ABSTRACT: This work attempted to establish the relationship between the dispersion morphology and the viscous flow behavior of clay dispersions in soybean oil fatty acid ethyl ester (FAEE) at 2 and 65 °C. The clays used in this study include raw montmorillonite (Mt) and three kinds of organoclays prepared by ion exchange modification of Mt by cetyltrimethylammonium chloride (OC16), dihexadecyldimethylammonium chloride (ODC16), and trihexadecylmethylammonium chloride (OTC16), respectively. The X-ray diffraction and water contact angle results demonstrated that greater alkyl chain number of surfactants led to greater interlayer space and stronger hydrophobicity of organoclays. Due to the good affinity of the surfactant and FAEE, OC16 exhibited the most stable dispersion in FAEE between 2−65 °C, which resulted in the best flat rheological property. The molecular structures of multiple chain surfactants were quite different from that of FAEE, resulting in weak affinity between organoclays (ODC16 and OTC16) and FAEE. The sheets of ODC16 and OTC16 tended to aggregate at 2 °C, forming a gel structure, thus significantly increasing the low shear rate viscosity (LSRV) and yield stress. At 65 °C, with the expansion of FAEE and the stronger thermal motion of sheets, the dispersions of ODC16 and OTC16 were improved, destroying the original gel structure and resulting in significant decreases in LSRV and yield stress. This study confirmed that stable clay/FAEE dispersions tended to exhibit flat rheology, which could serve as a basis for the application of clay/biodiesel dispersion in deep-water drilling.

1. INTRODUCTION

Drilling fluid is a general term for various circulating fluids during drilling and is always divided into two types according to the continuous phase, the water-based ones and the oil-based ones.1−3 Drilling fluids have a variety of functions including (1) carrying and suspending the cuttings, (2) stabilizing the wellbore and balancing geological pressure, (3) cooling and lubricating the drill bit, and (4) transmitting hydrodynamics, and so forth.4 In recent years, with the development of oil and gas exploitation, the number of drilling operations in deep water has been increasing gradually. Because of the nature of the continuous phase, oil-based drilling fluids exhibit better properties in shale inhibition, hydrate inhibition, lubrication, and reservoir protection than the water-based ones, endowing them with great advantages in deep-water drilling. However, in addition to conventional performance requirements, deep-water drilling places further demands on drilling fluids.

On the one hand, the drilling fluids used in the deep-water process should meet the marine environmental requirements. The environmental performance of the oil-based drilling fluid is mainly determined by the nature of the base oil. The traditional oil-based drilling fluid mainly uses diesel or white oil as the continuous phase. The aromatic content is relatively...
high and thus is not easy to be biodegraded.\textsuperscript{9} For solving this problem, synthetic organic media such as linear alpha olefins (LAO, CH\textsubscript{1}-C\textsubscript{18}, CH\textsubscript{1}=CH\textsubscript{1}-CH=CH\textsubscript{2}, n is 6 to 18) and gas-to-liquids (GTL, straight alkyl line C\textsubscript{10}H\textsubscript{20}, n is 12 to 21) have been gradually used as continuous phases in recent years.\textsuperscript{7} A comparison of the base oils is listed in Table 1. Compared with the traditional ones, these synthetic base oils are of high price, but more environmentally friendly, because they have low aromatic contents, which are easier to be biodegraded.

On the other hand, the special environment during deep-water drilling requires relatively stable rheological properties of drilling fluids over a wide temperature range. The temperatures encountered in each process during deep-water drilling are as follows: mud-line temperature is often lower than 4 °C; flow-line temperature is always between 12–21 °C; and bottomhole circulating temperature is usually higher than 65 °C.\textsuperscript{8} For traditional oil-based drilling fluids, organoclays have long been used as the basic rheologically controlling material, providing necessary rheological properties such as yield point (YP), low shear rate viscosity (LSRV), and gel strength for oil-based drilling fluids to meet the requirements of solids dispersion and wellbore cleaning.\textsuperscript{10} Organoclays are always hydrophobically modified from montmorillonite (Mt), making it easier for them to expand or even exfoliate in the organic phase, forming a card-house network with the lamellar structure originated from the raw Mt. Therefore, organoclays are often used as a tackifier for organic phase dispersions and enhancer for polymer nanocomposites.\textsuperscript{10–16} However, these key rheological properties would exhibit a great increase under the mud-line temperature, resulting in a much higher equivalent circulating density (ECD). As the narrow safe density windows were encountered in deep-water drilling operations, the high rheology of drilling fluids at low temperatures will always cause severe drilling fluid losses or even serious downhole accidents.\textsuperscript{17,18} To solve this problem, the first step is to select a base oil with viscosity that varies slightly with temperature. For example, the synthetic organic phases commonly used in deep-water drilling are just meeting the requirement. Then, a special rheological modifier should be added to interact with organoclays for changing the gel strength variation with temperature.\textsuperscript{19,20} Finally, the drilling fluid will exhibit relatively constant YP, LSRV, and gel strength, namely, the flat-rheology synthetic-based (FRSB) drilling fluid, which has long been successfully applied in the offshore field.

Despite the successful application of the FRSB drilling fluids in offshore drilling, they still have some defects among which the most important are cost and sustainability issues. Although the ocean environmental requirements are fulfilled, the synthetic base oils are always quite expensive and non-renewable.\textsuperscript{21} In contrast, vegetable oils are renewable and often cost-effective. Researchers have explored the use of vegetable oil derivatives such as biodiesel as an alternative to diesel since the early 90s.\textsuperscript{22–24} Some of them also tried to use biodiesel as a new continuous phase for oil-based drilling fluids.\textsuperscript{25,26} Biodiesel is a product of transesterification of vegetable oil with methanol. It is mainly composed of a mixture of fatty acid methyl esters, with much lower viscosity than the original vegetable oil and excellent environmental friendliness (meet the marine environmental requirements). It is feasible to use biodiesel-based drilling fluids in deep-water drilling to have a good control on the rheological properties over a wide temperature range. Additionally, with the development of transgenic technology, the price of transgenic vegetable oil is much lower than that of conventional ones, bringing greater advantages of large-scale production and application of biodiesel. Considering the wide application prospect of biodiesel-based drilling fluids in deep-water drilling, this work tried to study the morphological and rheological temperature responses of organoclay dispersions in fatty acid ethyl ester (FAEE). The organoclays used in this study were prepared by modifying the raw Mt with different quaternary ammonium salt cations. The FAEE was prepared by transesterification of genetically modified soybean oil with absolute ethanol in the laboratory because ethanol is less toxic than methanol.\textsuperscript{27} Also, the longer alcohol chain will provide biodiesel with a better flow performance at low temperatures, which is conducive to deep-water drilling.\textsuperscript{28} Based on the results of morphological and rheological experiments, the relationship between the morphologies and the rheological behaviors of clay/FAEE dispersions over a temperature range of 2–65 °C was explained. This study will be beneficial for the application of organoclay/biodiesel dispersions in deep-water drilling.

2. MATERIALS AND METHODS

2.1. Materials. The genetically modified soybean oil was bought from the Yihai Jiali Golden Dragon Fish grain, Oil and Food Co., Ltd. The anhydrous ethanol (purity ≥99.7%) and sodium hydroxide (powder, purity ≥96%) were bought from the Saan Chemical Technology (Shanghai) Co., Ltd. The raw Mt (cation exchange capacity (CEC) was 120 mmol/100 g) was kindly provided by the Shidabocheng Drilling Fluid Company (Beijing, China), milled, and sieved with a 200 mesh sieve. The X-ray fluorescence (XRF) result of Mt is listed in Table 2. Cationic surfactants (purity ≥90%) used for organoclay preparation are listed in Table 3. All of the surfactants were bought from Uosolf Chemical Industry Co., Ltd. (Jinan, China).

2.2. Preparation of the Soybean Oil Fatty Acid Ethyl Ester. Genetically modified soybean oil (500 mL, about 0.50 mol) was poured into a 1000 mL beaker and preheated at 60 °C for 1 h. Sodium hydroxide powder (2.00 g, 0.05 mol) was added into 138 g (3.00 mol) of anhydrous ethanol and stirred

| Table 1. Physical and Chemical Properties of Base Oils |
|----------------|-----------------|-----------------|------------------|
| base oil       | kinematic viscosity at 40 °C (mm²/s) | density at 20 °C (g/cm³) | aromatic content (wt %) | flash point (closed cup, °C) |
| diesel         | 3.5             | 0.86            | ≥25               | 78                     |
| white oil      | 4.0             | 0.82            | ≥5                | 120                    |
| LAO            | 2.8             | 0.79            | ≤0.05             | 117                    |
| GTL            | 2.7             | 0.78            | ≤0.05             | 112                    |

Table 2. XRF Result of Raw Mt

| component | SiO₂ | Al₂O₃ | MgO | CaO | Fe₂O₃ | K₂O | Na₂O | others | total |
|-----------|------|-------|-----|-----|-------|-----|------|--------|-------|
| content % (w/w) | 76.37 | 14.99 | 2.99 | 2.41 | 1.56 | 0.84 | 0.57 | 0.27 | 100   |
with a magnetic stirrer at 1000 rpm and 60 °C until the sodium hydroxide was totally dissolved. Then, the sodium hydroxide/anhydrous ethanol solution was added into the soybean oil and stirred with a magnetic stirrer at 1000 rpm and 60 °C for 1 h. During the reaction, the beaker was sealed with plastic wrap. Then, the mixture was kept at room temperature for the glycerol to settle at the bottom of the beaker by gravity. After the separation was completed, the bottom glycerin layer was removed and the upper ester layer was moved to a rotary evaporator to remove the residual ethanol at 80 °C and provide the soybean oil fatty acid ethyl ester (FAEE). The component of the obtained product was analyzed by gas chromatography−mass spectrometry (Agilent 7890A-5975C USA), and the results are shown in Table 4.

2.3. Preparation of Organoclays. All the organoclays were prepared in aqueous solution in the following way: 50 g of raw Mt powder was dispersed in 1000 mL of deionized water and stirred at 1000 rpm at 75 °C for 1 h; then, the surfactant (1.0 CEC of the raw Mt) was added into the previous solution and stirred for another 2 h; the final dispersion was settled at room temperature for 24 h; then, the supernantant was removed and the precipitate was filtered with an API medium pressure filter to remove the residual water; the filter cake was collected, dried at 90 °C for 24 h, and milled, and sieved with a 200 mesh sieve, providing the organoclay. Organoclays prepared with C16, DC16, and TC16 were named OC16, ODC16, and OTC16, respectively.

2.4. Preparation of Clay/FAEE Dispersions. Mt (1.00 g) and organoclays modified with different surfactants were added into 50 mL of FAEE (concentration of 0.02 g/mL) and stirred at 1000 rpm and 60 °C for 24 h, and then the dispersions of clays in FAEE were obtained.

2.5. Characterization of Organoclays. The X-ray diffraction (XRD) analyses of the clay powders were recorded by a D8 Focus diffractometer at a current of 40 mA and a voltage of 40 kV with Cu filtered radiation and a scan speed of 1° (2θ)/min. The patterns were collected with 2θ angle scanning from 1 to 10°. The basal spacing of organoclays was calculated by the Bragg equation shown in eq 1.

\[ 2d \sin \theta = n\lambda \]  

where \( d \) is the interlayer space, \( \theta \) is the diffraction angle, \( \lambda \) is the wavelength, and \( n \) is the reflection order. In our test, the \( \lambda \) of X-ray was 1.5406 Å and \( n \) was 1. Before the analysis, XRD samples were packed in standard sample holders and pressed flat.

Water contact angle was determined with the static sessile drop method using a digital camera equipped on a contact angle tester (HARKE-SPCA, Beijing HARKE Testing Equipment Factory). Before the test, the clay powders were placed on a glass sheet and pressed flat.

Thermogravimetric analysis (TGA) curves of the clay powders were obtained using a NETZSCH STA 409 PC (Bayern, Germany) at a heating rate of 10 °C/min and in a temperature range from 30 to 800 °C in a high-purity Ar atmosphere.

2.6. Morphology Study. Clay/FAEE dispersions (50 mL) were added into 100 mL graduated cylinders and settled for 10 h at 2, 25, and 65 °C, observing the total and the gel volume variation with time and temperature. The micrographs of clays dispersed in the FAEE were observed by a Leica DM4 M microscope. The particle size (diameter) distributions of clay dispersions were determined using a Malvern Mastersizer 2000 particle size analyzer.

2.7. Temperature-Controlled Rheology Experiment. The steady shear viscosity test focused on clay/FAEE dispersions was conducted by a HAAKE MARS60 rheometer (Thermo Electron Corporation, Germany) in the rate scan mode. The rheometer was operated under a plate model using a C35 1°/Ti rotor with a sample volume of 0.2 mL and a gap distance of 0.053 mm. The shear rate was controlled from 1000 to 0.1 s⁻¹, and the testing temperatures were 2 and 65 °C.

Table 3. Cationic Surfactants Used for Organoclay Preparation

| Cationic surfactants       | Abbreviation | Chemical structure |
|---------------------------|--------------|--------------------|
| Cetyltrimethylammonium chloride | C16          | ![Chemical structure](image) |
| Dihexadecyldimethylammonium chloride | DC16         | ![Chemical structure](image) |
| Trihexadecylmethylammonium chloride | TC16         | ![Chemical structure](image) |

Table 4. Main Components of FAEE

| FAEE      | corresponding fatty acid | wt % |
|-----------|--------------------------|------|
| ethyl myristate  | C14:0                     | 0.62 |
| ethyl palmitate   | C16:0                     | 13.25|
| ethyl hexadecenoate | C16:1                    | 10.34|
| ethyl stearate     | C18:0                     | 3.34 |
| ethyl oleate       | C18:1                     | 36.29|
| ethyl linoleate    | C18:2                     | 35.86|
| ethyl arachidate   | C20:0                     | 0.13 |
3. RESULTS AND DISCUSSION

3.1. Characterization. 3.1.1. XRD. The XRD patterns of raw Mt and organoclays are presented in Figure 1. The raw Mt exhibited a basal reflection at $2\theta = 5.62^\circ$, corresponding to a basal spacing of 15.69 Å. When modified by cationic surfactants, the reflections exhibited significant changes. On one hand, with the increased number of alkyl chains in surfactants, the basal reflections shifted to smaller angles, indicating the increase in the interlayer space. The basal reflections of OC16, ODC16, and OTC16 shifted to $2\theta = 4.46, 2.09, \text{and } 1.76^\circ$, respectively, corresponding to basal spacing values of 19.79, 42.32, and 50.04 Å. According to previous studies, the phenomenon could be explained by the differences in the molecule size of surfactants inserted into the Mt layers. The greater the number of alkyl chains, the bigger the molecule size of the surfactants and, consequently, the intercalation results in a greater interlayer space. On the other hand, the number of reflections also exhibited an increase with the number of alkyl chains. For raw Mt and OC16, only the 001 reflection could be observed. The 002 and 003 reflections of ODC16 emerged at $2\theta = 4.22$ and 6.33°, corresponding to $d$ values of 20.94 and 13.95 Å (1/2 and 1/3 of the basal spacing, respectively). For OTC16, the 002, 003, and 004 reflections emerged at $2\theta = 3.52, 5.26, \text{and } 7.03^\circ$, corresponding to $d$ values of 25.12, 16.77, and 12.56 Å (1/2, 1/3, and 1/4 of the basal spacing, respectively). According to the literature, it indicated the more ordered internal lattice of ODC16 and OTC16 caused by the surfactants with multiple alkyl chains. As the loading of surfactants was constant (1.0 CEC), a greater number of alkyl chains resulted in a denser and ordered arrangement.

3.1.2. Contact Angle. The contact angles of clays with deionized water are shown in Figure 2. The water contact angle of Mt was $25.61^\circ$, which was similar to the result in the literature, indicating the great hydrophilicity of the raw Mt. The hydrophilicity changed when it was modified with the quaternary ammonium salt cations. As the number of surfactant alkyl chains increased, the water contact angle of organoclays exhibited an increasing trend. The contact angles of OC16, ODC16, and OTC16 increased to 51.04, 74.14, and $88.82^\circ$, respectively. It indicated that the alkyl chain number of surfactants had a great influence on the clay surface property. The greater the alkyl chain number, the stronger the hydrophobicity. On one hand, the phenomenon was determined by the nature of surfactants. The surfactants with more alkyl chains would exhibit stronger hydrophobicity and their adsorption on the layer surface would enlarge the water contact angle of organoclays. On the other hand, with the same addition of surfactants (1.0 CEC), the denser arrangement of alkyl chains would occupy more area of the hydrophilic Mt surface, thus resulting in stronger hydrophobicity.

3.1.3. Thermal Analyses. The TG curves (Figure 3) reflect the thermal stability of clays. According to the literature, the thermal decomposition of organo-montmorillonite mainly occurred in three regions. The first tended to occur before 200 °C, corresponding to the mass loss of adsorbed water. The second one always occurred between 200–500 °C, corresponding to the oxidation and thermal decomposition of the surfactants. The last mass loss region above 500 °C was assigned to the dehydroxylation of Mt. In this test, 9.7% of mass loss was observed in the TG curve of the raw Mt before 200 °C, corresponding to the evaporation of adsorbed water. The mass losses of OC16, ODC16, and OTC16 decreased to 3.2, 2.2, and 1.2% before 200 °C, exhibiting a decreasing tendency with the increasing alkyl chain number. It indicated that the surfactants intercalated into the interlayer space and replaced most of the adsorbed water molecules. As the denser arrangement of DC16 and TC16 alkyl chains would occupy more interlayer space, thus replacing more water, it resulted in lesser mass loss before 200 °C than OC16. The initial degradation temperatures of OC16, ODC16, and OTC16 were 188, 183, and 181 °C, respectively, exhibiting a decreasing tendency with the increasing alkyl chain number. Additionally, the mass losses assigned to surfactant decomposition of OC16, ODC16, and OTC16 were 29.8, 38.8, and 42.8%, respectively, exhibiting an increasing tendency with the increasing alkyl chain number. A greater alkyl chain number caused worse thermal stability of organoclay. Several literature reports mentioned that the Mt layers would provide protection for the intercalated surfactant molecules, slowing down their thermal decomposition. As the greater alkyl chain number would result in a greater interlayer space of organoclays, it would be easier to expose the surfactants to the air; thus, they are easier to be decomposed.

3.2. Morphology. 3.2.1. Macromorphology. Gel formation of organoclays in base oil plays a necessary role in controlling the rheological properties of oil-based drilling fluids. The gel volumes of Mt and organoclays in FAEE are...
shown in Figure 4. The fresh dispersions were homogeneous with a gel volume of 50 mL (0 min). Mt exhibited the fastest sinking in FAEE, resulting in a rapid decline in the gel volume. After settling for 120 min, the reduction in the gel volume significantly slowed down and the final gel volume at 600 min was 11 mL. Compared with Mt, the sedimentation rates of organoclays in FAEE were significantly slower, showing better dispersion stability and greater gel volume. OC16 did not sink when it was left standing for 240 min, exhibiting the best settlement stability, and the gel volume at 600 min was 42 mL. ODC16 and OTC16 presented faster sinking and less gel volume than OC16. ODC16 had a gel volume of 24 mL at 600 min and that of OTC16 was 23 mL. According to the results, the organoclay modified by surfactants with single 16 carbon alkyl chain exhibited better dispersion in FAEE than that modified by surfactants with double and triple 16 carbon alkyl chains. It was in contrast to the results in the literature that organo-montmorillonite modified by surfactants with double 18 carbon alkyl chains exhibited a better dispersion state in the No. 5 white oil than that modified by surfactants with single 18 carbon alkyl chain. Although the swelling mechanism of organoclay in organic solvents is still not clearly understood, many literature reports pointed out that the dispersion of organoclay in organic solvents is highly dependent on parameters including the interaction between the surfactant and solvent, polarity of solvent, and duration of shearing. In this study, the duration of shearing was fixed. The base oil FAEE was mainly a mixture of 16 carbon and 18 carbon fatty acid ethyl esters and thus had stronger polarity than white oil (mixture of saturated alkanes). Compared with DC16 and TC16, the carbon chain structure of surfactant C16 was closest.
to that of FAEE; thus, it was more compatible. Also, due to the
looser arrangement of C16 molecules on the surface of Mt, a
more hydrophilic surface was retained in OC16 than those in
ODC16 and OTC16, prospectively exhibiting a greater
interaction with FAEE molecules.

To study the effect of temperature on the clay dispersions,
the samples were settled at 2 and 65 °C for 10 h and the
changes of total and gel volumes with temperature were
observed. As shown in Figure 5, the temperature affected both
the total and gel volumes of the clay dispersions. On one hand,
the total volumes of dispersions decreased at 2 °C while they
increased at 65 °C. The range of the total volume with
temperature was not affected by the kind of clay, indicating
that it was mainly determined by the nature of the FAEE. The
phenomenon might be explained by the thermal expansion and
cold contraction of FAEE molecules. At 2 °C, the carbon
chains of FAEE molecules shrunk, decreasing the distance
between molecules and resulting in a decrease in the total
volume. At 65 °C, the carbon chains of FAEE molecules were
stretched, enlarging the molecule distance and resulting in an
increase in the total volume. On the other hand, the gel
volume, which was mainly dependent on the dispersion state of
clay particles in FAEE, also exhibited a decrease at 2 °C and an
increase at 65 °C. The possible reasons are as follows: the
thermal motion of clay particles at 2 °C weakened, coupled
with the effect of the shrinking FAEE volume, and the diffusion
of clay particles was hindered. Conversely, at 65 °C, both the
stronger particle thermal motion and expanded FAEE volume
were beneficial to the particle diffusion, resulting in a greater
gel volume. It could be observed that the gel volume ranges of
ODC16 and OTC16 with temperature were greater than those
of Mt and OC16, indicating the greater impaction of
temperature change on their dispersion state.

3.2.2. Micromorphology. The optical micrographs and
particle size distributions of the clay dispersions are shown in
Figures 6 and 7. The clays modified with different surfactants
exhibited different microstructures and particle size distribu-
tions when dispersed in FAEE. In the Mt dispersion (Figure
6a), many large particles were observed to coexist with smaller
ones. The average particle size was 35.12 μm, and the biggest ones even
exceeded 100 μm. It might exhibit such behavior because of
the strong hydrophilic Mt surface and great amount of
interlayer-adsorbed water, which made it hard for the FAEE
molecules to infiltrate into the gallery to swell Mt particles. As
a result, the dispersion of Mt mainly depended on the
mechanical agitation, which was hard to disperse completely.
When modified with surfactants, the alkyl chain number had a great effect on the microscopic dispersion state of organoclays. The OC16 was most evenly dispersed (Figure 6b) because of the better affinity of C16 with FAEE and the polar interaction between OC16 sheets and FAEE molecules. The particle size of OC16 displayed a comparatively narrow distribution with an average particle size of 3.58 μm. The particle size distributions of ODC16 and OTC16 were almost the same, both exhibiting a narrow distribution with average particle sizes of 6.15 and 6.37 μm, respectively. It indicated that ODC16 and OTC16 were swollen in FAEE. However, different from OC16, ODC16 and OTC16 were not uniformly dispersed in FAEE but tended to aggregate and form a network. It might be due to the lower compatibility of DC16 and TC16 with FAEE molecules and the less polarity of ODC16 and OTC16 sheets, making it hard for ODC16 and OTC16 to interact with FAEE molecules.

**3.3. Rheological Properties at Different Temperatures.** The low shear rate viscosity (LSRV) and yield stress are the most critical parameters for the evaluation of the abilities of solid suspension and wellbore cleaning of drilling fluids. These two rheological properties are mainly determined by the network strength formed by clay particles, which would be mainly affected by the clay concentration, the interaction between clay and the continuous phase, and the concentration of polar components. In this work, all the clay concentrations were fixed at 2.0 wt % and no other polar components existed in the dispersions to study the effect of clay morphology on LSRV and yield stress variation between 2−65 °C. The apparent viscosity/shear rate behaviors of clay dispersions at 2 and 65 °C are presented in Figure 8. The pure FAEE exhibited Newtonian-like flow behaviors at both 2 and 65 °C. When added with clays, all the dispersions exhibited a shear-thinning behavior at 2 °C, responding to non-Newtonian flow behaviors deriving from the interaction between clay particles. With the temperature increased to 65 °C, the apparent viscosity of the dispersions experienced significant changes. As with FAEE, dispersion of Mt exhibited a Newtonian-like flow behavior, indicating the disappearance of particle interaction. The apparent viscosity values of OC16, ODC16, and OTC16 were almost identical and maintained a shear-thinning behavior. In deep-water drilling fluid technology, the change of low shear rate viscosity with temperature is also one of the most important indicators for determining fluid rheology. Taking the viscosity of dispersions at 0.1 s⁻¹ as an example (Table 5), the viscosity of the OC16 dispersion at

![Figure 7](https://i.imgur.com/3Q5Q5Q5.png)

**Figure 7.** Particle size distributions of clay/FAEE dispersions

![Figure 8](https://i.imgur.com/3Q5Q5Q5.png)

**Figure 8.** Apparent viscosity/shear rate behaviors of clay dispersions at (a) 2 °C and (b) 65 °C.

| clay | temperature (°C) | viscosity at 0.1 s⁻¹/mPa·s | ratio of 2 °C/65 °C |
|------|------------------|----------------------------|-------------------|
| Mt   | 2                | 1369.93                    | 2.694             |
|      | 65               | 50.86                      |                   |
| OC16 | 2                | 667.02                     | 1.57              |
|      | 65               | 425.62                     |                   |
| ODC16| 2                | 2725.68                    | 6.50              |
|      | 65               | 419.39                     |                   |
| OTC16| 2                | 7830.33                    | 18.89             |
|      | 65               | 414.52                     |                   |

0.1 s⁻¹ was the lowest at 2 °C and the highest at 65 °C and ended with the smallest viscosity ratio of 2 °C/65 °C (1.57). As a result, the low shear rate viscosity of OC16 dispersion varied minimally with temperature, indicating the relatively stable dispersion state of OC16 in the temperature range of 2−
However, the LSRV of other three clay dispersions exhibited a significant change with the temperature, corresponding to the great effect of temperature change on their dispersion state. These results were consistent with those in section 3.2.1.

The shear stress/shear rate behaviors of clay dispersions at 2 and 65 °C are shown in Figure 9. Based on the rheological data, the Herschel–Bulkley model was used to determine the yield stress of each sample, as shown in eq 2.

\[
\tau = \tau_0 + k\gamma^n
\]

where \(\tau\) is the shear stress, \(\tau_0\) is the Herschel–Bulkley yield stress (it mainly reflects the strength of the internal gel network during the flow of the drilling fluid), \(k\) is the consistency index and \(n\) is the flow index. The Herschel–Bulkley model parameters of all the samples are presented in Table 6. The Herschel–Bulkley model fitted all the experimental results fairly well (\(R^2 > 0.9\)). At 2 °C, the yield stress (\(\tau_0\)) of OC16 dispersion was almost the same with that of Mt. With the increase in the surfactant’s alkyl chain number, the yield stress exhibited a significant increase, indicating the formation of greater network strength by the organoclay particles. When the temperature increased to 65 °C, the yield stress values of Mt, ODC16, and OTC16 dispersions decreased to 0.0254, 0.0256, and 0.0372 Pa, respectively, and the ratios at 2 °C were 6.45, 21.95, and 21.47. It indicated that the network formed by clay particles weakened under 65 °C. The yield stress of the OC16 dispersion was 0.0544 Pa, which is the largest at 65 °C. The 2 °C/65 °C yield stress ratio of the OC16 dispersion was only 2.92, exhibiting the best temperature stability. Traditional oil-based drilling fluids are always focusing on the value of yield stress, determining whether the drilling fluid has sufficient abilities of solid suspension and wellbore cleaning. However, in deep-water drilling, the stability of yield stress over a wide temperature range (always between 4–65 °C) is more important because it will greatly affect the ECD, the key to determine the success of offshore drilling operations. Therefore, deep-water drilling is more inclined to optimize the base slurry (organoclay dispersion) with stable yield stress with temperature change to ensure the controllability of ECD. When the yield stress is insufficient to meet the requirements of solid dispersion and wellbore cleaning, it would be enhanced with a rheological modifier such as a dimer fatty acid amide.41

The rheological results confirmed that the OC16 dispersion exhibited the best flat rheology property. In comparison, the LSRV and yield stress of the other three, especially ODC16 and OTC16 dispersions, exhibited significant temperature sensitivity.

### 3.4. Temperature Influence Mechanism

Based on the former results, the relationship between the morphology and rheological properties of clay dispersions between 2–65 °C was established, as graphically explained in Figure 10. For Mt, the small interlayer space (no surfactant intercalation) and strong hydrophilic properties prevented the intercalation of FAEE molecules, thus leading to a poor expansion and dispersion of the sheets. As a result, big particle size and small particle amount existed in the Mt dispersions. At 2 °C, the

| Clay  | Temperature (°C) | \(\tau_0\) (Pa) | \(k\) (Pa·s) | \(n\) | \(R^2\) |
|-------|-----------------|----------------|-------------|------|--------|
| Mt    | 2               | 0.164          | 0.0194      | 0.911 | 0.9991 |
|       | 65              | 0.0254         | 0.0026      | 1.006 | 0.9995 |
| OC16  | 2               | 0.159          | 0.0222      | 0.863 | 0.9994 |
|       | 65              | 0.0544         | 0.00433     | 0.956 | 0.9989 |
| ODC16 | 2               | 0.562          | 0.00123     | 1.192 | 0.9737 |
|       | 65              | 0.0256         | 0.00346     | 0.962 | 0.9995 |
| OTC16 | 2               | 0.799          | 0.00416     | 1.110 | 0.9908 |
|       | 65              | 0.0372         | 0.00182     | 1.016 | 0.9992 |

Figure 9. Shear stress/shear rate behaviors of clay dispersions at (a) 2 °C and (b) 65 °C.

Figure 10. Microstructure variations with temperature in clay/FAEE dispersions.
particles tend to aggregate and form a network, exhibiting a non-Newtonian flow behavior during the shearing process. When temperature was increased to 65 °C, the stronger thermal motion of particles and the expansion of the continuous phase led to a greater particle spacing, destroying the origin network and exhibiting a Newtonian-like flow behavior. The organoclays exhibited better swelling in FAEE than in Mt. However, their dispersion states were greatly affected by the number of surfactant alkyl chains. The molecular structure of C16 was close to that of FAEE and thus had higher compatibility. In addition, the loose arrangement of C16 alkyl chains on the Mt surface occupied a less hydrophilic area, and thus, the sheets of OC16 exhibited stronger polarity than the other two organoclays and interacted much easier with FAEE molecules. As a result, OC16 was highly dispersed in FAEE, which would not be significantly changed by the thermal motion of sheets and the volume of FAEE variation caused by temperature changes. Therefore, temperature was shown to have a less effect on the LSRV and yield stress of OC16/FAEE dispersions. For ODC16 and OTC16, the greater interlayer space and hydrophobicity allowed the penetration of FAEE molecules into the galleries and thus could result in swelling in the base oil. However, due to the denser arrangement of alkyl chains and the difference between the molecular structures of surfactant and FAEE, the affinities of ODC16 and OTC16 to FAEE were limited. At low temperatures, the swollen sheets tended to aggregate and form a gel structure, with LSRV and yield stress much greater than those of Mt and OC16 dispersions. As the temperature increased to 65 °C, the gel structure broke up due to the dispersion of sheets, which was promoted by the stronger thermal motion of layers and the expansion of FAEE. The LSRV and yield stress were close to those of OC16 dispersion due to their similar dispersion states. As a result, the dispersions of ODC16 and OTC16 were more sensitive to temperature change than that of OC16.

4. CONCLUSIONS

In this work, three kinds of organoclays including OC16, ODC16, and OTC16 were prepared by modifying Mt with different types quaternary ammonium salt cations. Then, the effects of surfactant types on the interlayer spacing, hydrophobicity, and thermal stability of organoclays were characterized by XRD, contact angle, and TGA. The continuous phase FAEE was prepared by transesterification of transgenic soybean oil with ethanol. Then, the morphological differences of Mt and organoclays in FAEE dispersions and their effects on the viscous flow behaviors in the temperature range of 2–65 °C were studied. For the raw Mt, the small interlayer space and strong hydrophilicity made it difficult for FAEE molecules to penetrate the interlayer, preventing the swelling and dispersion of the sheets. At 2 °C, the big Mt particles tend to aggregate and form a network, leading to a non-Newtonian flow behavior and exhibiting yield stress. The network was destroyed at 65 °C because of the promotion of particle dispersion due to strong thermal motion and FAEE volume expansion. As a result, the Mt/FAEE dispersion exhibited a Newtonian-like flow behavior at 65 °C. When modified with quaternary ammonium salt cations, the swelling and dispersion of organoclays in FAEE were significantly improved. However, their dispersion states at different temperatures were greatly influenced by the alkyl chain number of the surfactants. The OC16 exhibited the most stable dispersion due to the high compatibility of C16 with FAEE molecules and the greater polar surface. The LSRV and yield stress of OC16 dispersion varied the least between 2–65 °C, exhibiting the best flat rheology. With the increase in the alkyl chain number, the affinity of the surfactants and FAEE molecule weakened. In addition, the denser arrangement of alkyl chains led to less polar regions on the surface of organoclays. Therefore, the dispersions of ODC16 and OTC16 were less stable and more sensitive to temperature changes. At low temperatures, the sheets of ODC16 and OTC16 tended to aggregate and form a stronger network, thus the LSRV and yield stress exhibited a significant increase, which were much greater than those of OC16. As the temperature increased, the network broke up due to the strong thermal motion and FAEE volume expansion. As a result, ODC16 and OTC16 exhibited similar dispersion states to OC16 in FAEE, with their LSRV and yield stress close to those of OC16. In summary, the higher the degree of affinity between the clay surface and the continuous phase, the better the dispersion stability and the less the influence of temperature changes on rheological properties.

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Notes
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■ REFERENCES

(1) Huang, X.; Jiang, G.; He, Y.; An, Y.; Zhang, S. Improvement of rheological properties of invert drilling fluids by enhancing interactions of water droplets using hydrogen bonding linker. *Colloids Surf., A* 2016, *506*, 467–475.

(2) Sun, J.; Huang, X.; Jiang, G.; Lyu, K.; Liu, J.; Dai, Z. Development of key additives for organoclay-free oil-based drilling mud and system performance evaluation. *Pet. Explor. Dev.* 2018, *45*, 764–769.

(3) He, Y.; Jiang, G.; Deng, Z.; Liu, F.; Peng, S.; Ni, X.; Shi, Y.; Cui, W. Polyhydroxy gemini surfactant as a mechano-responsive rheology modifier for inverted emulsion drilling fluid. *RSC Adv.* 2018, *8*, 342–353.
Hermoso, J.; Martínez-Boza, F.; Gallegos, C. Influence of viscosity modifier nature and concentration on the viscous flow behaviour of oil-based drilling fluids at high pressure. *Appl. Clay Sci.* 2014, 87, 14–21.

Rocha, L. A. S.; Junqueira, P.; Roque, J. L. Overcoming Deep and Ultra Deepwater Drilling Challenges. In *Offshore Technology Conference*; Offshore Technology Conference, 2003, OTC-15233. DOI: 10.4043/15233-ms.

Bastidas, H. A. N.; Perez, J. S. C.; Castellanos, C. V. Development of an Environmentally Friendly Oil Based Drilling Fluid Using Castor Oil with Polar Activator and In Presence of Strong Bases Lime. In *SPE Latin America and Caribbean Petroleum Engineering Conference*; Society of Petroleum Engineers, 2017. DOI: 10.2118/185451-ms.

Steve Young, J. F., John Lee and Ole Iacob Prebensen. A New Generation of Flat Rheology Invert Drilling Fluids. In *SPE Oil and Gas India Conference and Exhibition*; Society of Petroleum Engineers, 2012. SPE-154682. DOI: 10.2118/154682-ms.

Zamora, M.; Brousard, P. N.; Stephens, M. P. The Top 10 Mud-Related Concerns in Deepwater Drilling Operations. In *Proceedings of SPE International Petroleum Conference and Exhibition in Mexico*; Society of Petroleum Engineers, 2000. SPE 59019. DOI: 10.2523/59019-ms.

Zhuang, G.; Zhang, Z.; Yang, H.; Tan, J. Structures and rheological properties of organo-sepiolite in oil-based drilling fluids. *Appl. Clay Sci.* 2018, 154, 43–51.

Ma, L.; Zhu, Y.; Feng, P.; Song, G.; Huang, Y.; Liu, H.; Zhang, J.; Fan, J.; Hou, H.; Guo, Z. Reinforcing carbon fiber epoxy composites with triazine derivatives functionalized graphene oxide modified sizing agent. *Composites, Part B* 2019, 176, 107078.

Zhang, Y.; Shao, Q.; Zhao, B.; Zhang, B.; Murugdoss, V.; Wu, S.; Ding, T.; Guo, Z. Facile bioactive yeast cell templated synthesis of laser stealth antimony doped tin oxide hollow microspheres. *Colloids Surf., A* 2019, 583, 123965.

Zhu, G.; Cui, X.; Zhang, Y.; Chen, S.; Dong, M.; Liu, H.; Shao, Q.; Ding, T.; Wu, S.; Guo, Z. Poly (vinyl butyral)/Graphene oxide/poly (methylhydrosiloxane) nanocomposite coating for improved aluminum alloy anticorrosion. *Polymer* 2019, 172, 415–422.

Gong, X.; Liu, Y.; Wang, Y.; Xie, Z.; Dong, Q.; Dong, M.; Liu, H.; Shao, Q.; Lu, N.; Murugdoss, V.; Ding, T.; Guo, Z. Amino graphene oxide/dopamine modified aramid fibers: Preparation, epoxy nanocomposites and property analysis. *Polymer* 2019, 168, 131–137.

Jiang, D.; Wang, Y.; Li, B.; Sun, C.; Wu, Z.; Yan, H.; Xing, L.; Qi, S.; Li, Y.; Liu, H.; Xie, W.; Wang, X.; Ding, T.; Guo, Z. Flexible Sandwich Structural Strain Sensor Based on Silver Nanowires Decorated with Self-Healing Substrate. *Macromol. Mater. Eng.* 2019, 1900074.

Lou, C.; Jing, T.; Tian, J.; Zheng, Y.; Zhang, J.; Dong, M.; Wang, C.; Hou, C.; Fan, J.; Guo, Z. 3-Dimensional graphene/CuFe3O4 composites: Immobilized laccase electrodes for detecting bisphenol A. *J. Mater. Res.* 2019, 34, 2964–2975.

Zhang, Y.; An, Y.; Wu, L.; Chen, H.; Li, Z.; Dou, H.; Murugdoss, V.; Fan, J.; Zhang, X.; Mai, X.; Guo, Z. Metal-free energy storage systems: combining batteries with capacitors based on a methylene blue functionalized graphene cathode. *J. Mater. Chem. A* 2019, 7, 19668–19675.

Gandelman, R. A.; Leal, R. A. F.; Gonçalves, J. T.; Aragão, A. F. L.; Lomba, R. F.; Martins, A. L. Study on Gelation and Freezing Properties Comparison of Different Polyetheramines in Water-Based Drilling Fluids. In *SPE/IADC Drilling Conference*; Society of Petroleum Engineers, 2007. SPE-105881-MS. DOI: 10.2523/105881-ms.

Rojas, J. C.; Daughtery, B.; Renfrow, D.; Bern, P.; Greene, B.; Irby, R.; Gusler, B.; Grover, P.; Trotter, N.; Dye, B. Increased Deepwater Drilling Performance Using Constant Rheology Synthetic-based Mud. In *AADE National Technical Conference and Exhibition*; American Association of Drilling Engineers, 2007, AADE-07-NTCE-20.

Rojas, J. C.; Bern, P.; Platt, L. J.; Romo, L.; Greene, B.; Irby, R.; Trotter, N.; Dye, B.; Sharma, N. New Constant-Rheology Synthetic-Based Fluid Reduces Downhole Losses in Deepwater Environments. *SPE Annual Technical Conference and Exhibition*; Society of Petroleum Engineers, 2007. SPE-109586. DOI: 10.2118/109586-ms.

Helwani, Z.; Othman, M. R.; Aziz, N.; Fernandez, W. J. N.; Kim, J. Technologies for production of biodiesel focusing on green catalytic techniques: A review. *Fuel Proc. Technol.* 2009, 90, 1502–1514.

Ma, F.; Hanna, M. A. Biodiesel production: a review. *Bioresour. Technol.* 1999, 70, 1–15.

Pereira, R. G.; Oliveira, C. D.; Oliveira, J. L.; Oliveira, P. C. P.; Fellows, C. E.; Piamba, O. E. Exhaust emissions and electric energy generation in a stationary engine using blends of diesel and soybean biodiesel. *Renewable Energy* 2007, 32, 2453–2460.

Kwanchareon, P.; Luengnaruemitchai, A.; Jai-In, S. Solubility of a diesel–biodiesel–ethanol blend, its fuel properties, and its emission characteristics from diesel engine. *Fuel* 2007, 86, 1053–1061.

Sulaimon, A. A.; Adeyemi, B. J.; Rahimi, M. Performance enhancement of selected vegetable oil as base fluid for drilling HPHT formation. *J. Pet. Sci. Eng.* 2017, 152, 49–59.

Said, M. M.; El-Sayed, A.-A. H. The use of palm oil fatty acid methyl ester as a base fluid for a flat rheology high-performance drilling fluid. *J. Pet. Sci. Eng.* 2018, 166, 969–983.

Zhang, Y.; Zheng, Y.; Yang, S.; Guo, Z.; Zhang, T.; Song, H.; Shao, Q. Esterification synthesis of ethyl oleate catalyzed by Bronsted acid–surfactant-combined ionic liquid. *Green Chem. Lett. Rev.* 2017, 10, 202–209.

Wang, Y.; Ma, S.; Zhao, M.; Kuang, L.; Nie, J.; Riley, W. W. Improving the cold flow properties of biodiesel from waste cooking oil by surfactants and detergent fractionation. *Fuels* 2011, 90, 1036–1040.

Zhuang, G.; Zhang, H.; Wu, H.; Zhang, Z.; Liao, L. Influence of the surfactants’ nature on the structure and rheology of organo-montmorillonite in oil-based drilling fluids. *Appl. Clay Sci.* 2017, 135, 244–252.

Zhuang, G.; Zhang, Z.; Jaber, M.; Gao, J.; Peng, S. Comparative study on the structures and properties of organo-montmorillonite and organo-polyglycerite in oil-based drilling fluids. *J. Ind. Eng. Chem.* 2019, 56, 248–257.

Liu, T.; Lees, G. C.; Rothon, R. N.; Wilkinson, A. N.; Limpanapittayaporn, P. Evaluation of an alternative modification route for layered silicates and synthesis of poly(styrene) layered silicate nanocomposites by in-situ suspension polymerization. *Compos. Interfaces.* 2007, 14, 361–386.

Joly, S.; Sarnaud, G.; Ollitrault, R.; Bokobza, L.; Mark, J. E. Organically Modified Layered Silicates as Reinforcing Fillers for Natural Rubber. *Chem. Mater.* 2002, 14, 4202–4208.

Zhang, H.; Qiu, Z.; Sun, D.; Zhang, D.; Huang, W. Inhibitive properties comparison of different polyetheramines in water-based drilling fluid. *J. Nat. Gas Sci. Eng.* 2015, 26, 99–107.

Fan, Z.; Zhang, L.; Liu, S.; Luan, L.; Li, G.; Sun, D. Mechanism of High Temperature Induced Destabilization of Nonpolar Organobentonite/Oil-based Drilling Fluid. *J. Colloid Interface Sci.* 2019, 555, 53–63.

Ghavami, M.; Hasanzadeh, B.; Zhao, Q.; Javadi, S.; Kebrka, D. Y. Experimental study on microstructure and rheological behavior of organobentonite/oil-based drilling fluid. *J. Mol. Liq.* 2018, 263, 147–157.

Hermoso, J.; Martínez-Boza, F.; Gallegos, C. Influence of aqueous phase volume fraction, organoclay concentration and pressure on invert-emulsion oil mud rheology. *J. Ind. Eng. Chem.* 2015, 22, 341–349.

Zhuang, G.; Zhang, Z.; Gao, J.; Zhang, X.; Liao, L. Influence of surfactants on the structures and properties of organo-polyglycerite in...
oil-based drilling fluids. *Microporous Mesoporous Mater.* 2017, 244, 37–46.

(39) Thompson, J.; Dino, D.; Jobbins, R.; Matyi, M., Jr. Compositions for Drilling Fluids Useful to Provide Flat Temperature Rheology to Such Fluids Over a Wide Temperature Range and Drilling Fluids Containing such Compositions. Mar. 18, 2008. US 7,345,010 B2.

(40) Wenjun, H.; Xiong, X.; Honglie, Y. Research and Application of FLAT-PRO Constant Rheology Synthetic Base Drilling Fluid in Deepwater Operation. *Drilling Fluid and Completion Fluid.* 2017, 34, 15–20.

(41) Hilfger, M. G., Thaemlitz, C. J.; Moellendick, E. Investigating the Chemical Nature of Flat Rheology. In *SPE Deepwater Drilling & Completions Conference,* Society of Petroleum Engineers, 2016, SPE-180320. DOI: 10.2118/180320-ms.