

Evaluation of Polymer Properties for Potential Selection in Enhanced Oil Recovery

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This study analyzes the rheological properties of polymer under various shear rate, polymer concentration and molecular weight, temperature, salinity and divalent for potential Enhanced Oil Recovery (EOR) application. The polymers used were Xanthan Gum (XG), Guar Gum (GG), Arabic Gum (AG), Polyvinylpyrrolidone (PP) and Partial Hydrolyzed Polyacrylamide (HPAM). Fann, Grace Instrument and Brookfield viscometers were employed for viscosity measurement. The results recommended GG, AG and PP based on their shear thickening behaviour, XG and HPAM for their high molecular weight, PP and AG for their ability to withstand high temperature and salinity condition, and GG, PP and AG in high divalent concentration.

1. Introduction

The Enhanced Oil Recovery (EOR) process using polymer methods have been employed for the past 20 to 30 years ago in order to obtain maximum recoverable oil. There are many benefits of using polymers; they can increase the viscosity of water solution, enhance sweep efficiency and also reduce mobility ratio between water and oil (Niu et al., 2001). According to Achim et al. (2015), gelled polymer technology could be applied to seal high permeability zones and fractures, resulting in improving sweep efficiency and oil recovery. PETRONAS found that polymer flooding can be justified economically and environmentally because polymers are non-toxic and do not cause serious environmental problems (Caenn et al., 1989). It is simple and has a relatively low operating cost compared to other EOR methods. This EOR process could be monitored using a real-time approach of streaming potential measurement using electrodes permanently installed downhole (Mohd et al., 2017b), which is potential to monitor alkaline-surfactant-polymer (ASP) flooding (Mohd et al., 2017a). In the Daqing field of Northern China, an increase of 12 % petroleum production was achieved when polymer flooding was used instead of water flooding (Lee et al., 2009). A previous simulation study from the Daqing field indicated that this polymer flood might reach an oil recovery factor of up to 61 % of original oil in place (OOIP). In Malaysia, a chemical EOR application has also been implemented and proven positive in core flood studies using alkali surfactant flooding and ASP flooding, resulting in an average incremental oil recovery of about 14.6 % OOIP and 28.6 % OOIP, respectively (Ibrahim et al., 2006). Besides its potential application in EOR, polymer provides a significant contribution to polymer electrolytes, which is a mixture of organic polymer and inorganic salt. This study includes the use of polymer based electrolytes such as cellulose acetate (Abidin et al., 2014) and poly(ethylene oxide) (Chan and Kammer, 2014) on impedance spectroscopy (Chan and Kammer, 2016). It is the usual practice to select polymer based on its rheological characterization and its effect on oil recovery (Zheng et al., 2011). As polymer passes through the reservoir, there is a change in its physical and chemical properties due to formation absorption, shearing and chemical reactions. Generally, there are two commonly used polymers in EOR applications which are those produced synthetically and those that are natural products of wood and seed or those produced by bacteria or fungi. All of these polymers have their rheological properties compromised by the conditions found in the reservoirs such as high temperature, high salinity, the presence of malignant bacteria, and the hardness of connate water (Mothe et al., 2006). Different rheological regimes have been discovered when polymers with elastic

properties are injected into a porous medium (Zhang et al., 2011). Shear thickening and thinning occurs at high and low fluid velocities in porous media, respectively. Further increase of velocity could result in polymer degradation due to rupture of the polymer chain (Al Hashmi et al., 2013). In EOR applications, polymer must be stable at reservoir condition for an expected residence time in the reservoir rock as it can degrade under certain conditions. As the rheological properties of polymer depend on several parameters, this work therefore analyzes the rheological properties of polymer under various shear rate, polymer concentration and molecular weight, temperature, salinity and divalent. Such an approach would help the study to select the most potentially suitable polymer for potential EOR application.

2. Methodology

2.1 Materials

Five types of polymers were selected for this experiment, namely Xanthan Gum (R&M Chemical), Guar Gum (R&M Chemical), Arabic Gum (System), Polyvinylpyrrolidone (Merck), and Partial Hydrolyzed Polyacrylamide (Vchem). These polymers were selected based on specific rheological properties and their common use in EOR applications (Mothe et al., 2006). These types of polymer have different molecular weight, as shown in Table 1. Other materials such as Sodium Chloride (NaCl), Calcium Chloride (CaCl₂) and Magnesium Chloride (MgCl₂) were used for salinity and divalent test.

Table 1: Types of polymer used in this study

Polymer	Description	Molecular weight (x10 ⁶)
Xanthan Gum	XG	8.0
Partial-hydrolyzed Polyacrylamide	HPAM	6.0
Guar Gum	GG	2.2
Polyvinylpyrrolidone	PP	3.6
Arabic Gum	AG	2.5

2.2 Preparation of polymers

The aqueous polymer solution was prepared by slowly adding the powder into distilled water, which was stirred with a floating magnetic stir bar. The solution was stirred slowly for a minimum of 16 hours before being used to ensure full hydration of the polymer powder. Then, the filtration test was performed to ensure that the proper polymer hydration had been achieved. Approximately 250 ml of aqueous polymer solution was filtered through a 5 micron Millipore cellulose filter. To calculate the filtration ratio (FR), the collection time of the filtered fluid was recorded at 60, 80, 180 and 200 ml, as shown in Eq(1) (Levitt and Pope, 2008).

$$FR = \frac{(t_{200ml} - t_{180ml})}{(t_{80ml} - t_{60ml})} \quad (1)$$

Where t_{200ml} , t_{180ml} , t_{80ml} and t_{60ml} were the times recorded for 200, 180, 80 and 60 ml, respectively. After the test, the filter paper was inspected to see if any remaining polymer micro-gel was present due to improper hydration. A polymer solution with FR below 1.2 was used for rheological test (Lee et al., 2009).

2.3 Rheological properties measurement

The rheological properties were measured using a Fann Viscometer (below room temperature) and a Grace Instrument Viscometer (above room temperature) for temperature effect, as well as a Brookfield DV-LI+ Viscometer (shear rate, molecular weight, polymer concentration, salinity and divalent effects). The measurement of shear rate was related to the spindle speed of the Brookfield DV-II+ Viscometer. For shear rate and salinity (monovalent and divalent) tests, the polymer concentration was fixed at 1500 ppm. The shear rate was kept constant at 50 rpm in the polymer concentration and salinity tests, while 300 rpm for temperature test. The molecular weight of the polymer with its viscosity as a function of concentration was investigated. NaCl solution was selected for salinity test, while CaCl₂ and MgCl₂ were used as divalent salts for divalent ions effect.

3. Results and discussion

3.1 Filtration test

A filtration test was conducted to ensure proper polymer hydration in the study. The results are shown in Table 2. Most of the polymer hydration was done properly because the filtration ratio was below 1.2.

Table 2: Summary of rheological measurement

Polymer	Mixing time	Filtration ratio	Polymer presence on filter paper	Color
XG		1.17	No	White
HPAM		1.18	Small amount of polymer micro gel-remain	Clear White
GG	24 hours	1.15	No	Pale white
PP		0.98	No	Clear White
AG		0.88	No	Yellow gold

There was a small amount of HPAM in the filter paper after the filtration test. The unfiltered polymer occurred because of poor hydration due to improper mixing of distilled water and polymer. However, the filtration ratio was still below 1.2. Hence, these polymers were also used for the next test.

3.2 Rheological properties of polymer

3.2.1 Effect of shear rate

A Polymer solution is generally classified as a non-Newtonian fluid. The viscosity changes with shear rate and the change is not constant. Figure 1 shows the effect of shear rate on the viscosity of the selected polymers. The results showed two types of fluid rheology when the shear rate was applied; a pseudo-plastic fluid and a dilatant fluid (Zhang et al., 2011). XG and HPAM behave like pseudo-plastic fluid when the shear rate was less than 60 rpm and the viscosity changed slightly when the shear rates were larger than 60 rpm. This change was due to an association effect, in which the polymer chain contains a small fraction of an attractive group along the backbones. In pseudo-plastic fluids, known as shear thinning, viscosity decreases as the shear rate increases, and as such the majority of polymer solutions are shear thinning in their nature. At high shear rate, the high elongational viscosities caused by the elasticity of the polymer tear the polymer chain (Al Hashmi et al., 2013). Other types of polymer which are GG, AG and PP behave like dilatant fluid when the shear rate is applied as shown in Figure 1. In the dilatant fluid, known as shear thickening, viscosity increases simultaneously as the shear rate increases. This type of fluid occurs because there are colloidal suspension transitions from a stable state to a flocculation state. In an EOR application, shear thickening is desired because it results in improvement of the vertical and areal sweep efficiency, thus increasing oil recovery (Algharaib et al., 2011).

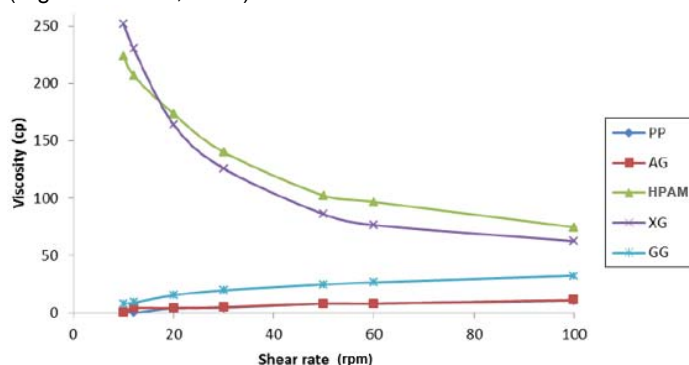


Figure 1: Effect of polymer on shear rate test

3.2.2 Effect of polymer molecular weight and concentration

Higher molecular weight and concentration of the polymer result in higher adsorption, resistance, and viscosity (Sharma et al., 2008). This is because polymer concentration changes the interactions among polymer molecules, while the molecular weight directly affects a change in size. The increased number of polymer molecules results in more interaction between the polymer chains, which then causes more frictional effects that increase viscosity. Figure 2 shows the effect of polymer concentration on viscosity at 50 rpm. The result demonstrates the viscosity of XG, HPAM and GG increasing steadily with increasing polymer concentration. Meanwhile, for PP and AG, the viscosity of the polymers is constant with only a small increment in viscosity. It can be clearly seen that the viscosity of polymer solutions increases rapidly at a concentration of above 1500 ppm. This is because at this concentration level, aggregation of the hydrophobic group occurs and physical cross-linking has also taken place. The polymer concentration at this point is called the critical aggregation concentration (Niu et al., 2001). In our analysis, it can be seen that polymers with a higher molecular weight produces a higher viscosity (Levitt and Pope, 2008). Those with a high molecular weight exhibit viscoelasticity, which is associated with shear degradation in porous media (Zhang et al., 2011). At a high shear rate, the high elongational viscosities caused by the elasticity of the polymer tear the polymer chain that significantly impacts

a high-rate polymer flow near the wellbore region. This elastic behavior also potentially contributes to the shear thickening of the polymer solution, where the apparent viscosity greatly increases when the polymer flows at a high shear rate in porous media (Al Hashmi et al., 2013). Figure 2 indicates that XG has the highest viscosity followed by HPAM, GG, PP and AG. Thus, XG and HPAM are recommended to be used in EOR applications because they have high viscosity and correspondingly the largest molecular weight compared to other polymers.

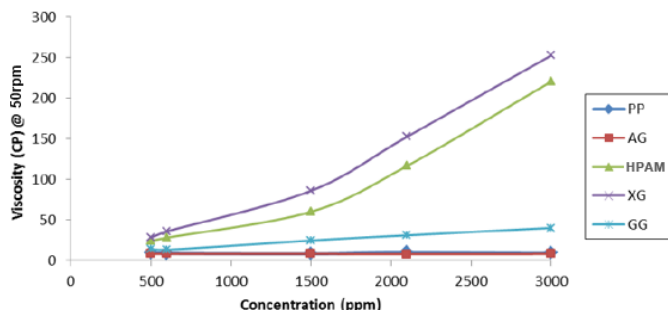


Figure 2: Polymer concentration test

3.2.3 Effect of temperature

Temperature is a significant cause of viscosity reduction. Figure 3 shows the relationship between the viscosity of polymer solutions and temperature at 300 rpm. Malaysian oil fields which are located offshore have a high reservoir temperature of more than 100 °C. Since the reservoir temperature is greater than the boiling point of the solutions, the test had to be conducted at temperatures ranging below 100 °C. The trends of the result were then observed and extrapolated to reservoir temperature (Ibrahim et al., 2006). Figure 3 shows the viscosity of all polymers decreasing steadily with increasing temperature. Similar results were obtained by Niu et al. (2001) who tested on HPAM. GG shows a greater viscosity reduction than HPAM, while PP and AG show the smallest viscosity reduction when the temperature is increased. The viscosity of HPAM, AG and PP is mostly stabilized at temperatures above 50 °C. Viscosity reduction is due to the stronger thermal vibration of water molecules that retard the association effect at high temperature (Niu et al., 2001), since the reservoir temperature for an EOR application is above 100 °C. PP and AG compared to other polymers have a minimum reduction in viscosity as the temperature increases. Thus, PP and AG are recommended as they are able to withstand the higher reservoir temperature with a minimum reduction in viscosity.

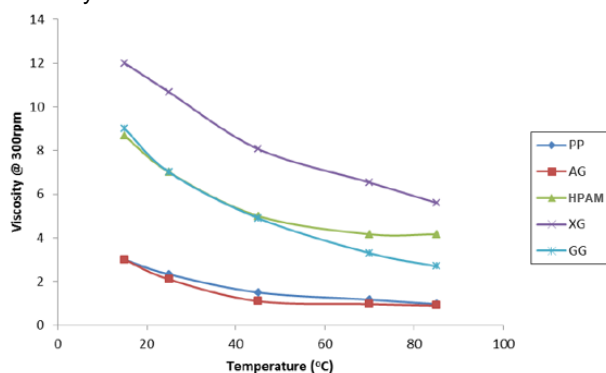


Figure 3: Effect of polymer on temperature test

3.2.4 Effect of salinity (monovalent)

Salinity is a parameter which imposes a limitation on the application of polymer flooding due to viscosity reduction. Since adding NaCl salt has a shielding effect on electrostatic resistance among polymer ions, the polymer tends to coil up. The negative charge of the polymer molecule is neutralized in the presence of salt. This results in a decrease in viscosity of the polymer solutions with increasing concentration of NaCl. This is supported by Niu et al.'s (2001) salinity test for HPAM. The result shown in Figure 4 is proof that salinity indeed decreases viscosity. The figure shows the effect of polymer on a salinity test with a viscosity reading at 50 rpm at a constant polymer concentration of 1500 ppm. XG and HPAM have maintained their viscosities from 3000 ppm to 7000 ppm of NaCl concentration and continue to decrease above 7000 ppm, while the

viscosity of PP, AG and GG steadily decreases with increasing NaCl concentration. Due to the shielding of negative charges, a drastic viscosity reduction of HPAM has occurred resulting from the presence of electrolytes or protons (Sharma et al., 2008). The level of aggregation has also been reduced. However, at a higher ionic strength (higher salt concentration), the addition of NaCl has led to macroscopic flocculation (Dautzenberg, 1997). Figure 4 indicates that HPAM has a drastic decline in viscosity followed by XG and GG, while PP and AG have the smallest reduction in viscosity. In a real condition, most reservoirs have high water salinity. Thus, PP and AG are potentially the best polymers for a high salinity reservoir application.

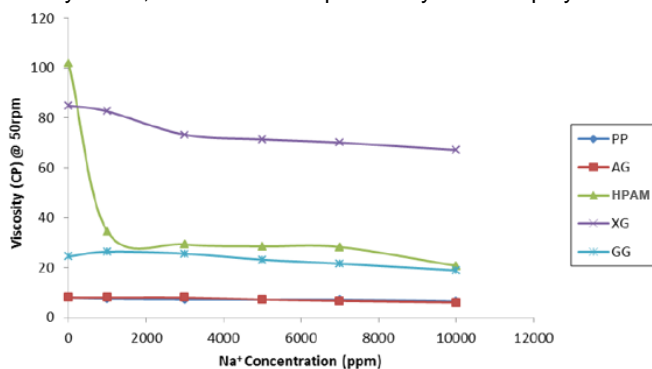


Figure 4: Effect of polymer on salinity test

3.2.5 Effect of divalent

The divalent ions (Ca^{2+} or Mg^{2+}) are known to tightly bind the anions along the polyelectrolyte chain because it has a higher charge and polarizability causing the polymer chain to contract to its minimum size and reduce its viscosity. According to Sharma et al. (2008) divalent ions have considerably more effect on viscosity than the monovalent ions. Figure 5a shows the effect of polymer in CaCl_2 concentration while Figure 5b shows the effect of polymer in MgCl_2 concentration.

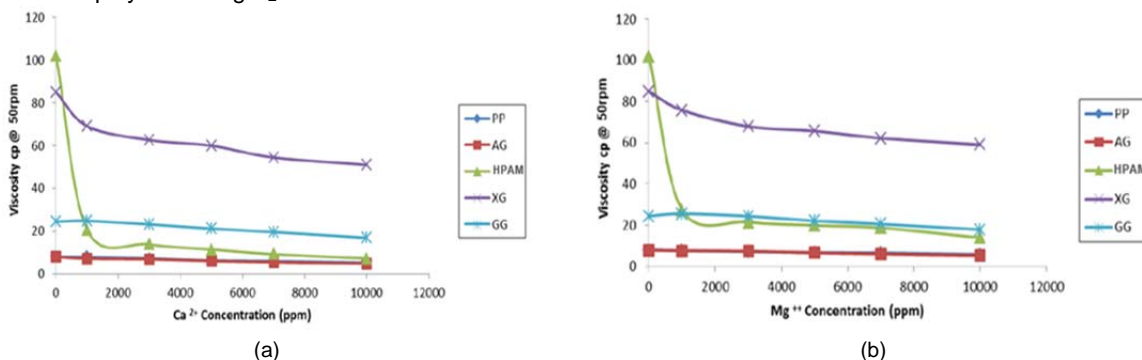


Figure 5: Effect of polymer viscosity on (a) CaCl_2 concentration; (b) MgCl_2 concentration

Both figures demonstrate all tested polymers becoming less viscous in the presence of divalent ion and increase in divalent ion concentration leads to a greater reduction in viscosity of the polymers except for PP and AG, which exhibit a minimum change in viscosity reduction. HPAM has a large molecular weight compared to GG, but Figure 5a shows that HPAM has become less viscous than GG. Meanwhile, in Figure 5b, in low concentration of MgCl_2 , HPAM has a higher viscosity than GG but at a higher concentration of MgCl_2 , GG is more viscous than HPAM. This situation has probably occurred because HPAM is more sensitive and has a strong cation interaction compared to GG. It is generally accepted that divalent ions (Ca^{2+} and Mg^{2+}) cause greater viscosity reduction than monovalent ion (Na^+) (Sharma et al., 2008). This happens due to the greater amount of cation in divalent than monovalent ion and also that divalent ions have strong binding to the carboxylate group (COO^-) than monovalent ion. Moreover, calcium ions cause a greater viscosity reduction than magnesium ion (Ibrahim et al., 2006). At a low but similar concentration of divalent ion of Mg^{2+} and Ca^{2+} , the viscosity of XG in Ca^{2+} is slightly lower than Mg^{2+} . Generally, reservoir fluid often contains a high concentration of divalent cations. The presence of this divalent ion in the reservoir can cause the polymer to become unstable, thus reducing its viscosity. In an EOR application, the use of GG, PP and AG is recommended to as they exhibit less viscosity reduction in comparison to HPAM and XG.

4. Conclusion

Based on the shear rate test, GG, AG and PP are selected for EOR application as they behave like dilatant fluid (shear thickening), resulting in improvement of sweep efficiency, thus higher oil recovery. Based on the molecular weight and concentration test, it is recommended that XG and HPAM be selected for their larger molecular weight compared to other polymers. In a harsh environment such as at high salinity and high temperature, PP and AG are recommended as they can withstand such conditions with a small viscosity reduction. In the salinity and divalent test, Ca^{2+} ion causes a greater reduction of polymer viscosity than Mg^{2+} followed by Na^+ . It shows that divalent ions have a more pronounced effect on viscosity than the monovalent ions. In high concentrations of divalent, it is recommended that GG, PP and AG be used in an EOR application due to the stability of polymer in increasing concentrations of divalent cation.

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