Preparation and Evaluation of PPGs for High-Temperature Conformance Control

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Abstract. In this paper, the synthesis and thermal behavior of nanocomposite performed particle gels (PPGs) was investigated. The nanocomposite PPGs were synthesized via free radical polymerization at room temperature, using acrylamide (AM), N-vinylpyrrolidone (NVP) as monomers and N, N-methylenebis (acrylamide) (MBA) as crosslinker. Thermal stability evolutions were conducted by aging PPGs at 130℃ and salinity of 2.2×10^5 mg/L for 90 days. Swelling ratio (Sw) and modulus were measured as a function of aging time. A three-stage swollen history was discovered by means of rheological experiments and swelling measurements. Experimental results show that increasing the concentration of monomer, crosslinker and clay lead to higher swelling ratio and lower modulus during the aging term. PPGs prepared with 30 wt % monomers, NVP: AM ratio of 6:4, 0.25 wt % crosslinker and 3.0 wt % clay exhibited optimum properties for conformance control at high temperature reservoir condition.

1. Introduction
Polyacrylamide gels have been widely used for conformance control and water shut off in oil reservoirs[1,2]. The applications of these gels are limited due to poor mechanical properties and thermal stabilities, especially at harsh reservoir environment. In recent decades, prepared particle gels (PPGs), polyacrylamide gels that formed underground and then cut into micrometer-scale pieces, were proposed and have shown advantages at elevated temperature and high salinity reservoirs. Compared with conventional in-situ gels, the properties of PPGs are enhanced mainly because of higher polymer content and controllable gelation reaction[3].

Several approaches have been investigated to enhance the strength and toughness of polymer gels, including topological gel, double network gel and nanocomposite gel, et al. In particularly, nanocomposite gel which is produced through polymerization in the presence of inorganic clay have been shown to exhibit excellent toughness relative to their organic chemically cross-linked compound[4]. In nanocomposite gels, the gel network is uniformly distributed in the layers of clay, make the gels more homogeneous. Therefore, mechanical properties of these gels are improved.

At elevated temperature, the network of polyacrylamide gels would be broken as a result of oxidative degradation of the molecular chains. Besides, the hydrolysis reaction of amide groups is accelerated by higher temperature, which turn to carboxyl group. The formed carboxyl groups are easily coordinated with divalent metal ions in water and then produce insoluble complex compound. Consequently, the hydrophilicity of the network is decreased and the gel becomes brittle, especially in salinity water. Function monomers, such as AMPS, NVP, were introduced into polyacrylamide chains to improve their high temperature and high salinity tolerance. To propose a gel that suitable for high temperature reservoir, nanocomposite PPGs consists of AM-NVP bi-copolymer were studied in this paper.
Mechanical properties of gels are often performed by rheological experiments, including compression, tension and shear tests[5]. It has been demonstrated that polyacrylamide gels deform linearly to large strain, like rubbers, implying modulus of these gels are constants in deformation. The mechanical properties of PPGs were characterized by shear modulus in this paper. When PPGs are placed at harsh environment, the modulus would be dynamic as results of the continuously crosslinking reaction, variation of polymer volume fraction due to swelling, as well as broken of network.

Nanocomposite PPGs were prepared and the thermal stabilities were evaluated at 130°C and salinity of 2.2×10⁴ mg/L in this paper. Swelling behaviors and modulus were studied as functions of aging time and components. PPGs prepared with 30 wt % monomers, NVP: AM ratio of 6:4, 0.25 wt% crosslinker and 3.0 wt% clay exhibit optimum properties for conformance control at high temperature reservoirs.

2.Materials and methods

AM and NVP were used as monomers, MBA was used as crosslinker. Ammonium persulfate and sodium formaldehyde sulfoxylate were used as initiators. All the materials above were analytically pure and purchased from Aladdin. Also, a kind of nano clay was kindly donated by Tonkun and was used without further purification. A brine with salinity of 2.2×10⁵ mg/L was used in this paper. The syntheses of PPGs were performed in distilled water by free radical polymerization. Firstly, clay suspension of 8wt% was prepared by dispersing clay particles in Na2CO3 solution. The gelling solution was prepared by dissolving amount of AM, NVP and MBA powders in distilled water. Then the gelling solution was poured into the clay suspension and the mixture was stirred at 500 r/min for 2 hours. Finally, amount of initiator powders, 0.5 wt% of total monomer, was added into the mixture directly. After mixing, the resulting solution was poured into a glass container and kept in a 40°C bath for 12 hours. The formed gels were dried and cut to different size as needed.

The swelling behaviors measurements were conducted in metal containers. In order to measure dynamic swelling at harsh environment, PPGs, cut into small cubes with length of 1cm, were put into the metal containers and then immersed by brine. The metal containers were taken into a 130°C oven, and taken out in internals. After cooling to room temperature, PPGs were taken out and sponged gently to remove water on the surface. Then the mass of PPGs was weighed. The swelling ratio of PPGs was defined as:

\[ S_w = \frac{(w_t-w_0)}{w_0} \]

Where w0 was the initial weight of PPGs before aging, wt was the weight of PPGs after aging. All the PPGs were aging for 90 days unless their structure strength became too weak.

Strain-controlled oscillatory measurements were conducted on an Anton Paar MCR 92 rheometer. At room temperature, storage modulus G’ and loss modulus G” were measured as a function of strain amplitude, ranging from 1 % to 1000 %, at frequency of 1 Hz. Data were obtained in so-called linear viscoelastic region (LVER), in which G’ and G” were independent of strain amplitude. Since G’ was 100 times larger than G” in all measurements, G” was ignored.

3.Results and discussions

Figure 1 presents the effect of monomer ratio on Sw and G’ of PPG versus aging time. PPGs with NVP:AM ratios ranging from 4:6 to 7:3 were synthesized, while the concentrations of the total monomer, crosslinker and clay were 30 %, 0.3 % and 3 %, respectively. As can be seen from the figure, PPGs became weaker while at higher NVP content. By increasing NVP ratio from 0.4 to 0.7, G’ was reduced from 3.0 KPa to 0.7 KPa after aging one day, although Sw was two times larger. At equilibrium stage, Sw of PPGs with monomer ratio lower than 6:4 exhibited dehydration, that is Wt was smaller than W0 since water was extruded from gel network.

As shown in figure 1, PPG that treated at 130°C underwent three stages: (1) The first stage: PPGs were rapidly swollen in the first three days. At this stage, G’ was continuously decreased along with the expansion of gel. At the third day, the values of Sw and G’ reached their maximum and minimum, respectively. (2) The second stage: From aging time of 7 to 45 days, Sw was gradually decreased for all PPGs with different monomer ratio, while G’ appeared conversely. (3) The third stage: After 45 days, a
swelling equilibrium was observed, where Sw reached a plateau, basically no longer changed with the aging time. This three-stages thermal behavior was observed in all experiments in the following study, indicating it was a common phenomenon for PPGs treated by high temperature.

Figure 1. Effect of monomer ratio on Sw and G’

To summarize the effect of monomer ratio, the mechanical strength of PPGs was decreased by the increase of NVP content, and Sw increased. Considering the fluctuation of gel volume was not expected in a plug treatment, the ratio of 0.6:0.4 was determined and used in the following study. Influence of other components of PPGs, including monomer concentration, crosslinker and clay, on the thermal behaviors of PPGs were discussed as well. The aging histories of stable PPGs are similar, independent of the compositions. However, values of Sw and G’ were measured and the optimum usage of each component was determined.

PPGs with monomer concentration of 0.20, 0.25, 0.30, and 0.35, respectively, were synthesized, while the concentrations of crosslinker and clay were 0.5 % and 3 %, respectively. Data of the dynamic Sw and G’ of PPGs were plotted in figure 2. During the whole aging term, PPGs with higher monomer content exhibited lower Sw and larger G’. It was found that when the monomer concentration was 0.20, G’ was monotonously declined with the aging time although the volume of PPG was decreased since the third aging day, implying collapse of the network structure. At concentration of 0.35, PPG was shrunk to its initial volume (Sw≈0) at equilibrium state. Considering a slightly swollen gel was preferred to better plug performance, as well as the cost, an eclectic monomer concentration of 0.30 % was determined.

Figure 2. Effect of monomer concentration on Sw and G’

Figure 3 shows the influence of crosslinker concentration, ranging from 0.1 % to 0.3 %, on the thermal properties of PPGs. It was found that when the concentration of MBA was lower than 0.1 %, PPG can not be formed; when the concentration was increased to 0.1 %, the formed PPGs were weak and would loss its strength to a fluid state after aging 10 days. As for the stable PPGs, Sw was always declined, from 0.4 to 0.0, by the increase of MBA content, which results to a higher modulus. Similarly, the optimum concentration was used as 0.25 %.
Clay was a kind of inorganic materials with layer structure, which was composed of Al-O octahedron and Si-O tetrahedron. When dispersed in water, clay was hydrated and the spacing of layer was increased, the middle of which was filled with water and exchangeable cations. During the synthesis, the polymeric monomers, such as AM, AMPS, NVP can be inserted between the crystal layers, and a regular organic-inorganic compound was formed. In the other word, clay acted as crosslinker in the composited PPGs. By means of the regular structure, the strength, swelling behavior, ultimate properties were significantly enhanced. The effect of clay on the thermal behavior was shown in figure 4. It can be seen that PPGs without clay endured no more than 10 days at 130℃, while the composited PPGs obtained higher strength with the increasement of clay content. However, when the clay concentration reaches 4 %, G’ of PPG was up to 10 KPa, which implying the PPG was hardly deformable. Therefore, a moderate concentration of 3 % was chosen.

4. Conclusion
The stability of gel at high temperature needed a fundamental structure strength, which was related to the crosslinker density. If the components contents were insufficient, PPGs would fail in a few days. The increasing the concentration of monomer, crosslinker and clay leaded to higher swelling ratio and lower modulus during the aging term. PPGs prepared with 30 wt % monomers, NVP: AM ratio of 6:4, 0.25 wt % crosslinker and 3.0 wt% clay exhibited optimum properties for reservoir treatment.

References
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