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## EFFECT OF NON-IONIC POLYMERS ON YIELD STRESS AND KINETIC STRUCTURE OF ALGERIAN BENTONITE USED IN DRILLING FLUIDS

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### Abstract

This paper reports the effect of two polymers on the rheological behavior of Algerian bentonite. This latter was sourced from Mostaganem –M'zila- and was used as drilling fluid in Algerian oil and gas wells. The two evaluated polymers were hydroxyethyl cellulose with a molecular weight of $9.5\times10^5$ g/mol and polyethylene glycol with molecular weight of $6\times10^3$ g/mol and $1\times10^4$ g/mol. Steady-state and dynamic shear rheology measurements were performed on a controlled stress rotational rheometer at a controlled temperature of $25\pm0.1°C$. It was found that all mixtures 'water-bentonite-HEC' and 'water-bentonite-PEG' exhibit shear-thinning behavior and the flow curves could be described by the Herschel-Bulkley (H-B) model. The obtained results show that (HEC) increased the rheological properties of bentonite dispersion such as yield stress and consistency index and deleted the gel time of this dispersion contrary to (PEG), which decreased these rheological properties and increased the gel time. It was also noticed that the rheological behavior of bentonite dispersion enhanced with increasing (PEG) molecular weight.

*Keywords*: non-ionic polymers; drilling fluids; Algerian bentonite; rheological behavior; hydroxyethyl cellulose; polyethylene glycol.

## 1. Introduction

Bentonite represents a very important clay material for a multitude of processes due to the exceptional properties of its dispersions in water [1]. Water-bentonite dispersions are used in different industries including oil and gas industry where these dispersions are used as drilling fluids [2-3]. These drilling fluids are designed to carry out several functions such as to transport cuttings to the surface, to prevent cuttings from sedimentation, to cool and lubricate bits and drill pipes, to minimize friction between formation and drilling equipment, to stabilize walls of the wellbore and to control formation pressure [4-6]. It is true that bentonite-water based drilling fluids are performant, but the high bentonite contents can have detrimental effects on drilling operations such as the reduction of the drilling operation productivity, thick filter cake, potential pipe sticking, and formation damage [7-8]. To overcome these problems, polymer-clay based drilling fluids are normally used [9]. These polymers have low cost, good rheological properties, and scant environmental impact.

In the last decade, it is found that non-ionic polymers can inhibit shale dispersion or clay swelling [10-11]. These non-ionic polymers are used in drilling fluids for different purposes, including building viscosity, reducing fluid loss, stabilizing bentonite dispersions and modifying drilling fluids rheology. Among the non-ionic polymers used in the drilling of oil and gas wells, hydroxyethyl cellulose (HEC), is used primarily for viscosity and fluid-loss-control in drilling and completion fluids [12-13] and polyethylene glycol (PEG), which has good performance concerning shale and gas-hydrate inhibition [14-15]. The addition of these polymers to water-bentonite dispersions affects the rheological behavior of these dispersions. Consequently, it is more important for rheological behavior to control the mixture water-clay-polymer.

Alemdar and Güngör [16], Tunç and Duman [17] and Ebagninin *et al.* [18], have studied the influence of polyethylene glycol of different molecular weight on the rheological behavior of bentonite dispersions. All these studies showed that the kinetic structure of the mixture 'bentonite-PEG', which is a significant property of drilling fluids, did not receive any attention. In addition, those previous studies did not make relationships between the obtained results and their application in the field.

The aim of this article is to investigate the effect of adding different non-ionic polymers to drilling mud sample containing Algerian bentonite followed by a comparison of different changes caused by these polymers. For this purpose, an experimental data from steady state shear rheology are obtained and fitted to the Herschel-Bulkley (H-B) model to study the non-Newtonian behavior of the drilling fluids formulated based on bentonite, (HEC) or (PEG) of different molecular weight over wide shear rate range, from $10^{-3}$ to $10^3$ $s^{-1}$. The knowledge of the (H-B) model rheological parameters is important. (H-B) yield stress data allows mud engineers to predict the minimum force required to initiate fluid flow. Meanwhile, the knowledge of the fluid consistency ($k$) and index flow ($n$), gives drilling engineers information on the type of fluid. The effect of the two non-ionic polymers on the bentonite dispersions kinetic structure is also investigated by measuring the viscoelastic moduli evolution as a function of time, which grants field engineer idea about the gelation time of the mixture bentonite-polymers. To our knowledge, it is the first time that the rheological behavior of the drilling fluid, 'water-bentonite-HEC' is studied.

## 2. Experimental study

### 2.1 Materials

A bentonite sample obtained from an Algerian field (Mostaganem, M'zila) was the constitute material of this study. This bentonite had this chemical composition, which was supplied by ENOF (Algerian Public Company of the Mining Products non-ferrous and useful Substances): 55-65 % $SiO_2$, 12-19 % $Al_2O_3$, 0.20 % $TiO_2$, 1-3.4 % $Fe_2O_3$, 1-3 % $Na_2O$, 1-2 % $CaO$, 0.5-1.18 % $K_2O$ and 2-3.4 % $MgO$. It was confirmed by X-ray fluorescence (XRF) analysis that the major components of the studied bentonite were 60.49 % $SiO_2$, 13.87 % $Al_2O_3$, 3.14 % $Fe_2O_3$, 3.95 % $CaO$, 2.37 % $MgO$, 0.24 % $SO_3$, 1.69 % $K_2O$, 3.54 % $Na_2O$, 0.08 % $P_2O_5$ and 0.29 % $TiO_2$.

To the base bentonite dispersion (3 wt%), two non-ionic polymers were added separately:

- The first polymer was hydroxyethyl cellulose (HEC), a water-soluble polymer considered as cellulose derivatives. Its molecular weight was $9.5×10^5$ g/mol [19], and it was used as an additive to the bentonite dispersions for controlling the rheological behavior of these dispersions. This polymer was supplied from UK Ltd. It was a cellulose ether, which was essentially non-ionic in nature and was widely used as a rheology modifier or stabilizer in drilling, completion and work-over fluids with good environmental acceptability [20]. For drilling fluids application, this linear polymer was used as a viscosifier especially to reduce filtrate volume [13].

-Polyethylene glycol (PEG), a water-soluble polymer of the polyether family, was supplied by Acros Organics. The molecular weight of the studied (PEGs) was $6×10^3$ g/mol and $1×10^4$ g/mol. This polymer was also non-ionic in nature, used principally for inhibiting shale and gas-hydrate in drilling fluids applications [14-15].

### 2.2. Samples preparation

Drilling fluids were formulated as follows: in the first step, a 3 wt% of bentonite powder was immersed slowly in distilled water under magnetic stirring conditions to achieve the best swelling of bentonite and to well disperse these particles of clay in water. After four hours of agitation, (HEC) powder of different concentrations ranged from 0.02 to 0.1 wt% or (PEG) powder of different molecular weight was added to the mixture. The obtained mixture (water-bentonite-HEC or water-bentonite-PEG) was left under magnetic agitation for twenty hours.

## 2.3. Rheological measurements

The rheological measurements were performed on a controlled-stress rheometer (Anton Paar-Physica MCR-301) equipped with coaxial cylinders geometry ($R_e$=14.464 mm, $R_i$=13.325 mm, $R_e$/ $R_i$=1.088, h=39.997 mm) at a controlled temperature of 25±0.1°C.

Before each test, the samples were gently stirred for twenty min; afterward, the samples were carefully loaded to the measuring geometry of the rheometer. In the measurement geometry, samples were subjected also to a preshear of 1000 $s^{-1}$, then left to rest time prior to the measurements because the domain structure of bentonite dispersions is quite sensitive to shear deformation history. In dynamic rheological tests, a thin layer of low-viscosity paraffin oil was used to prevent sample evaporation via covering the free surface of the sample.

The flow curves were obtained by applying an increasing shear stress ramp at 20 s for each stage and were measured at a shear rate ranging from $10^{-3}$ to $10^3$ $s^{-1}$.

The linear viscoelastic properties of the mixture 'water-bentonite-HEC' and 'water-bentonite-PEG' were studied by measuring the evolution of storage (G') and loss (G'') moduli as a function of time for five hours. This time sweep was measured by applying a chosen stress and frequency values equal to 0.15 Pa and 10 rad/s respectively, allowing measurements within the linear viscoelastic region.

## 3. Results and discussion

### 3.1 Steady-state shear rheology of water-bentonite-polymers dispersions

Flow curves extracted from shear stress-shear rate measurements for the bentonite dispersions in the presence of non-ionic polymers are shown in Figure 1 (a and b). On the one hand, it was noticed, that shear stress enhanced with the increase in (HEC) concentration, indicating that higher force was required to start the flow of the fluids.
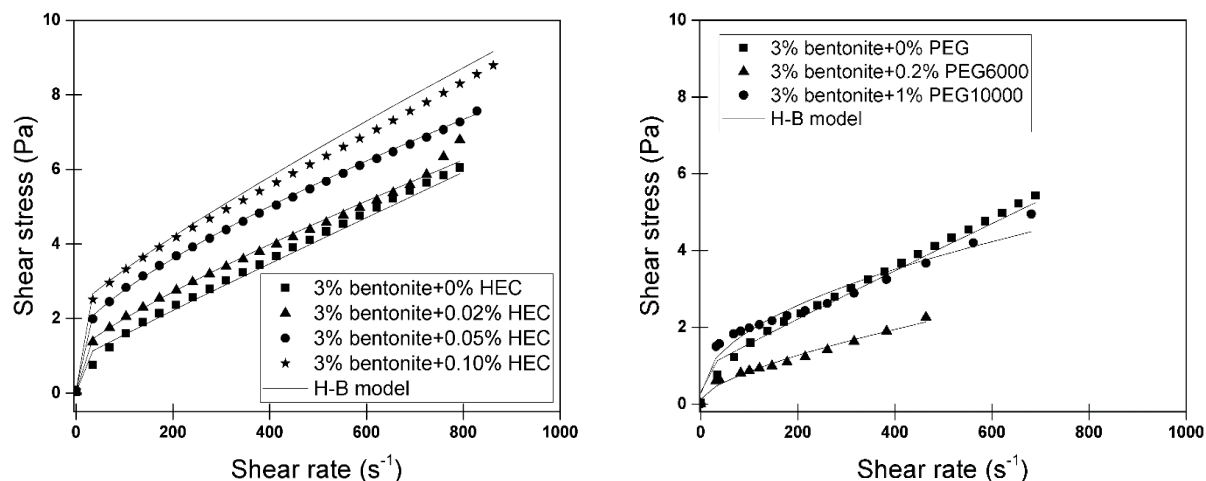


Figure 1. Flow curves of water-bentonite-polymers dispersions predicted by the Herschel-Bulkley model: (a) water-bentonite-HEC (b) water-bentonite-PEG6000 and water-bentonite-PEG10000

This enhancement in shear stress was attributed to the highly entangled (HEC), which could hold bentonite particles and consequently a flexible three-dimensional network was formed throughout the fluid system. On the other hand, it was also noticed that (PEG6000) addition to the bentonite dispersion decreased the shear stress, due to the fact that (PEG) reduced the interactions particle-particle and favored the interactions particle-additive [21]. In the case of (PEG10000), it can be observed that shear stress increased at low shear rate and decreased at a high shear rate, this effect is attributed to the fact that (PEG) acts inversely with increasing its molecular weight. The latter result was in good agreement with that of Ebagninin *et al.* [18],

who studied the effect of different molecular weight (PEG) on the rheological behavior of bentonite dispersions and found that the rheological properties of the mixture increased with increasing (PEG) molecular weight.

Experimental data are analyzed and fitted to the (H-B) model, which has already used to describe the drilling fluids rheological behavior [22-24]. It can be expressed as follows:

$$\tau = \tau c + k \dot{\gamma}^n \qquad\qquad (1)$$

where ($\tau$) is the shear stress (Pa), ($\tau c$) is the yield stress (Pa), ($k$) is the consistency index (Pa.s$^n$), ($\dot{\gamma}$) is the shear rate (s$^{-1}$) and ($n$) is the flow index.

From Table 1, which represents the (H-B) model rheological parameters of the mixture 'water-bentonite-HEC' and 'water-bentonite-PEG', it is clear that all mixtures have shear-thinning behavior with yield stress. In the case of mixtures obtained with (HEC), it was found that yield stress and consistency index increased with increasing in (HEC) concentration inversely to the flow index, which decreased. The increase in yield stress and consistency index was due to entanglements of polymer macromolecules, which were adsorbed onto the clay surface. This adsorption favored either flocculation or steric stabilization of the system 'water-bentonite-HEC' [17]. However, according to Güngör and Ece [25], bridging flocculation was induced at very low polymer concentration.

Table 1. The Herschel-Bulkley model rheological parameters of water-bentonite-HEC and water-bentonite-PEG mixtures

| Drilling fluid formulation | The Herschel-Bulkley model rheological parameters | | | |
|---|---|---|---|---|
| | $\tau_c$ (Pa) | $k$ (Pa.s$^n$) | $n$ (-) | $R^2$ |
| 3% Bentonite | 0.892 | 0.008 | 0.964 | 0.996 |
| 3% Bent+ 0.02% HEC | 1.080 | 0.02 | 0.831 | 0.996 |
| 3% Bent+ 0.05% HEC | 1.510 | 0.042 | 0.738 | 0.997 |
| 3% Bent+ 0.10% HEC | 2.238 | 0.02 | 0.865 | 0.994 |
| 3% Bent+ 0.2% PEG6000 | 0.129 | 0.033 | 0.669 | 0.995 |
| 3% Bent+ 1.0% PEG10000 | 0.272 | 0.167 | 0.495 | 0.993 |

For 'water-bentonite-PEG' dispersions, the results showed that this polymer induced a decrease in yield stress, which can be explained by the fact that the presence of (PEG) decreased the interactions between clay particles, which were rigid and benefited the interactions particle-additive, which were less rigid [26]. This decrease in yield stress was significant in the case of (PEG6000) in despite that the concentration used for (PEG6000) was lower than that used in the case of (PEG10000). This was mainly due to the reinforcement of the bonds between bentonite particles with the increase in polymer molecular weight [18]. Otherwise, the polymer molecules were adsorbed simultaneously on two or more particle surfaces. This phenomenon is accentuated, with the molecular weight where the length of the polymer chains allows the adsorption on more than one particle. This forms what is known as "polymer bridge flocculation", causing an increase in the rheological properties of the colloidal system [27-28].

### 3.2. Dynamic rheology of water-bentonite-polymers dispersions (kinetic structure)

To highlight the effect of (HEC and PEG) polymers on the gelation mechanism of the mixture 'water-bentonite-HEC' and 'water-bentonite-PEG', the evolution of the storage and loss moduli as a function of time for five hours was followed. On the one hand, the results (Fig. 2) showed that (HEC) addition to the basic bentonite dispersion allowed accelerating the mixture gel time, i.e., for the basic bentonite dispersion, it was found that the gel time closed to 109 s (determined by the crossing of modulus, G'=G'' according to Tung and Dynes [29]), whereas this transition from liquid to solid state did not exist for all 'water-bentonite-HEC' mixtures, these mixtures behaved like a gel from the beginning. One can say that (HEC) accelerates the kinetics of aggregation of clay particles. Focusing on these results, it can be concluded that the gel time disappearance by adding (HEC) to the basic bentonite dispersion (gel behavior in

the beginning) was due to the bridging of clay particles, this phenomenon favored the flocculation of the system while increasing (HEC) concentration and consequently mixture rigidity was reinforced.
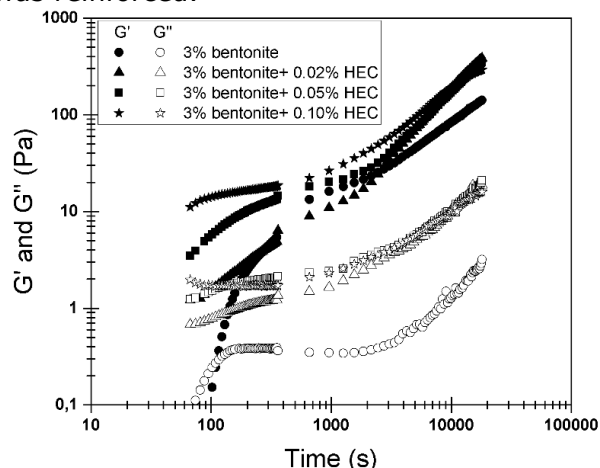


Figure 2. Kinetic structure of the basic bentonite dispersion and the mixture water-bentonite-HEC

On the other hand, the gel time ($T_{gel}$) evolution according to (PEG) molecular weight presented in Table 2 confirmed that (PEG) addition to the bentonite dispersion increased the gel time, which means that the basic dispersion gel time was always inferior to that of the mixture 'water-bentonite-PEG'. Therefore, (PEG) acts inversely to (HEC), it slows down the kinetics of aggregation of clay particles. This result can be explained by the way that (PEG) is adsorbed between one or several clay particles, but this adsorption is done without bridging phenomenon [26]. It can also be noticed that the gel time with (PEG1000) was inferior to that obtained with (PEG6000), which means that increasing

(PEG) molecular weight decreased the gel time. Consequently, one can think that the increase in (PEG) molecular weight allowed the appearance of bridging phenomenon between the clay particles and thereafter flocculation of the system would occur. Indeed, these results are in good agreement with the results obtained in steady state shear rheology

Table 2. Gel time of water-bentonite-PEG mixtures

| Drilling fluid formulation | 3% Bentonite | 3% Bent+ 0.2% PEG6000 | 3% Bent+ 1.0% PEG10000 |
|---|---|---|---|
| $T_{gel}$ (s) | 109 | 123 | 116 |

In summary, non-ionic polymers can act with different mechanisms on the clay particles such as: adsorbing onto the clay surface, intercalate the clay interlayer.

## 4. Conclusions

The rheological properties of water-bentonite-polymer dispersions were investigated using two different non-ionic polymers. The results revealed that (HEC) and (PEG) addition to Mostaganem bentonite dispersions resulted in different changes in the rheological behavior of these dispersions. On the one hand, the presence of (HEC) in drilling fluids formulation allowed yield stress and consistency index to be increased whereas it decreased the flow index. In addition, (HEC) accelerated the kinetics of aggregation of clay particles by favoring system flocculation. Consequently, a small (HEC) amount can replace high bentonite quantity, which avoids high solid content drilling-fluids. On the other hand, (PEG) addition to drilling fluids containing Mostaganem bentonite resulted in decreasing the yield stress and increasing the gel time. Furthermore, an increase in (PEG) molecular weight allowed an increase in the yield stress and a decrease in the gel time. As a consequence, low molecular weight (PEG) are recommended to be added to the drilling fluids when drilling operation is stopped, which allowed decreasing yield stress because this parameter increased significantly in this case due to a gelation mechanism. However, high molecular weight (PEG) is recommended to stabilize or increase slightly drilling fluids rheological properties.

### Symbols

| | | | |
|---|---|---|---|
| H-B | Herschel-Bulkley | K | Consistency index (Pa. $s^n$) |
| HEC | Hydroxyethyl cellulose | N | Flow index |
| PEG | Polyethylene glycol | $\dot{\gamma}$ | Shear rate ($s^{-1}$) |

| G′ | Storage modulus (Pa) | T | Shear stress (Pa) |
| G″ | Loss modulus (Pa) | $\tau_c$ | Yield stress (Pa) |

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