

EFFECTS OF ETHOXYLATED POLYAMINE ADDITION ON WATER-BASED DRILLING FLUID

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Abstract

Drilling fluid is a major component of a successful drilling process. However, the interaction between the drilling fluid and the shale with hydration property has led to the high fluid loss rate and shale swelling issues. Advance additives such as Ethoxylated Polyamine or typically known as Clayseal Plus (CP) is used as a shale control agent in water-based muds (WBM) which retard the rate of clay swelling and thus reduced the wellbore instability problems. Swell inhibition test showed that 3.5 v% CP was the optimum concentration in the drilling fluid. DSC analysis showed the crystallinity temperature and melting point of the filter cake samples were at 122.5 °C and 250 °C, respectively. Addition of CP into the drilling fluid also produced a filter cake with a smoother surface with lower filtrate volume. As expected, higher distribution of N in filter cake sample +CP was indicated to confirm the presence of CP as a polyamine base additive. The rheological analysis displayed that sample +CP yield superior viscoplastic behavior while drilling fluid -CP has uneven rheological trends at the lower shear rates regime. Methylene blue capacity test showed that drilling fluid sample +CP has lower value of methylene blue capacity (C_{MBT}). In addition, the study found that the concentration of ion $[OH^-]$ of both filtrate samples +CP and -CP were 0 mg/L while the concentrations of ion $[CO_3^{2-}]$, ion $[HCO_3^-]$, chloride ion (c_{Cl}), sodium chloride (c_{NaCl}) and total hardness (c_{CA+Mg}) for sample +CP were higher than sample -CP.

Keywords: Clayseal Plus, Ethoxylated polyamine, Fluid loss, Shale inhibitor, Shale swelling.

1. Introduction

Drilling fluid (typically known as drilling mud) plays a vital role in an oil and gas wellbore to ensure a successful drilling process and delivers a quality reservoir for production. Generally, drilling fluid aids the wellbore stabilization by maintaining good cuttings transport over wide ranges of shear rates, eliminating or minimizing physical and chemical microscopic scale reaction that negatively alter the formation properties, and preventing deep influx of filtrate and fine impurities into a reservoir in an overbalance condition [1, 2]. To a certain extent, a high quality drilling fluid should possess the ability to minimize the effects on formation properties alteration due to the filtrate and/or impurities influx into the reservoir of interest. A properly performed drilling fluid is supposed to be able to form a filter cake on the surface of the wall of a wellbore and a thin 'protective' layer that encapsulated cuttings being transported from downhole to surface before being separated from drilling fluids system by solids control equipment. The conventional drilling fluid system consists of mixtures from inorganic salts, fine-grained solids and organic liquid/compounds. Considering an overbalance drilling sector, drilling fluids can be divided into three main types: water-based mud (WBM), oil-based mud (OBM) and synthetic-based mud (SBM).

In view of the technical performance perspective for all types of drilling muds, the superior fluid that has been repeatedly reported is OBM, which is known for the good performance in terms of wellbore stability [3]. However, the major drawback of utilizing OBM is the negative effect on environment when OBM cuttings are to be discharged to the ocean at the offshore drilling areas [4]. On the other hand, SBM possesses better properties than OBM in terms of low toxicity, biodegradable and made up of synthetic organic compound. Nonetheless, several studies reported that OBM and SBM cuttings may affect the benthic communities on the seafloor due to the oxygen depletion caused by the extensive hydrocarbons biodegradation in drilling fluids [5]. Besides, the guidelines issued by OSPAR Convention in year 2000 have prohibited the release/discharge of either OBM or SBM into the ocean. To avoid high handling cost of OBM and SBM waste and the awareness of environmental protection, more studies are being conducted on WBM to improve its overall properties, which can technically perform as a replacement to OBM and SBM. Although WBM is highly environmental-friendly, there are still drawbacks in terms of thermal stability to inhibit shales compared to OBM and SBM.

There are several major problems encountered by the drilling and completion engineers when drilling into a high temperature wellbore using WBM. The most common difficulties are the high fluid loss rate into the formation and shale swelling issues. The addition of clay and weighing agent mixture is shown obviously not sufficient to improve the WBM filtration capability in determining the quality of filter cake formed and filtration volume limitation. Hence, the employment of fluid loss control additive which are currently available in the industry has received attention in overcoming the fluid loss issues [6]. These additives such as shale inhibitor are needed to improve the ability of WBM to retard reaction with shale either in the wellbore (with cuttings and wall of wellbore) or in the formation. Besides, the utilization of starch and its derivatives can be manipulated to function effectively as fluid loss additives as proven by many researchers, and as a surplus, they are abundantly available. For fluid loss control measures, a mixture of polyanionic cellulose (PAC) and starch are often selected

compared to hydroxypropyl starch (HP starch), carboxymethyl starch (CM starch), sodium polyacrylate (SPA) and carboxymethyl cellulose [7].

In general, the mechanisms of filter cake formation could be divided into mechanical and chemical interactions. It is well noted that with the current development and advancement of additives added into a fluid system, investigation of filter cake formations should also include the study of electro-chemical interactions to evaluate the relation between static and dynamic filtration under wellbore condition. Differential pressure occurs when borehole pressure is higher than the pressure in the permeable formation, resulting liquid from the drilling fluid flowing into the permeable formation and leaving a filter cake layer on borehole surface as filtrate to develop into inner and outer layer. The second mechanism is through cation exchange capability between the clay and/or shale with the aqueous drilling fluids, which initiates the impregnation of desirable components onto the wellbore wall surface and induced further development of filter cake at inner layer. The study by Elkatatny et al. [8] is to observe the filter cake build-up under static condition, suggested a thicker filter cake are features with small to large size particles, built of heterogeneous layers and poor in sorting. It is common to expect the fluid loss additives are supposed to delay or prevent an extent fluid loss under both dynamic and static condition.

It is a known fact that clay and shale minerals, such as kaolinite, smectite and chlorite possess great affinity with water. Hensen and Smit [9] commented that this situation promotes the shale swelling tendency when water-sensitive shales and clays (rich with reactive minerals) absorb water from the WBM, which might cause severe problems in drilling operation and greatly affect the wellbore stability. The swelled shale and clay would not only affect the WBM viscosity but also causing significant reduction of the borehole stability. An unstable borehole may lead to several drilling problems such as cuttings disintegration, bit balling, stuck pipes, and in the worst scenario, it may cause failure of re-entry and completion of a drilled well. Thus, swelling and hydration of shales and clays are directly related to reduction of drilling performance. Over the past few years, many researchers have proposed ways to overcome clay hydration and dispersion issues by using inorganic salts (potassium chloride (KCl) and sodium chloride (NaCl)), polymers, silicates, sugars and its derivatives, glycol and polyglycerols [10]. These inhibitors however only bring marginal success when used in the drilling fluids.

Among the most commonly used shale inhibitors, KCl has high ability to inhibit shale hydration due to its appropriate hydrational energy and cationic size [11]. Even so, it has several drawbacks including WBM failing at concentration above 1 % mass based on the mysid shrimp bioassay test done by Anderson in 2010, which indicated KCl is affecting the environment and may impose high cost for disposal and props relatively higher corrosion rates [12, 13]. In an unconventional drilling fluids system, quaternary amine compounds are among the top shale inhibitors other than KCl, that are used in the industries nowadays. However, their toxicity, incompatibility with anionic drilling fluid additives and fluids flocculation with high concentration of solids limits their applications in the industries [14]. Therefore, cationic organic polymer, for instance, quaternary polyamine and quaternary polyacrylamide have been used as additives to stabilize and inhibit clay swelling [15]. Due to these constraints as briefly discussed above, the aim of this study is to investigate the effects of advanced shale inhibitor addition, which is

made up of cationic organic polymer such as ethoxylated polyamine or typically known as Clayseal Plus (CP) in a WBM system.

2. Experimental

2.1. Materials

Drilling fluid formulation consisted of Bentonite, Polyanionic Cellulose, Xanthan Gum, Soda Ash, Sodium Hydroxide, Barium Sulphate, and Ethoxylated Polyamine (typically known as Clayseal Plus - CP) were obtained from Halliburton Energy Services (M) Sdn Bhd.

2.2. Methodology

2.2.1. Drilling fluid formulation and filter cake formation

Drilling fluid samples were prepared using a mechanical mixer and mixed according to the following sequence in a 500 ml beaker:

- i. Salt – Potassium chloride (KCl)
- ii. pH adjuster – Sodium Hydroxide (NaOH)
- iii. Fluid loss additives – Primary and secondary Polyanionic Cellulose
- iv. Viscosifier – Xanthan Gum
- v. Shale Inhibitor – Ethoxylated Polyamine/Clayseal Plus (CP)
- vi. Weighting agent – API Barium Sulfate
- vii. Deionized (DI) water to final volume

The mixed slurry sample was let to shear at the mechanical stirrer for 45 to 60 min and the measurement of slurry density was obtained to reach the targeted density of 1.2 SG. Table 1 shows the formulation used to prepare the drilling fluid/slurry sample.

Table 1. Drilling fluid formulation (Control fluid and inhibitive fluid).

Product	Control Fluid	Inhibitive Fluid
Base Fluid – DI water	Fill up until 200 ml	Fill up until 200 ml
Potassium Chloride	15.00 g (6 wt%)	15.00 g (6 wt%)
Sodium Hydroxide	0.06 g	0.06 g
Xanthan Gum	1.14 g	1.14 g
Primary Polyanionic Cellulose	1.14 g	1.14 g
Secondary Polyanionic Cellulose	2.28 g	2.28 g
Ethoxylated Polyamine (CP)	-	7.0 ml
Barium Sulphate	41.45 g	41.45 g

As shown in Fig. 1, a dead-end stirred cell system (HP4750, STERLITECH) was used to form filter cake with the filtration of drilling fluid, while Novatexx 2413 Freudenberg was used as non-woven filter support in the cell. Two sets of drilling fluid sample containing shale inhibitor (+CP) and without shale inhibitor (-CP) were prepared. 200 ml of each slurry was poured into the cell to form filter cake under regulated pressure of 80, 100, 120 and 150 psi with pressurized nitrogen supply. At each of the determined pressure, the volume of filtrate for each samples was recorded at the intervals of 10, 20 and 30 min. Lastly, the respective filter cake thickness was measured.

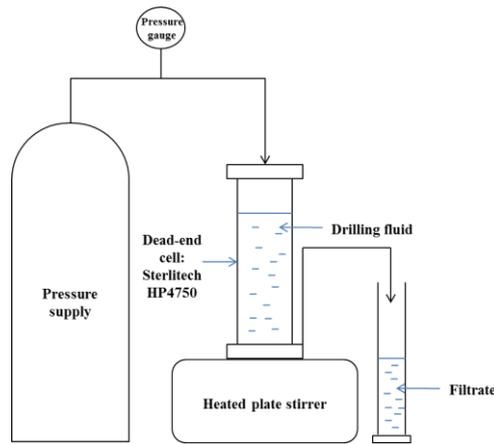


Fig. 1. Schematic diagram of dead-end filtration system.

2.2.2. Swell inhibition test

This test was carried out to determine the optimum concentration of CP, which could inhibit the clay swelling. Seven samples were prepared by using different concentrations of CP (0 v% as control sample, 0.5 v%, 1.0 v%, 2.0 v%, 3.0 v%, 4.0 v% and 5.0 v%). For each sample, 1 g of Bentonite was weighed on a digital balance and then mixed with CP at respective concentration in a vortex container separately. DI water was added up to 10 ml and it was mixed for 1 min with rotation of 2500/min using MS 1 Minishaker. The mixture was then poured into a 50 ml measuring cylinder. DI water was then added into each cylinder to reach a final volume of 50 ml. Changes of volume for each sample was recorded after 1 hr, 2 hr, 4 hr, 8 hr and 24 hr interval. The optimum concentration of CP obtained from this test was used to form the filter cake for samples with CP (+CP), while samples without CP (-CP) were prepared as the comparative measure.

2.2.3. Samples characterization

The drilling fluid and filtrate samples were characterized based on 3 main properties, i.e., physical, chemical and rheological. These characterization tests were important to evaluate the performance of drilling fluid with/without the addition of shale inhibitor (CP).

I. Physical properties

Physical characterizations were carried out by several techniques involving thermal and morphological analysis with Differential Scanning Calorimeter (DSC) and Field Emission Scanning Electron Microscope (FESEM), respectively. DSC analysis (Mettler Toledo DSC1, USA) was carried out to determine the exothermic and endothermic reaction of samples. Heating rate of 10 °C/min with temperature ranging from 30 °C to 300 °C was used for this analysis. Four samples were chosen for DSC analysis; filter cake +CP (80 psi and 150 psi) and filter cake -CP (80 psi and 150 psi). All filter cakes were dried in a desiccator for 24 hr prior to the DSC test. On the other hand, FESEM analysis was carried out to determine the surface morphology of the samples. This analysis aimed to examine the filter cake surface

and the shale inhibitor effect on the drilling fluid samples beside to determine the average qualitative chemical compositions of the samples.

II. Rheological properties

Rheological properties were important aspects to characterize drilling fluid. As non-Newtonian fluids, the rheology imposed by drilling fluids slurry is expected to exhibit pseudo-plastic behavior (Herschel Bulkley model), in which a typical polymer solution showed continuously shear-thinning behavior as shown in Fig. 2. In this study, the rheological tests were conducted for two drilling fluids samples: +CP and -CP. The rheological properties of drilling fluid samples were determined using rheometer MCR 500 (Anton Paar, Germany).

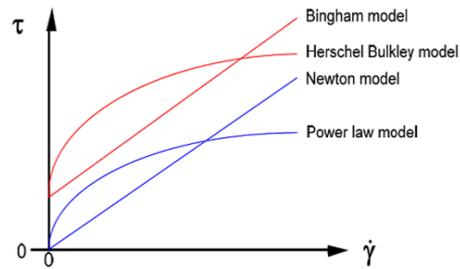


Fig. 2. Rheological models [16].

III. Chemical properties

The chemical properties of drilling fluid and filtrate samples were characterized using Fourier Transform Infrared Spectroscopy (FTIR), and several standard titration tests namely methylene blue capacity, filtrate alkalinity, chloride ion content and total hardness. FTIR analysis was performed to analyse the functional groups in the following samples: pure CP, drilling fluid +CP and drilling fluid -CP. Besides, methylene blue capacity test was conducted to indicate the extent of reactive clay content in the drilling fluid by determining cation exchange capacity of the sample. Filtrate alkalinity test was also conducted to determine the concentration of hydroxyl ions $[\text{OH}^-]$, carbonate ions $[\text{CO}_3^{2-}]$ and bicarbonate ions $[\text{HCO}_3^-]$ in the filtrate samples. There were two parts of filtrate alkalinity tests; 1) phenolphthalein and methyl orange filtrate alkalinities, and 2) phenolphthalein drilling fluid alkalinity. On the other hand, chloride ion test was carried out to determine the concentration of chloride ion while total hardness test was conducted to determine the concentration of calcium and magnesium ions in the filtrate samples.

3. Results and Discussion

3.1. Swell inhibition test

In this study, various concentrations of CP (ethoxylated polyamine) were added to bentonite being exposed to distilled water, in an attempt to indicate the optimum amount required to inhibit the bentonite swelling. According to the findings in Fig. 3, the addition of CP at concentration between 0 v% to 2.0 v% to the bentonite

samples shows a positive dynamic of bentonite swelling but the addition of 0.5 v% of CP does not provide any inhibition improvement. However, it could be observed from the plot in Fig. 3 that the magnitude of bentonite swelling started to slow down when CP concentrations increased from 1.0 v% to 3.0 v%. Further addition of CP from 4.0 v% to 5.0 v% resulted in a negative dynamic of bentonite swelling, a total swift over compared to the lower CP concentration. This scenario is not significant and it implies that a higher addition is not requisite. Considering the time required to observe the magnitude of volume changes, it could be seen that the magnitude happens within 1 hr of exposure time, except for samples without or very low CP concentrations. This phenomenon suggests that the swelling of bentonite is a longer period process under the laboratory testing condition; meanwhile the inhibition with CP is a much faster process.

The ability of CP to retard the clay swelling have been reported by several researchers [12, 17, 18]. The cationic nitrogen of CP attached to the surface of the clay, in which the hydrophobic carbon chain formed a layer to prevent the displacement of clay particles. Thus, it reduced the adsorption rate of water molecules, which contributes to the clay swelling inhibition [15]. Besides, Zhong et al. [12] has analyzed the inhibitive mechanisms by polyamine, which are possibly due to the existing dynamic dissociation balance of amine groups in aqueous solution, making the amine groups being protonated into ammonium ions when dissolving in water. The protonated ions will then neutralize the negatively charged clay surface. On the other hand, the hydrophobic carbon segments presence at the surface of clay would form a hydrophobic film. This combination may prevent water ingresses in the clay. Further analysis of the magnitude of bentonite volume changes in Fig. 3 suggests that proper inhibition by CP could be started at concentrations between 3.0 v% and 4.0 v%. Thus, it can be concluded that the optimum concentration of CP is at 3.5 v%.

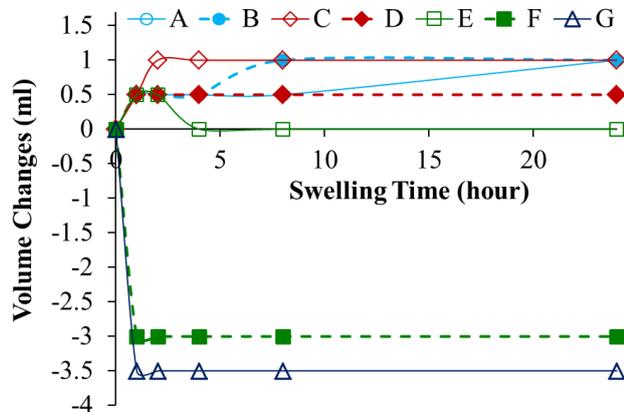


Fig. 3. Bentonite inhibition test: Effect of CP concentrations on bentonite swelling-inhibitive profile: (A) 0 v% (B) 0.5 v% (C) 1.0 v% (D) 2.0 v% (E) 3.0 v% (F) 4.0 v% (G) 5.0 v%.

Theoretically, the clay swelling occurs due to adsorption of water molecules on the crystal surface of clay. The ability of clay to swell is possibly caused by the cation exchange between the layers involving magnesium, calcium, sodium,

potassium and hydrogen ions [19]. Bentonite is Montmorillonite clay, which can be easily exfoliated and consists of aggregates of particles that can be dispersed in water or broken up by shearing, which contains layers of silicate bonded together by inclusions of atom such as calcium. A gel with finely divided bentonite clay is a result of exchanging the calcium with a larger cation and having strong attraction to water, such as sodium, and then expose to fresh water. The kinetics of the bentonite swelling is determined by the critical relative humidity, aggregates size, nature of inter-lamellar cation and composition of the expansive clay, and experimental condition (i.e., time, pH, pressure and temperature) [20].

3.2. Filter cake thickness and filtrate volume

The filter cakes and filtrate volume were developed and collected under varied pressure filtration of inhibitive drilling fluid and the control sample. Inhibitive drilling fluid with optimum concentration of CP (3.5 v%) was used in comparison with control sample (drilling fluid without CP) for further investigation. The proposed pressure regime is to help the researchers to understand the static filtration profile between applied filtration pressure of 80 psi to 150 psi for a WBM system in the presence of CP. Standard API test guidelines however have standardized the field test at only 100 psi within 30 minutes. Based on Fig. 4(a), it shows the filter cake height profile that was developed within 30 minutes in a dead-end cell. It has been generally accepted that the cake permeability decreases with the increase of static filtration pressure, nonetheless with the resultant cake solidification. Hence, in a laboratory observation, this scenario could mean a thicker mud cake and lower filtrate volume produced. Extrapolation of Fig. 4(a) to reproduce Fig. 4(b) indicates that the filter cake formed in the sample +CP is developing with non-linear profile under filtration pressure below 100 psi; in transient regime between 100 psi to 150 psi; but nearly constant (close to steady-state) above 120 psi. However, the filter cake height for sample -CP shows a strictly non-linear build up over the tested pressure regime of 80 psi to 150 psi. Literatures reveal the relation of filter cake build-up and resultant mud cake permeability exposed to static filtration against varied pressure are defined as in Equation 1 (Approximate equation of static and dynamic filtration from non-Newtonian fluid under unsteady-state to transient regime across a compressible filter cake) [21]:

$$\varepsilon(x, t) = \varepsilon_o \left[1 - \frac{x}{\sqrt{\gamma t}} + \frac{2}{\pi} \sum_{n=1}^{\infty} \left(\frac{1}{n^2} \sin n\pi \frac{(1-x)}{\sqrt{\gamma t}} e^{-\frac{n^2 \pi^2 x^2 2\pi x}{\gamma t \sqrt{\gamma t}}} \right) \right] \quad (1)$$

where ε is the stress function; t is time; x is cake thickness, γ is coefficient of cake thickness.

On the other hand, Fig. 4(b) exhibits the cumulative filtrate volume collected in several time intervals as a function of square-root of time for varied pressure between 80 psi to 150 psi. The filtration across the filter cake from drilling fluid sample without CP shows a linear trend, which could be assumed that the static filtration profile will never achieve steady-state and this is applied over the investigated pressure regime only. The solid lines, which represent the static filtration profile from the drilling fluid sample with addition of 3.5 v% CP, are shifted to a lower cumulative volume for all the pressures investigated. The shift tendency is obvious especially at lower pressure (i.e., 80 psi). Additionally, the filtration profile also reveals that two different linear relations of different

magnitude as a function of time are complied. In our case, the shifted time is at 20 min of continuous static filtration. This finding might suggest that the addition of CP not only alters the filter cake build up mechanisms and the resultant filter cake quality, but it may also affect the filtration rate performance at the early stage (spurt loss) and when it is exposed to lower differential pressure (i.e., 80 psi and below). However, when tested at a prolong time (i.e., up to 30 min and over) with a higher static pressure (i.e., 150 psi and beyond), the filtration performance could be extrapolated to indicate no significant differences with addition of CP.

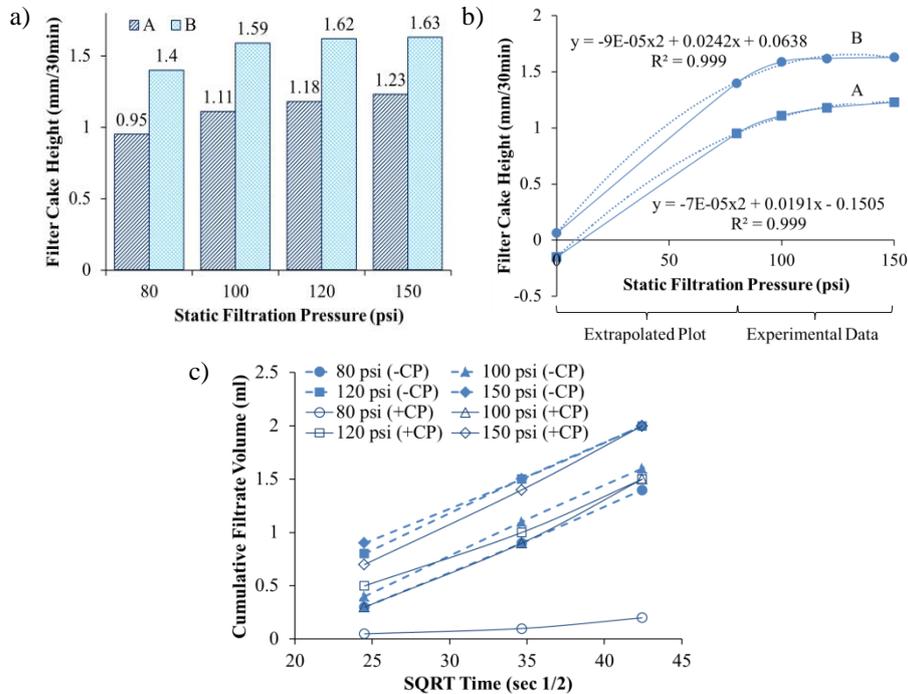


Fig. 4. (a) Filter cake height against static filtration pressure for (A) 3.5 v% CP (B) 0 v% CP; (b) Filter cake height involving back extrapolation based on polynomial equation; (c) Cumulative filtrate volume against square-root of time with 3.5 v% CP and without CP at different pressures.

3.3. Physical properties characterization

3.3.1. Thermal analysis

According to Critchley [22] and AME [23], DSC analysis is used to measure the thermal properties of samples such as melting point, heat of fusion, latent heat of melting, reaction energy and temperature, glass transition temperature, crystalline phase transition temperature and energy, precipitation energy and temperature, denaturation temperatures, oxidation induction times and specific heat or heat capacity. DSC measures the amount of energy absorbed or released by a sample when it is heated or cooled, providing quantitative and qualitative data on endothermic (heat absorption) and exothermic (heat evolution) processes. Based on the findings in Fig. 5, three noticeable peaks were found at the range of 30 to 100 °C (exothermic), 120 to 125 °C (endothermic) and 240 to 260 °C (exothermic). The first occurring peak signified the

removal of moisture content in the sample. The second peak centering at 122.5 °C represented the crystallinity temperature while the third peak (250 °C) detected was related to the melting point temperature. The DSC profiles for filter cake samples with and without CP at various pressures (80 and 150 psi) reveal similar trend in terms of crystallinity temperature and melting point. This is an encouraging scenario as the addition of CP as the shale inhibitor does not alter the temperature resistance profile of the drilling fluid system. Hence, it could be concluded that the addition of CP did not impose significant thermal effects on the drilling fluid operation.

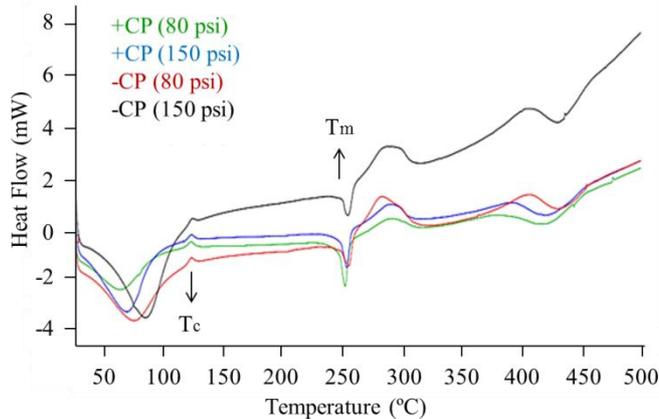


Fig. 5. DSC analysis for filter cakes with/without CP at 80 psi and 150 psi.

3.3.2. Morphological analysis

FESEM analysis was conducted to observe the microstructure and morphology while Energy Dispersion X-ray Spectroscopy (EDX) analysis was performed to determine the percentage distribution of elements on the surface for several fluid samples at different pressures: +CP (80 psi), +CP (150 psi), -CP (80 psi) and -CP (150 psi). The results of FESEM in Fig. 6 shows that sample without CP: -CP (80 psi) and -CP (150 psi) have smaller particles size and larger flat surface compared to sample with CP addition: +CP (80 psi) and +CP (150 psi). The addition of shale inhibitor (CP) has covered the surface of Barite (Ba) effectively, resulting in larger particles size and smaller surface of the clay. This scenario has indirectly reduced the contact surface area between water and clay, which could further enhance the clay stabilization [12]. On the other hand, the EDX analysis has shown that for all filter cake samples, Ba represents the highest distribution of elements in each filter cake sample as Ba is the largest component added into the drilling fluid sample. The addition of CP (ethoxylated polyamine) which yield amino groups are detected in EDX with the presence of nitrogen (N) as the main element. The presence of amino groups in CP is proven by FTIR analysis, which will be discussed in the next section (3.4.1). According to Fig. 7, it shows that sample +CP at higher pressure (150 psi) has a higher percentage distribution of N compared to sample +CP at lower pressure (80 psi). This is possibly due to distribution of more CP adsorption onto the clay surface at higher operating pressure with sample +CP (150 psi) compared to sample +CP (80 psi), which therefore increasing the percentage distribution of N in sample +CP (150 psi).

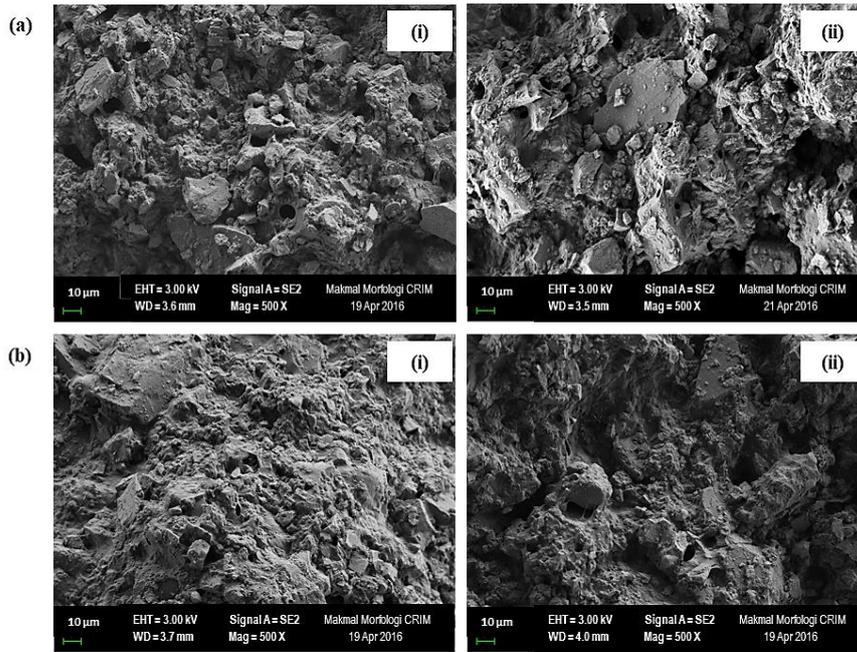


Fig. 6. FESEM analysis for filter cakes: (a) with CP (i) 80 psi (ii)150 psi; (b) without CP (i) 80 psi (ii) 150 psi.

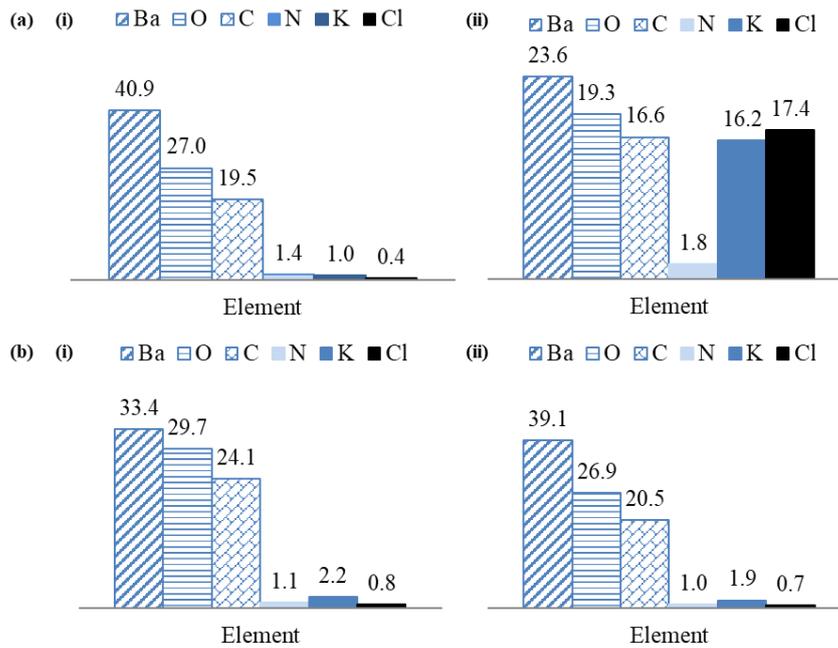


Fig. 7. EDX analysis for filter cakes: (a) with CP measured at (i) 80 psi, and (ii)150 psi; (b) without CP measured at (i) 80 psi, and (ii) 150 psi.

3.3.3. Rheological analysis

The effects of CP addition on the rheological properties of the drilling fluid was evaluated by conducting rheological analysis at low shear rate regime of below 100 per second. According to the rheological behavior shown in Fig. 8, the fluid sample +CP exhibits a stable viscoplastic flow properties while fluid sample -CP shows an uneven trend, in which the flow properties was difficult to determine. It could be proven that the fluid sample +CP follows the Herschel Bulkley model, which has been mentioned in Section 2.2.3. Barry et al. [24] explained that this model is the most appropriate model to describe the flow properties of a non-Newtonian drilling fluid. In this way, the stability of sample +CP at low rheology regime was improved, which helps the fluid system to perform better in terms of solids suspension capability. Apart from that, the higher shear stress value over the same shear rate are more preferable when dealing with cutting suspension over low shear regime. In this way, it could enhance the hole cleaning in the drilling operation.

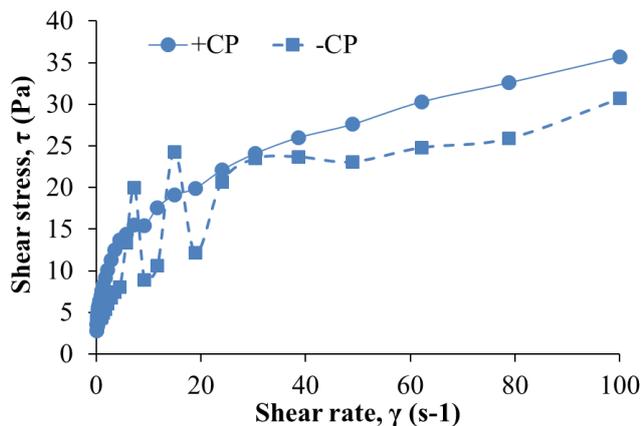


Fig. 8. Low end rheological regime for drilling fluid samples with/without CP.

3.4. Chemical properties characterization

3.4.1. FTIR

Chemical properties characterization with FTIR was conducted to determine the functional groups present in all three samples: CP, drilling fluid +CP and drilling fluid -CP. Table 2 shows the wavenumber of functional groups exist in each sample based on the FTIR analysis as presented in Fig. 9. Peak was detected at region 3300 cm^{-1} proved the presence of amine functional groups originated from the CP, which is a type of polyamine. Besides, the peak spotted at 1640 cm^{-1} region was alkene groups while the peaks detected at 1459 cm^{-1} was alkane group. Additionally, CP also contains alcohol and ether groups, which were seen at peak 1136 cm^{-1} and 1040 cm^{-1} , respectively in the spectrum of CP sample. On the other hand, the drilling fluid samples with and without CP have approximately the same spectrum. Both samples exhibit the presence of alkenes and alkynes (at wavenumber region of 670 cm^{-1} and 1640 cm^{-1}) in the spectrum, which was possibly due to the existence of barite and xanthan gum originated from the drilling fluid formulation. The only difference spotted for both fluid samples was the presence of amine groups for the sample with CP addition. The amine groups are originated from the CP, which is

typically known as ethoxylated polyamine to serve as shale inhibitor in drilling fluid system.

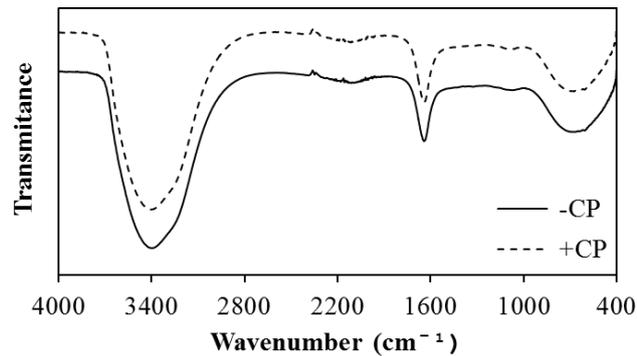


Fig. 9. FTIR spectra for drilling fluids with/without CP.

Table 2. FTIR wavenumber and functional groups.

Sample	Functional group	Wavenumber (cm ⁻¹)
CP	Amine (N-H, stretch)	3326.94
	Alkynes (C≡C-H, stretch)	2154.29
	Alkenes (C=C, stretch)	1639.03
	Alkanes (C-H, bending)	1459.31
	Alcohol (C-O, stretch)	1136.45
	Ether (C-O, stretch)	1040.70
	Alkenes (C-H, bending)	838.33, 922.74, 991.24
Drilling fluid +CP	Amines (N-H, stretch)	3397.50
	Alkynes (C≡C-H, stretch)	1644.20
	Alkenes (C=C, bending)	667.10
Drilling fluid -CP	Amine (N-H, stretch)	3405.60
	Alkynes (C≡C-H, stretch)	1644.40
	Alkenes (C=C, bending)	676.10

3.4.2. Methylene blue capacity and total hardness

Methylene blue capacity test was conducted to determine the amount of reactive clay in drilling fluid sample, whereby it can provide an estimation of the total cation exchange capacity of the drilling fluid. Pre-treatment with hydrogen peroxide is intended to eliminate the effects of organic materials such as lignosulfonates, lignite, cellulose polymer, polyacrylate and etc. Due to the cationic properties of methylene blue, it sticks to the negatively charged surfaces [25]. CP has cationic properties whereby its ammonium cations will neutralize the negatively charged surface of the fluid sample, hence preventing the methylene blue from sticking to the surface. Based on the result obtained as shown in Fig. 10, it shows that sample +CP has C_{MBT} of 10.69 kg/m³, which is lower than the sample -CP with 14.25 kg/m³. This proves that the negatively charged surface was neutralized by CP and successfully prevent the surface adsorption of methylene blue. Thus, the C_{MBT} reading for sample +CP is lower compared to sample -CP.

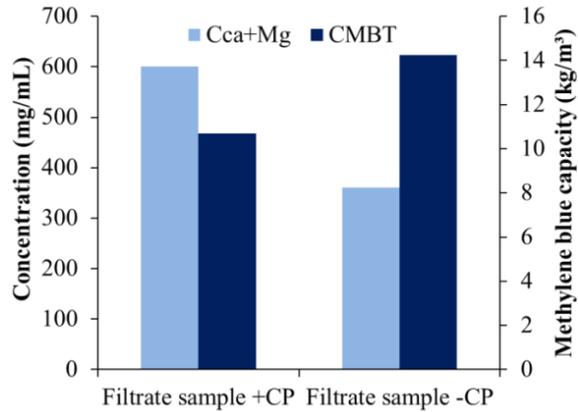


Fig. 10. Methylene blue capacity and total hardness for filtrate samples.

Meanwhile, total hardness test was conducted to determine the concentration of calcium (Ca) and magnesium (Mg) ions content in the filtrate sample. The total of calcium and magnesium plasticity is known as total hardness. Both ions will replace sodium ions in the drilling fluid and thus reducing the rate of fluid hydration in addition to increase the flocculation and aggregation of fluid or clay platelet which might lead to an increase in the yield point, gel strength and drilling fluid loss [19]. As shown in Fig. 10, the total hardness obtained for the two samples (+CP and -CP) were greater than 200 mg/L, whereby the c_{CA+Mg} in the filtrate sample +CP was 600 mg/L while the filtrate sample -CP was 360 mg/L. When the c_{CA+Mg} exceeded 200 mg/L, it will cause pH value and plastic viscosity of the drilling fluid to decrease. Further treatment such as the addition of soda ash and caustic soda is necessary to get rid of Ca and Mg. Soda ash will precipitate Ca and caustic soda will precipitate Mg so that both elements can be removed from the drilling fluid sample.

3.4.3. Filtrate alkalinities

Phenolphthalein alkalinity is the amount of sulphuric acid (in ml) needed to neutralize the filtrate sample to a pH of 8.3, which is the color change end point of phenolphthalein indicator solution. Methyl orange alkalinity measurements are the amount of acid needed to lower the pH of the fluid sample to a pH of 4.5, which is the color change end point of methyl orange indicator solution. This test was performed to determine the concentration of hydroxyl ions $[OH^-]$, carbonate ions $[CO_3^{2-}]$ and bicarbonate ions $[HCO^-]$ in the filtrate sample. $[CO_3^{2-}]$ will react with acid to produce $[HCO^-]$. The reaction occurs when the pH decreased to 8.3 and at the same time, the neutralization of $[OH^-]$ also occurs at this pH. Therefore, the phenolphthalein alkalinity is a combined measurement of hydroxyl and carbonate alkalinity. When the pH dropped to 4.5, it shows that the $[HCO^-]$ is being converted to carbon dioxide (CO_2) and water (H_2O) when it reacts with acid. The results obtained are as shown in Fig. 11. Concentration of $[OH^-]$ for the filtrate sample +CP and the filtrate sample -CP were 0 mg/L. For $[CO_3^{2-}]$, the filtrate sample +CP has a concentration of 1080 mg/L while the filtrate sample -CP has a concentration of 240 mg/L. Finally, the filtrate sample +CP has a $[HCO^-]$ concentration of 2318 mg/l while the filtrate sample -CP is 1220 mg/L.

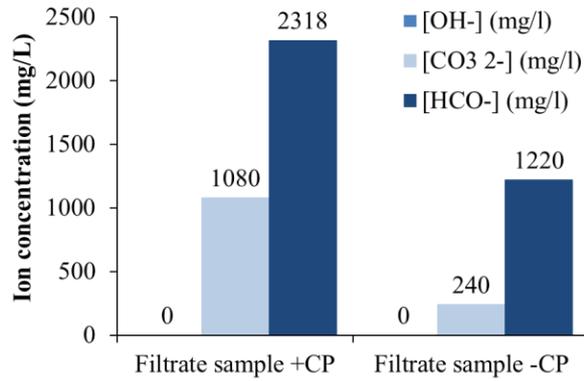


Fig. 11. Concentration of [OH⁻], [HCO⁻] and [CO₃²⁻] for filtrate samples.

3.4.4. Chloride ion content

Drilling fluid salinity levels were measured by titration with silver nitrate to determine the concentration of chloride ions content in the filtrate and then recorded as the chloride ion concentration or sodium chloride concentration in mg/L. The degree of hydration of drilling fluid will decrease if the fluid salinity increases [19]. Fig. 12 shows that the chloride ion concentration of the filtrate sample +CP was higher with value of 4600 mg/l compared to the filtrate sample -CP, which was only 2700 mg/L. On top of that, the concentration of sodium chloride for filtrate sample +CP was higher compared to the filtrate sample -CP whereby the reading obtained was 7590 mg/L for filtrate sample +CP and 4455 mg/L for filtrate sample -CP. High content of chloride ions in the filtrate sample +CP shows that it has lower degree of drilling fluid hydration. Drilling fluid hydration decrement could promote flocculation tendency, which would affect the filtration and flow properties of fluid. As a result, it may reduce the plastic viscosity and increase fluid loss [19]. Therefore, it is necessary to monitor the salinity level by observing the concentration of chloride ions in the mud filtrate.

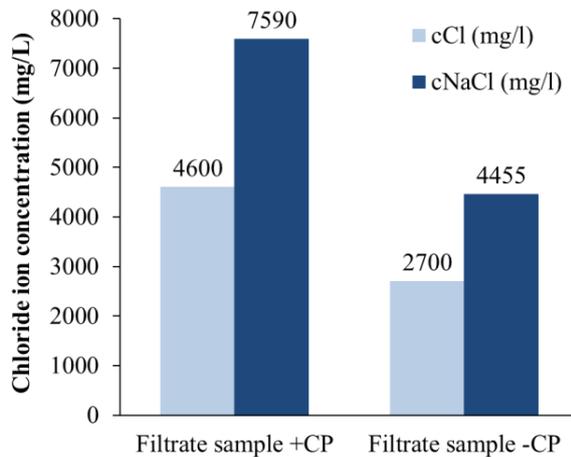


Fig.12. Concentration of c_{Cl} and c_{NaCl} for filtrate samples.

4. Conclusions

The effects of shale inhibitor, Ethoxylated Polyamine (Clayseal Plus) addition into the water-based drilling fluid was successfully investigated in this study. Based on the swell inhibition test, the optimum CP concentration obtained is at 3.5 v%. At this optimum concentration, CP would attach to the clay surface effectively to inhibit the clay swelling when the water molecules adsorption rate decreases. The result obtained for filter cake thickness and filtrate volume reveals that the drilling fluid +CP has thicker filter cake with lower filtrate volume compared to drilling fluid -CP. Besides, the DSC analysis shows that the chosen filter cake samples have crystallinity temperature at 122.5 °C and melting point at 250 °C. FESEM analysis also exhibits that the filter cake samples +CP have larger particles size and smaller flat surface than the filter cake samples -CP, which lead to smaller clay surface in contact with water. In addition, the filter cake sample +CP (150 psi) has higher distribution percentage of N due to the presence of CP. The rheological analysis proves that sample +CP is exhibiting viscoplastic rheological behaviour compared to sample -CP with uneven rheological trends. Apart from that, the chemical properties characterization for methylene blue capacity indicates that the drilling fluid sample +CP has lower methylene blue capacity (C_{MBT}) than the drilling fluid sample -CP. In addition, the results of several chemical tests conducted found that the concentration of ions $[OH^-]$ for both filtrate samples were 0 mg/L. However, the concentration of carbonate ion $[CO_3^{2-}]$, bicarbonate ion $[HCO_3^-]$, chloride ion (c_{Cl}), sodium chloride (c_{NaCl}) and total hardness (c_{Ca+Mg}) for samples +CP were higher than the samples -CP. These ion concentrations were in an acceptable range limit without affecting the drilling fluid operation performance. Therefore, it can be concluded that the presence of CP in WBM greatly reduces the shale-water affinity and its presence in the filter cake formation reduces the amount of filtrate penetrating the layer.

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Nomenclatures

C_{Ca+Mg}	Concentration of Ca + Mg
C_{MBT}	Capacity of methylene blue
c_{Cl}	Concentration of chloride ion
c_{NaCl}	Concentration of sodium chloride
t	time
x	cake thickness

Greek Symbols

ε	stress function
γ	coefficient of cake thickness

Abbreviations

+CP	With shale inhibitor
-CP	Without shale inhibitor
Ba	Barite
CM	Carboxymethyl
CP	Clayseal Plus
DI	Deionized
DSC	Differential Scanning Calorimeter
EDX	Energy Dispersion X-ray Spectroscopy
FESEM	Field Emission Scanning Electron Microscope
FTIR	Fourier Transform Infrared Spectroscopy
HP	Hydroxypropyl
OBM	Oil-based mud
PAC	Polyanionic cellulose
SBM	Synthetic-based mud
SPA	Sodium polyacrylate
WBM	Water-based mud

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