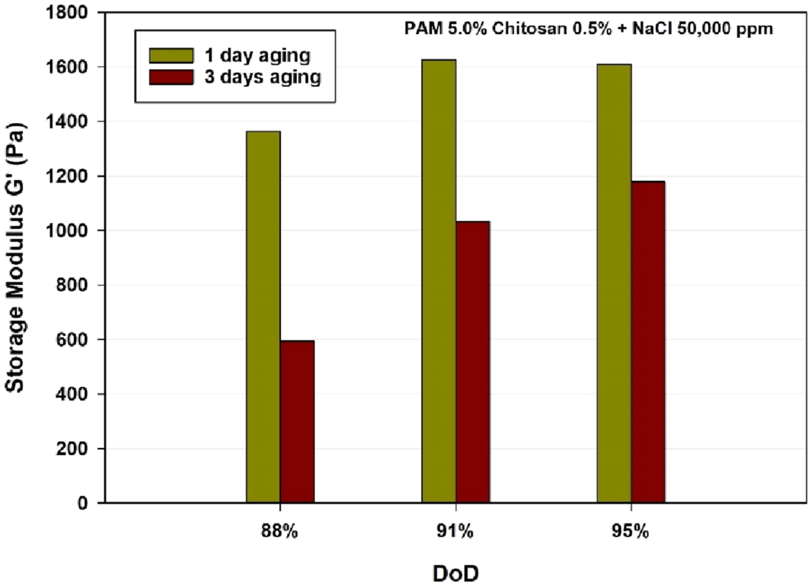

Figure 6. Thermal degradation of PAM/chitosan in a brine solution aging at 100 °C for 1 and 3 days.

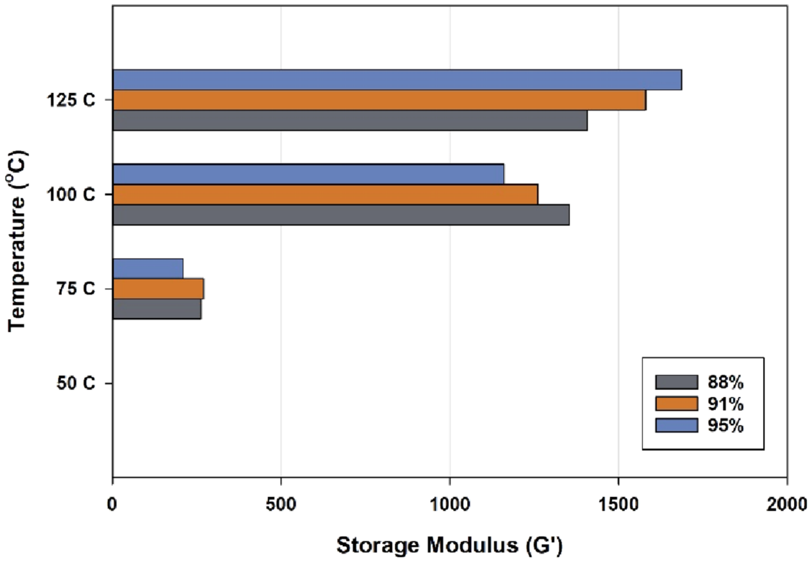

Figure 7. Effect of aging temperature on the storage modulus of PAM (5 wt %)/chitosan (0.5 wt %) gel.

PAM/chitosan gel strength could be explained by the shielding effect reported in previous studies for PAM/PEI gels.[33,34]

3.3. Effect of Temperature. Among the many factors affecting the gelation process of the PAM/chitosan gelant, the temperature is a crucial parameter to define the temperature window of applicability. Figure 7 displays the PAM/chitosan gel strength evaluation when the aging temperature is varied between 50 and 125 °C. The solution successfully produced a gel with sufficient strength when the temperature was 100 °C or above, marking a more than 1000 Pa storage modulus. Nevertheless, it failed to do so when the temperature was lower than 100 °C within 24 h of aging. While a very soft gel was noticed when the aging temperature was 75 °C, there was no sign of any gel-forming when the temperature was set for 50 °C. Comparing the similarities in the chemistry of chitosan and PEI, it is speculated that both crosslinkers undergo the same crosslinking mechanism with PAM. Figure 7 agrees with the above statement as the application of PEI was reported to be limited to the high-temperature reservoirs when the temperature exceeds 80 °C.[12,35] Overall, the gel strength was observed to increase with the temperature, which is suggested to be caused by the increasing crosslinking due to the acceleration in the degree of hydrolysis in PAM at high temperatures.

3.4. Gelation Kinetics of the PAM/Chitosan System. Studying the gelation kinetics is vital as it can define the ability of the gelant to solve the problem. Timing is a critical factor in the success of the gel treatment in oil and gas reservoirs. A successful gelant should have a sufficient gelation time to allow for the injection and the penetration of the solution to the designated zones but should also be low enough for quick responses to decrease the nonproductive time as much as possible.[12]

Gelation kinetics is evaluated by observing the storage and loss moduli as a function of time. The storage modulus (G') represents the solid-like behavior, and the loss modulus (G'') represents the liquid-like behavior of a viscoelastic system. Hence, a gelant system is expected to have a more loss modulus initially ($G'' > G'$) because the solution is in the liquid form where the storage modulus will exceed the loss modulus as the

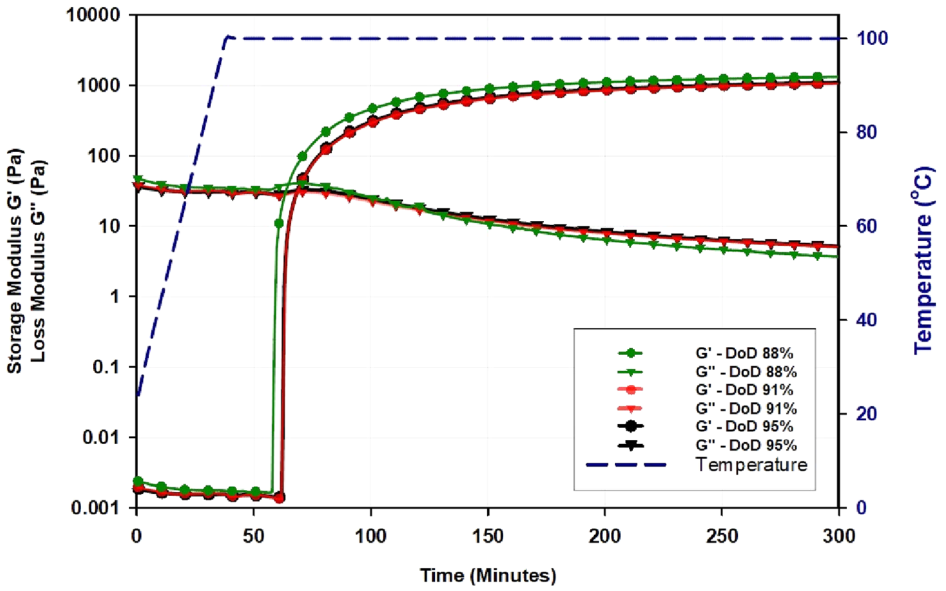

Figure 8. Gelation kinetics of 5 wt % PAM + 0.5 wt % chitosan with different DoD values.

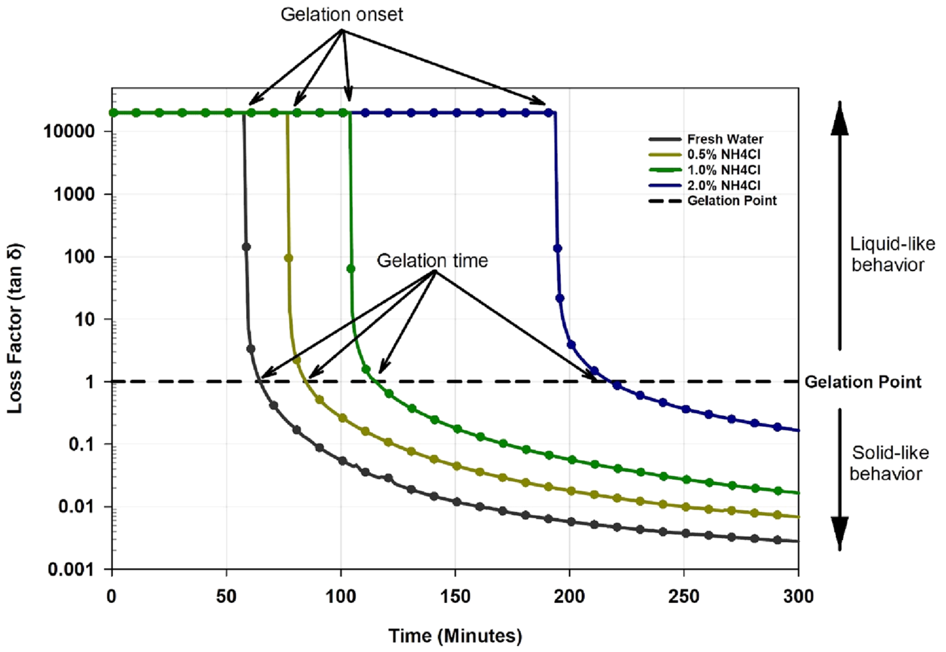

Figure 9. Effect of NH_4Cl on the gelation profile of PAM/chitosan.

gelation goes on ($G' > G''$) because it turns into a solid gel. Gelation time refers to the onset point where both loss and storage moduli are equal ($G' = G''$).

Another method of representing the gelation kinetics can be through the loss factor described in eq 2 below. A decreasing gelation factor can be interpreted by the process of gelation when the solution is liquid-like when $\tan \delta > 1$ and in the solid form when $\tan \delta < 1$, where gelation time is when $\tan \delta = 1$.

$$\text{loss factor } (\tan \delta) = \frac{\text{loss modulus } (G'')}{\text{storage modulus } (G')} \quad (2)$$

Figure 8 presents the gelation profile for the previously defined optimum PAM/chitosan system with different DoD values. The results demonstrate two things. First, the DoD does not affect the gelation mechanism as all systems had a similar gelation profile. Second, the gelation time of PAM/chitosan (around 60 min) is comparable to the gelation time of the unmodified PAM/PEI system (60−70 min), suggesting its suitability for field applications.[36] While ammonium chloride was ineffective in controlling the gelation time in systems with inorganic crosslinkers,[37] it succeeded in the PAM/chitosan system (Figure 9). As illustrated in the figure, the gelation point is at the crossover point with the line $y = 1$. NH_4Cl delayed the gelation from 60 min to more than 200 min when 2.0 wt % concentration was used, as shown in Figure 9.

Although adding NH_4Cl to the polymeric matrix is advantageous to delay the crosslinking reaction, it has the downside of weakening the final gel strength. Figure 10 shows that the storage modulus decreased from around 1500 to 1100 Pa when a solution of 2.0 wt % NH_4Cl is used instead of freshwater. Although salts delay the gelation time, however, the gel reaches

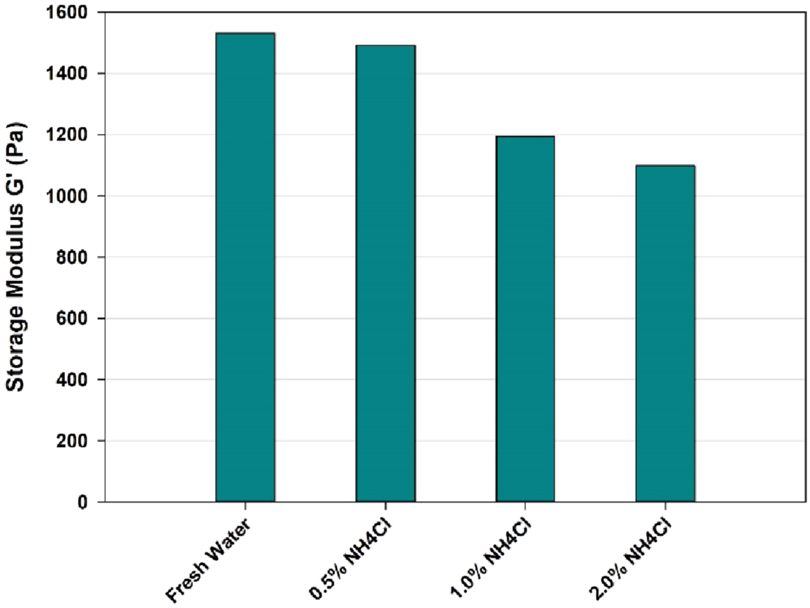

Figure 10. Effect of NH_4Cl on the equilibrium gel strength of PAM (5 wt %)/chitosan (0.5 wt %).

almost the same ultimate gel strength as shown in our previous work.[38] Hence, the formulation must be optimized according to the depth of application to have the minimum amount of salt needed to delay the gelation to keep high gel strength.

3.5. PAM/Chitosan Crosslinking Mechanism. The transamidation reaction is generally responsible for the crosslinking between PAM and PEI.[25,31] This study performed a detailed rheological analysis on the PAM/chitosan gelant system. The findings show similarities between the gelation of PAM/PEI and PAM/chitosan. For the similarities in the chemistry, both crosslinkers have the same functional group (amine) that is believed to be the site of crosslinking. Second, the onset temperature for crosslinking is the same for both systems, where no or soft gel is formed when the temperature is less than 80 °C. Third, the gelant system of PAM/chitosan response to the addition of ammonium chloride was the same as the response for PAM/PEI. The gelation was delayed, and the final gel strength was reduced to similar extents. The gel strength produced from PAM/PEI and PAM/chitosan is within the same range (1500−2000 Pa) and has the same gelation behavior.[20,39] Last, both systems had comparable gelation times and storage modulus. Yet, the main difference between PEI and chitosan in the process of crosslinking PAM is that the chitosan has two available sites for crosslinking (amino and hydroxyl groups), compared to only one active side in the structural backbone of PEI.[40] These findings support the notion that the transamidation reaction is also responsible for the gelation of the PAM/chitosan system, as illustrated in Figure 11.

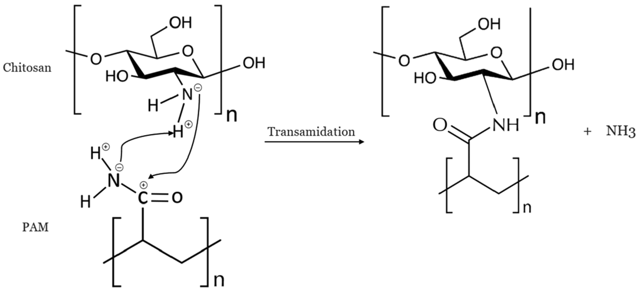

Figure 11. Proposed mechanism for the PAM/chitosan crosslinking reaction.

4. CONCLUSIONS

Chitosan is a natural biopolymer with unique properties, being green, biodegradable, and abundant in nature, which attracted the attention of researchers. The applications of chitosan have recently extended to the petroleum-engineering sector. Many researchers have recommended using it as a crosslinking agent for plugging and water control in oil and gas reservoirs, yet few studies have investigated this system. In this study, an extensive rheological assessment of the gelation characteristics of PAM/chitosan gelant has been conducted. The findings from this study provide evidence on the ability of chitosan to compete in the market and to replace the available commercial crosslinkers. The main conclusions from this investigation are as follows:

1. The optimum concentrations for PAM and chitosan in the formulation are 5 and 0.5 wt %, respectively. This formulation has an acceptable initial viscosity with a sufficient and sustainable final gel strength in the reservoir.
2. The DoD had a minimum effect on the gel rheological properties; however, it impacted the long-term thermal stability. The syneresis was observed to increase with the increase in the DoD.
3. The formulation yielded a gel with a sufficient strength exceeding 1000 Pa when the temperature is 100 °C; nonetheless, no or weak gel was produced below 80 °C, making it only suitable for high-temperature applications.
4. Ammonium chloride has effectively retarded the gelation and delayed the gelation time from 60 to 210 min when 2 wt % is added. However, the final gel strength was compromised as it dropped from 1530 to 1098 Pa.
5. The PAM/chitosan crosslinking reaction mechanism is suggested to be a transamidation reaction, similar to PAM/PEI, due to the high similarities in the chemistry and the gelation behavior between both formulations.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors would like to acknowledge the Qatar National Research Fund (a member of Qatar Foundation) for funding through grant # NPRP13S-1231-190009. Al-Salam Petroleum Services Company, Qatar, is also acknowledged for co-funding this project. The findings achieved herein are solely the responsibility of the authors. The authors would also like to thank SNF Floerger Company for supplying the polyacrylamide samples. The authors would also like to acknowledge Qatar University for providing Graduate Assistantship to R.E. in her graduate studies.

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