This paper aims at evaluating the flat-rheology performance of a novel associative polymer (AP) on synthetic-based drilling muds (SBM) for deepwater drilling and exploring the mode of action. The associative polymer was synthesized by dimer acid, triethylenetetramine and polyoxyethylene lauramine on the basis of chemical modification in aqueous, and the adjusting rheology performance of AP was evaluated through mud making tests at two densities and oil/water ratios (OWR). The results show that AP performs extremely well on adjust the rheology of SBM within a broad temperature range from 4°C to 65°C, especially for the key rheological parameters of deep-water drilling, such as yield point, gel strengths and 6-rpm reading. Based on a combined use of FT-IR, XRD, particle-size distribution, polarizing microscope, rheology test of emulsions and TEM analysis, the probable flat rheology mechanism was determined due to the specific adsorption structure at interphase. The results indicate that the enhancement of slippage between the dispersed droplets and the layer of organic clay is primarily responsible for the excellent adjusting rheology ability of AP.

**Keywords:** flat-rheology, associative polymer, synthetic-based muds, deep-water drilling, adsorption structure.

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1. Introduction

Deepwater drilling fluids technology is a hot and difficult spot in the field of deep-water drilling all over the world. For the reason that the temperature is below 5 °C in deep water, so the drilling fluids will rapidly cool down and even be gelling. It finally causes the increase of the viscosity, the equivalent circulating density, fluid column pressure and even complicated down-hole problems. So, it is significant to maintain drilling fluids flat-rheology in a broad range of temperature to prevent lost circulation and other accidents [1,2]. Now, synthetic-based drilling fluids are widely used in deep-water drilling for its practicality and reliability.

Van Oort (2004) and Rojas (2007) provided an unique stability of rheological properties of these very special fluids. They pointed out that the «flat-rheology» of the drilling muds remained relatively stable yield point, gel strengths, 6-rpm reading in a large range of temperatures (4 °C ~ 65 °C) [3,4]. The stability of «flat-rheology» drilling muds (FR-SBM) was steadily improved with rheology modifiers improving, and it was applied successfully in the South China sea (2009) and the Gulf of Mexico (2012) [5-7]. However, their research more focused on the improvement of drilling muds system and engineering applications. Robert Schlemmer (2011) [8] had cited the studies on rheology and dynamics of associative polymers in shear and extension by Tripathi [9], which offered a possible view of the energy landscape for the detachment of a terminal hydrophile of an associative polymer. However, little information has been done on the critical rheology modifier, and their studies were lack of systematic research and the targeted, moreover, there were no detailed analysis mechanism of the associative polymer in water in oil (C_{14} liner alpha olefin) emulsions.

This paper focuses on that how to adjust and stabilize the rheology of synthetic-based invert emulsion drilling fluids at low temperature with a novel associative polymer. First, the associative polymer (AP) was synthesized by the method of macromolecular chemical modification. Next, the influence of polymer was researched on the rheological properties of the emulsions at low temperature. Finally, the adsorption characteristics of the polymer between the interfaces of clay and dispersed droplets were analyzed, and then, the probable flat rheology mechanism was deduced after summarizing thoroughly this paper.

2. Experimental

2.1. Materials

Dimer acid (dibasic acid, 90 wt%, monobasic acid, 3 wt%, polybasic acid, 7 wt%) was purchased from Jiangxi aturex industrial Co., Ltd., China. Triethylenetetramine, PEG lauramine, CaO and CaCl_{2}, all of analytical reagent grade, were purchased from Sinopharm Chemical Reagent Co.China. C_{14} liner alpha olefin (LAO) was purchased from Chevron Phillips Chemical Company LLC, USA. Organic Clay, emulsifier and wetting agents, all of industrial grade reagent grade, were purchased from M-I SWACO, USA Barite (325 mesh, BaSO_{4} 95 wt%) was purchased from Shanghai Chemical Reagent Co., China. All the materials were used without further purification.
2.2. Methods
2.2.1. Synthetic method
Dimer acid (10.0 g) were placed in a preweighed reactor equipped with a barrel distilling receiver and a condenser. The fatty acids were heated to 80 °C maintained 15 min, and then triethylenetetramine (2.5 g) were added while dropping time control in 30 min. The contents were heated to 180 °C under a nitrogen blanket while mixing at 200 RPM. The reaction was allowed to continue until the acid value was ≤2.0 (mg KOH/gram). Once the acid value was ≤2.0 (mg KOH/gram), polyoxyethylene lauramine (12 g) was added slowly while mixing for another two hours at 180 °C. The resulting product was poured into storage containers.

2.2.2. Preparation of test samples
2.2.2.1. Preparation of the samples
The organic clay (OC) (2.0 wt%) were added in the emulsions with an oil/water ratio (OWR) of 80:20, and then 1.0% and 2.0 wt% APs were respectively dispersed in 300 g emulsions. The hybrids sheared sufficiently at 10000 rpm for 15 min and then hot rolled at 80 °C for 16 h. The hybrids were centrifuged at 8000 rpm for 10 min after cooling down to room temperature, and then the solid samples were washed with alcohol to eliminate the dissociative AP molecules. The washing and centrifugation processes were repeated several times until the supernatant was clear. Finally, the dark brown solid were dried at 120 °C and ground to fine powders for the analysis of XRD.

2.2.2.2. Preparation of emulsions and muds
1) Preparation of emulsion. The emulsions with 70:30 OWR and 80:20 OWR were prepared. To compare the effect of APs in the emulsions, 2.0 wt% polymers were added respectively in the emulsions. The emulsions were sheared at 10000 rpm for 20 min.
2) Preparation of emulsion with organic clay. 2.0 wt% organic clay were added in the emulsions with two OWR. In order to determine the effect of AP in the emulsion with organic clay, 2.0 wt% polymers were respectively added in the above emulsions. The emulsions were sheared at 10000 rpm for 20 min.
3) Preparation of muds. The emulsions with 80:20 OWR were prepared, and then the auxiliary treatment agents were added successively, such as 2 wt% of the organic clay, 1.5 wt% wetting agent and 1.5 wt% CaO, and then 35 wt% and 85 wt% Barite were added respectively as SBM at two kinds of density. In order to determine the effect of AP in the SBM, 2.0 wt% polymers were respectively added in the above SBM. The emulsions were sheared at 10000 rpm for 20 min.

2.2.3 Mud making Test
2.2.3.1 Rheology measurements
Experiments are performed by the FANN 75 rheometer. with a thermostatic device. Then, the following procedure is applied for each temperature (4 °C ~ 65 °C): The sample is placed in the cell at 4°C and with a constant shearing of 600 r/min, 300 r/min, and 3 r/min, and then stable 5 min at each shear rate every temperature, next record the values at each temperature. The yield point of the sample was calculated from the readings at the rotating speed of 600 rpm and 300 rpm (Φ600 and Φ300) using the following formulas: yield point (YP)=Φ300–Φ600/2. The measurement of gel strength (Gel) was that the sample could be steady shear at 600 rpm for 10 seconds, and then standing for 10 minutes, and then take the highest reading at 3 rpm. The Gel of the sample is calculated using the following formulas: Gel = Φ3/2(10 min) [10].

2.2.3.2. Electrical stability test
Fann23D electrical stability tester (Fann Instrument Company, U.S.A) can measure the stability of the emulsion. The electrode was placed in the test solution, and then the breaking voltage value could be read out from the device, and then repeated 5 times for the average.

2.2.4. Analysis methods
2.2.4.1. Fourier transforms infrared spectroscopy (FT-IR) measurements. Magna-IR 560 infrared spectrometer with the wavenumber range of 4000-400 cm⁻¹ and the resolution of 4 cm⁻¹ was used to analyze the structure of the polymer.

2.2.4.2. Particle-size distribution analysis (PSD analysis)
Malvern Zetasizer Nano ZS was used to analyze the particle size and distribution. The equipment is suitable to the sample with the partial size of 0.6-6000 nm and the concentration range of 0.01 mg/ml ~ 5% w/v.

2.2.4.3 XRD analysis
XRD analysis was performed using D8 Advance Diffractometer (Bruker, Germany) with a voltage of 40 kV, a current of 40 mA and Cu Kα (λ=1.5406 nm) filtered radiation. Diffraction patterns were collected with 20 angle scanning between 2° and 15°.

2.2.4.4 Polarizing microscope
Emulsion with organic clay was selected as sample. First, appropriate amount of sample was dipped with a cell scraper, uniformly spread out on slide and then put on the measuring platform with the temperature of 10°C. After that, the sample was observed by the OPTIPHOT2-POL transmitted light polarizing microscope (Nikon, Japan) and photographed by CoolSN AP 3.3M CCD microscopes dedicated digital camera (Roper Scientific Company LLC, USA). Finally, image processing software ImageJ (National Institutes of Health, USA) was used to analyze and process the image.

2.2.4.5 Transmission electron microscopy (TEM)
TEM analysis were performed using JEM-2100 transmission electron microscope (JEOL, Japan). The samples were prepared by dipping the prepared alcohol suspension onto the amorphous carbon-coated copper TEM grids and dried under an infrared lamp.
3. Results and discussions

3.1. Structural Characterization

Figure 1 is the infra-red spectrogram of the associative polymer, which contains feature region (4000~1300 cm⁻¹) and the fingerprint region (1300 ~ 650 cm⁻¹). Some of the major absorption peaks [11] are: stretching bands of structural -N-H- (3299 cm⁻¹), stretching bands of –CONHR amide I (1650.40 cm⁻¹), II (1548.27 cm⁻¹) and III (1464.81 cm⁻¹) and stretching vibration of C-H (2924.68 cm⁻¹, 2852.69 cm⁻¹). The superimposition of -CH₃ asymmetric deformation vibration peaks and -CH₂ scissor vibration of laminated (1464.81 cm⁻¹ and 1352.37 cm⁻¹). In the fingerprint region, the absorption peak out plane vibration of -CH₂ at 780~720 cm⁻¹, stretching vibration absorption peak of structural -(CH₂)ₙ-(n≥4)(722.18 cm⁻¹), deformation vibration of structural an unsaturated hydrocarbon =C-H(936.85 cm⁻¹, 888.14 cm⁻¹), asymmetric stretching vibration of structural -C-O-C-(1124.67 cm⁻¹). Associative polymer is successfully synthesized by the spectral analysis.

Figure 2 shows the polymer structure. The polymer chain has both -CH₂CH₂O- reactive hydrophilic blocks and amide blocks, and also has long carbon chain hydrophobic group (-C₃H₆₂), and then such a functional group structure consistent with the experimental results of infrared.

3.2. Mud making test

Figure 3 Mud making test results:

a) Rheology of 1.35 g/ml SBM;

b) Rheology of 1.35 g/ml FR-SBM after hotting rolled at 150°C;

c) Rheology of 2.0 g/ml SBM;

d) Rheology of 2.0 g/ml FR-SBM after hotting rolled at 150 °C

Figure 3 shows the rheology of different specific gravity SBM and FR-SBM between 4 °C ~ 65 °C. As can be seen from figure 3a and figure 3c, the YP, Φ6 and Gel of SBM appeared significantly alteration cover a broad temperature range (4 °C ~ 65 °C) and decreased by more than 50%. The rheology shows significantly changes after the associative polymer added from figure 3b and figure 3d, that the certain key rheological parameters are lower than 15% from 4 °C to 65 °C after hotting rolled at 150 °C. That is, the rheology of system remained stable and showed flat rheological properties after adding the polymer treatment agent. Rheological stability for deep-water drilling is very essential. The flat-rheology characteristic allows for a higher viscosity to be maintained without negatively affecting drilling rate or ECD, and ensure that deep-water drilling fluids do not occur gelling in a low temperature environment. Moreover, cuttings carrying capacity and barite suspension properties are greatly improved.

3.3. Rheology and stability of emulsion

It is an effective way of investigating the effect of associative polymer on rheological profiles of emulsions The YP and Gel of emulsions without OC are shown in (fig.4a) and (fig.4b). Apparently, the rheology of the emulsion is not significantly changed within normal dosage (2.0 wt%) of APs, and the YP and Gel maintain at low value (<2). However, the values increase significantly after adding organic clay (fig.4c and 4d). The value of the YP and Gel reduced by more than 50% from 4 °C to 65 °C without APs. By contrast, the YP and Gel values were only reduced by less than 15% from with 2.0 wt% AP added. That is, the APs can be used as a rheology modifier to adjust the cryogenic rheology of synthetic based drilling fluids.

Table 1 shows that the emulsion-breaking voltage does not fall and has no substantial change after
Fig.3. Mud making test results: a) Rheology of 1.35 g/ml SBM; b) Rheology of 1.35 g/ml FR-SBM after hotting rolled at 150 °C; c) Rheology of 2.0 g/ml SBM; d) Rheology of 2.0 g/ml FR-SBM after hotting rolled at 150 °C.

Fig.4. The impact of AP on the rheology of two OWR emulsion: a) yield point of emulsion; b) gel strength of emulsion; c) yield point of emulsion with OC; d) gel strength of emulsion with OC.
adding the associative polymer, which indicates associative polymer does not affect the stability of the emulsion.

Results indicate that the rheology of invert oil-emulsion drilling fluid depend on the organic clay [12]. The emulsion mixer gathers at the interface between two liquids to form a more stable interfacial film with certain strength, which reduces the oil-water interfacial tension, so the aqueous phase droplets disperse in the oil phase as isolated discrete sphericity. In highly dispersed emulsion multiphase system, there is certain affinity between organic clay and droplets with surfactants, so some tiny droplets spontaneously adsorb on the surface of organic clay particles and link some clay particles together to form network structure and even gel structure. Of course, the structure can be destroyed by shearing. In brief, the rheology of invert oil-emulsion drilling fluid depends on the dispersion of the organic clay and the interaction between water droplets and the organic clay [13-15]. When barite is added, the probability of contact between clay particles is reduced, so the structure is more difficult to form. However, barite particles gather together and form a network structure, which enhance YP, Gel and low shear viscosity. That is why emulsions exhibit strong thixotropic in macroscopic view. At low temperature, the interaction between dispersed droplets and the organic clay become stronger and the friction between the solid particles become larger, so the system has a strong thixotropic property without associative polymer. It is believed that the associative polymer, as the key agent, is able to change the characteristics of the interaction between the interfaces, and reduce the thixotropic of emulsion or adjust rheology, to build a «flat-rheology» system.

3.4. X-ray diffraction

Figure 5 XRD patterns of OC/AP hybrids. The percentages in parentheses represent the concentrations of polymer solutions

The XRD patterns of OC/AP hybrids as compared with pristine OC is presented in figure 5. For pristine OC, the XRD pattern displays an interlayer d(001) spacing of 1.30 nm. The interlayer adsorption and polymerization of polymer immediately modified the XRD patterns of OC. For OC/AP hybrid with 1.0 wt% polymer loading, the d(001) spacing increases from 1.30 nm to 1.39 nm. Subtracting the layer thickness of about 0.96 nm, the gallery height are around 0.34 nm and 0.43 nm. Increase of the polymer loading to 2.0 wt% leads to the expansion of d(001) spacing to 1.45 nm.

The gallery height in this case is approximate 0.49 nm, almost equals the thickness of bilayer DHI oligomers plus the length of bond forming between the H atoms of catechol OH and O atoms on the siloxane surfaces. This indicates the AP molecule can be inserted OC molecular layer.

3.5. Particle-size distribution

Figure 6 Particle size distribution of emulsion with organic clay at different polymer dosage (Ultrasound 10 min)

Figure 6 shows the volume distribution of clay particles in the systems after adding different amount of polymer. It shows that D50 (d=458.07 nm) account for 21.8 % without polymer, D50 (d=122.4 nm) account for 24.9% with 1.0 wt% polymer, and D50 (d=68.06 nm) account for 25.6% with 2 wt% polymer was added. That is, the organic clay separated into smaller blocks with the polymer added, and then the acting force between dispersed droplets and the organic clay reduced at continuous shearing force.

Table 1

<table>
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<th>Groups</th>
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<tbody>
<tr>
<td>1</td>
<td>OWR(7:3)</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td>OWR(7:3) + 2.0 wt% AP</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>OWR(8:2)</td>
<td>205</td>
</tr>
<tr>
<td></td>
<td>OWR(8:2) + 2.0 wt% AP</td>
<td>210</td>
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<tr>
<td></td>
<td>OWR(7:3) + 2 wt% OC</td>
<td>350</td>
</tr>
<tr>
<td>2</td>
<td>OWR(7:3) + 2 wt% OC + 2.0 wt% AP</td>
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</tr>
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<td></td>
<td>OWR(8:2) + 2 wt% OC</td>
<td>475</td>
</tr>
<tr>
<td></td>
<td>OWR(8:2) + 2 wt% OC + 2.0 wt% AP</td>
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</table>

Fig.5. XRD patterns of OC/AP hybrids. The percentages in parentheses represent the concentrations of polymer solutions.

Fig.6. Particle size distribution of emulsion with organic clay at different polymer dosage (Ultrasound 10 min)
3.6 Polarizing microscope

Figure 7 is the microscopic photographs through digital image processing by Image-J. Micrograph reveals the connection between the organic clay particles and dispersed water droplets. The black part is dispersed droplets while the gray part is the organic clay particles. As can be seen from (fig.7a), the organic clay particles form a regular cyclic structure which interact with droplets. At low temperatures, the rheology significantly increased because of the greater interaction force between cyclic structure and water droplets. However, the cyclic structure is broken after the addition of the polymer treatment agent (fig.7b). The organic clay particles form the bridge construction with associative polymers, which weaken the interaction between the dispersed droplets and the organic clay.

3.7. Transmission electron microscopy

The TEM images (fig.8) reveal the association modes of APs. Figure 8a shows the dispersion state of the clay particles, and then the cyclic structure between the dispersed droplets and the clay particles can be seen from it. Figure 8b shows the AP molecules are inserted into the clay layers. The molecular chains of APs distribute in the clay layers, and show a disordered state, which is the primary reason to change the drilling fluid rheology.

In the previous report, researchers have proposed the mechanism of organic clay dispersion in polymers during melt processing. They believed that exfoliation of platelets is achieved through a combination of shear and molecular diffusion [16-18]. However our experimental results obtained from the intermediate states of the morphology evolution. Here, we propose a model based on our experimental observations (fig.9). In the synthetic-based drilling fluids system, the active hydrophilic and hydrophobic chains form a multi-point link structure in oil-water interface to replace the strong adsorption structure between the original organic clay particles and dispersed water droplets. Thereby, it is form a layer «weak link» composite structure by polymer molecular film. So, the polymer film adsorption layer form on the surface of solid particles and increase the repulsion between particles weighting agent, which can reduce the friction between solid-solid, and then promote the inter-layer slippage bentonite particles with dispersed droplets. Further more, it can improve the drilling fluid rheology. At low temperature, viscosity and gel strength significantly increase because the activity of the dispersed phase in emulsion decreased and the adsorption force become greater between dispersed droplets and solid particles. The electrical stability experiments show that the «weak link» structure of multi-point adsorption can reduce the force between the interfaces without affecting the stability of emulsion, and maintain emulsion relatively stable in a wide the temperature range.
4. Conclusions

In summary, the associative polymers can significantly improve the rheology of synthetic base drilling muds at low temperature (4 °C ~ 65 °C), especially for barite-weighted muds. The drilling muds have stable yield point, gel strength and 6-rpm reading in the temperature range, which can reduce complex deep-water drilling problems caused by the radical change of drilling fluid viscosity. So, flat rheology drilling muds play a significant effect on the smooth development of deep-sea drilling project. On the other hand, the comprehensive and accurate mechanism of “flat-rheology” cannot be determined so far. In this paper, it is explained qualitatively why the rheology is flat at low temperature through inference and adsorption mechanism of polymer. According to the mechanism have been analyzed above, associative polymer will effectively reduce the specific surface area of organic clay and further reduce the force between the organic clay and dispersed water droplets for its unique amphiphilic structure. It can reduce the joint strength between the clay particles and liquid droplets, and the friction between barite particles and the clay particles. So the slipping and the dispersion between the layer of particles and water droplets can be promoted. It is particularly obvious in deep water to keep flat rheology of drilling fluids at low temperature environment in deepwater drilling. Moreover, the amount of polymer in drilling fluid should be kept within 2~2.5 wt% in order to achieve the best rheology performance.

References

Применение синтетических буровых растворов для глубоководного бурения на основе нового ассоцативного полимера

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Реферат

В статье рассматриваются вопросы регулирования и стабилизации реологических свойств синтетического бурового раствора (СБР) для глубоководного бурения скважин с помощью нового ассоцативного полимера (АП). АП синтезирован путем химической модификации димерной кислоты, триэтилентетрамин и полиоксизитиленового лаурина в водном растворе. Регулирование свойств СБР с помощью АП оценивалось в процессе тестов по приготовлению бурых растворов при двух разных значениях плотности и водонефтяного фактора. Показано, что АП очень хорошо регулирует реологические свойства СБР в широком диапазоне температур от 4 °C до 65 °C, особенно ключевые для глубоководного бурения параметры, такие как предел прочности и статическое напряжение сдвига. Результаты исследований показали, что увеличение скольжения между диспергируемыми частицами и слоем органической символизируется первоочередной хорошего регулирования реологических свойств с помощью АП.

Darın sularda qazma üçün yeni associativ polimer əsaslı sintetik qazma məhlullarının tətbiqi

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(Çin Neft Universiteti)

Xülasa

Maqalədə yeni associativ polimer (AP) vasitəsi ilə quyuların darın sularda qazələması üçün sintetik qazma məhlulünün (SQM) relojə xassalarının tənzimlənməsi və stabilloşdırılması məsələləri nazordan keçirilir. AP dimer tərəf, triətiəntetrəmin və polioksiətiilen laurinin su məhlulunda kimyov modifikasiyasi yolu ilə sintez olunmuşdur. AP vasitəsi SQM-nın xassalarının tənzimlənməsi şxilşin və su-neft faktorun iki müxtəlif göstəricilərdə qazma məhlullarının hazırlanması testlərinin aparılması zaman qiymətlədirlənmədi. Göstərilmişdir ki, AP 4 °C-dan 65 °C-dən geniş temperatur diapazonunda SQM-nin relojə xassalarını - xüsusi də, darın sularda qazma üçün vacib olan mühümli haddi və sürüşmənin statik gərginliyi kimi xassaları çox yaxşı tənzimləyir. Tədqiqatların nəticələri göstərilmişdir ki, relojə xassalarının AP tərəfindən yaxşı tənzimlənməsinin asas səbəbi dispersləmiş hissəciklərə orqanik qılı qatış arasında sürüşmənin artmasıdır.