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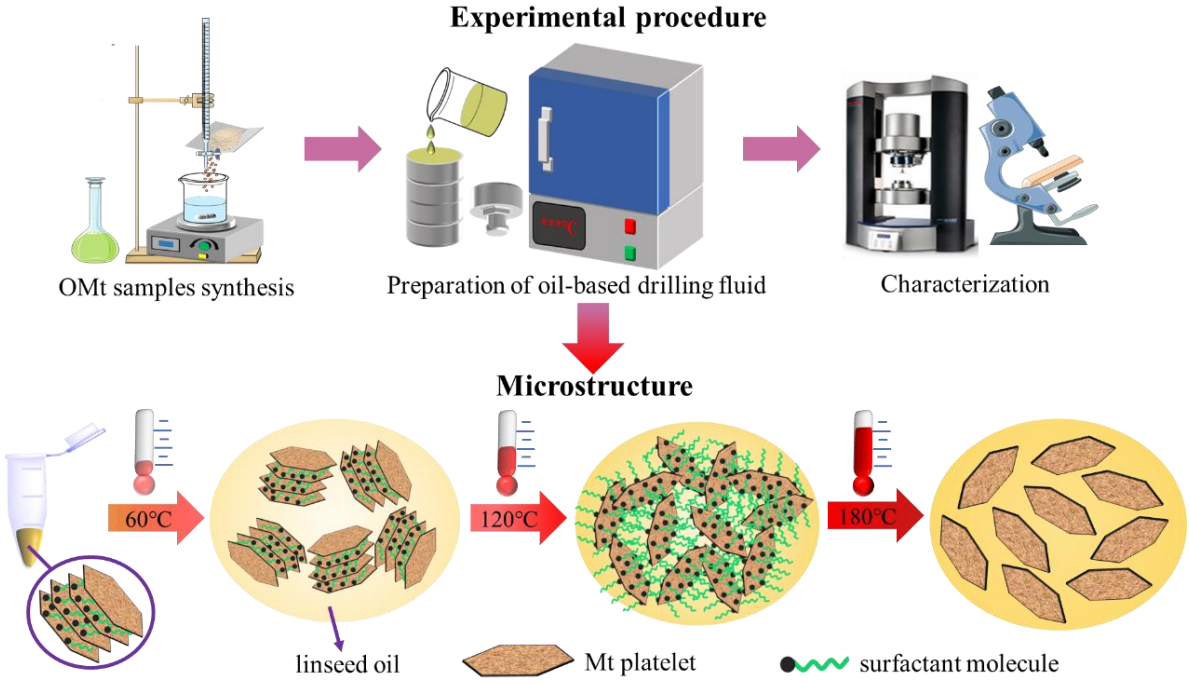
Abstract

The application of organoclays as an additive to improve the performance of oil-based drilling fluids has long been a subject of research. In this work, montmorillonite containing zinc cations was modified by lecithin to synthesize organic montmorillonite (ZnOMt), which was then dispersed in vegetable and mineral oils for the preparation of oil-based drilling fluids. Their viscoelastic properties were evaluated and linked to ZnOMt microstructure information obtained by X-ray diffraction (XRD) and transmission electronic microscopy (TEM). The nature of the oil used and the heating temperature are key parameters influencing the performance of oil-based drilling fluid. The favorable properties of vegetable oil-based drilling fluids containing organoclays provide great potential for their application in drilling

engineering.

Graphical abstract



Keywords: oil-based drilling fluids; organoclay; vegetable oil; microstructure; rheology; viscoelasticity

1. Introduction

The depletion of easily accessible hydrocarbon resources has prompted the petroleum industry to develop more complex and challenging reservoirs, such as unconventional shales and high-temperature and high-pressure (HTHP) fields. Shale reservoirs are rich in clay minerals, and various reactions will occur when exposed to water-based drilling fluids, which may cause wellbore instability (Deville et al., 2011; Aramendiz and Imqam, 2019). Drilling in HTHP conditions is a challenging task as the harsh environments adversely affect drilling fluid performance (Zhong et al., 2023). Consequently, the selection of the appropriate drilling fluids plays a pivotal role in trouble-free and safe drilling operations. Oil-based drilling fluids have high thermal stability and can provide low friction, shale inhibition, and salt resistance to overcome some undesirable characteristics of water-based drilling fluids (Zhuang et al., 2019). Therefore, oil-based drilling fluids are more suitable for shale and HTHP drilling.

The ideal oil-based drilling fluid is a non-Newtonian fluid with appropriate rheological and viscoelastic properties. Organoclays are the most important additives used to adjust the colloidal and rheological properties of oil-based drilling fluids. The organoclays is known for its ability to swell and form thixotropic gels in organic media (Moraru, 2001). Most oil-based drilling fluids are formulated with clays modified with quaternary ammonium salts, although these salts are toxic and difficult to degrade. Bio-organoclays are considered to have the potential to replace traditional

toxic organoclays. These bio-organoclays can be obtained by modifying clay minerals with biosurfactants. Phospholipids, especially lecithin, have been investigated as promising candidates for the synthesis of bio-organoclays owing to their exceptional zwitterionic properties (Li et al., 2023b). Lecithin is usually extracted from soybeans and is mainly composed of phosphatidylcholine (PC). PC contains a choline part characterized by a negatively charged phosphate group and a positively charged trimethyl-amino group. It can prepare organic montmorillonite through ion-dipole interactions under alkaline conditions (Li et al., 2023a).

The rheology of oil-based drilling fluids is not only influenced by the properties and concentration of organoclays, but also affected by the composition and nature of base oil (Hermoso et al., 2014). Diesel and mineral oil are common organic dispersion mediums for preparing oil-based drilling fluids, but these materials will cause serious pollution. The drilling cuttings contaminated with oil-based drilling fluids, drilling fluid wastes and other potential contaminants pose several risks to the terrestrial, aquatic and aerial environments if not disposed of properly (Pereira et al., 2022). To address this problem, some eco-friendly, cheap and easily available vegetable oil such as palm oil (Sulaimon et al., 2017) and soybean oil (Agwu et al., 2015) have been gradually utilized as dispersion mediums in recent years.

The main components of most vegetable oils are triglycerides and fatty acids. Some vegetable oils, referred to as siccative oils (such as linseed oil), contain unsaturated fatty esters which can undergo a complex autoxidation mechanism followed by crosslinking, resulting in the formation of a polymer network (Orlova et

al., 2021). This network structure has the ability to cure and form a solid film. The curing process can be accelerated by heating or adding metallic driers (i.e. Pb^{2+}, Zn^{2+}), which is a common practice in oil paints (de Viguerie et al., 2016; Artesani, 2020). Zn^{2+} in the siccative oil leads to the formation of carboxylic salts that behave as ionic cross-links and act as a reinforcing site for the ionomer network (Artesani, 2020). The metallic driers and siccative oils are commonly employed in oil paints, but are rarely reported in the field of oil-based drilling fluids. Additionally, temperature can have an adverse impact on the performance of organoclays in oil-based drilling fluids. Although previous studies have evaluated the macro-rheological properties of oil-based drilling fluids at high temperatures (Patel et al., 2019b; de Brito Buriti et al., 2022), the response of organoclay microstructure in oil to temperature still deserves further investigation.

In this study, inspired by the zinc cations and siccative oil in oil paints, the biosurfactant lecithin was used to modify Mt containing Zn^{2+} to prepare organoclays, which were then mixed with linseed oil to produce oil-based drilling fluid colloidal systems. The microstructure of ZnOMt in mineral oil (paraffin oil) and vegetable oil (linseed oil) and its effect on the rheological behavior of oil-based drilling fluids were comparatively evaluated. The X-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques were employed to study the microstructure of ZnOMt suspensions.

2. Materials and methods

2.1 Materials

The chemicals used for the synthesis of the Mt are hydrofluoric acid (40% w/w; Fluka), sodium acetate (99%; Sigma-Aldrich), magnesium acetate tetrahydrate (99%; Sigma-Aldrich), aluminium oxide (99%; Sigma-Aldrich) and silica (99.8%; DEGU). The materials used to prepare ZnOMt include: zinc acetate dihydrate (98%; Sigma-Aldrich), lecithin (94%; Sigma-Aldrich), CH_3CH_2OH (96%; Sigma-Aldrich), NaOH (1 mol/L; Sigma-Aldrich). The base oil utilized for formulating oil-based drilling fluid is categorized into two types: paraffin oil and linseed oil, both procured from Sigma-Aldrich. Their physical and chemical properties are shown in Table 1. All chemicals were used directly without additional purification.

Table 1 Physical and chemical properties of paraffin oil and linseed oil

	freezing point	boiling point	flash point	density	viscosity (Pa·s, 25℃)	color	main components
linseed oil	< -24 ℃	>316 ℃	>113 ℃	0.93 g/ml at 25 ℃	0.05	yellow	triglycerides
paraffin oil	< -15 ℃	260~450 ℃	>215 ℃	0.83~0.89 g/ml at 20 ℃	0.13	colorless	higher alkanes

2.2 Synthesis of Mt

The Mt employed in this work was synthesized according to the previous method (Jaber and Miéhé-Brendlé, 2005; de Oliveira et al., 2021) and had the ideal formula per half unit cell: $Na_{0.4}[Si_4Al_{1.6}Mg_{0.4}O_{10}(OH, F)_2]$. The solution is obtained by adding the reagents in the following order: deionized water (65.61g: 3.65mol), hydrofluoric acid (0.81g: 2.02mmol), sodium acetate (0.32g: 3.90mmol), magnesium acetate tetrahydrate (0.86g: 4.01mmol), aluminium oxide (1.11g: 10.89mmol) and silica (2.42g: 0.04mol). The initial hydrogel was continuously stirred at 25℃ for 4.0h and then transferred to an autoclave and heated at 190℃ for 7days. The autoclave was

cooled to room temperature and the product was thoroughly washed with distilled water and centrifuged. Finally, the synthesized Mt was dried at 60℃ for 48h. The cation exchange capacity (CEC) of the synthesized Mt is 130meq/100g.

2.3 Synthesis of ZnOMt

The Mt structure are negatively charged due to isomorphic substitution, resulting in the presence of exchangeable hydrated cations in the interlayer space to neutralize the negative charges (Malamis and Katsou, 2013). This property of Mt makes it easy to exchange interlayer cations with other metal cations in solution to prepare Mt containing different interlayer cations. This practice has been reported in numerous literatures (Yan and Zhang, 2021). To ensure that Na^+ in the Mt is completely replaced by Zn^{2+}, Mt was dispersed in 5.0CEC of zinc acetate solutions for 12h under magnetic stirring at 25℃. Then, the obtained mixture solution was centrifuged, and the same process was repeated twice. Finally, the sample was dried in an oven at 60℃ for 48h. The sample will be designated as ZnMt.

The preparation of ZnOMt was performed using the following procedure: 2g of ZnMt was dispersed in 100mL of distilled water and stirred for 2h. 1.0CEC of lecithin was dissolved in 100mL ethanol and stirred for 2h. Next, the lecithin solution was slowly added to the ZnMt dispersion and then NaOH was added dropwise to confirm that the pH of the mixture solution was 9.0. The mixture suspension was sonicated 5 min and stirred 2h at 60℃, and then the suspension was centrifuged, washed 3 times with 1:1 ethanol-distilled water solution, and the resulting precipitate was dried in an oven at 60℃ for 48h.

2.4 Preparation of oil-based drilling fluid

ZnOMt powder was added to paraffin oil and linseed oil, respectively, and stirred for 1h to prepare oil-based drilling fluid with a concentration of 50kg/m^3. The drilling fluids should be aged at different temperatures to simulate the effect of formation temperature on drilling fluid properties during drilling operations. The resulting fluid was placed in a rotary oven heated to 60℃, 120℃, 180℃ and kept for 16h. All the procedures follow the standards of American Petroleum Institute (API), i.e., API RP 13D-2017 and API RP 13B-2-2018. The procedure for preparing ZnMt/oil drilling fluid and Zn/oil drilling fluid is the same as that for preparing ZnOMt/oil drilling fluid. The oil-based fluids were named following the template of ZnOMt/oil-temperature. For example, ZnOMt/paraffin-60 is prepared with ZnOMt and paraffin oil aged at 60℃.

2.5 Characterization

The X-ray diffraction (XRD) patterns of all samples were conducted using Cu-Kα radiation (λ=0.15406 nm) on a Bruker D8 Advance X-ray powder diffractometer, which was performed at 40 kV, 30 mA and a scanning step of 0.05°. In particular, the XRD test procedure for ZnOMt/oil structure is described in detail in Section 3.1. The small drop of drilling fluid was placed on copper grids covered with an ultrathin carbon membrane for TEM analysis. The experiment was carried out with a JEOL 1011 transmission electron microscope, operating at the accelerating voltage of 100 kV (beam current around 86 μA). The samples were imaged in Bright Field (BF) mode and were examined in high vacuum mode. Optical microscopy was carried

out by using an Olympus BX51 microscope to obtain the dispersion of ZnOMt in oil.

Rheology measurements were performed with a Thermo Fisher Scientific HAAKE MARS 40 rheometer, equipped with stainless steel cone plate fixtures to obtain a uniform flow field. Each measurement was repeated at least twice to check reproducibility. The geometry and parameters of the cone plate are shown in Fig. 1. The flow curves were measured in controlled shear rate mode, with the shear rate increasing linearly from $0.1s^{-1}$ to $1000s^{-1}$ in 180s. The thixotropy measurement process for oil-based drilling fluid was performed according to the following procedure: the shear rate linearly increased from $0.1s^{-1}$ to $1000s^{-1}$ in 180s (up-sweep), and then linearly decreased from $1000s^{-1}$ to $0.1s^{-1}$ in 180s (down-sweep). The calculation of the thixotropic loop area is performed using RheoWin 4.87. The dynamic viscoelastic properties of the samples were collected by oscillatory rheology tests. The strain amplitude sweep test from 0.1 to 100% strain was carried out at ω=6.28 rad/s to evaluate the linear viscoelastic range (LVER).

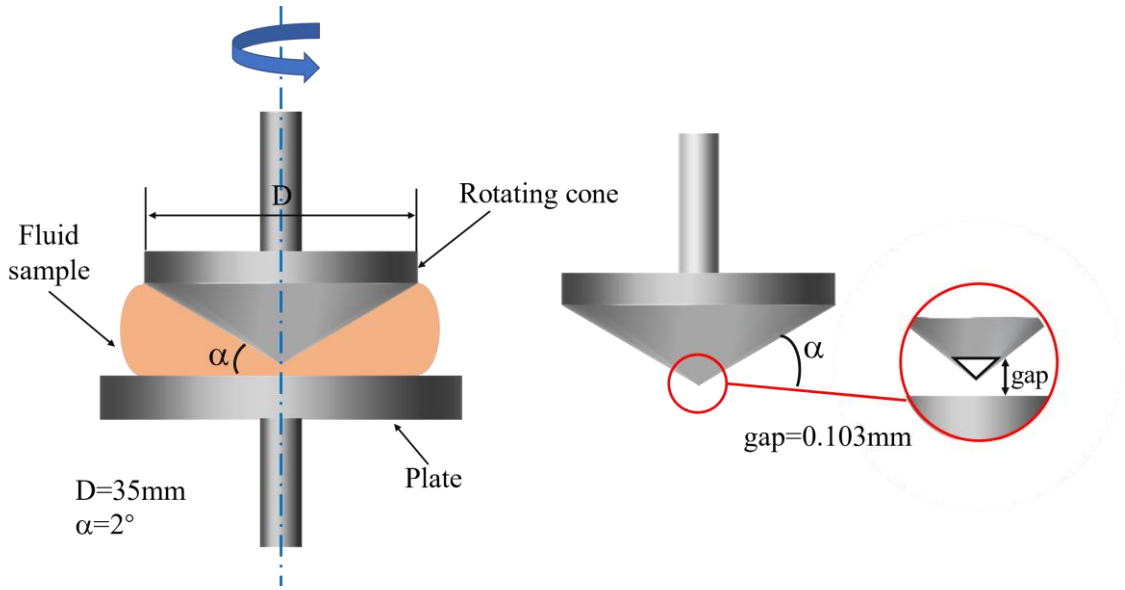


Fig. 1 The geometry and parameters of the cone plate fixture

2.6 Rheological Modeling

Rheological modeling aims to describe the flow behavior of drilling fluids mathematically. The rheological modeling for drilling fluid can facilitate the calculation of fluid flow dynamics (Agwu et al., 2021). Rheological models can generally be divided into two groups: (i) the relationship between shear rate and shear stress; (ii) the relationship between shear rate or shear stress and viscosity. In this study, the rheological data of the drilling fluid at different temperatures were fitted with three rheological models, including two-parameter models (i.e., Bingham-plastic, Casson) and three-parameter models (i.e., Herschel-Bulkey). More details and description of the rheological modeling are provided in the Supporting Information.

3. Results and Discussion

3.1 X-ray diffraction

The XRD patterns of the synthesized Mt and ZnOMt obtained by lecithin modification are presented in Fig. 2. The XRD pattern of synthesized Mt (Fig. 2A) matched well with the standard PDF card of Mt and no other reflections are observed, suggesting that Mt has been successfully synthesized and has a high purity. The Mt exhibited a reflection at 2θ=6.02° with a d_{001}-value of 1.47nm. The XRD pattern of the ZnMt indicated little change in the intensity and position of the (001) reflection, which is consistent with the results of previous studies (Daković et al., 2012). After modification with lecithin, this reflection shifted to 2θ=1.65°, corresponding to a basal spacing of 5.35nm. The basal spacing of ZnOMt increased from 1.45nm to 5.35nm (Fig. 2B), indicating the successful intercalation of lecithin into the interlayer space of

Mt.

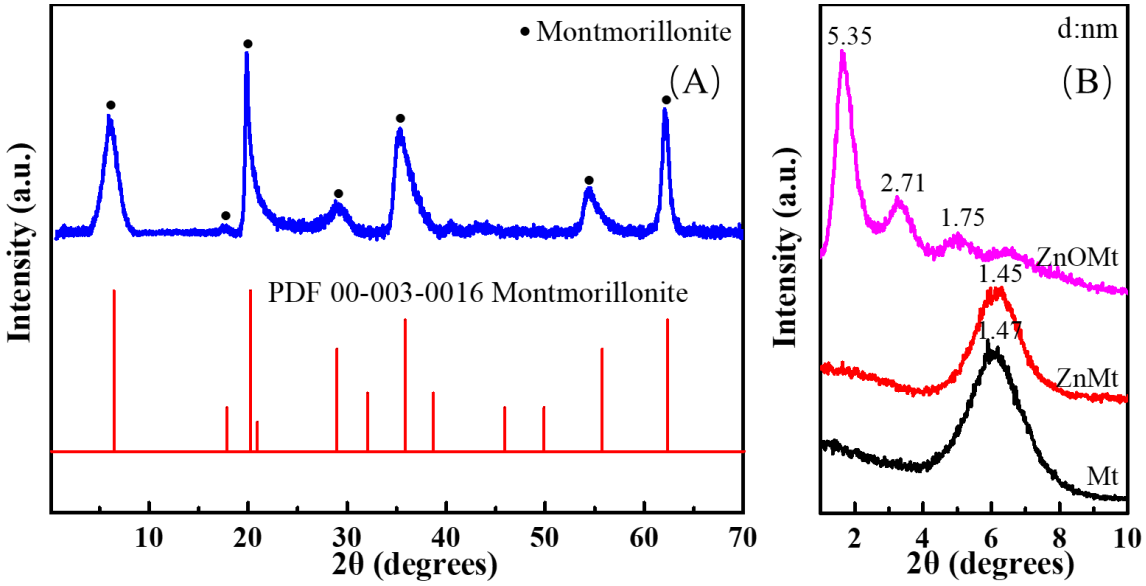


Fig. 2 XRD patterns of synthesized Mt, ZnMt and ZnOMt

The structure of ZnOMt in oil is characterized by the XRD technique using a suitable method (Fig. 3A). Firstly, a high-speed centrifuge was used to remove excess oil from the aged drilling fluid to obtain ZnOMt sediment. The ZnOMt sediment was then uniformly smeared on the glass. Finally, the ZnOMt sediment can be measured using the X-ray diffractometer, similar to powder samples.

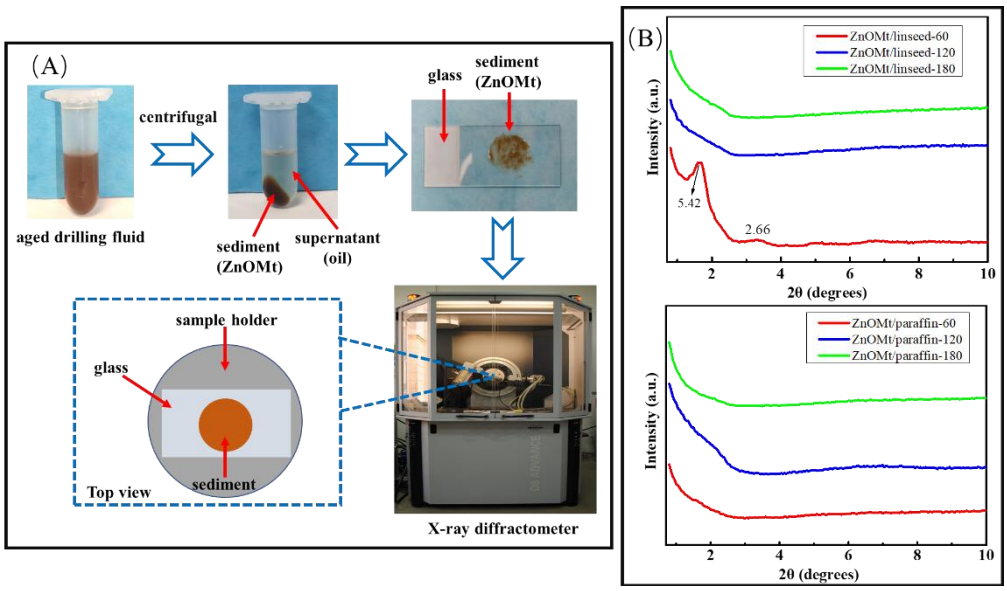


Fig. 3 Interpretation diagram (A) of XRD test for ZnOMt sediment, and XRD patterns

(B) of ZnOMt/linseed, ZnOMt/paraffin aged at different temperatures

The XRD patterns of ZnOMt sediment in linseed and paraffin oil aged at different temperatures are presented in Fig. 3B. The base spacing of the synthesized ZnOMt powder was 5.35 nm. However, the XRD results of ZnOMt/linseed and ZnOMt/paraffin showed different trends after aging at various temperatures. The basal spacing of ZnOMt/linseed-60 increased from 5.35 nm to 5.42 nm, suggesting the penetration of oil molecules into the interlayer of ZnOMt and subsequent expansion of the basal spacing. Based on previous research (Zhuang et al., 2017; Patel et al., 2019a), high temperatures can promote the thermal motion of oil molecules, leading to the swelling of ZnOMt in oil. There was no detectable reflection from Mt lattices in the XRD patterns of ZnOMt/linseed aged at 120℃ and 180℃. The same results can also be observed in ZnOMt/paraffin systems. Several scholars suggested that the disappearance of the (001) reflection is caused by the exfoliation of organoclays in oil (Luckham and Rossi, 1999; Zhuang et al., 2016a; Zhuang et al., 2017). As the temperature increased, more oil molecules intercalated into the interlayer space of the ZnOMt, resulting in the exfoliation of clay platelets and reducing the attractive force between Mt sheets. The exfoliated clay platelets form a “house of cards” structure through three different modes of particle association : face-to-face (FF), edge-to-face (EF) and edge-to-edge (EE) (van Olphen, 1964). Others believed, however, that the qualitative structural information on d-spacing provided by XRD can not explain the different rheological properties observed in ZnOMt/oil systems, indicating that the basal spacing can not predict the fluid flow behavior (Burgentzlé et al., 2004;

237 Hermoso et al., 2014).

238 ***3.2 TEM analysis***

239 In order to illustrate the microstructure of ZnOMt in oil-based drilling fluid,
240 taking the ZnOMt/linseed system as an example, the TEM images of drilling fluid at
241 different temperatures are shown in Fig. 4. The ZnOMt powder sample obtained by
242 lecithin modification exhibited a layered structure. When it was dispersed in linseed
243 oil and subjected to aging at 60℃, the layered structure remained unaltered, which is
244 consistent with the XRD results. A large number of aggregated layered ZnOMt
245 particles dispersed in the linseed oil. As the temperature increased to 120℃, the
246 ZnOMt platelets exfoliated. The exfoliated nanoclay platelets were not randomly
247 dispersed in the oil but formed compact clay tactoids and then a kind of network
248 structure was formed. The ZnOMt/linseed-180 sample was completely exfoliated but
249 presented a different dispersion state from ZnOMt/linseed-120. The ZnOMt platelets,
250 of approximately 60 nm, were homogeneously dispersed in the linseed oil, without
251 contact with each other. The network structure formed by the clay platelets was
252 destroyed, because of the degradation of the surfactant in the ZnOMt at high
253 temperature. The effect of temperature on the microstructure of ZnOMt is mainly
254 reflected in the exfoliation and the degradation of surfactants. The relationship
255 between the microstructure and rheological properties of ZnOMt in oil will be
256 explained in detail in the following sections.

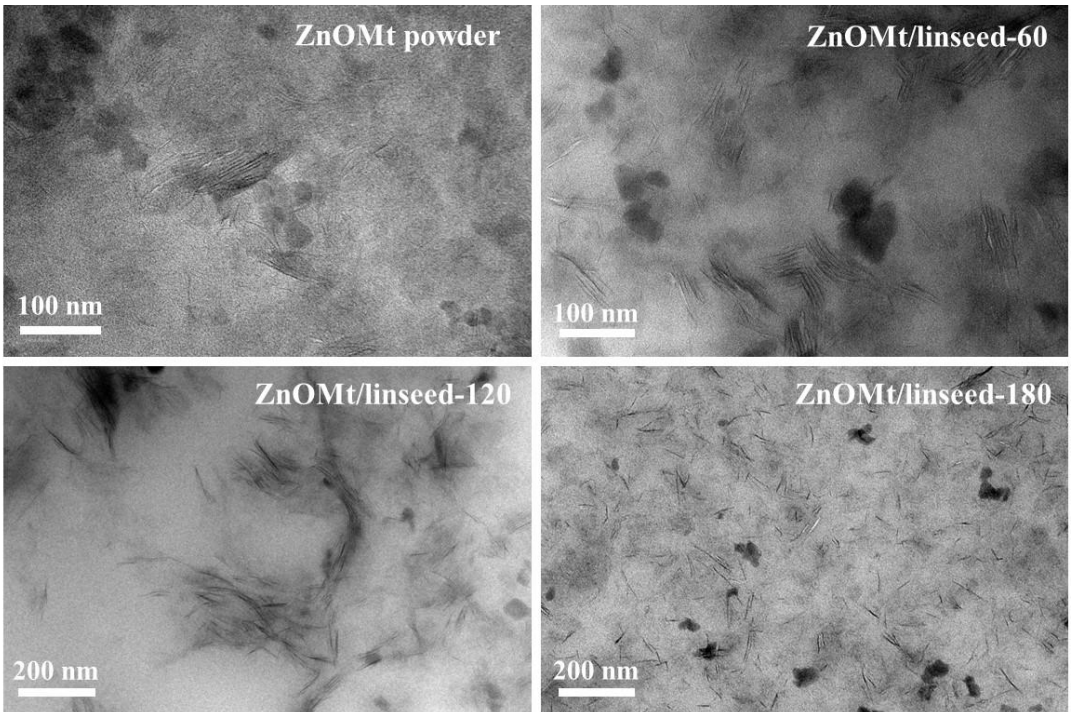


Fig. 4 TEM images of ZnOMt powder, and ZnOMt/linseed aged at different temperatures

3.3 Dispersion

The dispersion states of ZnOMt and ZnMt powder in paraffin oil and linseed oil at different temperatures were obtained mainly by optical microscopy for observing the overall size distribution of the particles. As shown in Fig. 5, the ZnMt samples were not uniformly dispersed throughout the organic medium for either paraffin oil or linseed oil. Due to the strong hydrophilicity of ZnMt, it is difficult for oil molecules to penetrate into the interlayer space to swell the clay particles. However, it is worth noting that the dispersion of ZnMt in paraffin and linseed oil is distinct. The ZnMt samples were randomly dispersed in linseed oil without any contact, whereas in paraffin oil they were interconnected. These particles tend to gather and partially overlap each other and form a net-like structure. The organo-modification of ZnMt with lecithin evidently improved its dispersion in oil. Although the dispersion of

ZnOMt in both oils was stable, the dispersion of ZnOMt in linseed oil was more homogeneous and the particle size was smaller. The ZnOMt in paraffin oil presented a large number of aggregated particles. In contrast, the aggregated particles in linseed oil were very limited at any temperature. This is probably due to the fact that linseed oil is polar compared to non-polar paraffin oil, which has a stronger affinity for ZnOMt modified by polar molecules of lecithin (Jones, 1983; Ma et al., 2023). In addition, temperature contributes to the dispersion of ZnOMt in oil-based drilling fluids.

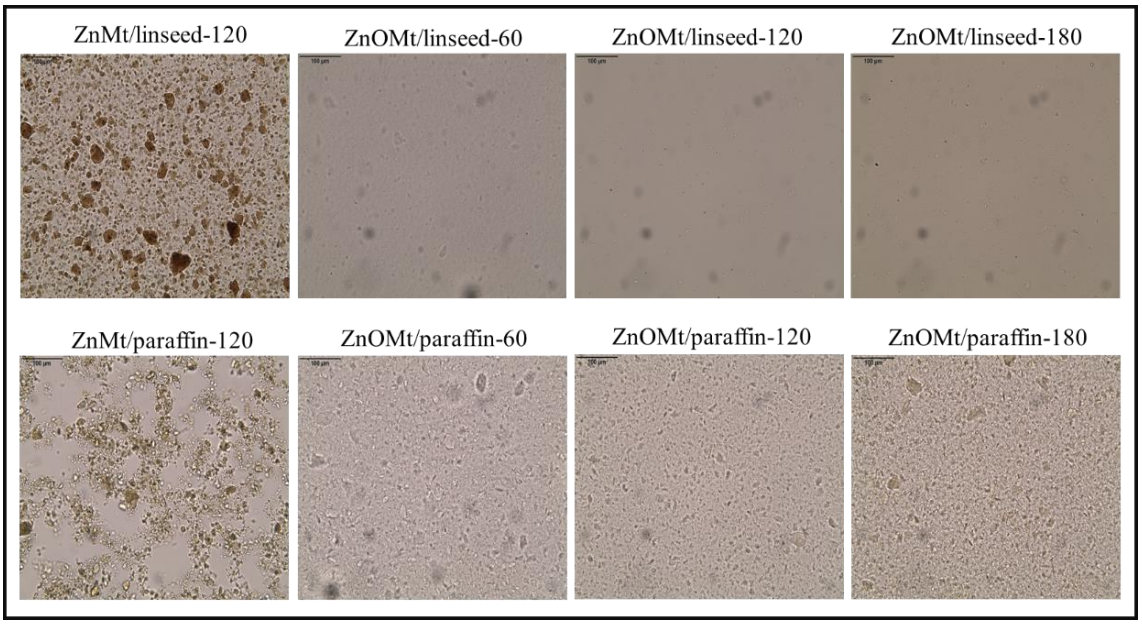


Fig. 5 Optical microscope images of ZnMt and ZnOMt in oil-based drilling fluid

3.4 Rheological properties

The relationship between shear stress and shear rate is the most accurate description of drilling fluid flow behavior (Arain et al., 2022). Fig. 6(A, B) illustrates the flow behavior of oil-based drilling fluid containing Zn^{2+}, ZnMt, ZnOMt samples as a function of shear rate at 120℃: different rheological behaviors were obtained in oil phases. Pure linseed and paraffin oil are Newtonian fluids, exhibiting a constant

viscosity at any shear rate. For linseed oil, the addition of Zn^{2+} remarkably increased the viscosity of linseed oil, and the viscosity of the system grew from 0.06 to 0.5 Pa·s, which may be caused by the saponification reaction between the zinc cations and the esters of the siccative oil, as commonly reported in the literature (Osmond, 2019; Artesani, 2020). The addition of ZnMt had no effect on the viscosity of linseed oil, while ZnOMt modified its rheological behavior from Newtonian to shear thinning: the ZnOMt/linseed oil system displayed high viscosity at low shear rates and the viscosity decreased with increasing shear rates, which is highly desirable in drilling operations. For paraffin oil, Zn^{2+} did not affect the flow behavior of paraffin oil, as it is mainly composed of alkanes that cannot react with Zn^{2+}. Interestingly, paraffin oil containing ZnMt was a non-Newtonian fluid with shear thinning properties, while linseed oil containing ZnMt was a Newtonian fluid. This may be due to the different dispersion states of ZnMt in two oils. The net-like structure (Fig. 5) formed by ZnMt in paraffin oil leads to an increase in viscosity. Conversely, the dispersion of ZnOMt in paraffin oil did not yield satisfactory rheological properties. The ZnOMt showed better rheological performance and application potential for drilling fluid in linseed oil compared to paraffin oil.

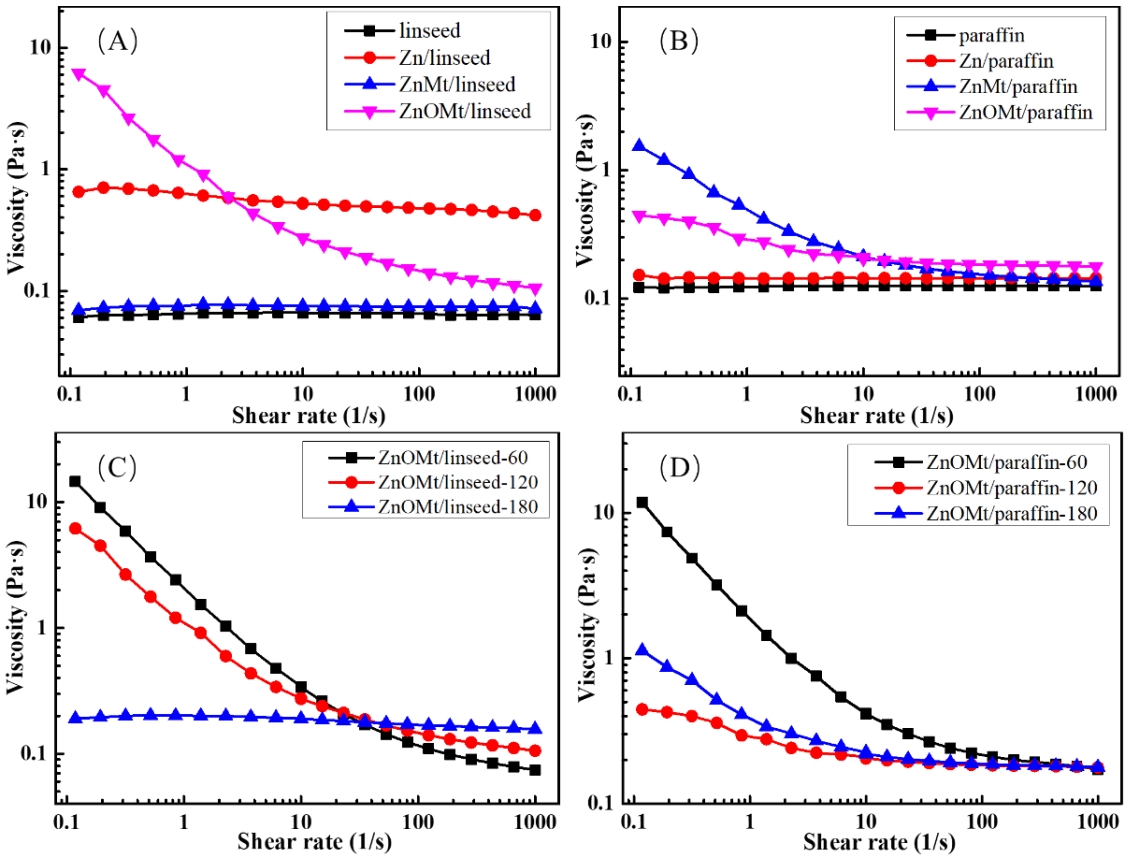


Fig. 6 Flow tests of oil-based drilling fluids prepared by Zn^{2+}, ZnMt, ZnOMt at 120℃ (A, B) and flow tests of ZnOMt/oil fluids at varying temperatures (C, D)

The rheological behavior of oil-based drilling fluid is not only affected by the oil nature, but also depends on the temperature. As shown in Fig. 6(C, D), the rheological properties of oil-based drilling fluids were altered as the temperature increased. At temperatures below 120℃, ZnOMt/linseed fluids exhibited shear thinning behavior at low shear rates. The viscosity measured at zero shear rate can be used to indicate the pumpability of drilling fluids and as a rheological parameter to evaluate barite sag, borehole cleaning, surge, and swab pressures (Maxey et al., 2008; Li et al., 2022). The viscosity of ZnOMt/linseed oil systems at low shear rates decreased gradually with increasing temperature. As the temperature increased to 180℃, the system viscosity decreased to 0.2 Pa·s and became a Newtonian fluid. This reduction may be due to the

fact that temperature (180℃) disrupts the structure of clay platelets and reduces the connection and bonding between clay particles. The ZnOMt lost its ability to adjust linseed oil-drilling fluid rheological properties at 180℃, indicating that the electrochemical attraction between clay particles has totally disappeared. The ZnOMt/paraffin oil system exhibited similar rheological behavior to the ZnOMt/linseed oil fluid at 60℃. However, when the temperature rose to 120℃, its viscosity dropped significantly and tended to exhibit the properties of Newtonian fluid. Comparing the rheological properties of ZnOMt in linseed oil and paraffin oil, it can be concluded that the ZnOMt/linseed oil system is more resistant to high temperatures.

3.5 Thixotropy

The thixotropy of the drilling fluid plays a crucial role in controlling the rate of penetration at low shear rates within the well annulus and ensuring effective suspension of cuttings (Celino et al., 2022). The microstructure of drilling fluid is disrupted in the up-sweep, while rebuilt in the down-sweep and hysteresis is induced in the flow curves. Fig. 7 illustrates the thixotropic loop curves of the ZnOMt/oil system at different temperatures. The loop areas of ZnOMt/linseed-60 and ZnOMt/linseed-180 fluids were minimal due to the lack of ZnOMt exfoliation at 60℃ and the degradation of surfactant molecules at 180℃, resulting in poor thixotropy. Conversely, the loop area is higher at 120℃ indicating greater thixotropy. According to XRD and TEM results, this is due to the exfoliation of ZnOMt and the resulting network structure in linseed oil. Based on the loop area values, the thixotropic loop

areas of the ZnOMt/paraffin system were not satisfactory, whatever the temperature.

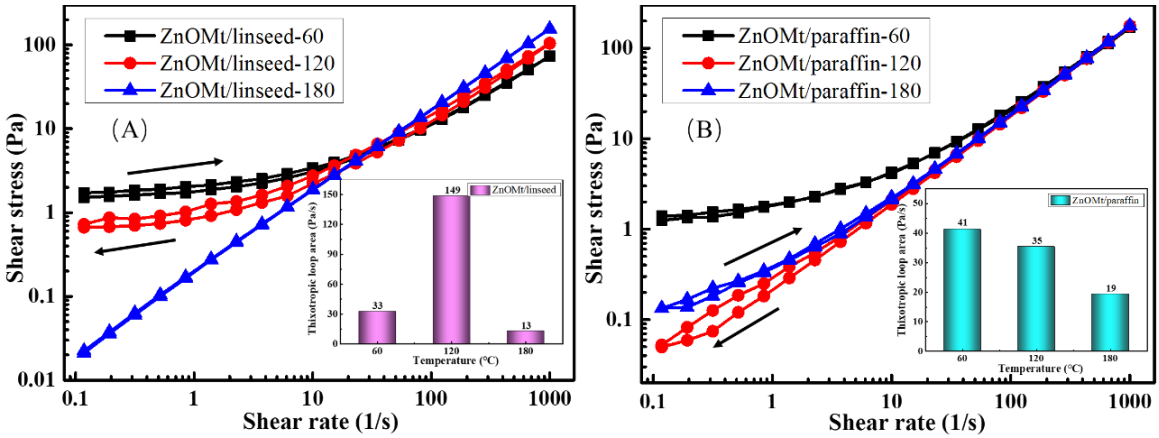


Fig. 7 The thixotropic loop curves and areas of the ZnOMt/linseed (A) and ZnOMt/paraffin (B) system at different temperatures

3.6 Rheological modeling

The knowledge of the drilling fluid rheological model is crucial, as the accuracy of fitting the model to the actual properties of the drilling fluid will dramatically affect the drilling hydraulics calculations (Wiśniowski et al., 2020). In this work, the R^2, SSR, and RMSE are used to determine the performance of the rheological models. These parameters were defined by fitting constants using regression analysis obtained from rheological data. The curve fitting of the rheology model at different temperatures, including the obtained rheological constants and derived statistical parameters, is provided in the Supporting Information.

A satisfactory model to characterize the rheological properties of drilling fluids at different temperatures was determined based on the values of fitted parameters such as R^2 (greater than 0.99), SSR (less than 5) and RMSE (less than 0.2) (Rafieefar et al., 2021). As expected, the Bingham-plastic model was not suitable for describing the rheological behavior of non-Newtonian drilling fluid because the model expresses a

linear relationship. In comparison with the Bingham-plastic model, the Casson model fitted better, revealing the nonlinear relationship between the shear stress and shear rate. The Herschel-Bulkey model represents the most accurate fitting results of drilling fluids at different temperatures. This is why the Herschel-Bulkley model is selected for utilization in the drilling fluid field.

Rheological parameters such as flow behavior index (*n*) and consistency coefficient (*k*) obtained by the Herschel-Bulkley model provide more valuable information. The *n* value can be used to evaluate the ability of drilling fluids to carry cuttings, and *k* is the measure of the consistency of the fluid, which is proportional to the effective viscosity (Maiti et al., 2021). The drilling fluid with the lowest *n* value and the highest *k* value has a greater ability to suspend and carry drill cuttings. The fitting results obtained from the Herschel-Bulkley model revealed that the ZnOMt/linseed system exhibited an n value of 0.8884 and a k value of 0.2263 at 120℃. These findings indicate that the linseed oil-based drilling fluid demonstrated the most favorable rheological properties at 120℃.

3.7 Viscoelastic properties

Dynamic measurements were also performed on ZnOMt/oil systems to understand their structural behavior (Werner et al., 2017). The amplitude sweep tests are presented in Fig. 8, indicating the viscoelastic properties (storage and loss modulus) of the ZnOMt/oil system at different temperatures.

The linear viscoelastic range (LVER) is defined by the strain range where G′ and G″ are approximately constant: the limit of the LVER was 3% for ZnOMt/linseed-60

and 8% for ZnOMt/linseed-120, respectively. The microstructure of the drilling fluid within the LVER remains intact; it is a solid-like structure as the value of G′ was higher than that of G″. When the drilling fluid is subjected to greater strain after the LVER, micro-cracks begin to appear, which spread throughout the drilling fluid system and this behavior persists until the flow point is achieved (Medhi et al., 2021). The flow point (G′=G″) represents the overlapping point of G′ and G″, implying a transition from solid-like to liquid-like characteristics. As the strain increased after the flow point, G′<G″ and the drilling fluid behaved more like a liquid-like and viscous structure. With increasing temperature, the flow point shifted towards higher shear strain. The flow points corresponding to ZnOMt/linseed-60 and ZnOMt/linseed-120 were 25% and 34%, respectively. Higher flow point normally related to stronger inner structure and suspension capacity. At 180℃, G″ > G′ regardless of the applied strain, indicating liquid-like behavior: the internal structure of the sample was completely disrupted, which is consistent with the TEM results. The ZnOMt/paraffin systems did not exhibit any viscoelasticity with G″ always greater than G′ at both high and low temperatures. This result suggested that ZnOMt prepared from lecithin could not form a network structure in paraffin oil. The composition and nature of the base oil is also an important factor in the viscoelasticity of the drilling fluid.

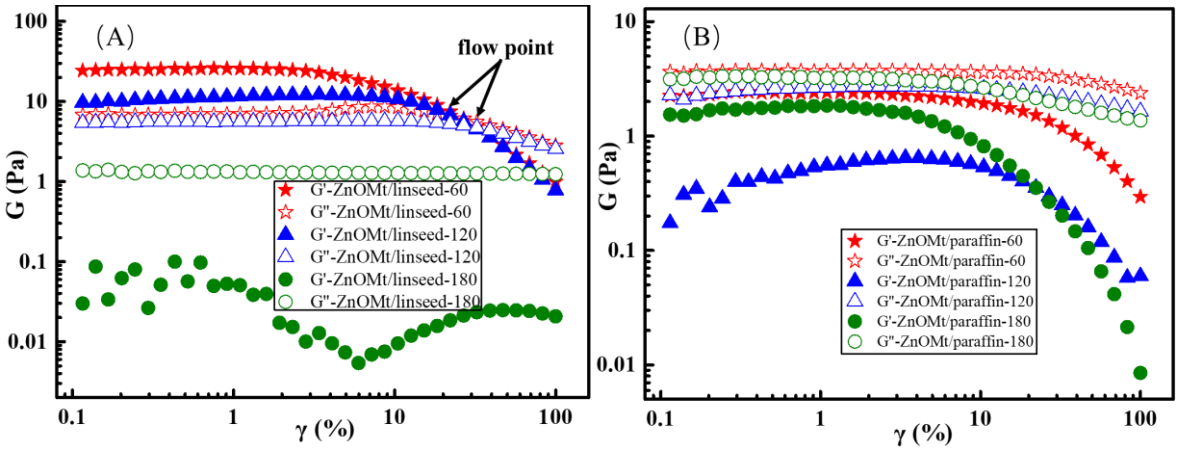


Fig. 8 The amplitude sweep tests of the ZnOMt/linseed (A) and ZnOMt/paraffin (B) systems at different temperatures

3.8 Discussion of rheological mechanism

Based on the experimental findings, a comprehensive analysis of the impact of temperature on the rheological properties of linseed oil-based drilling fluid and the microstructure of ZnOMt in linseed oil is thoroughly discussed. A schematic representation of the microstructure of ZnOMt in linseed oil at different temperatures is proposed in Fig. 9. The synthesized ZnOMt maintained the layered structure while exhibiting an increased interlayer spacing, suggesting the intercalation of lecithin. This observation is further supported by the XRD and TEM results. After the dispersion of ZnOMt in linseed oil at 60℃, no exfoliation has been observed. The aggregation of larger clay particles impeded the flow of drilling fluid and resulted in higher viscosity. In addition, the high aspect ratio of the ZnOMt further reinforced this flow resistance (Cruz et al., 2019). When the temperature rose to 120℃, the oil molecules intercalated into the interlayer space and caused exfoliation of the ZnOMt (van Olphen, 1964; Luckham and Rossi, 1999). Lecithin molecules adsorbed on the surface of ZnOMt possess long and flexible alkyl chains, which facilitated their

entanglement with each other, leading to a physical attraction (Zhuang et al., 2016b; Liu et al., 2023). By increasing the temperature up to 180℃, lecithin molecules started to degrade, and the network structure of the drilling fluid was completely destroyed. The exfoliation of ZnOMt leading to its homogeneous dispersion in oil was confirmed by observations using optical microscopy and TEM.

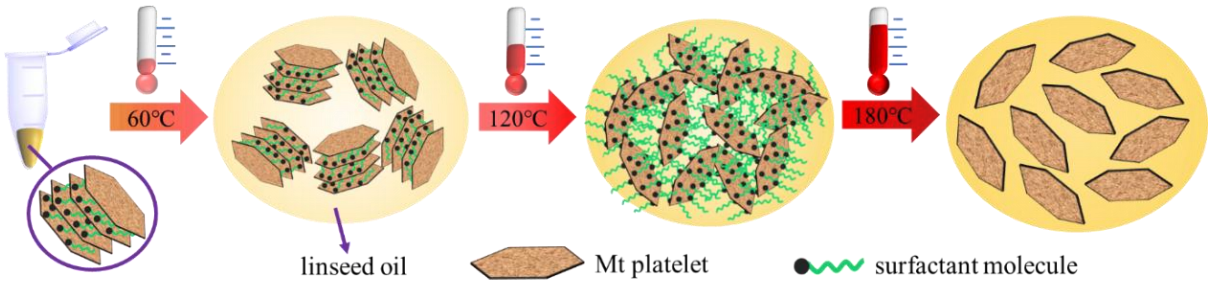


Fig. 9 The microstructure of ZnOMt in linseed oil at different temperatures

4. Conclusions

A systematic and in-depth experimental work was performed to probe the potential of siccative oil (linseed oil) as an alternative to mineral oil-based drilling fluid. The viscoelasticity, thixotropy, and microstructure of ZnOMt in linseed oil and paraffin oil at different temperatures were compared and investigated. The ZnOMt prepared by zinc ions and lecithin showed viscoelastic behavior in linseed oil when the temperature didn't succeed 120 ℃. The microstructure of ZnOMt in linseed oil undergoes three stages with rising temperature: swelling→exfoliation→high dispersion. The association of exfoliated clay platelets and the intertwining of surfactant molecules adsorbed on the clay surface are the basis for forming a network structure and thixotropy in drilling fluids. In addition, the paraffin oil-based drilling fluids always displayed liquid-like behavior, while linseed oil-based drilling fluids exhibited viscoelastic properties and maximum thixotropy at 120℃. The favorable

properties of vegetable oil-based drilling fluids containing organoclays provide great potential for their application in drilling engineering.

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References

Agwu, O.E., Akpabio, J.U., Ekpenyong, M.E., Inyang, U.G., Asuquo, D.E., Eyoh, I.J., Adeoye, O.S., 2021. A critical review of drilling mud rheological models. Journal of Petroleum Science and Engineering 203, 108659.

Agwu, O.E., Okon, A.N., Udoh, F.D., 2015. A comparative study of diesel oil and soybean oil as oil-based drilling mud. Journal of Petroleum Engineering 2015, 1-10.

Arain, A.H., Ridha, S., Mohyaldinn, M.E., Suppiah, R.R., 2022. Improving the performance of invert emulsion drilling fluid using boron nitride and graphene nanoplatelets for drilling of unconventional high-temperature shale formations. Journal of Molecular Liquids 363, 119806.

Aramendiz, J., Imqam, A., 2019. Water-based drilling fluid formulation using silica and graphene nanoparticles for unconventional shale applications. Journal of Petroleum Science and Engineering 179, 742-749.

Artesani, A., 2020. Zinc oxide instability in drying oil paint. Materials Chemistry and Physics 255, 123640.

Burgentzlé, D., Duchet, J., Gérard, J., Jupin, A., Fillon, B., 2004. Solvent-based nanocomposite coatings: I. Dispersion of organophilic montmorillonite in organic solvents.

458 Journal of colloid interface science 278, 26-39.

459 Celino, K.N., Fernandes, R.d.S., de Morais, S.C., de Souza, E.A., Balaban, R.d.C., 2022.
460 Emulsion-based drilling fluids: Rheological properties preservation facing changes on the
461 temperature, pressure and dispersed phase. Journal of Molecular Liquids 352, 118753.

462 Cruz, N., Forster, J., Bobicki, E.R., 2019. Slurry rheology in mineral processing unit operations:
463 A critical review. The Canadian Journal of Chemical Engineering 97, 2102-2120.

464 Daković, A., Kragović, M., Rottinghaus, G.E., Ledoux, D.R., Butkeraitis, P., Vojislavljević, D.Z.,
465 Zarić, S.D., Stamenić, L., 2012. Preparation and characterization of zinc-exchanged
466 montmorillonite and its effectiveness as aflatoxin B1 adsorbent. Materials Chemistry and
467 Physics 137, 213-220.

468 de Brito Buriti, B.M.A., Barsosa, M.E., da Silva Buriti, J., de Melo Cartaxo, J., Ferreira, H.S., de
469 Araújo Neves, G., 2022. Modification of palygorskite with cationic and nonionic surfactants for
470 use in oil-based drilling fluids. Journal of Thermal Analysis and Calorimetry 147, 2935-2945.

471 de Oliveira, L.H., Trigueiro, P., Rigaud, B., da Silva-Filho, E.C., Osajima, J.A., Fonseca, M.G.,
472 Lambert, J.-F., Georgelin, T., Jaber, M., 2021. When RNA meets montmorillonite: Influence of
473 the pH and divalent cations. Applied Clay Science 214, 106234.

474 de Viguerie, L., Payard, P.A., Portero, E., Walter, P., Cotte, M., 2016. The drying of linseed oil
475 investigated by Fourier transform infrared spectroscopy: Historical recipes and influence of
476 lead compounds. Progress in Organic Coatings 93, 46-60.

477 Deville, J.P., Fritz, B., Jarrett, M., 2011. Development of Water-Based Drilling Fluids
478 Customized for Shale Reservoirs. SPE Drilling & Completion 26, 484-491.

479 Hermoso, J., Martinez-Boza, F., Gallegos, C., 2014. Influence of viscosity modifier nature and

480 concentration on the viscous flow behaviour of oil-based drilling fluids at high pressure.
481 Applied Clay Science 87, 14-21.
482 Jaber, M., Miéhé-Brendlé, J., 2005. Influence du milieu de synthèse sur la cristallisation de
483 saponite : proposition de mécanisme réactionnel en milieux acide et basique. Comptes
484 Rendus Chimie 8, 229-234.
485 Jones, T.R., 1983. The properties and uses of clays which swell in organic solvents. Clay
486 Minerals 18, 399-410.
487 Li, Q., Berraud-Pache, R., Souprayen, C., Jaber, M., 2023a. Intercalation of lecithin into
488 bentonite: pH dependence and intercalation mechanism. Applied Clay Science 244, 107079.
489 Li, Q., Berraud-Pache, R., Yang, Y., Souprayen, C., Jaber, M., 2023b. Biocomposites based
490 on bentonite and lecithin: An experimental approach supported by molecular dynamics.
491 Applied Clay Science 231, 106751.
492 Li, X.-L., Jiang, G.-C., Xu, Y., Deng, Z.-Q., Wang, K., 2022. A new environmentally friendly
493 water-based drilling fluids with laponite nanoparticles and polysaccharide/polypeptide
494 derivatives. Petroleum Science 19, 2959-2968.
495 Liu, S., Zhang, C., Du, J., Huang, H., Fang, S., Li, X., Duan, M., 2023. Effect of dispersants on
496 the stability of calcite in non-polar solutions. Colloids and Surfaces A: Physicochemical and
497 Engineering Aspects 672, 131730.
498 Luckham, P.F., Rossi, S., 1999. The colloidal and rheological properties of bentonite
499 suspensions. Advances in Colloid and Interface Science 82, 43-92.
500 Ma, G.-D., Zuo, H.-R., Pang, S.-Y., Duan, M., Xiong, Y., Li, X.-L., 2023. Anchoring polyamide
501 active layer to improve the thermal stability of polyacrylonitrile composite forward osmosis

membrane through interfacial enthalpic effect. Separation and Purification Technology 318, 123954.

Maiti, M., Bhaumik, A.K., Mandal, A., 2021. Performance of water-based drilling fluids for deepwater and hydrate reservoirs: Designing and modelling studies. Petroleum Science 18, 1709-1728.

Malamis, S., Katsou, E., 2013. A review on zinc and nickel adsorption on natural and modified zeolite, bentonite and vermiculite: Examination of process parameters, kinetics and isotherms. Journal of Hazardous Materials 252-253, 428-461.

Maxey, J., Ewoldt, R., Winter, P., McKinley, G., 2008. Yield stress: what is the True value, AADE Fluids Conference and Exhibition, pp. 1-10.

Medhi, S., Gupta, D.K., Sangwai, J.S., 2021. Impact of zinc oxide nanoparticles on the rheological and fluid-loss properties, and the hydraulic performance of non-damaging drilling fluid. Journal of Natural Gas Science and Engineering 88, 103834.

Moraru, V.N., 2001. Structure formation of alkylammonium montmorillonites in organic media. Applied Clay Science 19, 11-26.

Orlova, Y., Harmon, R.E., Broadbelt, L.J., Iedema, P.D., 2021. Review of the kinetics and simulations of linseed oil autoxidation. Progress in Organic Coatings 151, 106041.

Osmond, G., 2019. Zinc soaps: an overview of zinc oxide reactivity and consequences of soap formation in oil-based paintings. Metal soaps in art: Conservation research, 25-46.

Patel, H.A., Santra, A., Thaemlitz, C.J., 2019a. Exceptional flat rheology using a synthetic organic-inorganic hybrid in oil-based muds under high pressure and high temperature, SPE/IADC International Drilling Conference and Exhibition. OnePetro.

524 Patel, H.A., Santra, A., Thaemlitz, C.J., 2019b. Exceptional Flat Rheology Using a Synthetic
525 Organic-Inorganic Hybrid in Oil-Based Muds Under High Pressure and High Temperature,
526 SPE/IADC International Drilling Conference and Exhibition, p. D012S020R001.
527 Pereira, L.B., Sad, C.M.S., Castro, E.V.R., Filgueiras, P.R., Lacerda, V., 2022. Environmental
528 impacts related to drilling fluid waste and treatment methods: A critical review. Fuel 310,
529 122301.
530 Rafieefar, A., Sharif, F., Hashemi, A., Bazargan, A.M., 2021. Rheological Behavior and
531 Filtration of Water-Based Drilling Fluids Containing Graphene Oxide: Experimental
532 Measurement, Mechanistic Understanding, and Modeling. ACS Omega 6, 29905-29920.
533 Sulaimon, A.A., Adeyemi, B.J., Rahimi, M., 2017. Performance enhancement of selected
534 vegetable oil as base fluid for drilling HPHT formation. Journal of Petroleum Science and
535 Engineering 152, 49-59.
536 van Olphen, H., 1964. Internal mutual flocculation in clay suspensions. Journal of Colloid
537 Science 19, 313-322.
538 Werner, B., Myrseth, V., Saasen, A., 2017. Viscoelastic properties of drilling fluids and their
539 influence on cuttings transport. Journal of Petroleum Science Engineering 156, 845-851.
540 Wiśniowski, R., Skrzypaszek, K., Małachowski, T., 2020. Selection of a Suitable Rheological
541 Model for Drilling Fluid Using Applied Numerical Methods, Energies.
542 Yan, H., Zhang, Z., 2021. Effect and mechanism of cation species on the gel properties of
543 montmorillonite. Colloids and Surfaces A: Physicochemical and Engineering Aspects 611,
544 125824.
545 Zhong, H., Guan, Y., Qiu, Z., Grady, B.P., Su, J., Huang, W., 2023. Application of carbon

546 coated bentonite composite as an ultra-high temperature filtration reducer in water-based
547 drilling fluid. Journal of Molecular Liquids 375, 121360.
548 Zhuang, G., Gao, J., Peng, S., Zhang, Z., 2019. Synergistically using layered and fibrous
549 organoclays to enhance the rheological properties of oil-based drilling fluids. Applied Clay
550 Science 172, 40-48.
551 Zhuang, G., Zhang, H., Wu, H., Zhang, Z., Liao, L., 2017. Influence of the surfactants' nature
552 on the structure and rheology of organo-montmorillonite in oil-based drilling fluids. Applied
553 Clay Science 135, 244-252.
554 Zhuang, G., Zhang, Z., Sun, J., Liao, L., 2016a. The structure and rheology of
555 organo-montmorillonite in oil-based system aged under different temperatures. Applied Clay
556 Science 124-125, 21-30.
557 Zhuang, G., Zhang, Z., Sun, J., Liao, L., 2016b. The structure and rheology of
558 organo-montmorillonite in oil-based system aged under different temperatures. Applied Clay
559 Science 124, 21-30.
560