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Nonionic Polyol Esters as Thinner and Lubricity Enhancer for Synthetic-Based Drilling Fluids

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Abstract

This study evaluates the performance of polyol esters as thinners and lubricity enhancers in invert emulsion synthetic-based drilling mud (SBM). Three types of polyol esters, namely pentaerythritol ester (PEE), trimethylolpropane ester (TMPE), and neopentyl glycol ester (NPGE), were prepared at various concentrations of 1, 2, and 3% (v/v) in SBM. The results showed that polyol esters reduced the rheological properties of the drilling mud, such as yield point and gel strength, after the hot rolling test at 135°C. The rheology data was fitted to the Herschel-Bulkley model to describe the shear thinning behaviour of drilling mud. The model parameters showed that the polyol ester resulted in lower yield stress of SBM, which indicated
lower forces are needed to initiate a fluid to move. Their relative effectiveness as a lubricity enhancer was evaluated by measuring the coefficient of friction (COF), wear scar diameter, and scar topography. It was found that polyol esters reduced the COF of SBM by 22% at a concentration of 1% (v/v). PEE provided the best friction reduction and anti-wear performance due to a higher number of the ester group and molecular weight, in comparison with NPGE and TMPE. The lubricity improvement for SBM is recently required by off-shore regulations.

**Keyword:** polyol ester; rheology modifier; drilling mud; wear prevention.

1. Introduction

The main functions of drilling fluids or mud are to transport rock cuttings in the wellbore annulus to the surface, to cool and lubricate the drill bit, and to provide a hydrostatic head to maintain the wellbore stability. To provide these functions, the drilling fluids must be sufficiently viscous to be able to carry rock cuttings and to suspend barite and other weighting agents [1, 2]. However, unwanted increased viscosity due to multiple circulations of the mud in the wellbore might occur and result in a problematic sticking of the drill string, and increased circulating pressures that can contribute to the problem of loss circulation [3]. Wear and tear of the drilling tools are other common problems in the drilling operation, which are caused by poor lubrication. Consequently, it can lead to drill bit bearing wear, casing wear, over-pulls in trip-outs and drag, torque problem, and differential sticking [4, 5].

Increased viscosity commonly occurs when clay layers in the mud associate together and form an aggregated or flocculated structure, leading to higher rheological properties [6]. When the viscosity exceeds the rheological specifications, certain chemicals such as thinners are typically added to the drilling fluid to neutralize the edge charge of the particles and deflocculate the particles [7]. The types of thinners varied, ranging from natural and modified natural products, such as lignin, lignosulphonates, polyphosphates, tannins, low molecular...
weight polyacrylates, and surfactants [3, 8-10]. Hafshejani et al. [6] studied the performance of oak seed extract as a thinner/deflocculant for bentonite drilling mud. The study found that oak seed extract neutralized the positive edges of the bentonite by tannins (dominant constituent in oak seed extract), destroying the ability of the bentonite layers to link one another. Therefore, the capacity of bentonite to form a flocculated structure decreased, decreasing the rheological properties and fluid loss volume. In another study, Zhang and Yin [10] used a modified lignosulfonate thinner called Fe-tannin-lignosulfonate to reduce the viscosity of the water-based mud. The finding highlighted the superior thinning ability of the modified lignosulfonate at an elevated temperature up to 120°C in comparison with the widely used FeCr-lignosulfonate.

Currently, there is increasing interest in developing multifunctional additives, which combine different additive functionalities. Padavich and Honary [11] reported that sunflower thinning agents in Russian drilling operation were able to thin the mud as well as improve the lubricity and inhibition level. Ofei et al. [12] proposed ionic liquid as a rheology stabilizer and filtration control for water-based mud. The study suggested that ionic liquid would enhance effective wellbore cleaning through improved rheology up to a temperature of 180°C. In a similar study, Ahmad et al. [2] studied the performance of high molecular weight copolymers as rheology modifiers and filtration control for water-based mud that can withstand drilling temperatures up to 85°C.

Organic esters have been recommended for use as the base fluids, surfactants, lubricants, and thinners, to replace the harmful mineral oil in drilling fluid formulations [13, 14]. Particular esters may modify the relationship between the viscosity and the percentage of solids in the mud, acting as a thinner and a dispersant [15, 16]. Polyol esters, which are the products of a monobasic acid and a polyhydric alcohol, were reported to have superior characteristics compared to other types of esters [4]. The oxidation and thermal stability of this type of ester
had been improved by replacing glycerol with alcohol that did not contain β-hydrogen atoms [17], allowing polyol esters to be used at much higher temperatures. In addition, polyol ester also has higher polarity, lubricity, and anti-wear in comparison with paraffin oil or other commercial lubricity enhancer products [18, 19]. In drilling fluid application, esters have been known to be soluble with synthetic base fluid such as paraffin oil and can improve the solubility of other additives [4]. In a recent study, polyol esters successfully improved the lubricity of bentonite-based drilling mud by more than 80% due to their high polarity [20].

This study reports for the first time the application of nonionic polyol esters for SBM as an additive for synthetic-based mud (SBM). SBM is a water-in-oil invert emulsion system which is widely used to minimize the friction and to increase the penetration rate in the drilling operation. Only a few studies had been conducted on viscosity reducing and lubricity enhancer additives for SBM, as previous studies were more focused on water-based mud. Some drilling field regulations have recently demanded lubricity improvement for SBM [4, 14]. Development for an improved rheology-thinner is also necessary for invert-emulsion SBM when increased viscosity occurs [3, 7]. Anionic surfactants, particularly from the group of fatty alcohol sulfates, were commonly used as thinners for SBM. However, Silva et al. [21] described that several studies had shown that nonionic additives such as nonionic surfactants were less toxic and more biodegradable than ionic surfactants, and organophilic clays that reacted with them had higher thermal stability than those containing ionic surfactants. In terms of the sorption ability, nonionic surfactants indicated greater tendency to adsorb on solid surfaces at lower concentrations with predicted high efficiencies [22].

In this study, three types of nonionic polyol ester, namely neopentyl glycol ester (NPGE), trimethylolpropane ester (TMPE), and pentaerythritol ester (PEE), were evaluated as potential multifunctional thinners and lubricity enhancers for SBM. The polyol esters also have the molecular structure of surfactants which is made up of dissimilar groups such as hydrophobic
and hydrophilic. These polyol esters differ physically and chemically in a way that a better understanding of their effect on rheological properties and lubricity of the mud needed to be studied. The rheological properties, which include plastic viscosity, yield point, and gel strengths, were measured before and after hot rolling at 135°C for 16 hours. The standard high temperatures and high pressures (HTHP) filtration measurements were conducted to evaluate the effects of polyol esters on the fluid loss volume. Lastly, the lubricity enhancement of polyol esters was investigated by measuring the coefficient of friction (COF), wear scar diameter (WSD), and scar surface characteristic.

2. Experimental method

2.1. Materials

Three different polyol esters, NPGE, TMPE, and PEE, were the respective products of transesterification of palm oil methyl ester with NPG, TMP, and PE, as shown in Fig. 1. The reaction was carried out by reacting a 200 g of palm oil methyl ester and a known amount of polyol (NPG, TMP, or PE) in a 500 ml three-neck flask equipped with a mechanical stirrer. The weight of polyol was determined based on the required molar ratio and the calculated mean molecular weight of methyl ester. The mixture was then heated to the reaction temperature. Subsequently, the catalyst was added. The vacuum was gradually applied to the system until it reached the desired pressure and maintained at the same pressure until the reaction was completed. The polyol ester characteristics are presented in Table 1, while the fatty acid composition is shown in Table 2. The Fourier transform infrared FTIR spectra of each polyol ester is shown in Fig. 2. The displayed band at 1739 cm\(^{-1}\) is accountable for the carbonyl stretch C=O of aliphatic ester, while the bands at both 1241 and 1260 cm\(^{-1}\) indicates the C-O stretch of ester.
Fig. 1. The synthesis of (a) NPGE, (b) TMPE, and (c) PEE.

Table 1. The characteristics of different polyol esters

<table>
<thead>
<tr>
<th>Properties</th>
<th>NPGE</th>
<th>TMPE</th>
<th>PEE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, kg/m³</td>
<td>0.89</td>
<td>0.91</td>
<td>0.93</td>
</tr>
<tr>
<td>Viscosity at 40°C, cSt</td>
<td>21</td>
<td>45.7</td>
<td>68.4</td>
</tr>
<tr>
<td>Viscosity at 100°C, cSt</td>
<td>6.3</td>
<td>9.46</td>
<td>12.7</td>
</tr>
</tbody>
</table>
Table 2. Fatty acid composition of different polyol esters

<table>
<thead>
<tr>
<th>Fatty acid (%)</th>
<th>NPGE</th>
<th>TMPE</th>
<th>PEE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoester</td>
<td>9.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Diester</td>
<td>90.0</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>Triester</td>
<td>-</td>
<td>97.0</td>
<td>36.0</td>
</tr>
<tr>
<td>Tetraester</td>
<td>-</td>
<td>-</td>
<td>52.0</td>
</tr>
</tbody>
</table>

Fig. 2. Infrared spectra of polyol esters

2.2. Drilling fluid preparation

The invert-emulsion SBM was prepared by mixing Sarapar oil, emulsifiers, organophilic clay, gilsonite, lime, CaCl₂ brine, and barite, using Hamilton Beach Fann mixer. Table 3 shows the formulation of SBM used in this study. The mud weight was 1438 kg/m³ (12 lb/gal), the specific gravity was 1.44, and the oil-water ratio was 75:25. Next, various concentrations of polyol ester were added to the prepared SBM (1%, 2%, and 3% v/v respectively, i.e., 1% means 3.5 ml of polyol ester was added into 350 ml of the mud sample). To simulate the
circulation of drilling mud through the hole under the actual drilling conditions, all the mud samples were aged in a hot rolling oven at 135°C for 16 hours to allow the full viscosity to develop.

Table 3. Drilling mud composition

<table>
<thead>
<tr>
<th>Components</th>
<th>Function</th>
<th>Concentration (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sarapar oil</td>
<td>Base fluid/continuous phase</td>
<td>156.04</td>
</tr>
<tr>
<td>Confi-mul P</td>
<td>Primary emulsifier</td>
<td>3.00</td>
</tr>
<tr>
<td>Confi-mul S</td>
<td>Secondary emulsifier</td>
<td>6.00</td>
</tr>
<tr>
<td>Organophilic clay</td>
<td>Viscosifier</td>
<td>6.50</td>
</tr>
<tr>
<td>Gilsonite</td>
<td>Filtration control</td>
<td>4.00</td>
</tr>
<tr>
<td>Lime</td>
<td>Activates the emulsion</td>
<td>10.00</td>
</tr>
<tr>
<td>CaCl₂ Brine</td>
<td>Viscosifier</td>
<td>253.30</td>
</tr>
<tr>
<td>Barite</td>
<td>Weighing agent</td>
<td>229.04</td>
</tr>
</tbody>
</table>

2.3. Rheological properties measurement

The thinning effect of polyol esters was investigated by measuring the rheological properties of SBM samples according to the API 13B-2 standard. The rheological properties such as plastic viscosity (PV), yield point (YP), and gel strength were measured before and after hot rolling at a standard temperature of 48.8°C using a rotational viscometer Fann Model 35. The measurements consisted of measuring the shear stress at various shear rates, which ranged from 3 RPM (5.109 s⁻¹) to 600 RPM (1021.8 s⁻¹).

\[
PV = \theta_{300} - \theta_{600}, \text{ (cP)} \tag{1}
\]

\[
YP = \theta_{300} - PV, \text{ (lb/100 ft}^2) \tag{2}
\]

Gel strength is the shear stress of drilling mud measured at a low shear rate (3 RPM) after a static period of 10 sec and 10 min.
2.4. Herschel-Bulkley (1926)

The rheological behaviour of SBM containing polyol ester additive was fitted to the Herschel-Bulkley model. The Herschel-Bulkley model provides three parameters, which are yield stress ($\tau_0$), fluid consistency index ($K$), and flow behaviour index ($n$), to describe the relation between the shear rate and shear stress [23]. The equation of Herschel-Bulkley model (Eq. 3) was fitted to the rheology data by using the Generalized Reduced Gradient Nonlinear algorithm implemented in Excel Visual Basic with the use of the Solver library. $\tau$ represents the shear stress.

$$\tau = K (\gamma)^n + \tau_0$$ (3)

The Herschel-Bulkley model covers the range of yield stress values represented in both Bingham plastic and power law models. The power law represents the case of zero yield stress, while the Bingham plastic model describes the yield stress ($\tau_0$) equals to the yield point (YP). Herschel-Bulkley model characterizes the yield stress of drilling fluid by the criteria in Eq. 4.

$$0 \leq \tau_0 \leq YP$$ (4)

2.5. HTHP filtration characteristic

The filtration test was measured using the Fann HTHP filter press to provide a relative measure of mud filtrate invasion into a porous formation of the wellbore under static condition in accordance with a standard procedure described by API 13B-2. The test was conducted using a 175 ml static filter press equipped with a heating jacket, a regulated pressurization system and a filter paper. The mud’s HTHP fluid loss was measured at test conditions of 500 psi pressure, 135°C operation temperature, and 30 minutes operation time. The volume of collected filtrate and the thickness of the mud cake deposited on the filter paper were reported.
2.6. Four-ball lubricity tester

The effect of polyol ester on the tribological properties of SBM was investigated using a four-ball lubricity tester in accordance with ASTM D 4172. The tester consisted of three steel balls, with a diameter of 12.7 mm, held stationary in a ball cradle filled with the mud sample and a fourth ball held in a rotating spindle. The illustration of the tester is presented in Fig. 3. A 40 kg load was applied through a lever system, which pushed the three stationary balls upward against the fourth ball. The test was conducted with a rotational speed of 1200 RPM for 60 minutes at room temperature. The friction torque encountered within the contact was continuously monitored and gathered using the data acquisition software. The measured frictional torque was converted into the coefficient of friction (COF).

![Fig. 3. Schematic diagram of a four-ball tester](image)

After the test, the diameter of the wear scar developed on the balls was measured by using a calibrated microscope to assess the anti-wear behaviour of the polyol ester in the mud. The smaller the wear scar diameter (WSD), the better the performance of the polyol ester. The steel balls were thoroughly cleaned with toluene before and after each experiment. Experiments were done in triplicate to observe if any error occurs. The wear scar on the worn balls were
characterized using a scanning electron microscope (SEM) Hitachi S-3400N to compare the wear modes for different polyol esters.

3. Results and discussion

3.1. The effect of polyol esters on drilling mud rheological properties

The measured shear stress of SBM containing polyol esters as a function shear rate and polyol ester concentration after hot rolling is presented in Fig. 4 (a), (b), and (c). The data was collected at the standard temperature of 48.8°C. A control sample (without polyol ester) is plotted as “SBM” in each graph. General observation shows that SBM containing NPGE, TMPE, and PEE have lower shear stress compared to SBM without polyol esters; the shear stress decreases with the increase of polyol ester concentration. At 5.1 s⁻¹ shear rate, 1% of the polyol esters have reduced the shear stress of the SBM by approximately 45%. The decrease of shear stress is more pronounced at higher shear rates, particularly for NPGE and TMPE treated SBM. The results clearly indicate a thinning effect of polyol esters in SBM. The nonionic polyol ester adsorbs onto the surface of organophilic clay and neutralizes the negative sites of the clay particles. Accordingly, the interaction between the organophilic clay particles is reduced, resulting in the dissociation of the aggregated clay particles.

Luckham and Rossi [24] described that the mechanism of surfactant adsorption on clay surfaces are related to ion-dipole interactions, the formation of hydrogen sites, increased entropy, and Van der Waals forces. Particularly for the nonionic surfactants, Shen [25] found that nonionic surfactants demonstrated higher sorption ability onto clay surface than cationic surfactants since the sorption capacity was not limited by the clay’s cation-exchange capacity. Silva et al. [21] studied the organophilization of bentonite clay using nonionic surfactants, aiming at their use as a dispersant in diesel and kerosene-based drilling mud. The study found
that small increments of surfactant concentration in clay can lead to significantly different mud rheology, even though the rheology was only described by apparent viscosity.
**Fig. 4.** Rheogram comparison of SBM with different polyol esters; (a) NPGE, (b) TMPE, and (c) PEE, at various concentration after hot rolling.

The rheological properties of SBM in the presence of polyol ester, which comprise of yield point (YP), gel strength, and plastic viscosity (PV) are presented in Figure 5-7. A control sample is plotted as “SBM” in each graph. It is seen that all the rheological properties, except for PV, experience a sharp decrease in the presence of NPGE, TMPE, and PEE, after hot rolling (AHR). The graphs also show that the changes in mud properties due to polyol esters before hot rolling (BHR) are not seen. This is possibly because the interparticle force between the mud particles mainly occurs after hot rolling at the elevated temperatures [26].

Fig. 5 (a), (b), and (c) illustrate the change in the rheological parameter YP of SBM for each polyol esters. Theoretically, YP measures the electro-chemical or attractive forces in a fluid under flow conditions. The YP depends on the surface properties of the mud solids, the volume concentration of the solids, and the electrochemical environment of these solids, particularly the concentration and type of ions present [27-29]. Fig. 4 (a) indicates that SBM containing 1% of NPGE and TMPE demonstrate a substantial reduction in YP AHR from 19 lb/100ft² for the control sample to 9 and 11 lb/100ft² respectively. In comparison, 1% of PEE resulted in higher YP, which is 15 lb/100ft². When the organophilic clay is dispersed in the drilling mud, the
emulsifier additive chains form the links between the dispersed particles, increasing the YP [29]. However, when the polyol ester is present, the emulsifiers may be less polar than the polyol ester. Polyol esters are adsorbed to the organophilic clay surface and reduce the interactions between the organophilic clay particles. Thus, it leads to low mud viscosity and gel strength. Further experimental data presented in Fig. 5 (b) and (c), shows the SBM is tested at a higher polyol concentration of 2% and 3%. It shows that the YP decreases with the increase of polyol ester concentration.

The rheology of SBM treated with polyol ester differs based on the molecular weight and molecular structure of the polyol ester. Overall, the results indicate that NPGE caused the lowest mud YP, followed by TMPE and PEE. This might occur because a straight chain molecule of NPGE has a more compact arrangement in the interlayer and lower molecular weight, generating a more compact clay lattice in the mud suspension. Therefore, the change in YP is more prominent due to the strong interactions between the NPGE and clay. Meanwhile, the branched-chain molecules of TMPE and PEE have weaker molecular interactions between the branch chains. Four ester groups of PEE are able to bond the adjacent lattice of clay together, but its high molecular weight causes a more expanded clay lattice. This may lead to the ingress of water-in-oil emulsion molecule and a weaker bond between the additive and clay [30]. Hence, the PEE results in higher YP, compared to TMPE and NPGE with the same concentration.
Fig. 5. Effect of different polyol ester; (a) 1%, (b) 2%, and (c) 3%, on yield point.
The electrical stability (ES) of mud after hot rolling is also plotted in Fig. 5, to evaluate the emulsion stability of the mud with the change of YP under a simulated wellbore condition. Higher ES indicates a more stable and compacted emulsion. ES is a function of continuous phase viscosity, solid concentrations and type, and emulsifiers/surfactants [31]. Generally, increasing the concentration of the oil base fluid, barite, or emulsifier increases the ES. The lower the interfacial tension can be made, the smaller the droplets become, and the more stable the emulsion. The API standard value for ES of the SBM is above 400 Volts. Results show that all the mud samples meet the API standard for ES value. Most SBM containing polyol ester possess higher ES compared to SBM without polyol ester, demonstrating a more stable emulsion between oil and water phase in the mud.

The effect of polyol ester concentration on the 10 secs and 10 min gel strength of SBM after hot rolling is illustrated in Fig. 6 (a), (b), and (c). SBM containing 1% of polyol ester NPGE, TMPE, and PEE exhibit a substantial reduction of gel strength and a further reduction at an increased polyol ester concentration, following the trend for YP. At 1% polyol ester concentration, there is adequate range between the initial 10-sec gel and 10-min gel for all the samples. At 2% and 3% of NPGE and TMPE concentrations, the mud shows a flat and low gel, which might be undesirable. Sufficient gel strength is needed to hold the drill cuttings when the mud circulation is stopped. On the other hand, PEE mud maintains sufficient gels up to a concentration of 2%. Generally, this phenomenon suggests that the SBM containing PEE can suspend cuttings under static conditions better than the SBM containing NPGE or TMPE.
Fig. 6. Effect of polyol ester; (a) NPGE, (b) TMPE, and (c) PEE, on gel strengths after hot rolling.

Lastly, the change in the rheological parameter plastic viscosity (PV) of SBM as a function of polyol ester concentration is shown in Fig. 7. The PV of the controlled sample is plotted at 0% of polyol ester concentration. The results show that the PV is not substantially affected by the addition of the polyol esters. The calculated PV ranges between 21 to 25 cP. For most practical purposes, PV depends on the concentration of mud solids [29]. Hence, the addition of liquid polyol esters does not affect the value. It is also worth mentioning that low and stable PV is desirable. Excessive PV will cause an increase in the pump pressure that is required to pump the fluid, leading to an excessive equivalent circulating density [32].
Fig. 7. Effect of different polyol ester on plastic viscosity after hot rolling.

Based on experimental data, PEE and TMPE give a more controllable decrease in rheology, while NPGE causes a very low YP at the concentrations of 2% and 3%. Such low YP might lead to poor rock cuttings transport while drilling. According to Lyons and Plisga [16], the recommended range of YP for SBM with the properties described in this study is between 6 – 14 lb/100 ft². The drilling mud company may wish to control the amount of viscosity reduction by adding only an effective concentration of the thinner required to achieve the desired viscosity.

3.2. Statistical analysis of mud rheological properties

Table 4 shows the effect of polyol ester concentration on three Herschel-Bulkley parameters, which consist of yield stress ($\tau_0$), fluid consistency index ($K$), and flow behaviour index ($n$). The coefficients of correlation ($R^2$) and RMSE of the model are also shown. The results in Table 4 indicate that the Herschel-Bulkley model gives considerably high $R^2$ values (>0.99) and low RMSE (<0.41). Thus, the Herschel-Bulkley model could give a good prediction for SBM containing polyol esters. The yield stress represents the minimum amount of force that needed to be applied to initiate a fluid to move. The results show that yield stress decreases
with the concentration of polyol ester. The yield stress decreases from 4.11 Pa for SBM without polyol ester to 2.22, 1.86, and 1.96 Pa at 1% of PEE, TMPE, and NPGE respectively. Since the decrease of yields stress is more than 46% at a very low polyol ester concentration, it shows that the presence of polyol ester plays a significant role to determine the flow behaviour of the mud.

Table 4. Herschel-Bulkley parameters at various polyol ester concentrations

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\tau_0) (Pa)</th>
<th>K (Pa.s(^n))</th>
<th>n</th>
<th>(R^2)</th>
<th>RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBM</td>
<td>4.11</td>
<td>0.15</td>
<td>0.76</td>
<td>1.00</td>
<td>0.16</td>
</tr>
<tr>
<td>SBM+NPGE 1%</td>
<td>1.96</td>
<td>0.05</td>
<td>0.91</td>
<td>1.00</td>
<td>0.25</td>
</tr>
<tr>
<td>SBM+NPGE 2%</td>
<td>1.01</td>
<td>0.03</td>
<td>0.96</td>
<td>1.00</td>
<td>0.23</td>
</tr>
<tr>
<td>SBM+NPGE 3%</td>
<td>1.01</td>
<td>0.02</td>
<td>1.00</td>
<td>0.99</td>
<td>0.28</td>
</tr>
<tr>
<td>SBM+TMPE 1%</td>
<td>1.86</td>
<td>0.08</td>
<td>0.84</td>
<td>1.00</td>
<td>0.25</td>
</tr>
<tr>
<td>SBM+TMPE 2%</td>
<td>0.85</td>
<td>0.06</td>
<td>0.88</td>
<td>0.99</td>
<td>0.27</td>
</tr>
<tr>
<td>SBM+TMPE 3%</td>
<td>0.89</td>
<td>0.04</td>
<td>0.94</td>
<td>0.99</td>
<td>0.39</td>
</tr>
<tr>
<td>SBM+PEE 1%</td>
<td>2.22</td>
<td>0.09</td>
<td>0.83</td>
<td>0.99</td>
<td>0.41</td>
</tr>
<tr>
<td>SBM+PEE 2%</td>
<td>1.71</td>
<td>0.09</td>
<td>0.83</td>
<td>0.99</td>
<td>0.41</td>
</tr>
<tr>
<td>SBM+PEE 3%</td>
<td>1.92</td>
<td>0.05</td>
<td>0.91</td>
<td>1.00</td>
<td>0.15</td>
</tr>
</tbody>
</table>

The fluid consistency index, \(K\), decreases with the increase of polyol ester concentration, as illustrated in Fig. 8 (a). The \(K\) value shows the degree of significant changes of dependent variables (in this case the shear stress) as the result of changes in the independent variable (in this case the shear rate). The greater \(K\) value indicates greater shear stress [33], which replicates the experimental data. Furthermore, the flow behaviour index, \(n\), increases with increasing polyol ester concentration, as shown in Fig. 8 (b). The \(n\) values measure the degree to which the fluid is shear-thinning or shear-thickening. For SBM containing TMPE and PEE mud, the \(n<1\) implies that the mud has shear-thinning behaviour. Shear-thinning fluid refers to a fluid that demonstrates a lower apparent viscosity at higher shear rates and high viscosity at a low
shear rate [34]. As for NPGE treated SBM, the data of \( n = 1 \) suggests that at 3% of the NPGE concentration, SBM becomes Newtonian.

**Fig. 8.** The Herschel-Bulkley parameters (a) fluid consistency index \((K)\) and (b) flow behaviour index \((n)\) for SBM containing polyol ester.

In summary, the effect of polyol ester on the rheological behaviour of SBM is well-described by the Herschel-Bulkley model. The first parameter of this model, which is yield stress, suggests that polyol esters results in lower yield stress/lower horse-power pump to move the mud. The effect of the polyol ester type, including NPGE, TMPE, and PEE, lead to a similar effect on the yield stress. Mud yield stress appears to be higher when the polyol ester has more branched-chain molecules, such as PEE. The second model parameter, fluid consistency index, \( K \), is in good agreement with the experimental data of the shear stress, where the fluid with greater shear stress has a greater fluid consistency index. For fluid index, \( n \), it shows that the TMPE and PEE mud have shear-thinning properties while the NPGE mud shows the characteristic of a Newtonian fluid.
3.3. Analysis of mud filtration properties

The filtrate loss tests were conducted under a simulated drilling condition ($T=135^\circ C$, $P=500$ psi). Low filtrate loss with thin mud cake is desirable in the drilling operation. As presented in Fig. 9, the addition of TMPE and PEE results in a decrease of filtrate volume collected in 30 minutes, while the NPGE shows no improvement in filtration. At a low concentration of 1% of TMPE and PEE, the filtrate volume is reduced by 45.5% when compared with the control sample at 0% polyol ester. Usually, when the viscosity of the mud decreases, the filtrate volume becomes worse under an elevated temperature, as reported by Sami [35] and Wenjun et al. [36]. On the contrary to this understanding, the low viscosity of polyol ester added SBM did not lead to the high filtrate. This is in agreement with the modern use of thinner or dispersant where the thinners are also used to reduce filtration and mud cake thickness [7]. Rizvi [37] described a dispersant prevents colloidal particles from aggregating into a mass of particles or floc cells. It is also mentioned that polyhydric alcohols, including trimethylolpropane, pentaerythritol, and tris (hydroxymethyl) aminomethane, are commonly used to make ester dispersants. When solids in the mud disperse better, the packing density increases and the filtrates loss decreases [38].

Fig. 10 presents the mud cake thickness formed during the filtration tests. In accordance with the results of the filtrate volume, the presence of TMPE and PEE in SBM decreases the mud cake thickness. At 1% of TMPE and PEE concentration, the mud cake thickness is reduced by about 65%, compared to SBM without TMPE or PEE. However, NPGE leads to thicker mud cake, which is undesirable. Nevertheless, this shows a remarkable performance in maintaining the fluid retention behaviour, even though increasing the TMPE or PEE’s concentration does not consequently reduce the fluid loss and mud cake thickness any further.
Fig. 9. Filtrate volume of SBM treated with different polyol esters

Fig. 10. Mud cake thickness of SBM treated with different polyol esters

3.4. Effect of polyol ester on COF and WSD of the mud

Fig. 11 shows the measured coefficient of friction (COF) of SBM with different kinds of polyol esters at various concentrations. It can be seen that the COF of SBM with polyol esters is lower than the SBM without polyol ester (plotted at 0% of polyol ester concentration). At a concentration of 1%, all three polyol esters decrease the COF from 0.11 to 0.089 (22% reduction) approximately. The low COF of polyol ester mud is believed to be attributed to the
high polarity molecules of polyol ester that attach to the metal surface and form a lubricating film. It results in a decrease of contact friction between two moving surfaces.

![Graph showing COF vs. Polyol ester concentration](image)

**Fig. 11.** The coefficient of friction (COF) of drilling mud with different polyol ester

The TMPE treated SBM demonstrates the lowest COF in the volume fractions of 2% and 3%, compared to the NPGE and PEE mud. The difference, however, is not significant. Theoretically, the COF reduction should follow the nature of the ester content in each polyol ester. The tetraester content in PEE should be the most lubricious, followed by the triester of TMPE and diester of NPGE [39]. PEE has the highest viscosity due to high molecular weight. The high viscosity of PEE should have formed thicker film for better surface protection. However, in this study, all the polyol esters lead to similar COF. This indicates that the performance of polyol esters in reducing COF in SBM does not always relate to their viscosity.

The results also shows that increasing the concentration of polyol ester does not show further improvement of COF. The COF of TMPE mud at 1% and 2% is 0.089 and 0.079 respectively, but the COF increased at 3% of TMPE. The high polarity of polyol esters determines high surface affinity, hence they adhere to positively charged metal surfaces, even at a very low concentration of 1%.
Without the polyol ester, the lubricity is only provided by the base fluid, which is paraffin oil. The oil film layer is probably thinner compared to the layer created when the polyol esters are present in the system. When the base fluid fails to provide a separating film between the rubbing surfaces, the polyol esters will contribute to the boundary lubrication. In this regime, the polyol esters provide an anti-wear and extreme pressure additive function through surface adsorption and chemical break-down [19, 40, 41].

Fig. 12 presents the effect of polyol esters on the wear scar diameter (WSD) of the steel balls. A substantial improvement on WSD is obtained by TMPE and PEE at a low volume fraction from 1% to 3% in the mud. WSD is reduced by the increase of polyol ester concentration. The WSD of the mud without lubricant is 1.3 mm. TMPE and PEE reduce the WSD from 1 mm to 0.8 mm and 1 mm to 0.9 mm, respectively. Both polyol esters have the maximum WSD reduction at a volume fraction of 3%. At this point, the WSD is reduced by 34.5%, and 31.8% for TMPE and PEE treated SBM. These results indicate that TMPE and PEE protect the rubbing surface of the steel balls better.

Fig. 12. Wear scar diameter (WSD) of drilling mud with different polyol ester
As for NPGE, a slight improvement on WDS is also observed. At 1% of the NPGE concentration, 10% of WSD is obtained. Increasing the NPGE concentration does not decrease the WSD much further. The inferior performance of NPGE might be attributed to less number of carboxylate ester content, compared to TMPE and PEE. This is in accordance with previous studies which found that the scar is improved when the carboxylate group in ester and polarity increase [18, 42]. The difference is, however, those studies tested pure lubricants. In this study, it is evidence that even though the polyol esters were used as an additive at a very low concentration, they were still able to provide a protective layer. All the polyol esters have high polar molecules which were strongly attracted to the metal surface [43, 44]. Hence, a low concentration of polyol ester most likely attaches itself to the steel balls and remains adherent under the given surface pressure. Accordingly, lower COF and WSD are achieved.

3.5. Surface characteristics

The topography of the worn steel ball was examined by SEM. Fig. 13 presents the comparison of wear caused by the base mud (without polyol esters) and mud treated with 3% polyol esters. The maximum lubricant concentration of 3% was chosen for this examination as it gave the most significant effect on WSD.

As depicted in Fig. 13 (a), the wear scar for SBM, the controlled sample, reveals considerable rough river-vein patterned layers, mainly in the direction of sliding. This roughness is covered by a thin layer of oxidized wear debris. For polyol ester added mud, the appearance of scar varies depending on the type of polyol ester. SBM containing NPGE produces a severe prow formation and more oxidized wear debris, compared to the base mud. The oxidation of lubricant layer might be due to the hot aging process of mud preparation where a temperature of 135°C has been applied for 16 hours. It appears that different types of polyol esters lead to different kinds of corrosive acids that cause corrosive wear. For SBM+TMPE, the worn surface
shows minimal corrosive wear. However, TMPE accelerated deeper scar, which is indicated from several plowed tracks and rough surfaces formed. Polyol ester acts as a lubricating boundary film during severe and intense shearing strain. However, in this study, the TMPE film had completely broken down. This result is similar to the findings reported by Zulkifli et al. [45], who found that pure TMPE lubricant caused severe abrasive wear which led to polished wear on the metal surface. Apart from the load applied to the four-ball tester, solids contained in a drilling mud evidently contribute to friction and scar [46]. In this study, each mud consisted of 53% (w/w) solids which might lead to high friction.

For SBM+PEE, the results in Fig. 13 (d) implies that PEE has the best ability to protect the metal surface from wear. SBM with PEE results in smoother surfaces compared to TMPE mud. Although all types of polyol esters tested in this study gave a beneficial effect on COF, an increase in the number of the ester group and molecular weight, namely from diester and triester to tetraester leads to a higher tribology performance in general. Tetraester of PEE tends to increase the thickness of adsorbed lubricant film on the metal surface, thus increasing the protection on the area. Moreover, a higher number of ester groups leads to a greater binding between the molecules [19]. Hence, PEE shows greater resistance to shear forces under a high load of drilling mud solids.
4. Conclusion

The performances of three types of nonionic polyol esters as multifunctional thinners and lubricity enhancers for SBM have been examined. Experimental results show that adding polyol esters such as NPGE, TMPE, and PEE in SBM reduced the rheology of the mud by neutralizing the interaction between the clay particles in the mud, which would be beneficial when the mud viscosity exceeds the specifications. Furthermore, TMPE and PEE reduced the filtrate volume and mud cake thickness. The effect of polyol esters on the rheological behaviour
of SBM was well described by the Herschel-Bulkley model. Polyol esters were also able to reduce the COF of SBM by 22% at a concentration of 1% (v/v). Increasing the concentration of polyol ester does not improve the COF any further. A substantial improvement on WSD was achieved by TMPE and PEE at a concentration of 3%, which was more than 30%. The thinning and lubricating ability of polyol esters in SBM was closely related to the molecular structure of the polyol esters. By comparison, the PEE resulted in the best performance. The addition of PEE exhibited the most controllable rheological and filtration properties. Moreover, the tetraester of PEE gave the best protection on the metal surface against applied load and high solid additives of the mud. Overall, PEE has the highest potential to provide a thin mud rheology and lubricant film for the metal drilling pipe and casing.

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Highlights:

- Nonionic polyol esters give thinner rheology and better lubricity for synthetic based drilling mud.
- Polyol esters enhance the filtration properties of drilling mud.
- Increasing the number of the ester group and molecular weight leads to a higher tribology performance.
- PEE is the type of polyol ester that is most suitable for synthetic based mud.