

Enhancing the rheological properties and thermal stability of 1 oil-based drilling fluids by synergetic use of organo-montmorillonite and organo-sepiolite

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1	Enhancing the rheological properties and thermal stability of
2	oil-based drilling fluids by synergetic use of organo-
3	montmorillonite and organo-sepiolite
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23 Abstract

This work focused on improving the rheological properties and thermal stability 24 25 of oil-based drilling fluids by using the mixture of organo-montmorillonite (OMt) and 26 organo-sepiolite (OSep) as the rheological additive. OMt and OSep were prepared in 27 water. X-ray diffraction (XRD), scanning electron microscope and transmission 28 electron microscope were applied to characterize the structure of organoclays (OC). 29 The OC/oil gels were characterized using an appropriate XRD method. Dynamic 30 rheological test was used to appraise the rheological behavior, viscosity, gel strength 31 and thixotropy of OC/oil fluids aged at different temperatures. OMt firstly swelled in oil at low temperature, and then exfoliated above 150°C. OSep maintained its crystal 32 33 structure all the time. The mixing of these two OC did not obviously influence their 34 structures. However, the gel formation ability was promoted, resulting in improvement of rheological properties and thermal stability of oil-based drilling fluids. The 35 nanolayers of OMt and nanofibers of OSep interweaved with each other, reinforcing 36 37 the network structure and protected them form collapse at high temperatures. The mixture of OMt and OSep with mass proportion of 50% for each displayed the optimal 38 39 rheological properties and thermal ability.

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Keywords: Sepiolite, oil-based muds, rheological properties, organic modification,
high temperature.

43

45 1. Introduction

Over the next 30 years, global energy is projected to rise almost 60%, a 46 47 challenging trend that may be met only by revolutionary breakthroughs in energy 48 science and technology (Esmaeili, 2011). Although the technologies of some new or renewable energies (such as new battery, wind energy, nuclear energy, etc.) are 49 50 developing fast, oil and gas, as the traditional energy, are the main energy resource in 51 the world. The demand of oil and gas is increasing due to the rapid development of the society. However, the petroleum industry is increasingly drilling more technically 52 53 challenging and difficult wells. Drilling of deeper wells worldwide requires constants searching for adequate drilling fluids to overcome extreme conditions (Williams et al., 54 55 2011).

56 Drilling fluids are compared as "the bloods of drilling operations". By drilling operations, oil and gas can be extracted from the earth. Drilling fluids serve several 57 58 fundamental functions, such as (i) to remove the cuttings generated by the drill bit from 59 the borehole, (ii) to control the downhole formation pressures, (iii) to overcome the fluid pressure of the formation, (iv) to avoid damage to the producing formation and (v) 60 61 to cool and lubricate the drill bit, etc. (Chilingarian and Vorabutr, 1983; Caenn and Chillingar, 1996; Meng et al., 2012). Generally, drilling fluids can be divided into two 62 types based on the continuous phase, i.e., water-based drilling fluids and oil-based 63 64 drilling fluids. Water-based drilling fluids are limited by their abilities of dissolving salts, interfering with the flow of oil and gas through porous rocks, promoting the 65 disintegration and dispersion of clay minerals, and effecting the corrosion of iron 66

67 (Caenn et al., 2011). Oil-based drilling fluids, owing to their excellent lubricity, high 68 rate of penetration, shale inhibition, wellbore stability, high lubricity, high thermal 69 stability (Caenn and Chillingar, 1996; Khodja et al., 2010), are advised to be used to 70 drill difficult wells. In spite of the advantages of oil-based drilling fluids, drilling 71 practice always demand drilling fluids with greater rheological properties and better 72 thermal stability.

73 Organoclays (OC) are used in oil-based drilling fluids to control the rheological behavior. They perform specific functions in a base oil and are varied in amount to 74 75 furnish the properties required for satisfying the conditions of use. Organomontmorillonite (OMt) is mostly used in oil-based drilling fluids (Caenn et al., 2011; 76 Dino and Thompson, 2013; Zhuang et al., 2016, 2017b). Hermoso et al. (2014) reported 77 78 that the viscous flow behavior of oil-based drilling fluids is deeply influenced by OMt nature and concentration. (Schmidt, 1987) proposed that OC did not viscosify the oils 79 but built the structure through interactions with the aqueous face (water phase is usually 80 included in oil-based drilling fluids). But later work (Burgentzle et al., 2004) 81 82 demonstrated that OMt can viscosify organic solvents without water. Previous work (Zhuang et al., 2017b, d) reported the exfoliation of OMt in oil aged at high 83 temperatures. Exfoliated OMt produced many nanolayers to build a "house of cards" 84 structure, resulting in the improvement of gel formation and rheological properties. By 85 comparing studies on different modifiers, surfactants containing two long alkyl chains 86 87 was proved to be easier to result in exfoliation of OMt in oil and excellent rheological properties. However, distinct decline of the rheological properties occurred when best 88

fluids aged above 180°C, because of two potential ways, i.e., thermal decomposition
and desorption of organic surfactants.

Recently, the OC from palygorskite-sepiolite family were reported to be used in oil-91 based drilling fluids (Dino and Thompson, 2002; Zhuang et al., 2017a, c, d, 2018b; 92 93 Weng et al., 2018). They exhibited excellent rheological properties in oil by forming a 94 "haystack" structure. These clay minerals are natural nanofibrous materials. For 95 sepiolite (Sep), its fiber sizes generally range from 0.2 µm to 2 µm in length, 100 nm to 300 nm in width and 50 nm to 100 nm in thickness (Alvarez, 1984; Álvarez et al., 2011). 96 97 Accordingly, Sep shows preeminent rheological properties in polar solvents. By organic modification, organo-sepiolite (OSep) displays the lipophilicity and can perform 98 excellent rheological properties in oil (Zhuang et al., 2018a). 99

100 Some recent literature reported about the joint use of Mt and fibrous clay minerals 101 (Neaman and Singer, 2000; Chemeda et al., 2014; Al-Malki et al., 2016) to enhance the rheological properties of clay minerals in solvents. Al-Malki et al. (2016) found that 102 103 bentonite-based drilling mud with Sep nanoparticles showed a great stability in plastic 104 viscosity and yield point over a wide range of temperature and pressure, especially at high temperatures and pressures. The previous work enlightened that synergistic use of 105 106 OMt and OSep may also promote the rheological properties and thermal stability of oilbased drilling fluids. This is a promising way to sustain oil-based drilling fluids work 107 in difficult wells. 108

Aiming to improve the rheological properties and thermal stability of oil-based
 drilling fluids, OMt and OSep was synergistically used in oil-based fluids aged at

111 different temperatures and their structures and rheological properties were 112 characterized.

113

114 2. Materials and Methods

115 2.1 Materials

116 Na⁺-treated Mt was obtained from Kazuo, Liaoning, China, with the purity of ca. 84% and cation exchange capacity (CEC) of 120 cmol/kg. Sep was obtained from Spain, 117with the CEC of 35 cmol/kg. The purity of clay minerals was defined X-Ray diffraction 118 119 method according to the Chinese standard SY/T 5163-2010. Details of this method were reported in previous literature (Zhuang et al., 2018a). Some quartz (12%), calcite (4%) 120 and albite (2%) were included in the Mt sample (see Fig. 1 (A)). XRD pattern of Sep 121 122 (Fig. 1 (B)) matches well with the JCPDS card of Sep and no other reflections are observed, indicating the high purity of Sep. The chemical composition of Mt and Sep 123 were characterized by X-ray fluorescence (XRF) analysis and the results are listed in 124 125 Table 1. Both of these two clay minerals were milled and sieved with a 200-mesh sieve before use. Benzyl dimethyl octadecyl ammonium chloride (C18, purity of 97%) and 126 dimethyl dioctadecyl ammonium chloride (DC18, purity of 98%) were bought from 127 Anhui Super Chemical Technology Co., Ltd, China. The white oil (No. 5) was bought 128 from China National Petroleum Corporation. 129

130

131 2.2 Preparation of OC

132 OMt was prepared in aqueous solution as the following steps: 100 g of Mt was

added into 1 L deionized water, stirring for 0.5 h; then DC18 (1.0 CEC of Mt) was added into the previous dispersion, stirring for 1 h; at last, by centrifugation, drying at 60°C for 24 h, milling and sieving with a 200-mesh sieve. OSep was prepared as the following steps: C18 (35% of the mass of Sep) was firstly dissolved into 500 mL distilled water (keep at 60°C in the whole process), 100 g of Sep was added into the previous solution, stirred for 1 h and thickened slurry was obtained; at last, after drying at 60°C for 24 h, milling and sieving with a 200-mesh sieve, OSep was prepared.

140 2.3 Preparation of Sep/oil fluids

12 g of OC was added into 400 mL white oil (concentration of 30 kg/m³) and 141 blended at 10000 rpm for 20 min. A drilling fluid should be aged at different 142 temperatures to model the real drilling operation. According to the standards of API 143 144 SPEC 13A and API RP 13B-2, the resulting fluid was placed in a rotary oven heated to 66°C, 150°C, 180°C and 200°C where it was aged for 16 h. The mixtures of OC in oil-145 based drilling fluids are listed in Table 2. The corresponding fluid is named as OC/oil-146 temperature. For example, the oil-based fluid of OMt_{0.5}-OSep_{0.5} and oil aged at 150°C 147 is named as OMt_{0.5}-OSep_{0.5}/oil-150. 148

149

150 2.4 Characterization

The X-ray diffraction (XRD) analysis was conducted on a Bruker D8 Advance Xray powder diffractometer operating at Cu Kα radiation, 40 kV, 40 mA and a scan speed
of 0.05 s per step (step size: 0.02°). The XRD patterns were collected from 3° to 70°.
Particularly, the XRD test for OC/oil gels is described in the section 3.1. Scanning

155	electron microscope (SEM) images were obtained with a HITACHI SU8000 type SEM
156	and the operating voltage was 10 kV. The transmission electron microscope (TEM)
157	analysis was conducted on a JEM 1200EX TEM equipment and operated at the voltage
158	of 200 kV. Gel volume results were obtained by adding 100 mL aged fluid into a
159	graduated cylinder with a stopper and standing for 24 h. The dynamic rheological
160	behavior of oil-based fluids was tested by a Thermo Scientific HAAKE Roto Visco 1
161	rotational viscometer at 20°C. The tested program was: the shear rate linearly increased
162	from 0 s ⁻¹ to 100 s ⁻¹ in 5 min (up step), and then linearly decreased from 100 s ⁻¹ to 0 s ⁻¹
163	¹ in 5 min (down step).

164

165 **3. Results and discussion**

166 **3.1 XRD** analysis

The XRD patterns of Mt and OMt were presented in Fig. 1 (A). There were some 167 impurities, i.e., quartz and calcite in the Mt sample. The basal reflection of Mt occurred 168 at $2\theta = 7.05^{\circ}$, with the basal spacing of 1.25 nm. Modified with DC18, a group of 169 reflections emerged at 2.40° , 4.82° and 7.34° , which were attributed to the reflections 170 of (001), (002) and (003) crystalline planes. The basal spacing of OMt increased to 3.68 171 172 nm, indicating the successful intercalation of DC18 into the interlayer space. In Fig. 1 (B), the XRD pattern of OSep is nearly the same with that of Sep. This phenomenon 173demonstrated that the organic modification could not influence the crystal structure of 174Sep, similar with the modification of palygorskite (Zhuang et al., 2017a, c). This is 175176 because that the TOT (T refers [SiO₄] tetrahedron and O refers to [Al(Mg)O₆]

octahedron) layers were linked by covalent bonds. Based on the TGA results (see Fig.
S1, in supplementary materials), there were 40.8% and 23.4% of organic surfactants
included in OMt and OSep, respectively.

The OC/oil gels were also characterized by XRD using an appropriate method (see 180 181 Fig. 2 (A)). Firstly, the OC/oil fluid was dripped on oil-absorbing papers. After 24 h of 182 natural absorption, extra oil was removed and the OC/oil gel was obtained. OC/oil gels were marked following the template of "OC/oil-temperature". Finally, the OC/oil gels 183 184 can be tested using the X-ray diffractometer similar with powder samples. The XRD 185 patterns of sample holder and sample holder with oil are shown in Fig. 2 (B). The sample holder exhibited a small reflection with low intensity. However, a wider 186 reflection occurred in the XRD pattern of sample holder + oil, with higher intensity. 187 188 These two reflections are typical amorphous ones, in agreement with the previous literature (Ribotta et al., 2004; Bates et al., 2006; Ford et al., 2010; Rowe and Brewer, 189 2017). Thus, this reflection between 8 to 30° and centering at ca. 17° is assigned to the 190 amorphous reflection of oil. 191

The XRD patterns of OC/oil gels aged at different temperatures are presented in Fig. 3. A wide reflection in the range of $2\theta = 8-30^{\circ}$ emerged in the XRD patterns of OC/oil gels, centering at 17 to 18°. They are attributed to the oil as proved in Fig. 2 (B). These wide reflections demonstrated that oil molecules were packaged in the network structures of OC. The intensity of these reflections can be used to evaluate the oil contents in the gels. Compared with OMt, the XRD patterns of OMt/oil-66 and OMt_{0.8}-OSep_{0.2}/oil-66 showed that the basal spacing of OMt in these two gels increased to 5.04

nm: indeed, oil molecules are probably in the interlayer space due to the lipophilicity. 199 In the XRD pattern of OMt_{0.5}-OSep_{0.5}/oil-66, both intensities of reflections attributed 200 201 to OMt and OSep dramatically reduced, indicating disordered arrangements parallel to the c-axis of OMt and the b-axis of OSep. When the mass content of OSep increased to 202 203 80%, the basal reflection of OMt disappeared in the XRD pattern of OMt_{0.2}-204 $OSep_{0.8}$ /oil-66. Considering the changes in the XRD patterns of $OMt_{0.5}$ - $OSep_{0.5}$ /oil-66 205 and OMt_{0.2}-OSep_{0.8}/oil-66, the mixing of OMt and OSep facilitated the exfoliation of 206 OMt. The XRD pattern of OSep/oil-66 is similar with that of OSep powder, in spite of 207 the wide reflection from 8° to 30° .

With the temperature rising, the wide reflection of oil showed high intensity, 208 indicating more oil molecules contained in the gel structures. This fact proved that high 209 210 temperatures promoted the formation of a stronger network structure with large interspace. OSep/oil gels maintained the reflections of Sep at different temperatures. 211 However, the basal reflections of OMt/oil gels aged above 150°C disappeared, probably 212 suggesting the exfoliation of OMt. But the (100) reflection, which emerged at $2\theta =$ 213 214 19.7°, was kept in the XRD patterns of OMt/oil gels. This phenomenon implied that the 215 individual TOT structures were kept and changes just happened to the arrangement paralleling to the c-axis. The basal reflection of OMt was not observed in the mixture 216 of OMt and OSep aged at high temperatures, indicating the exfoliation of OMt. With 217 218 the increase of OSep, OC/oil gels exhibited higher intensity of the (110) reflection, because of the more proportion of OSep. Significantly, the XRD patterns of these 219 OC/oil aged from 150°C to 200°C showed the similar reflections, indicating that they 220

221 kept the structures in this temperature range.

222

223 **3.2 SEM and TEM**

224 The SEM and TEM images are presented in Fig. 4. OMt is associated with a large 225 number of silicate layers. To some extent, these layers are soft so that they may be 226 curved. Based on the TEM image of OMt, the lamellae contain at least 10 layers. The 227 distance between two adjacent layers was measured as 3.56 nm. This value is a little 228 smaller than the basal spacing derived from the XRD result. This is because the high 229 voltage of TEM test (200 kV) would destroy the interlayer surfactants and/or dehydration of the interlayer space (Kogure, 2013). Hence, the basal spacing calculated 230 231 from the TEM depended on the voltage, test time, thermal stability of organic 232 compounds and the thickness of samples. The exfoliation of OMt was defined as no further interaction occurs between the two delaminated units (isolated layers or stacking 233 of few layers) which become independently mobile in the liquid phase (Bergaya et al., 234 235 2012), so that the no long-range order was apparent along the c-axis. The exfoliated OMt layers would form a "house of cards" structure by surface to edge and edge to 236 237 edge arrangements.

The SEM and TEM images of OSep showed the disordered aggregation of OSep fibers. The length of fibers ranged from hundreds of nanometers to ca. 1 µm. Indeed, the OSep existed in the forms of individual fibers (rods), laths and bundles (García-Romero and Suárez, 2013). The crystal laths and bundles, which consist of nanofibers, are very hard to be disaggregated, due to the electronic attraction, Van der Waals forces and hydrogen bonding interaction (Haden and Schwint, 1967; Xu et al., 2014). The
aggregation of different forms of OSep built a "haystack" structure (Haden, 1963).

The SEM or TEM images of OC/oil gels can't be obtained, because of the high amount of oil present in the gels. Indeed, it is difficult to remove the oil because of its high boiling point and non-volatile ability.

248

249 **3.3 Gel volume**

250 The gel volume results (see Fig. 5) can directly show the gel formation ability and 251compatibility between oil and OC. At the initial time (t = 0 s), all the gel volumes of 252 OC/oil fluids were set as 100.0 mL. When the time went to 90 min, the gel volumes of 253 OMt, OMt_{0.8}-OSep_{0.2}, OMt_{0.5}-OSep_{0.5}, OMt_{0.2}-OSep_{0.8} and OSep in oil were 21.8 mL, 254 97.2 mL, 98.0 mL, 100.0 mL and 100.0 mL, respectively. After standing four 24 h, the gel volumes became 15.7 mL for OMt, 67.1 mL for OMt_{0.8}-OSep_{0.2}, 89.5 mL for 255OMt_{0.5}-OSep_{0.5}, 100.0 mL for OMt_{0.2}-OSep_{0.8} and 100.0 mL for OSep. OMt showed 256 257 the least gel volume in oil while OSep presented the gel volume of 100.0 mL. At room temperature, OMt can only absorb a part of oil molecules, resulting in the expanding of 258259 interlayer space. The swelling OMt particles dispersed and stacked in oil, without prominent contributions to promoting the network structure and gel formation. 260 However, TEM images testified that OSep is in the form of fibers, laths and bundles, 261 which are in nanoscale. These fibers laths and bundles could be easier to form "haystack" 262 structures, leading to the high and stable gel volumes. The gel volumes of OMt/OSep 263 mixture in oil increased with the increase of OSep proportion. This phenomenon 264

suggested that the addition of OSep contributed to the gel formation of OMt in oil.

267

3.4 Rheological properties

268 The dynamic rheological curves of OC/oil fluids are presented in Fig. 6. These 269 curves display the rheological behavior and thermal stability of corresponding OC/oil 270 fluids. Aged at 66°C, OMt/oil fluid showed the highest shear stress, indicating that 271 OMt/oil fluid displayed the best viscosity. OMt/oil and OSep/oil fluids aged at 66°C 272 showed the different curves of up step and down step. However, in the rheological 273 curves of the mixture of OMt and OSep fluids, the down step curves nearly followed the up step curves. This fact demonstrated that the network structures of OMt and 274275 OSep in oil obviously changed while no distinct structural changes happened in the 276 mixture fluids. The single OC built their own network structures in oil. But the new network structure didn't form well in the mixed oil fluids aged at 66°C. In addition, 277 the rheological curves of fluids aged at 66°C followed the Bingham plastic model at 278 10-100 s⁻¹, except for OSep/oil aged at 66°C. 279

When the temperature increased to above 150° C, the rheological curves became very different. Firstly, the shear stresses of fluids aged above 150° C is much larger than those of fluids aged at 66° C, demonstrating the promotion of network structures and viscosity by high temperatures. Furthermore, in the up step, a rapid climb was observed before 20 s⁻¹, and then a dramatical decline occurred. Consequently, there was a critical point which showed the highest shear stress. This critical point suggested that a large shear stress must be applied to break the connected aggregates

of OC and to disperse and orient stacked nanoplatelets or nanofibers (maybe nano laths and bundles) in the flow direction (Zhuang et al., 2017b). In the down step, the curves were nearly lines (in spite of the derivation at 0-20 s⁻¹), in agreement with the Bingham plastic model. No critical points were seen in the down step because the network had been sheared at high shear rate and the network structures were destroyed.

293 These critical points can indicate the gel strengths of network structures. The 294 shear stress results corresponding to these critical points are listed in Table 3. Aged at 295 66°C, OSep/oil fluid showed a little different rheological curve from other fluids, due to the changes at 0-40 s⁻¹ in up step. It was a critical range, instead of a point, because 296 297 the network structure was not enough strong. The critical shear stresses of OMt/oil 298 and OSep/oil fluids firstly increased and then decreased, indicating that the increase of aging temperature firstly improved the formation of network structure and higher 299 temperature would be harmful for the network structure, due to the thermal 300 301 degradation and/or desorption of organic surfactants. The critical shear stress of 302 $OMt_{0.8}$ - $OSep_{0.2}$ /oil fluid gradually decreased with the temperature rising. However, 303 OMt_{0.5}-OSep_{0.5}/oil and OMt_{0.2}-OSep_{0.8}/oil fluids showed basically stable critical shear stresses from 150°C to 180°C, and little higher ones at 200°C. This 304 phenomenon demonstrated the better stability of the mixture of OMt and OSep than 305 single OC in oil-based drilling fluids. 306 The shear stresses of samples at 100 s⁻¹ were applied to evaluate the viscosities (η) 307

308 of different fluids (Table 4). As $\eta = \tau/\gamma$ and γ was constant (τ refers to shear stress and

 γ refers to shear rate), i.e., 100 s⁻¹, τ can be used to indicate the changes of η . Aged at 309 66°C, the τ values of samples were very low, because the OC were not exfoliated 310 completely or dispersed well. With the temperature rising, the τ values dramatically 311 increased due to the fine formation of network structures which was promoted by high 312 313 temperatures. For example, the τ_{66-150} values of OMt/oil, OMt_{0.8}-OSep_{0.2}/oil, OMt_{0.5}-314 OSep_{0.5}/oil, OMt_{0.2}-OSep_{0.8}/oil and OSep/oil were 108%, 378%, 687%, 696% and 315 694%. Compared with the τ values at 180°C, OMt/oil, OMt_{0.8}-OSep_{0.2}/oil and OSep/oil at 200°C decreased by 49%, 26% and 18%. However, the τ values of OMt_{0.5}-OSep_{0.5} 316 317 and OMt_{0.2}-OSep_{0.8} at 200°C increased by 46% and 18%. These results also supported 318 that the mixture of OMt and OSep benefited the viscosity and thermal stability of oil-319 base drilling fluids.

Thixotropy represents a reversible isothermal transformation of a colloidal sol to a gel. It is caused by the clay mineral units slowly arranging themselves in positions of minimum free energy. In drilling practice, low resistance (low viscosity) is expected for the bit to ensure high drilling rate, while high viscosity is expected for carrying cuttings. Excellent thixotropy of an oil-based drilling fluid is necessary. The areas of thixotropic loops (abbreviated as A, see in Table 5) in Fig. 6 are applied to evaluate the thixotropy of OSep/oil fluids.

Aged at 66°C, the A value of OMt/oil fluid was 22.5 $Pa \cdot s^{-1}$ and that of OSep/oil fluid was 39.38 $Pa \cdot s^{-1}$. The A values of $OMt_{0.8}$ - $OSep_{0.2}/oil$, $OMt_{0.5}$ - $OSep_{0.5}/oil$ and OMt_{0.2}- $OSep_{0.8}/oil$ fluids ranged from 2.39 to 4.82 $Pa \cdot s^{-1}$, indicating nearly no thixotropy of these samples. High temperatures promoted the gel formation. The A

331	values of samples increased until aged at 180°C, except for those of OMt _{0.5} -OSep _{0.5} /oil
332	and $OMt_{0.2}$ - $OSep_{0.8}$ /oil. The decrease rates of OMt /oil, $OMt_{0.8}$ - $OSep_{0.2}$ /oil and
333	OSep/oil from 180°C to 200°C (A180-200) were 71%, 49% and 24%. OMt/oil declined
334	more than OSep/oil. OMt _{0.5} -OSep _{0.5} /oil and OMt _{0.2} -OSep _{0.8} /oil exhibited continuous
335	and slow augment of the A values until to 200°C, so that these two samples can be
336	basically regarded as stable samples. The A values of $OMt_{0.5}$ - $OSep_{0.5}$ /oil and $OMt_{0.2}$ -
337	OSep _{0.8} /oil at 150-200°C were much more than those of a single OC, demonstrating
338	that the mixture of OMt and OSep contributed to improving the thixotropy of oil-based
339	fluids.
340	Considering all the discussions of rheological properties, the mixture of OMt and
341	OSep, with the mass proportion of 50% for each, can effectively improve the viscosity,
342	gel strength, thixotropy and thermal stability of the oil-based fluids.
343	
344	3.5 Network structure
345	The rheological test proved that the $OMt_{0.5}$ - $OSep_{0.5}$ performed greater rheological
346	properties and better thermal stability in oil than each single OC did. This enhancement
347	was resulted by the mixed network structure (see Fig. 7). When mixing OMt and OSep
348	in oil, they firstly disperse following their own nature. At low temperature, oil
349	molecules were adsorbed into the interlayer space of OMt, resulting in swelling. OMt
350	was mostly in the form of swelled particles, perhaps with a little exfoliated nanolayers.
351	OSep fibers, laths and crystal bundles dispersed in oil. Although the mass proportions
352	of these two OC were identical, the number of OMt particles was much less than the

number of OSep fibers, laths and bundles. Due to the difference of these numbers, OMt
and OSep had no strong contact with each other. But the mixing of these two OC still
improved their gel formation in oil (see Fig. 5).

356 As the XRD results demonstrated that OMt exfoliated in oil above 150°C, one OMt 357 particle might divided into dozens or hundreds of nanolayers. Consequently, the number 358 of OMt layers dramatically increased. Influenced by the thermal motion, these nanolayers mixed and contact with the nanofibers, laths and bundles. Significantly, the 359 "house of cards" structure of OMt and the "haystack" structure were not independent. 360 361 These two different shapes of silicate units (layered OMt and fibrous OSep) interweaved with each other, leading to a stronger network structure. Previous work 362 testified that organic surfactants would decomposed or/and dissolved into oil at high 363 364 temperature, resulting the shrink of OMt (Zhuang et al. 2017b). In this mixed network structure, exfoliated OMt layers were supported by OSep fibers, and the OSep fibers 365 were also sustained by the nanolayers. 366

367

368 4. Conclusion

In summary, synergetic use of OMt and OSep can improve the rheological properties and thermal stability of oil-based drilling fluids. OMt firstly swelled in oil by adsorbing oil molecules while OSep showed stable dispersion due to its nanoscale fibers, laths and bundles. At high temperature, thermal motion promoted the exfoliation of OMt into nanolayers. The interweave of nanofibers (laths and bundles) of nanolayers enhanced the network structure, resulting in improvement of rheological properties.

375	The mutual	support	between	OMt	nanolayers	and	OSep	nanofibers	protected	this
376	network stru	cture for	m crush a	t high	temperature	es.				

378 4	Acknowledgement
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Fig. 1 XRD patterns of (A) Mt, OMt, (B) Sep and OSep.



Fig. 2 (A) Interpretive diagram of XRD test for OC/oil gel sample and (B) XRD patterns of the sample holder and sample holder with oil.



Fig. 3 XRD patterns of OC/oil gels aged at (A) 66°C, (B) 150°C, (C) 180°C and 200°C.



Fig. 4 SEM images of (A) OMt and (C) OSep; TEM images of (B) OMt and (D) OSep.



Fig. 5 Gel volume results of (A) OMt, (B) OMt_{0.8}-OSep_{0.2}, (C) OMt_{0.5}-OSep_{0.5}, (D)

 $OMt_{0.2}$ - $OSep_{0.8}$ and (E) OSep in oil.



Fig. 6 Dynamic rheological curves of OC/oil fluids aged at (A) 66°C, (B) 150°C, (C) 180°C and (D) 200°C for 16 h.



Fig. 7 the Interpretive diagram of the network structure of the mixed OMt and OSep in oil.

Figure captions:

Fig. 1 XRD patterns of (A) Mt, OMt, (B) Sep and OSep.

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Tables

Sampla	Composition (mass %)							
Sample	SiO ₂	Al_2O_3	CaO	MgO	Na ₂ O	Fe ₂ O ₃	others	
Mt	64.40	19.71	4.16	3.75	3.72	3.30	0.96	
Sep	63.68	9.88	1.26	19.41	0.87	3.35	1.55	

Table 1 Chemical composition of Mt and Sep (derived from XRF results)

Table 2 Details of the mixtures of OMt and OSep.

Sample	OMt (mass %)	OSep (mass %)
OMt	100	0
OMt _{0.8} -OSep _{0.2}	80	20
OMt _{0.5} -OSep _{0.5}	50	50
OMt _{0.2} -OSep _{0.8}	20	80
OSep	0	100

Sampla	Shear stress (Pa)					
Sample	66°C	150°C	180°C	200°C		
OMt/oil	none	15.62	31.41	15.28		
OMt _{0.8} -OSep _{0.2} /oil	none	31.50	29.33	22.05		
OMt _{0.5} -OSep _{0.5} /oil	none	50.12	51.08	62.67		
OMt _{0.2} -OSep _{0.8} /oil	none	41.52	44.49	53.81		
OSep/oil	none	19.64	36.53	33.06		

Table 3 A summary of shear stress results corresponding to the critical points.

Table 4 A summary of shear stress (τ) at the shear rate (γ) of 100 s⁻¹.

Sample	τ (Pa)		τ_{66-150}	$\tau_{180-200}$		
Sample	66°C	150°C	180°C	200°C	(%)	(%)
OMt/oil	4.02	8.36	21.53	10.96	108	-49
OMt _{0.8} -OSep _{0.2} /oil	3.13	14.95	17.60	13.10	378	-26
OMt _{0.5} -OSep _{0.5} /oil	1.80	14.16	13.96	20.34	687	46
OMt _{0.2} -OSep _{0.8} /oil	1.25	9.95	11.78	13.86	696	18
OSep/oil	1.91	15.16	13.29	10.85	694	-18

Note: $\tau_{66-150} = (\tau_{150} - \tau_{66})/\tau_{66} \times 100\%$, similarly, $\tau_{180-200} = (\tau_{200} - \tau_{180})/\tau_{180} \times 100\%$; τ_x refers to the shear stress at 100 s⁻¹ of fluids aged x°C.

	A (Pa \cdot s ⁻¹)				A ₆₆₋₁₅₀	A ₁₈₀₋
Sample	66°C	150°C	180°C	200°C	(%)	200
						(%)
OMt/oil	22.50	325.97	635.20	186.22	1349	-71
OMt _{0.8} -OSep _{0.2} /oil	3.46	600.86	710.46	361.12	17266	-49
OMt _{0.5} -OSep _{0.5} /oil	4.82	1097.75	1281.62	1497.10	22675	17
OMt _{0.2} -OSep _{0.8} /oil	2.39	907.37	1011.93	1080.78	37865	7
OSep/oil	39.38	275.34	842.99	644.85	599	-24

Table 5 The areas of thixotropic loops (A) in Fig. 6.

Note: $A_{66-150} = (A_{150}-A_{66})/A_{66} \times 100\%$, similarly, $A_{180-200} = (A_{200}-A_{180})/A_{180} \times 100\%$;

 A_x refers to the area of a sample aged at $x^\circ C$.