Preparation and evaluation of nonionic polyurethane polymers in improving the rheological properties and filtrate loss control of water base muds

El-Sayed Anter¹, Galal H. Sayed², Mahmoud I. Abdou³, Nasser R. Abdel-Rahman³, Hany E. Ahmed³, Nabel A. Negm³*

¹Egyptian Mud Engineering and Chemicals Company, Cairo, Egypt
²Chemistry Department, Faculty of Science, Ain Shams University, Cairo, Egypt.
³Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt.

Abstract

Polyurethanes are special nonionic polymers which had a wide range of applications nowadays. This work aims to produce different nonionic polyurethanes by the reaction of polyethylene glycols with different molecular weights (4000, 6000, 10,000, and 20,000 g/mole) and toluene diisocyanate. The obtained polyurethanes' structures were determined using molecular weight measurements, Fourier transform infrared spectroscopy (FTIR), and proton nuclear magnetic resonance (¹H-NMR). The effect of the synthesized polyurethanes on the rheological properties of two drilling fluids was studied. The polyurethane polymers were influenced by the filtrate loss of the drilling fluids in comparison to the blank. The results showed that the synthesized polyurethane nonionic derivatives effectively enhanced the shear-thinning non-newtonian drilling fluids following the modified power Law Model (Herschel Bulky Model). The other rheological properties of the formulated drilling water-base muds, including apparent viscosity (AV), plastic viscosity (PV), yield point (YP), and gel strength were improved considerably compared to the commercial formulation.

Key words: Drilling fluids; rheology; filtrate loss; yield point; plastic viscosity; polyurethane

Introduction

Polyurethane (PU) is a nonionic polymer used in many industrial fields such as elastomers, paints, insulators, liquid coatings, foams, elastic fibers, airplane wings, etc. Polyurethanes are: - rigid and flexible foams, ionomers, thermoplastic, binders, and elastomers [1]. The chemical structure of PU has a remarkable role in the physical properties of the polymer. PU is synthesized by the reaction between isocyanate groups and hydroxyl groups, leading to urethane groups (Scheme 1). Some parameters, like the cross-linking ratio, dictate the morphology of the resulted PU. The degree of cross-linking must be lowered by reducing (NCO/OH) ratio to achieve more elastic PU. Hydrophilic polyurethane (HPPU) is a special class of PU that is produced by small changes in the polyol and the degree of cross-linking. HPPUs have the capability to form several polyurethane dispersions in an aqueous medium like wound care products, medical supplies, soap-delivery systems, and a semipermeable membrane in protective fabrics [2, 3].

Drilling fluids or muds are considered one of the most important requirements and key factors for

*Corresponding author e-mail: nabelnegm@hotmail.com
Receive Date: 10 March 2020, Revise Date: 17 March 2020, Accept Date: 31 March 2020
DOI: 10.21608/EJCHEM.2020.25588.2499
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successful drilling processes. They are non-Newtonian fluids with shear thinning characteristics. Drilling fluids are composed of base fluid (water or oil) and a mixture of natural and synthetic chemical components to optimize the drilling process [4, 5]. Drilling fluids have different functions during drilling wells, including removing drilled cuttings from the bottom of the well to the surface, cooling and lubricating the drilling bit, and bottom-hole assembly and improving wellbore stability [6, 7]. Drilling fluids are classified into three main categories; synthetic-based mud (SBM), oil-base mud (OBM), and water-based mud (WBM). The choosing of a proper drilling fluid is convenient with its cost, easy and safe use, and environmentally friendly [4, 8, 9]. Despite SBM and OBM have higher efficiency and safety drilling operation than WBM. WBM is preferable to be used due to it is environmentally safe and cost-effective in comparison to other types [5, 6].

The main properties of water-base drilling muds (WBDF), according to the American Petroleum Institute (API), are the density of the fluid, which is responsible for wellbore stability. The common weighting materials are barium sulphate (BaSO₄), calcium carbonates (CaCO₃), hematite (Fe₂O₃), and galena (PbS) [4, 8, 10]. pH is the 2nd significant property. The alkalinity of WBM is obtained by the addition of sodium or potassium hydroxide. Decreasing pH is achieved by acids addition like citric acid. The preferable pH range in WBM is (9-10.5), promoting polymers to give its maximum tendency as a viscosifier or filtrate loss controlling agents [10, 11]. Viscosity and rheological properties are the 3rd characteristic properties, which are responsible for carrying drilled cuttings during circulation to the surface and suspending them, and weighting materials. Drilling fluids can be described by thixotrophic shear-thinning fluids with a yield stress, which capable to suspend drilled cuttings and weighting materials at low shear rates [8]. When the viscosity or rheological properties of drilling fluids are relatively high, this will result in excessive pump pressure, which badly affects the wellbore stability and may lead to fracturing the formation [6, 8]. On the other hand, when the viscosity or rheological properties (like yield point or gel strength) is relatively low, the slip velocity of cuttings (movement of cuttings towards downhole) will be high and consequently requires high flow pump rates to remove cuttings out of the well. When the circulation stops for any case, the cuttings and weighting materials will settle downhole and cause the sticking of string [12, 13]. The proper rheological properties lead to good hole cleaning and carrying drilled cuttings from downhole and, consequently, improve penetration [14]. Yield point (YP) is clearly defined by the tendency of drilling fluids to carry cuttings from downhole towards the surface to be removed by solids control equipment [15]. The last substantial characteristic property of WBM is the filtrate loss control; the filtrate loss refers to the invasion of base fluid (water or oil) into the pores of the permeable drilled formation by the effect of differential pressure [16].

2. Materials and technique.

The drilling formulations were prepared in two compositions. The first is the blank fluid formulation in the absence (M₀) and in the presence of NaCl (Mₙ). The second is the commercial fluid formulation in the absence (M₀) and the presence of NaCl (Mₙ). Table (1) represents the composition of the different studied formulations.

### Materials

Toluene diisocyanate (TDI); polyethylene glycol with different molecular weights (4000, 6000, 10000, and 20,000 g/mol); methyl ethyl ketone (MEK) obtained from Sigma Aldrich, Germany. Treated bentonite; calcium carbonate (medium grade) and XC-polymer were obtained from NETCO, Oil field supplier's company in El-Ammreya, Egypt. Sodium hydroxide was obtained from El-Naser Chemicals Co., Egypt. Synthetic of Nonionic Polyurethane Polymers

The nonionic polyurethane polymers were prepared (Scheme 2) by reacting toluene diisocyanate (0.125 moles) and polyethylene glycol (0.25 mole of 4000, 6000, 10000, and 20000 g/mole) separately in 2-butene (80 mL) as a solvent in a one-necked flask (500 mL) and the reaction was conducted at 140 °C under reflux for 12 h. The resulted matrix was cooled to room temperature, and the solvent was removed under reduced pressure (1/3 bar) at 40 °C. The afforded polyurethane polymers were washed twice with 2-butene and dried in an oven for complete dryness [17]. The obtained PU polymers were designated as PU₄, PU₆, PU₁₀, and PU₂₀ for polyethylene glycol derivatives of 4000, 6000, 10000, and 20000 g/mole.

### Formulation of drilling fluids

The drilling fluids used in the study were formulated according to Table 1. M₀ and Mₙ were: blank and commercial formulations, respectively, while Mₙ (n=4, 6, 10, 20) were the modified formulations using the prepared PU₄, PU₆, PU₁₀, and PU₂₀ polymers. Mₙ, M₂₅, and M₅₀ were prepared in the presence of NaCl. All components were mixed together using a standard Hamilton Beach high-speed mixer at 1500rpm for 30 minutes to obtain the sodium chloride inhibited mud sample (M₅₅-2₀S).
Table 1: Composition of the studied drilling fluid formulations

<table>
<thead>
<tr>
<th>Component</th>
<th>(M_b)</th>
<th>(M_{bs})</th>
<th>(M_c)</th>
<th>(M_{cs})</th>
<th>(M_n)</th>
<th>(M_{ns})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bentonite (g)/H(_2)O (mL)</td>
<td>109/225</td>
<td>109/175</td>
<td>109/175</td>
<td>109/125</td>
<td>109/175</td>
<td>109/125</td>
</tr>
<tr>
<td>NaOH (g)/H(_2)O (mL)</td>
<td>0.25/25</td>
<td>0.25/25</td>
<td>0.25/25</td>
<td>0.25/25</td>
<td>0.25/25</td>
<td>0.25/25</td>
</tr>
<tr>
<td>CaCO(_3) (g)/H(_2)O (mL)</td>
<td>10.5/50</td>
<td>10.5/50</td>
<td>10.5/50</td>
<td>10.5/50</td>
<td>10.5/50</td>
<td>10.5/50</td>
</tr>
<tr>
<td>Xanthan (g)/H(_2)O (mL)</td>
<td>0.5/25</td>
<td>0.5/25</td>
<td>0.5/25</td>
<td>0.5/25</td>
<td>0.5/25</td>
<td>0.5/25</td>
</tr>
<tr>
<td>NaCl (g)/H(_2)O (mL)</td>
<td>---</td>
<td>17.5/50</td>
<td>---</td>
<td>17.5/50</td>
<td>---</td>
<td>17.5/50</td>
</tr>
<tr>
<td>Starch (g)/H(_2)O (mL)</td>
<td>---</td>
<td>---</td>
<td>5/50</td>
<td>5/50</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>PU(_n) (g)/H(_2)O (mL)</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>5/50</td>
<td>5/50</td>
<td>5/50</td>
</tr>
</tbody>
</table>

**Rheological study**

The rheological properties of the prepared drilling fluid formulations were studied (\(M_{4.20}\)) using the chandler engineering laboratory model (API) Fan V-G meter viscometer (Chan Model 3500) [16-20]. The prepared drilling formulations were thermostated at 25 °C using American Petroleum Institute (API) standard cup. The steady dial readings were recorded at six different dial readings at standard speeds (600, 300, 200, 100, 6 and 3 rpm). The readings were designated as \(\Phi_{600,3}\), and were used to calculate the rheological parameters including: shear rate, shear stress, apparent viscosity, plastic viscosity, yield point, gels strength (10 s and 10 min) and thixotropy, using Equations 1-8 [8, 12, 21, 22]:

- Apparent viscosity \(\mu_a\), \(cp = \Phi_{600}/2\) (1)
- Plastic Viscosity \(\mu_p\), \(cp = \Phi_{600} - \Phi_{300}\) (2)
- Yield Point \(Y_P\), \(lb/100 \text{ ft}^2 = \Phi_{300} - \mu_p\) (3)
- Shear stress \(\tau\), \(lb/100 \text{ ft}^2 = 1065* \Phi\) (4)
- Shear rate \(\gamma\), Sec\(^{-1}\) = 1.7023*\(\omega\) (5)
- G10 s, \(lb/100 \text{ ft}^2 = \Phi_3\) after static for 10 sec. (6)
- G10 min, \(lb/100 \text{ ft}^2 = \Phi_3\) after static for 10 min. (7)
- Thixotropy = G10 min - G10 s (8)

where \(\Phi\): the dial reading \(lb/100 \text{ ft}^2\), \(\omega\): rotor speed (rpm), G 10 sec – G 10 min: highest \(\Phi\); reading (Gel strength) after 10 sec and 10 min, respectively.

**Filtrate loss**

API Filter press apparatus of low pressure-low temperature technique (LP/LT) was used to determine the filtrate loss of the different drilling formulations. The cell was loaded with drilling fluid, and pressure (100 psi) was applied through the cup attached to the nitrogen tank through the backpressure regulator. A graduated cylinder (25 mL) was placed under the support holding the stainless-steel cell for collecting discharged filtrate [18, 23, 24]. The collected filtrate volume was reported after 7.5 min (spurt loss), and after 30 min (total filtrate loss).

**3. Results and Discussion**

The prepared compounds (PU\(_4\), PU\(_6\), PU\(_{10}\), and PU\(_{20}\)) were synthesized by the reaction of toluene diisocyanate and polyethylene glycol with different molecular weights, according to Scheme 1.

![Scheme 1](image)

Scheme 1: Preparation of polyurethane (PU) polymer.

**Characterization of the synthesized compounds**

The prepared polymers were characterized using FTIR, \(^1\)H-NMR spectroscopy, and molecular weight determination.

Molecular weight
The molecular weights of the synthesized nonionic polyurethanes (PU₄, PU₆, PU₁₀, and PU₂₀) were determined using gas chromatography (model HP 5890), provided with a flame ionization detector. The obtained molecular weights were listed in Table 2.

Table 2: Average molecular weights of the synthesized polyurethane polymers (PU₄-2₀)

<table>
<thead>
<tr>
<th>PU</th>
<th>4</th>
<th>6</th>
<th>10</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWt. (g/mole)</td>
<td>40362</td>
<td>60240</td>
<td>100958</td>
<td>20196</td>
</tr>
</tbody>
</table>

It is clear from data in Table 2 that the average molecular weights of the different polymers were in the range of the expected molecular structure and monomer distribution along the polymeric backbones as represented in Scheme 2.

Scheme 2: Reaction of toluene diisocyanate with polyethylene glycol to form polyurethane (PU) polymers.

FTIR spectroscopy
FTIR spectroscopic analysis of the synthesized polyurethane polymer (PU₄) (Figure 1a) showed the following absorption bands: 3447 cm⁻¹ corresponding to stretching of (O-H) groups [25-27]; two overlapped absorption bands at 2887 cm⁻¹ corresponding to symmetric and asymmetric stretching of (C-H) group of ethylene glycol units; 1724 cm⁻¹ corresponding to (C=O) group of the formed amide in urethane group [28, 29]. Figure 1b-d showed the absorption bands of PU₆-₂₀ polyurethane nonionic polymers. PU₆-₂₀ polymers showed the appearance of the characteristic absorption bands of the different functional groups (including: O-H, C-H, and C=O).

Figure 1: FTIR spectra of: a) PU₄, b) PU₆, c) PU₁₀, and d) PU₂₀.

¹H-NMR spectroscopy
Figure 2 represents the ¹H-NMR spectra of the prepared nonionic polyurethane polymer (PU₂₀). PU₂₀ polymer represents the following signals δ (ppm) (Figure 2): 2.2 ppm (s, 3H, Ar-CH₃); 2.5 ppm (s, 6H, CH₃) of DMSO; 3.55 ppm (t, nH, -CH₂CH₂O-); 3.7 ppm (t, 4H, -CH₂CH₂O-CO-NH-Ar); 4.2 ppm (s, 2H, HO-); 4.45 ppm (t, 4H, -CH₂CH₂O-CO-NH-Ar); 7.0, 7.25, 7.5 ppm (Ar-H); 8.9 ppm (s, 2H, -CO-NH-Ar).
Rheological properties of the drilling fluids formulations

The rheological properties of the drilling formulations were studied in the absence and the presence of NaCl, including the following properties: flow behavior, apparent viscosity (AV), plastic viscosity (PV), yield point (YP), gel strength (G10 sec and G10 min), yield point/plastic viscosity (YP/PV), and filtration loss.

Flow behaviour

The flow behaviour of a fluid is defined as the relationship between shear stress (τ) and shear rate (γ). The direct variation between shear rate and shear stress represents Newtonian fluids such as water, alcohol, and light oil. On the other hand, an indirect shear stress shear rate relationship represents non-Newtonian fluids, like drilling fluids. Figure 3a,b represents the variation profile of the shear rate-shear stress of the different drilling fluids in the absence (a) and in the presence (b) of NaCl in their formulation. The nonlinear profiles represent the non-Newtonian behaviors of the different drilling fluids formulations under investigation.

Apparent viscosity (AV)

Apparent viscosity is the shear stress applied to the drilling fluid formulations divided by the shear rate at a constant temperature. During the management, AV is obtained by dividing the shear stress of the drilling formula by 2. Figure 4a-b represents the apparent viscosity values of the different drilling formulations. It is clear from Figure 4a that the lowest AV value was obtained in the case of M_b formulation. M_c formulation showed high AV value due to the presence of starch in its composition. Starch has a swelling tendency in the presence of water, which improves AV value compared to M_b. Addition of the prepared nonionic polyurethane polymers in the chemical composition of the formulated drilling fluids (M_4-20) showed considerable variation in AV values compared to M_b formulation. AV value of M_b formulation was obtained at 13 cP, while the presence of PU_4 as viscosity modifier increased AV value to 14 cP. The addition of PU_6 and PU_10 has gradually increased AV values to 16 and 18 cP. While the addition of PU_20 to the drilling fluid formulation increased AV value considerably to 21

Figure 2: 1HNMR spectra of PU_20.

Figure 3: The relation between shear rate and shear stress for the drilling fluids formulations using the prepared nonionic polyurethane polymers: (a) without NaCl, and (b) in the presence of NaCl.
The gradual increase in AV values of the formulations contains PU$_{4.20}$ additives can be attributed to the gradual increase in the polyethylene glycol chain length (number of ethylene glycol units). The increasing of polyethylene glycol chain length in the prepared polyurethanes increases these compounds’ hydration due to the gradual increase in their interaction by the aqueous medium. The increase in the aqueous medium's interaction is due to the increasing in hydration tendency as the ethylene glycol units increased. The maximum hydration tendency was reported for polyethylene glycol chains of 20000 g/mole. Figure 4b represents the influence of NaCl in addition to the drilling formulations (inhibited formulations). Analyzing data in Figure 4b reveals that NaCl's addition to the different formulations has a minor reducing influence on AV values. Additionally, the sequence of decreasing AV values was similar to AV values in the absence of NaCl in the formulation. The decrease of AV values can be attributed to the decrease in the hydration of polyethylene glycol chains due to the salting-out effect of NaCl on the nonionic species. AV values of M$_{20}$ formulation were the highest and were higher than M$_{c}$.

(b) Figure 4: A comparison between the apparent viscosities (AV) for the drilling fluids formulations using the prepared nonionic polyurethane polymers: a) without NaCl, and b) in the presence of NaCl.

Plastic viscosity (PV)

Plastic viscosity is defined as the resistance of a fluid to flow. PV of drilling fluid can be managed by controlling the size, concentration, and shape of the solids formulating the drilling formulations, and minimizing the liquid phase's viscosity. The lowest PV value is considered to be the best in drilling practice. When PU$_{4}$ was added to the tested drilling formulation M$_{4}$, the PV value was lower than its value for the blank drilling fluid (M$_{b}$). The PV values start to increase gradually with increasing MWt of PU$_{n}$ (PU$_{6.20}$) in the mud samples (M$_{6.20}$), as shown in Figure 5a. Addition of 5% NaCl salt (Figure 5b) to the different formulations increased the PV value comparing to uninhibited formulations (without NaCl). When PU$_{4}$ was added to the tested drilling formulation (M$_{48}$), the PV value was lower than its value for the blank drilling fluid (M$_{b}$). By increasing the MWt for added PU’s, PV value was increased gradually for 5% NaCl inhibited drilling fluids (M$_{48.208}$) Figure 5b.
Figure 5: A comparison between the plastic viscosities (PV) for the drilling fluids formulations using the prepared nonionic polyurethane polymers: a) without NaCl, and b) in the presence of NaCl.

Yield Point (YP)

The yield point (YP) of drilling fluids represents the fluid’s ability to carry out the produced cuttings during the drilling process. The proper and effective YP is required during drilling to provide good hole cleaning and avoid any harmful effect on the ECD (equivalent circulation density) [15]. Figure 6a,b represents the yield point values of the different drilling formulation at 25 °C. Figure 6a shows the YP of the uninhibited formulation and represents the lowest value at 12 Lb/100 ft² for M₄ formula, which contains PU₄. M₆ exhibit YP at 13 Lb/100 ft², while M₁₀ has YP at 16 Lb/100 ft². The presence of PU₆ in M₆ drilling fluid formulation increased YP to be similar to YP of M₆ formulation. The practical improvement in YP of the formulated formulations was started to appear by the addition of PU₁₀ nonionic polyurethane polymer in M₁₀ formula. The maximum improvement was achieved at 22 Lb/100 ft² in the presence of PU₂₀ polymer. As it is clear from Figure 6a, the addition of PU₁₅ and PU₂₀ in the drilling fluid formulations improved YP values of the drilling fluids M₁₀ and M₂₀ than the commercial drilling formulation (M₄). The identical trend in the yield points of the different formulations was observed after inhibiting the drilling formulations (M₄S, M₆S, M₁₀S, and M₂₀S) by the addition of NaCl salt to the formulations.

Figure 6: A comparison between the yield points (YP) for the drilling fluids formulations using the prepared nonionic polyurethane polymers: a) without NaCl, and b) in the presence of NaCl.

Gel strength (G10 sec and G10 min)

Gel strength is referred to as minimum shearing stress required to initiate a slip-wise movement of fluid. Gel strength is representing the measurement of electrochemical forces between drilling fluid’s
component in static conditions. Gel strength is responsible for drilling muds’ ability for suspending drilling fluids components and cuttings \([6, 18]\). Increasing the drilling fluids’ gel strength during the drilling process is required to increase the cleaning and to remove efficiencies of drilling products. The prepared formulations’ gel strength values at G10 sec and G10 min can be divided into two groups compared to the commercial formulation \(M_c\) (Figure 7(a)). The first group includes \(M_4\) and \(M_6\) showed lower gel strength at G10 sec and G10 min than \(M_c\) formulation. The second group includes \(M_{10}\) and \(M_{20}\) formulations, which represent higher gel strength at G10 sec and G10 min than those of \(M_c\). Inhibited drilling formulations by 5% NaCl showed a slight decrease in the gel strength values at G10 sec and drilling fluid. Higher YP/PV ratio indicates that the drilling fluid is shear thinning, which is quickly break gel to thin the drilling fluid when it is moved as the drilling is resumed again \([19]\). Figure 8a,b represents the variation of YP/PV by changing the type of the additives in the drilling fluid formulations either uninhibited (without NaCl) or inhibited (with NaCl). Generally, the addition of the prepared additives (\(PU_4, PU_6,\) and \(PU_{10}\)) lowers YP/PV than the commercial and the commercial and blank formulations \((M_c, M_b)\). Incorporating of \(PU_{20}\) nonionic polyurethane polymer in the drilling fluid formula \(M_{20}\) showed an increase in YP/PV value compared to the other additives.

![Figure 7](image1)

(a)

(b)

Figure 7: A comparison between the gel strength at 10 sec and 10 min for the drilling fluids formulations using the prepared nonionic polyurethane polymers: a) without NaCl, and b) in the presence of NaCl.

Yield Point/Plastic viscosity (YP/PV)
The ratio between the yield point and the plastic viscosity indicates the extent of shear thinning of the
polyurethane polymers: a) without NaCl, and b) in the presence of NaCl.

Filtrate loss control

The filtrate loss is referring to the volume of drilling formulations base fluid, which is invaded into a drilled rock due to the difference between hydrostatic and formation pressures, especially in the overbalance drilling [16]. The filtrate loss control was studied for the blank formulation (M_0) and was found at 13.5 mL. The addition of PU_4 and PU_6 in the drilling fluid formulations M_4 and M_6 increased the filtrate loss to 15 and 14.5 mL, respectively. Increasing the molecular weight of the prepared additives (PU_{10}, PU_{20}) was reduced the filtrate loss comparing to the blank fluid (M_0), as shown in Figure 9a. By the addition of NaCl salt to the drilling formulations, the filtrate loss was increased. A similar observation was reported for M_{4s-20s}, as shown in Figure 9b.

![Filtrate loss control of the drilling fluids formulations using the prepared nonionic polyurethane polymers: a) without NaCl, and b) in the presence of NaCl.](image)

Conclusions

The study presents several nonionic polyurethane polymers which are efficient as additives for water base muds to improve their rheological properties, including apparent viscosity (AV), plastic viscosity (PV), yield point (YP), and gel strength in the presence and in the absence of salts in the medium.

Conflicts of interest

“There are no conflicts to declare”.

References


*Egypt. J. Chem. 63, No. 11 (2020)*


