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1 Organoclays used as colloidal and rheological additives in
2 oil-based drilling fluids: an overview

3

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23 Abstract

24 The objective of this paper is to give an overview of the synthesis, properties of
25 different organoclays, including organo-montmorillonite, organo-sepiolite and
26 organo-palygorskite, and their use as rheological additives in oil-based drilling fluids.
27 The researches performed until the present moment are described and summarized. A
28 significant amount of work had been done in this area, including the rheological
29 behavior at normal and high temperature, the structure changes of organoclays in
30 oil-based system, thermal stability and the rheological mechanisms. The role of
31 layered and fibrous organoclays in oil-based drilling fluids in the enhancement of the
32 rheological properties and thermal stability is deeply reviewed.

33 Keywords: montmorillonite, palygorskite, sepiolite, oil-based muds, rheological
34 properties, thermal stability

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74 1. Introduction

75 Oil and gas, the main fossil fuels, not only provide us the major energy sources
76 but they are also the feedstocks for a great variety of manmade materials and products
77 that range from gasoline and diesel oil to varied petrochemical and chemical products,
78 including synthetic materials, plastics, and pharmaceuticals (Olah, 2005). The
79 petroleum products integrate our daily life involving food, clothes, house, electronic
80 products, etc. In some extent, oil and gas support the economic and cultural boom in
81 the past hundred years. With the development of human society and increasing
82 population in the world, oil and gas continue to be significantly depleted and will
83 become increasingly costly. Present estimates of the proven oil reserves reveal that
84 they would last for some 30 years at the current rate of consumption. Natural gas
85 reserves are comparable but somewhat larger. New developments and improved
86 recovery methods, however, could extend these estimates significantly.

87 To resolve this serious problem, two actions have been taken. Firstly, new energies
88 and materials are researched and developed to try to replace traditional energies and
89 materials. For example, much attention has been paid to the solar energy conversion
90 (Scaife, 1980; Schaller and Klimov, 2004; Grätzel, 2005; Crabtree and Lewis, 2007),
91 nuclear energy (Hodge, 2017; Ozcan and Ari, 2017) and other renewable energy
92 resources (Cheng, 2017; Hodge, 2017). In addition, new energy-storing materials
93 using nanotechnologies have been developed (Borenstein et al., 2017; Ouyang et al.,
94 2017; Pramudita et al., 2017; Xu et al., 2017; Zhao et al., 2017; Liang et al., 2018).

95 Secondly, more efforts have been spared to enhance the oil and gas production by
96 three ways: (i) looking for more oil and gas reservoirs by more geological surveys and
97 explorations, (ii) developing new technologies to exploit oil and gas from difficult
98 formations, such as high-temperature, high-pressure, high-angle, offshore wells, etc.
99 (Davison et al., 1999; Bland, 2006; Esmaeili, 2011; Kezirian and Phoenix, 2017), and
100 (iii) developing more unconventional energy, i.e., shale oil and shale gas (Curtis, 2002;
101 Kinnaman, 2011; Barati and Liang, 2014). Although, the new energies may be cleaner
102 and more environmentally friendly, they cannot satisfy the large demands of the
103 society at present. The best economic way is to take full advantage of petroleum oil
104 and gas now.

105 Drilling operation is the first and important step of extracting oil and gas from
106 underground. Drilling operation has been practiced for thousands of years. According
107 to Confucius (600 B.C.), wells were drilled in China for brine during the early part of
108 the Zhou dynasty (1122-250 B.C.). Many wells, some hundreds of feet deep, were
109 bored near the border of Tibet for brine, gas, and water. Water was poured into these
110 wells to soften the rock and to aid in the removal of cuttings. This water was the
111 inchoate drilling fluids. With the development of science and technology, drilling
112 operation and drilling fluids have become an important subject. The drilling fluids
113 used in rotary drilling are complex systems with many compositions. Today, the
114 successful completion of an oil well and its cost depends on a considerable extent on
115 the properties of the drilling fluids. The cost of the drilling fluid itself is relatively
116 small, but the choice of the right fluid and maintenance of the right properties while

117 drilling profoundly influence the total well costs. Hence drilling fluids play a very
118 important role in extracting oil and gas.

119 Drilling fluids were firstly used to remove the cuttings from the bore hole. But
120 now, the diverse applications for drilling fluids require specific functions. In a
121 summary, a drilling fluid severs fundamental functions such as (i) carrying cuttings
122 from beneath the bit, transporting them up the annulus, and permitting their separation
123 at the surface, (ii) cooling and cleaning the drilling tools, (iii) reducing friction
124 between the drilling string and the sides of the hole, (iv) maintaining the stability of
125 uncased sections of the borehole, (v) preventing the inflow of fluids oil, gas, or water
126 from permeable rocks penetrated, (vi) forming a thin, low-permeability filter cake that
127 seals pores and other openings in formations penetrated by the bit, (vii) assisting in
128 the collection and interpretation of information available from drill cuttings, cores,
129 and electrical logs (Caenn and Chillingar, 1996; Caenn et al., 2011).

130 Drilling fluids are classified according to their continuous phases: water-based
131 drilling fluids, oil-based drilling fluids and gas. Gas is used limitedly in practice. Thus,
132 only water-based drilling fluids and oil-based drilling fluids are discussed in this work.
133 Water-based drilling fluids were firstly developed and wildly used due to the low cost
134 (Caenn and Chillingar, 1996; Meng et al., 2012; Sadeghalvaad and Sabbaghi, 2015).
135 However, water-based drilling fluids are limited in difficult drilling operations, such
136 as offshore, high-temperature, high-angle wells, because of the sensitivity to salts and
137 poor shale inhabitation (Zhuang et al., 2015a). On the contrary, oil-based drilling
138 fluids exhibit excellent thermal stability and drilling performance by producing low

139 frictions, high rate of penetration, excellent shale inhabitation, wellbore stability, good
140 lubricity and prominent salt resistance (Khodja et al., 2010) to overcome some
141 undesirable characteristics of water-drilling fluids. Thus, oil-based drilling fluids are
142 more popular in the difficult drilling operations (e.g., offshore drilling,
143 high-temperature and high-angle wells).

144 Shale gas is a newly unconventional energy resource. It is mostly extracted by
145 hydraulic fracturing, which is a commonly used technique to stimulate hydrocarbon
146 production by creating a network of highly conductive fractures in the area
147 surrounding a wellbore (Curtis, 2002; Vidic et al., 2013; Barati and Liang, 2014;
148 Vengosh et al., 2014). A horizontal drilling is necessary for exploiting shale gas. The
149 instability of the wellbore resulted from the swelling of clay minerals by adsorbing
150 water is the most serious problem. Hence, oil-based drilling fluids are popular when
151 drilling shale formations. Most of the rest and newly found fields are difficult to
152 extract oil and gas due to difficult geological conditions, such as high temperature,
153 high pressure, high angle and offshore, etc. Thus oil-based drilling fluids are more
154 likely to be used in these fields.

155 The rheological properties (especially under high temperatures) of a drilling fluid
156 are always concerned, because the functions of drilling fluids are basically supported
157 by appropriate rheological properties. A drilling fluid is a thixotropic system; it
158 exhibits low viscosity when sheared, such as on agitation or circulation (as by
159 pumping) but, when such shearing action is halted, the fluid thickens to hold cuttings
160 in place. The fluid must become thick rapidly, reaching a sufficient gel strength before

161 suspended materials fall any significant distance. This behavior must be totally
162 reversible at all temperatures encountered. In addition, when a free-flowing liquid, the
163 fluid must retain a sufficiently high viscosity to carry all unwanted particulate matter
164 from the bottom of the hole back up to the surface. Moreover, the increasing
165 geothermal gradient may damage the fluids. Thus, a drilling fluid must accomplish a
166 number of these interrelated functions over a wide range of temperatures to satisfy the
167 requirements to be a commercial drilling fluid.

168 Hence, greater emphasis is placed on the rheological properties provided by the
169 colloidal and rheological additives. Clay minerals, such as montmorillonite (Caenn
170 and Chillingar, 1996; Abu-Jdayil, 2011; Caenn et al., 2011; Abdo and Haneef, 2013a),
171 palygorskite (Guyen et al., 1988; Dahab and Jarjarah, 1989; Dahab, 1991; Galan,
172 1996; Murray, 2000; Neaman and Singer, 2004; Baltar et al., 2009) and sepiolite
173 (Guyen, 1981; Guven et al., 1988; Galan, 1996; Altun and Serpen, 2005; Osgouei,
174 2010; Razali and Zafirah, 2011; Altun et al., 2014; Abdo et al., 2016; Al-Malki et al.,
175 2016) are widely used as colloidal and rheological additives in water-based drilling
176 fluids, due to their formation of network structure in water. Inspired by the use of clay
177 minerals in water-based drilling fluids, organoclays (OC), which are obtained by
178 reacting clay minerals with organic compounds, are developed to be used in oil-based
179 drilling fluids as rheological additives for many years. It has been admitted that OC
180 can be used to thicken organic compositions and particularly oil-based drilling fluids.
181 Organic modification results in appropriate colloidal and rheological properties of OC
182 in oil-based system. Addition of OC in the continuous phase enables to achieve

183 suitable properties of the fluid during the different well drilling phases. Consequently,
184 OC promotes a thixotropic behavior combining a low viscosity under shear i.e. during
185 the drilling process, and also the ability to form rapidly a gel retaining suspended
186 materials when the shear is halted. Hence, they have to maintain the rheological
187 properties of the oil-base drilling fluids at different depth i.e. over a wide temperature
188 range. Furthermore, OC has to minimize interaction of oil-base drilling fluids with the
189 bearing rocks by forming a low permeability protective cake on the bore wall and
190 developing adequate physicochemical characteristics to avoid the swelling of drilled
191 shale rocks.

192 In the past years, much literature had been reported about the synthesis, structures,
193 properties and applications, especially in clay/polymer nanocomposites (CPN). Many
194 scientists have also made efforts to study the application of OC in oil-based drilling
195 fluids. Most of the work focused on the applied properties of OC that modified with
196 different organic compounds. Some scientific and technical problems are still
197 unsettled. Mineralogists and engineers paid much attention to the use of OC in
198 oil-based drilling fluids. However, mineralogists usually concern about the structure
199 and properties of OC while engineers always emphasize the applied properties in
200 drilling practice. Anyone concerned with oil-based drilling fluids technology should
201 have a good basic knowledge of clay mineralogy, colloidal chemistry and rheological
202 properties, as OC provides the colloidal and rheological base of in oil-based drilling
203 fluids. In this paper, an overview of recent research and development about
204 application of OC (including organo-montmorillonite (OMt), organo-palygorskite

205 (OPal) and organo-sepiolite (OSep)) in oil-based drilling fluids are presented. The
206 structures, colloidal and rheological properties, and rheological mechanisms of OC in
207 oil-based drilling fluids are summarized.

208

209 2. Organo-montmorillonite

210 2.1 Montmorillonite

211 Montmorillonite (Mt), the main component of bentonite, belongs to the general
212 family of clay minerals. An ideal Mt layer is composed of two continuous $[\text{SiO}_4]$
213 tetrahedral sheets (T) and a $[\text{AlO}_6]$ octahedral sheet (O) (Fig. 1). Thus, the structure of
214 Mt is described as TOT type (Bergaya et al., 2012; Brigatti et al., 2013). Due to
215 isomorphism, Mt layers are often negatively charged. A negative charge layer arises
216 from the substitution of Mg^{2+} and other lower charge cations for Al^{3+} in octahedral
217 sites (Brigatti et al., 2013; Jaber et al., 2014). Consequently, some exchangeable
218 cations, such as Na^+ and Ca^{2+} present in the interlayer space counterbalance the deficit
219 of positive charges (Murray, 1991; Chiou, 1997; Bergaya and Lagaly, 2001; Brigatti et
220 al., 2013). Thus, Mt exhibits high cation exchange capacity (CEC). Murray (1999)
221 reported that the CEC of Mt generally lied in the range of 60-100 cmol/kg. Some
222 recent papers demonstrated higher CEC values which were more than 100 cmol/kg
223 (He et al., 2010; Karaca et al., 2012; Sun et al., 2013; Fernández et al., 2014; Luo et
224 al., 2015). An extremely high CEC of Mt was reported as 174 cmol/kg by Fernández
225 et al. (2014). Mt occurs normally as thin flakes of small particles. The special

226 structure and features result in large specific surface area, swelling properties in polar
227 solvents, adsorptive property and rheological properties of Mt. When mixed with
228 water, the high charge and fine particle size give the fluid a very high viscosity. These
229 basic properties of Mt are related to many industrial uses such as rheological additives
230 in drilling fluids, as foundry bond clays, for pelletizing iron ores, and as sealants in
231 irrigation ditches, farm ponds, earthen dams, landfill liners, etc. (Murray, 1991, 1999).
232 Particularly, raw Mt is widely used in water-based drilling fluids and OMt is also
233 extensively used in oil-based drilling fluids.

234

235 2.2 Synthesis of OMt

236 Due to the exchangeable cations, organic cations can intercalate into the interlayer
237 space (Bergaya and Lagaly, 2001; de Paiva et al., 2008; He et al., 2010, 2014; Lagaly
238 et al., 2013; Bardziński, 2014; Tangaraj et al., 2017), resulting in the expansion of
239 interlayer space. Organic cations do not only intercalate into the interlayer space of
240 Mt, but also coat on the surface (Juang et al., 2002; Hedley et al., 2007; Zhu et al.,
241 2011; Zhuang et al., 2015a, 2016), leading to the increase of the hydrophobicity.
242 Besides cation exchange, surface adsorption, grafting and other chemical interactions
243 can be applied to obtain OMt.

244 Generally, OMt can be prepared by aqueous solution and solid-state reaction.
245 Reacting in aqueous solution is the most common method to prepare OMt in
246 laboratory or even at the industrial scale. OMt is easily obtained by contact with

247 surfactants in aqueous solutions. In aqueous solution thanks to the osmotic pressure,
248 intercalation of organic cations occurs quickly at room temperature. Heating to
249 50-80°C was also employed in some reports. Usually, OMt prepared by aqueous
250 solution exhibits ordered interlayer arrangement, especially at a high surfactant's
251 loading level.

252 Reacting in aqueous solution was criticized because the use of large amount of
253 water. Hence, solid-state methods, including grinding, ball milling and heating the
254 mixtures, were tried to prepare OMt. At first, heating the mixture of Mt and organic
255 compounds was applied. Organic molecules such as acrylamide, methacrylamide, and
256 urea (Ogawa et al., 1989) and bipyridine or hydroxyquinolines (Ogawa et al., 1991;
257 Khaorapong and Ogawa, 2007). However, in these examples, the driving force for
258 intercalation of the organic molecule was the formation of a coordination complex
259 with the preexisting interlayer cations. A mechanochemical route to the interlayer
260 polymerization of polyaniline and polypyrrole in montmorillonite has also been
261 proposed (Yoshimoto et al., 2004a,b, 2005a, b, c), but there are few data regarding
262 non-polymerizing solid-state intercalation of surfactants. OMt was prepared by
263 heating the mixture of Mt, cetyl trimethyl ammonium bromide (CTAB) and silane
264 coupling agent with vigorous stirring (Ge and Jia, 2008, 2009). Recently, grinding and
265 ball milling attracted much attention when preparing OMt (Hrachová et al., 2007).
266 Ball milling method had been employed to modify Mt with nonionic surfactants and
267 accompanying with anionic surfactants (Zhuang et al., 2015b). Nonionic and anionic
268 surfactants successfully intercalated into the interlayer space and increased the basal

269 spacing. Afterwards, Xie et al. (2014) compared the structures of OMt prepared with
270 Mt and CTAB in aqueous solution and ball milling method. They found that ball
271 milling method is a promising way to produce OMt and the basal spacing of the
272 corresponding OMt was as large as 4.55 nm.

273 Many organic compounds can be used to prepare OMt, e.g., cationic surfactants
274 (mostly quaternary ammonium salts and quaternary phosphonium salts) (Lee et al.,
275 2005; Xi et al., 2007; Vazquez et al., 2008; Zhou et al., 2009; Zhu et al., 2009a;
276 Bardziński, 2014), anionic surfactants (Yılmaz and Alemdar, 2005; Yang et al., 2007;
277 Sarier et al., 2010; Zhang et al., 2010b), nonionic surfactants (Platikanov et al., 1977;
278 Shen, 2001; Nourmoradi et al., 2012; Ouellet-Plamondon et al., 2014; Silva et al.,
279 2014b; Guégan et al., 2015; Yin et al., 2015; Zhuang et al., 2015a) and even the
280 mixture of these modifiers, such as cationic and anionic surfactants (Regev and Khan,
281 1996; Chen et al., 2008; Chen et al., 2011; Zhang et al., 2013; Wu et al., 2014; Fu et
282 al., 2016), cationic and nonionic surfactants (Zhang et al., 2012b; Yin et al., 2015;
283 Zhuang et al., 2015a) and anionic and nonionic surfactants (Yang et al., 2005; Zhang
284 et al., 2012a; Zhuang et al., 2015b).

285 Different organic modifiers were used with Mt via different interaction
286 mechanisms. Displacement reactions occur when water molecules in the interlayer
287 space of Mt. Polar molecules enter the interlayer space by replacing water molecules.
288 Neutral organic compounds can form complexes with the interlayer cations. The
289 adsorption of neutral molecules is driven by various chemical interactions: hydrogen
290 bonds, ion-dipole interaction, co-ordination bonds, acid base reactions, charge transfer,

291 and van der Waals forces (Lagaly et al., 2013). Anionic surfactants are difficult to
292 intercalate into the interlayer space due to the negative charges. However, they can
293 also enter the interlayer space by accompanying with cations (Zhang et al., 2010b; Fu
294 et al., 2016).

295 Although cationic surfactants are criticized due to the poor thermal stability and
296 toxicity, they are mostly employed in OMt industry because of the low-cost, easy
297 reaction and controllable hydrophobicity (by the length and/or number of long alkyl
298 chains). OMt modified with two or more kinds of surfactants is very attractive
299 because some properties of OMt can be adjusted by changing the type and amount of
300 surfactants. For example, the basal spacing of OMt prepared with
301 cetyltrimethylammonium bromide and sodium dodecyl sulfonate was reported as
302 large as about 6 nm (Wu et al., 2014), and the dispersity of this OMt was much more
303 homogeneous in organic solvents (Sun et al., 2016). OMt modified with nonionic
304 surfactants usually show worse hydrophobicity due to the polar groups such as –OH.
305 But using nonionic surfactants with cationic surfactants together could improve the
306 hydrophobicity and thermal stability of OMt (Zhuang et al., 2015a).

307 OMt often shows compatibility with organic matrix, swelling ability in organic
308 solvents, adsorption ability to organic matters. The swelling or even exfoliation of
309 OMt in organic solvents contributes to the increase of viscosity and thixotropy. Hence,
310 OMt is usually used in the applications such as CPN, adsorbents of organic pollutants,
311 rheological control agents, paints, cosmetics, refractory varnish, thixotropic fluids, etc.
312 (Patel et al., 2006; Liu, 2007; Utracki et al., 2007; de Paiva et al., 2008; Jaber and

313 Miché-Brendlé, 2009; Zhu et al., 2009b; Bergaya et al., 2011; He et al., 2014).

314

315 2.3 Rheological properties of OMt in oil-based drilling fluids

316 OMt also plays an important role in petroleum industry, which affects our daily
317 life everywhere today. Jordan (1963) reported OMt as the thicker in organic solvents.
318 After decades of years, OMt is the most widely used and commercial rheological
319 additive in oil-based drilling fluids. OMt control the rheological behavior of an
320 oil-based drilling fluid by dispersing, swelling and even exfoliation in base oil, due to
321 the hydrophobicity and large basal spacing. A few works have examined the
322 rheological behaviors, filtration properties and thermal stability of oil-based drilling
323 fluids when OMt were used as an additive to improve the drilling operations. They
324 exhibited that rheological properties of organoclay/oil fluids depend on the type of
325 organoclay, size, shape, surface properties, concentration, and medium composition.

326 A recent study by Hermoso et al. (2014) showed that viscous flow behaviors of
327 oil-based drilling fluids with two commercial OMt samples (B34 and B128) as
328 additives at different pressure are strongly influenced by OMt nature and
329 concentration (Fig. 2). Higher concentration of OMt in oil resulted in larger viscosity.
330 The viscosity of OMt/oil fluids increased with the increase of pressure. This
331 phenomenon might be due to the compression of base oil under high pressure, which
332 led to the increase of concentration of OMt. They also observed that shear-thinning
333 behavior of the OMt/oil fluids at different concentrations is related to the development

334 of various microstructures, which depend on the type of surfactants. Hermoso et al.
335 (2015) investigated the rheological properties of OMt in invert-emulsion oil-based
336 drilling fluids with the influences of concentration and pressure, and they found the
337 similar phenomenon. In addition, the water fraction also positively affected the
338 viscosity of the fluids. Afterwards, Hermoso et al. (2017) jointly researched the
339 influence of aqueous phase volume fraction, OMt concentration, pressure and
340 temperature on density of oil-based drilling fluids. They studied the
341 pressure-temperature-density behavior of the OMt/oil fluids by Tait equation, with a
342 maximum relative error lower than 0.21%. The density of the OMt/oil fluids
343 decreased as temperature increased while the density increased as pressure augmented
344 (Fig. 3).

345 Moreover, Zhuang et al. (2016) investigated the structure of OMt/oil fluids and
346 their viscous flow behaviors under different temperatures. They observed that
347 swelling and gel formation of organoclay dispersion were positively affected by
348 compatibility between base oil and OMt, basal spacing and surfactant loading level.
349 Temperature rising promoted the viscosity and thixotropy before 150°C and
350 continuous increase of temperature resulted in damage to the rheological properties,
351 due to the loss of surfactants within organoclay interlayers. But they just investigated
352 the OMt modified by CTAB. Later, Zhuang et al. (2017b) investigated the structures
353 and rheological properties of OMt modified by different quaternary ammonium salts
354 in oil-based drilling fluids. The selected surfactants included dodecyl trimethyl
355 ammonium chloride (C12), octadecyl trimethyl ammonium chloride (C18-A), benzyl

356 dimethyl octadecyl ammonium chloride (C18-B) and dimethyl dioctadecyl
 357 ammonium chloride (DC18). The results demonstrated that longer or more long alkyl
 358 chains gave rise to greater gel formation (Table 1). Accordingly, they evaluate the
 359 rheological properties using dynamic rheological test (Fig. 4). Usually, the rheological
 360 properties of a drilling fluid, such as apparent viscosity (AV), plastic viscosity (PV)
 361 and yield point (YP), are determined by a Fann type viscometer, which assumes the
 362 flow behavior conforms to Bingham model. The dynamic rheological curves indicated
 363 three models, i.e., Newtonian for OMt modified with badly lipophilic surfactants,
 364 power law model for OMt modified with moderately lipophilic surfactants and very
 365 good shear thinning behavior with critical points for OMt modified with highly
 366 lipophilic surfactants. The temperature significantly influenced the rheological
 367 properties of OMt modified with highly lipophilic modifiers. Temperature rising
 368 before 180°C improved the viscosity and thixotropy while continuous rising led to
 369 decline. Surfactants with longer and/or more long alkyl chains are advised to prepare
 370 OMt, aiming to provide greater viscosity, thixotropy and thermal stability for
 371 oil-based drilling fluids.

372

373 Table 1 Gel volume of different OMt/oil fluids aged at different temperatures (Zhuang
 374 et al., 2017b).

Samples	Gel volume (mL)			
	66°C	150°C	180°C	200°C
C12-Mt/oil	9.0	9.2	8.1	7.8

C18-A-Mt/oil	35.0	39.5	37.8	31.3
C18-B-Mt/oil	100.0	100.0	100.0	100.0
DC18-Mt/oil	100.0	100.0	100.0	100.0

375

376 As mentioned previously, more new types of OMt were synthesized to be
377 potential rheological additives for oil-based drilling fluids. Cationic surfactants are
378 criticized for their poor thermal stability and toxicity. Nonionic and/or anionic
379 surfactants-modified OMt may improve the rheological properties and thermal
380 stability of OMt in oil-based drilling fluids. Silva et al. (2014b) prepared OMt
381 samples with two nonionic surfactants (TA20 and TA50) and evaluated the swelling
382 properties and viscosities in different oils. The basal spacing of OMt increased to the
383 highest of 5.81 nm, which was derived from the XRD results. Among the solvents
384 used here, diesel and kerosene were the ones that led to the highest swell indices, i.e.,
385 7 mL/2 g. The combined use of these two nonionic surfactants produced better
386 swelling and viscosity results than using them separately. However, this work didn't
387 compare the swelling ability and rheological properties with OMt modified with
388 cationic surfactants. Furthermore, the properties of this kind of OMt in oil-based
389 drilling fluid at high temperatures also need to be evaluated.

390 Zhuang et al. (2015a) comparatively studied the rheological properties of OMt
391 modified with cationic (CTAB) and nonionic (OP-10) surfactants in oil-based drilling
392 fluids. OP-10-modified OMt showed worse lipophilicity than CTAB-modified OMt,
393 due to the $-C-O-$ and $-OH$ groups of OP-10. OMt modified with both CTAB and

394 OP-10 showed better compatibility to oil, swelling ability and rheological properties
395 in oil than OMt modified by only one surfactant. This work proved that synergetic use
396 of two or multiple surfactants to prepare OMt may be a potential way to enhance the
397 rheological properties. But the rheological properties of OMt prepared with optimized
398 cationic and nonionic surfactants should be continuously investigated. Fan et al. (2015)
399 investigated the filtration properties of OMt prepared with both cationic and nonionic
400 surfactants in oil-based drilling fluids (Fig. 5). The optimized OMt sample with the
401 concentration of showed a colloidal fraction of 100% in white oil after 16 h
402 (concentration of 2 g/100 mL). The optimized OMt sample exhibited a low fluid loss
403 of 5.7 mL and left a filter cake approximately 68 mm thick after 30 min. Zhou et al.
404 (2016) reported the rheological and filtration properties in oil-based drilling fluids
405 containing OMt which was modified with cationic and anionic surfactants (CA-OMt).
406 In comparison to a commercial OMt (DG-OMt), CA-OMt presented better
407 rheological properties and filtration results than DG-OMt. However, the oil-based
408 drilling fluids containing many other agents, such as emulsifier, wetting agent and
409 barite. It was not convincing that the improvement of rheological properties of
410 oil-based drilling fluids was contributed by the addition of CA-OMt. The
411 compatibility between OMt and any other agents may result in unexpected changes.

412

413 2.4 Rheological mechanism of OMt in oil

414 Understanding the structure and mechanism of OMt in oil would benefit to

415 develop appropriate OMt for oil-based drilling fluids. In the case of Mt in water-based
416 drilling fluids, the rheological behavior of montmorillonite is highly related to several
417 factors such as the type of bentonite, shape, and size of bentonite particles, the
418 exchangeable inorganic ions, and electrostatic properties of the bentonite particles.
419 Two different electrical double layers of flat surface and edge of Mt/water dispersion
420 formed in water. The gel formation and network structure of Mt in water are mainly
421 created by connection between parallel plates, through positive edge to negative
422 surface linkages, to form a “house of cards structure” (Van Olphen, 1964a, b, 1977)
423 and also the edge-to-edge ribbons (M'Ewen and Mould, 1957; M'Ewen and Pratt,
424 1957). Luckham et al. (1999) concluded the structure of Mt in water as dispersion,
425 face-to-face, face-to-edge and edge-to-edge (Fig. 6), but only face-to-edge and
426 edge-to-edge can form network structures.

427 However, it is quite different for OMt in oil. Schmidt et al. (1987) reported that
428 the interaction between OMt and water in base oil contributed to the viscosity of
429 oil-based drilling fluids. Recent researches also demonstrated that more water
430 percentages increased the viscosity of oil-based drilling fluids (Hermoso et al., 2015;
431 Zhuang et al., 2015a). But this point of view ignored the interaction between OMt and
432 base oil. In all-oil-based drilling fluids, OMt may present excellent rheological
433 properties even without any water. Silva et al. (2014a, b) found the positive
434 relationship between the swelling ability of OMt in oil and the viscosity of oil-based
435 drilling fluids. Generally, the excellent swelling ability of OMt caused great viscosity
436 while poor swelling resulted in inferior viscosity. This phenomenon was also testified

437 by Zhuang et al. (2015a). Zhuang et al. (2016, 2017b, d) studied the structures of
438 OMt/oil gels aged at different temperatures by X-ray diffraction and noticed the
439 exfoliation behavior of DC18-Mt at high temperature (Fig. 7). The rheological
440 properties of OMt in oil are influenced by the basal spacing and ability of swelling
441 and exfoliation, which are deeply affected by the surfactants' nature. According to the
442 previous investigation (Zhuang et al., 2017d, 2019a,b), the structural changes of
443 different OMt in oil are summarized in Fig. 8. Surfactants with a single short alkyl
444 chain (< 12 C atoms), showing poor lipophilicity, led to small basal spacing and poor
445 compatibility with oil, and finally resulted in inferior swelling and even shrinking.
446 Organic surfactants with a single long alkyl chain (> 16 C atoms) resulted in good
447 swelling at normal temperature but shrinking at high temperature. Most important,
448 surfactants with double long alkyl chains, exhibiting excellent lipophilicity,
449 contributed to large basal spacing and appropriate compatibility with base oil, which
450 brought about the easier intercalation of oil molecules and consequently resulted in
451 exfoliation in oil. Although the use of OMt samples modified with more alkyl chains
452 in oil-based drilling fluids has never been reported, these OMt samples may present
453 considerable rheological properties. Moreover, the surfactants' loading level also
454 affects the rheological properties of OMt in oil-based drilling fluids. Generally, more
455 surfactants should promote the rheological properties of oil-based drilling fluids by
456 increasing the basal spacing and compatibility of OMt with oil. But the occupation of
457 organic surfactants in the interlayer space is limited.

458 Like Mt in water, Zhuang et al. (2016) concluded that OMt network was resulted

459 from the percolation of stacked OMt units (layers, particles, and aggregates) to form a
460 gel at multiscale (Fig. 9(A)). Obviously, exfoliation of OMt, which can result in more
461 OMt layers, is an effective way to enhance the rheological properties of oil-based
462 drilling fluids containing OMt. Zhuang et al. (2016) proposed that OMt units formed
463 “edge-to-edge” and “face-to-edge” structures via absorbed surfactants by physical
464 attraction (e.g. enwinding) instead of the attraction between different double electrode
465 layers of Mt units. But this hypothesis needs further verification. Oil-based drilling
466 fluids containing OMt showed shear thinning behavior and thixotropy due to the
467 structural change at different shear rates (Fig. 9(B)). At high shear rate, the network
468 structure is destroyed, leading to the decrease of gel strength and viscosity. At low
469 shear rate, however, the dispersed OMt units formed network structure again,
470 contributing to the increase of gel strength and viscosity.

471 Geothermal high temperature is another challenge for drilling fluids. Thermal
472 stability of OMt in oil should be considered. Two possible changes of the organic
473 modifiers in OMt can be proposed: (i) thermal degradation and (ii) dissolving into the
474 base oil. Xie et al. (2001) proved that the initial degradation of the quaternary
475 ammonium cations in OMt followed a Hoffmann elimination reaction by
476 TG-FTIR-MS and pyrolysis/GC-MS analysis. Zhuang et al. (2019a) investigated the
477 thermal stability of different OMt samples in oil by XRD, thermal analysis and N
478 elemental analysis. The results demonstrated that both desorption and degradation
479 influenced the thermal stability of OMt/oil fluids. Surfactants with short alkyl chains
480 desorbed in oil even at low temperatures, while organic modifiers having long alkyl

481 chains did not. Quaternary ammonium salts degraded into olefins and amines before
482 200°C, and continuous oxidation occurred at higher temperatures. The resulting
483 olefins and amines first stayed in the interlayer space and then gradually dissolved
484 into the base oil at higher temperatures (Fig. 10). Consequently, surfactants with two
485 or three long alkyl chains were suggested to contribute to excellent thermal stability
486 and rheological properties of OMt in oil-based drilling fluids. For example, OMt
487 prepared with DC18 can suffer from thermal attack at 250°C for 16 h, while the
488 viscosity at 100 s⁻¹ decreased by only 12.8% and the gel volume remained 100.0%
489 (Zhuang et al., 2019a).

490

491

492 3. Organo-palygorskite and organo-sepiolite

493 3.1 Palygorskite and sepiolite

494 Compared with the large deposit of Mt, palygorskite (Pal) and sepiolite (Sep) are
495 less on the earth. But these two clay minerals attract more interests due to their special
496 adsorptive, colloidal-rheological, and catalytic properties which are the basis for many
497 technological applications. Pal and Sep are clay minerals inasmuch as they contain a
498 continuous two-dimensional tetrahedral sheet; however, they differ from other layer
499 silicates in that they lack continuous octahedral sheets. The apical oxygen atoms of
500 the tetrahedra partially form the coordination unit of the octahedral sheet. Therefore,
501 there is a region of the structure where a channel may form adjacent to the basal

502 oxygen planes between two 2:1 layers (Fig. 11). Channels are $3.7 \times 10.6 \text{ \AA}$ in
503 sepiolite and $3.7 \times 6.4 \text{ \AA}$ in palygorskite. As the octahedral sheet is discontinuous at
504 each inversion of tetrahedra, oxygen atoms in the octahedra at the edge of the ribbons
505 are coordinated to cations on the ribbon side only, and coordination and charge
506 balance are completed along the channel by protons, coordinated water and a small
507 number of exchangeable cations. Also, a variable amount of zeolitic water is
508 contained in channels (Bradley, 1940; Alvarez, 1984; Krekeler and Guggenheim,
509 2008; Álvarez et al., 2011; Guggenheim and Krekeler, 2011; Suárez and
510 García-Romero, 2011).

511 Both of them show fibrous morphology (Fig. 11). Fiber sizes vary widely but
512 generally range from 100 \AA to $4\text{-}5 \text{ \mu m}$ in length, 100 \AA to 300 \AA in width, and 50 \AA to
513 100 \AA in thickness (Galan, 1996; García-Romero and Suárez, 2013). The presence of
514 micropores and channels in these minerals together with the fine particle size and
515 fibrous habit account for their high surface area. The BET surface area of Sep is ~ 300
516 m^2/g compared to $150 \text{ m}^2/\text{g}$ for Pal (Galan, 1996; Álvarez et al., 2011). Sep is a
517 Mg-rich silicate close to trioctahedral phyllosilicates, while Pal appears to lie midway
518 between dioctahedral and trioctahedral phyllosilicates. Due to the isomorphism
519 substitution, Pal and Sep exhibit extra negative charges which were balanced by
520 cations in the channels. These cations are also exchangeable. But the CEC of both
521 minerals is quite lower than Mt, ranging from 4 to 40 cmol/kg (Galan, 1996; Álvarez
522 et al., 2011). Usually, Pal shows less CEC than Sep.

523 The principal applications of Pal and Sep colloidal grades generally involve

524 thickening, gelling, stabilizing or other modification of their rheological properties.
525 These minerals are used in paints (especially where high thixotropy is advantageous),
526 adhesives, sealants, fertilizer dispersions and cosmetics (e.g. milks, masks), in
527 addition to fluid carriers for pre-germinated seeds (Galan, 1996; Murray, 1999, 2000;
528 Álvarez et al., 2011). They are also used in water-based drilling fluids (Dahab and
529 Jarjarah, 1989; Dahab, 1991; Neaman and Singer, 2004; Altun and Serpen, 2005;
530 Baltar et al., 2009; Abdo and Haneef, 2013b; Altun et al., 2014; Abdo et al., 2016;
531 Al-Malki et al., 2016).

532

533 3.2 Synthesis of OPal and OSep.

534 Pal and Sep are usually used as adsorbents, rheological agents, catalytic carriers,
535 and fillers for polymer nanocomposites. In some applications, organic modification is
536 necessary before use due to the poor compatibility between these clay minerals and
537 organic compounds. For example, the adsorption of organic compounds from waste
538 water and polymer nanocomposites. The modifiers include cationic surfactants,
539 amines, organosilanes and polymers. The synthesis of OPal and OSep are summarized
540 in Table 2. Most of OPal and OSep were prepared using quaternary ammonium salts
541 in aqueous solution. In some cases, heating was employed to help the reactions. Only
542 a few examples were prepared in organic solvents. The interaction between modifiers
543 and clay minerals not only occurred on the external surface, but also may penetrate
544 into the structural channels. Maya blue, an ancient hybrid pigment, was proved as a

545 hybrid, in which the natural indigo dye molecules penetrated into Pal channels,
546 resulting in outstanding resistance to acids, bases, solvents and light (Chiari et al.,
547 2003; Río et al., 2011).

548 The possibility to induce versatile intercrystallite adsorption either of atoms or of
549 neutral molecules and charged species, and even polymers, into the structural tunnels
550 of sepiolite, appears as a feasible way to prepare organic-inorganic materials with
551 predetermined behavior. Ruiz-Hitzky (2001) illustrated in the adsorption of methylene
552 blue into Sep channels and tunnels by pore volume distribution and infrared. Li et al.
553 (2003) investigated the removal of anionic contaminants from water by using
554 surfactant-modified Pal and Sep. The hexadecyltrimethylammonium (HDTMA)
555 adsorption capacities were 520 and 260 mmol/kg for Pal and Sep, respectively. These
556 authors proposed a mechanism as shown in Fig. 12. The first layer of cationic
557 surfactants intercalated into the channels of clay minerals by the polar head via
558 electrostatic attraction. Then the second layer of cationic surfactants were adsorbed
559 due to the affinity between alkyl chains. The molecular access to the channels and
560 tunnels of Pal and Sep is of great interest in the field of hybrid pigments, water
561 treatment as well as rheological agents.

562

563 Table 2 A summary of the synthesis of OPal and OSep

Clay mineral	Modifiers	Method	Reference
Pal	Octodecyl trimethyl ammonium	Reacting in water with	(Huang et al., 2007a;
	chloride (OTMAC)	ultrasonication	Huang et al., 2007b;

			Huang et al., 2008)
Pal	Hexadecyl trimethyl ammonium bromide (HDTMAB)	Reacting in water (100°C) with ultrasonication	(Lei et al., 2009)
Pal	3-mercaptopropyltrimethoxysilane and 3-aminopropyltrimethoxysilane	Reacting in water	(Liang et al., 2013)
Pal	Chitosan	Stirring in toluene (60°C)	(Peng et al., 2013)
Pal	Dioctadecyl dimethylammonium bromide (DODMAB)	Reacting in water at 80°C	(Sarkar et al., 2012)
Pal	Octadecyl trimethyl ammonium bromide (ODTMAB) and DODMAB	Reacting in water at 80°C	(Xi et al., 2010; Sarkar et al., 2011)
Pal	cetyl trimethyl ammonium chloride (CTAC) and chloride alkyl dimethyl benzyl ammonium (BKC)	Reacting in water	(Silva et al., 2014c)
Pal	4,4'-methylene bis(phenyl isocyanate) (MDI)	Reacting in acetone	(Wang et al., 2008)
Pal	Butyl acrylate	Reacting in toluene	(Wang and Sheng, 2005)
Pal	3-aminopropyl triethoxysilane	Reacting in toluene	(Xue et al., 2010, 2011)
Pal	Silane coupling agents KH550 and KH972	Reacting in toluene	(Zhang et al., 2010a)
Pal	Series of quaternary ammonium salts	Reacting in water	(Zhuang et al., 2017a;

			Zhuang et al., 2017c)
Sep	dodecylamine	Reacting in water	(Akçay et al., 2005)
Sep	N-cetylpyridinium	Reacting in water	(Bakhtiary et al., 2013)
Sep	Silane coupling agents KH550	Reacting in mixture of water and ethanol	(Chen et al., 2012)
Sep	benzyl dimethyl hydrogenated tallow quaternary ammonium (B2MTH), trimethyl hydrogenated tallow quaternary ammonium (3MTH) and N-Hydrogenated tallow-1,3-diaminopropane (DIAMIN T)	Details not given	(Garcia-Lopez et al., 2013)
Sep	trimethyl hydrogenated tallow quaternary ammonium	Details not given	(García-López et al., 2010)
Sep	quaternary amine salts (SDBAC and DDAC)	Reacting in water	(Lemić et al., 2005)
Sep	Polyethylene glycol (PEG)	Reacting in water	(Mejía et al., 2014)
Sep	Alkoxysilane	Reacting in water	(García et al., 2011)
Sep	Dodecylethyldimethylammonium (DEDMA) bromide	Reacting in water	(Özcan and Özcan, 2005)
Sep	DDTMAB and HDTMAB	Reacting in water	(Sabah and Çelik, 2002; Sabah et al., 2002)

Sep	Series of quaternary ammonium salts, amines and organosilanes	Adsorption and grafting	(Tartaglione et al., 2008)
Sep	Series of quaternary ammonium salts	Reacting in water	(Zhuang et al., 2018a; Zhuang et al., 2018b; Zhuang et al., 2018d)
Sep	Series of quaternary ammonium salts and sodium dodecyl sulfate (SDS)	Reacting in water	(Weng et al., 2018)
Pal and Sep	HDTMAB and dodecyl trimethyl ammonium bromide (DDTMAB)	Reacting in water	(Li et al., 2003)
Pal and Sep	Triton X-100, Sodium dodecyl sulphate and ODTMAB	Reacting in water	(Sanchez-Martin et al., 2006; Sánchez-Martín et al., 2008)
Pal and Sep	(3-aminopropyl) triethoxysilane	Mixing under nitrogen gas for 48 h at 180°C	(Moreira et al., 2017)

564

565 3.3 Rheological properties of OPal and OSep in oil-based drilling fluids

566 Mt is the most used clay mineral for water-based drilling fluids, since it presents
567 excellent viscosity and thixotropy in fresh water. However, when in contact with salts,
568 Mt tends to coagulate reducing its viscosity and losing its thixotropic properties,
569 because the network structure of Mt in water is affected by the electrolytes. Pal and
570 Sep, in contrast, remains a viscous dispersion in the presence of dissolved salts (Galan,

571 1996; Baltar et al., 2009; Abdo and Haneef, 2013b). It is because these two clay
572 minerals form a “haystack” structure by organizations of nanofibers and it is not
573 sensitive to electrolytes. It is thus used as a component of drilling fluids for wells
574 drilled off shore or those that cross layers of soluble salts. The desired rheological
575 properties remain relatively constant even at high electrolyte concentrations over a
576 wide pH (Neaman and Singer, 2000a).

577 Due to the excellent performance of Pal and Sep in water-based drilling fluids,
578 OPal and OSep were suggested to be used in oil-based drilling fluids. Pal and Sep
579 need to be organically modified because of the poor compatibility between clays
580 surface and base oil. House (1984) reported OPal and OSep as rheological additives
581 for oil-based drilling fluids in his patent. OPal and OSep were prepared from raw clay
582 minerals and a kind of quaternary cationic organic compound or some mixtures. He
583 found that these OC prepared by extruding a mixture of a clay selected from the group
584 consisting of Pal, Sep, and mixtures thereof, a quaternary cationic organic compound,
585 water and an alcohol having from 1 to 5 carbon atoms in certain specified ratios are
586 readily dispersible in oleaginous liquids provided that the organophilic clay is not
587 dried to remove the moisture or alcohol therefrom. The API (American Petroleum
588 Institute) rheological value (20 g OC in 262.5 mL diesel oil) exhibited 9-22 mPa•s for
589 plastic viscosity (AV), 2-19 mPa•s for yield point (YP) and 2-5 Pa for gel strength
590 after 10 s. Later, some patents (Van Slyke, 1994; Dino and Thompson, 2007; Miller,
591 2009, 2011; Dino and Thompson, 2013) also reported the use of OPal or OSep as a
592 supplementary rheological agent with OMT in oil-based drilling fluids. The previous

593 work introduced the application of OPal and OSep in oil-based drilling fluids.
594 However, some scientific problems, such as the interaction between organic modifiers
595 and clay minerals, gel structure of OPal and Sep in oil and the influence of
596 temperatures, etc., were still unsolved.

597 Zhuang et al. (2017a) reported the rheological properties of OPal in white oil and
598 investigated the influence of temperatures. The rheological properties of OPal in oil
599 were not only influenced by the compatibility between OPal and oil, but also affected
600 by the insertion of organic cations into the channels of Pal. OPal modified with worse
601 lipophilicity showed less gel volume in oil, but better rheological properties than OPal
602 modified with better lipophilicity. This phenomenon was explained by the insertion of
603 smaller modifiers into the Pal channels and the appropriate polarity improved the
604 stability of organic cations in OPal and the gel formation. The OPal/oil fluids were
605 aged at a rotary oven at 66°C, 150°C, 180°C and 200°C for 16 h. With the increase of
606 temperature, the rheological properties of OPal/oil fluids were improved until 180°C.
607 At extremely high temperature, the rheological properties declined might because of
608 the desorption of surfactants.

609 Later, the use of OSep in oil-based drilling fluids were also studied. Zhuang et al.
610 (2018d) modified Sep with benzyl dimethyl octadecyl ammonium chloride (C18-B)
611 and investigated the rheological properties of OSep in oil. The optimized amount of
612 surfactant equals to 35 wt.% of raw Sep. OSep showed excellent viscosity and
613 thixotropy in oil. The temperature rising below 180°C promote the rheological
614 properties. By calculating the size of organic modifier, surface area test and thermal

615 analysis, a part of surfactants were testified to insert into the Sep channels. Later,
616 Zhuang et al. (2018b) researched structures and rheological properties of three
617 surfactant-modified OSep (Fig. 13). The pore width and micropore volume
618 distribution demonstrated that C18-A and C18-B inserted into the Sep channels while
619 DC18 cannot. Compared with the channel size, C18-A is much smaller, C18-B is a
620 little smaller with one side almost identical, and DC18 is much larger. Consequently,
621 C18-B can block the channels and fixed on the surface, resulting in the best
622 rheological properties and thermal stability.

623 Weng et al. (2018) comparatively investigated the structure and rheological
624 properties of OSep modified with cationic surfactants alone and mixture of cationic
625 and anionic surfactants in oil. The addition of anionic surfactants decreased the
626 lipophilicity of OSep. OSep modified with cationic and anionic surfactants showed a
627 little higher viscosity than OSep modified with cationic surfactants alone. But the
628 improvement was not significant.

629

630 3.4 Rheological mechanism of OPal and OSep in oil

631 It is difficult to identify the gel structure of OPal and OSep in oil, because it is
632 very difficult to remove the oil in the gels, and the structure should be destroyed if the
633 oil is removed. Thus, there is no reports about the microscopic evidence about the gel
634 structures of OPal and OSep in oil. Zhuang et al. (2017c,d , 2018b) researched the gel
635 structure of OPal in oil by gel formation ability and X-ray diffraction test for the

636 OPal/oil gels. They found that OPal kept the crystal structure in oil. This was very
637 different from OMT which swelled and even exfoliated in oil. According to the fibrous
638 morphologies (See Fig. 14), Pal and Sep form a “haystack” or “brush heap” structure
639 in solvents. Hence, OPal and OSep were considered to form the similar “haystack”
640 structure in oil. Due to the lipophilic surface, OPal and OSep fibers can disperse in oil
641 and form a network structure by natural stack and connection. The rheological
642 properties of OPal and OSep in oil were influenced by the compatibility between OC
643 and oil. OPal and OSep presented three possible structures in oil (Fig. 15(A)), i.e.,
644 stack, network structure and dispersion. Surfactants of poor lipophilicity led to
645 inferior compatibility between OC and oil, resulting in stack of nanofibers. Oppositely,
646 OPal and OSep modified with surfactants of great lipophilicity usually led to excellent
647 compatibility with oil, consequently causing fine dispersion in oil. Neither stack nor
648 dispersion contributed to prominent rheological properties of oil-based drilling fluids,
649 due to the weak interaction between nanofibers. The selection of appropriate
650 surfactants is very important for enhance the rheological properties of oil-based
651 drilling fluids containing these OC. According to the previous investigations (Zhuang
652 et al., 2017a, 2018b), C18-A (mass 25% of Pal) was optimal for the rheological
653 properties of OPal in oil while C18-B (mass 35% of Sep) improved most for OSep
654 among the selected surfactants. In addition, the aggregations of OPal and OSep also
655 influenced the rheological properties. OPal and OSep existed in the form of different
656 aggregations, i.e., particles, aggregations, crystal bundles (including several fibers)
657 and individual fibers (Fig. 15(B)). Except for organic modification, high temperature

658 can also promote the disaggregation of crystal bundles and aggregates, resulting in
659 more individual fibers and small aggregates. This disaggregation contributed to a
660 stronger network structure. Extremely high temperature (usually $> 180^{\circ}\text{C}$) would
661 damage the rheological properties Thermal degradation and desorption of organic
662 surfactants may be responsible, but more details need be specified.

663 Zhuang et al. (2017b, 2018b) studied the interactions between these two clay
664 minerals and organic surfactants, and their influences on the rheological properties.
665 Surfactant cations stayed in OPal and OSep at four possible locations (Fig. 16), i.e., (i)
666 completely inserting into the channels and/or tunnels, (ii) partially inserting into the
667 channels and/or tunnels, (iii) blocking the channels and/or tunnels and (iv) covering
668 on the surface. Two possibilities were proposed for the thermal stability of OPal and
669 OSep in oil: (i) thermal degradation of organic modifiers and (ii) dissolution of
670 organic modifiers detached from OC and dissolution into oil. The insertion of
671 surfactants into the channels is significant for the stability of OPal and OSep in oil. In
672 the previous study (Zhuang et al., 2017b), DC18-Mt presented the best rheological
673 properties and thermal stability in oil-based drilling fluids. But the optimized
674 modifiers were C18-A for OPal and C18-B for OSep. This fact demonstrated that the
675 decline of rheological properties of OPal and OSep in oil below 200°C is mostly due
676 to the desorption of organic surfactants and accordingly resulted in poor compatibility
677 between clay minerals and oil. Obviously, the insertion of modifiers enhanced the
678 fixation of modifiers in oil, even under high temperatures. The insertion of organic
679 modifiers was testified by pore volume distribution (Zhuang et al., 2018b). By

680 comparing the molecular size, C18-A and C18-B were possible to insert into Sep
681 channels while DC18 was not (Fig. 17). Because C18-A is much smaller than the
682 channel size, it is not as stable as C18-B in the channels and tunnels of Sep.
683 Accordingly, based on the molecular size, C18-A is possible to penetrate into Pal
684 channels and tunnels while C18-B and DC18 are not.

685

686 4. Synergetic use of organoclays in oil-based drilling fluids

687 4.1 Rheological properties of synergetic use of different OC.

688 Some literature reported about the joint use of two clay minerals to enhance the
689 rheological properties of clay minerals in aqueous dispersion or water-based drilling
690 fluids. Neaman and Singer (2000b) researched the rheological properties of mixed Mt
691 and Pal in aqueous dispersion and they found that small montmorillonite additions (\leq
692 10 wt.%) increased the rheological parameters (plastic viscosity and Bingham yield
693 value). Au and Leong (2013) found that the mixture of Mt and kaolinite in aqueous
694 dispersion could adjust the optimized pH value and rheological properties by
695 changing the amount of these two clay minerals. Aiming for using in water-based
696 drilling fluids, İşçi and Turutoğlu (2011) researched the mixture of Mt and Sep in
697 water. They found the mixture is not adequate for water-based drilling fluids and
698 stabilizers were necessary. Afterwards, Chemedá et al. (2014) investigated the
699 rheological properties of dispersions of fibrous clay minerals (Pal and Sep) mixed
700 with Mt with different layer charge. The degree of interaction between Mt and fibrous

701 clay particles and its effect on the apparent viscosity and yield point of the dispersions
702 depend on the concentration, layer charge and charge localization of the Mt in the
703 mixture. The physical and chemical properties of the fibers (fiber length, specific
704 surface area and CEC) also affect the interaction of fibrous clays with smectite and
705 consequently the rheological properties of the mixtures. The rheological properties
706 were affected by layer charge of Mt and the proportion of fibrous clay minerals. An
707 appropriate mixture of Mt and fibrous clay minerals enhanced the rheological
708 properties by the interaction of particle-particle linkages. Al-Malki et al. (2016) found
709 that bentonite-based drilling mud with Sep nanoparticles showed a great stability in
710 plastic viscosity and yield point over a wide range of temperature and pressure,
711 especially at high temperatures and pressures.

712 The previous work enlightened that synergistic use of OMt and OSep may also
713 promote the rheological properties and thermal stability of oil-based drilling fluids.
714 This is a promising way to sustain oil-based drilling fluids work in difficult wells.
715 Zhuang et al. (2017d) comparatively studied the rheological properties of OMt and
716 OPal in oil-based drilling fluids. Although OMt presented greater viscosity and
717 thixotropy than OPal in oil, OPal exhibited better thermal stability and dispersity.
718 Mainye and Teutsch (2015) researched the mixture of OMt and OPal (or OSep) as a
719 rheological additive to improve the ultra-low shear rate viscosity and to increase the
720 carrying capacity of oil-based drilling fluids. The clay minerals were modified with
721 quaternary amines and/or quaternary ammonium salts. The mass percentage of OPal
722 or OSep was 10%. They found the mixture of different organoclays significantly

723 yielded stable gels that were non-progressive compared to each individual organoclay
724 used separately. But this work didn't systematically study the synergetic use of two
725 organoclays in oil-based drilling fluids.

726 Later, Zhuang et al. (2018c) systematically reported the synergetic use of OMt
727 and OSep in oil-based drilling fluids aged at different temperatures. They found that
728 synergetic use of OMt and OSep can improve the rheological properties and thermal
729 stability of oil-based drilling fluids. OSep showed better gel formation ability than
730 OMt at room temperature and the addition of OSep improved the gel formation ability.
731 Aged at low temperature, OMt presented the highest viscosity. However, the mixture
732 of OMt and OSep with mass ratio of 1:1 exhibited the optimized rheological
733 properties aged at 150-200°C (Fig. 18). The oil-based fluids containing the mixture of
734 OMt and OSep showed a little increase of viscosity and thixotropy aged from 150°C
735 to 200°C for 16 h while dramatic decline was observed in the fluids only containing
736 OMt or OSep. The rheological properties of oil-based drilling fluids containing a
737 mixture of OMt and OPal was also researched (Zhuang et al., 2019c). The results
738 indicated a similar phenomenon with the mixture of OMt and OSep in oil. This
739 investigation thus also supported that synergetic use of layered and fibrous OC
740 enhanced the rheological properties and thermal stability of oil-based drilling fluids.

741

742 4.2 Rheological mechanism of mixed OC in oil

743 There is no microscopic evidence about the gel structure of the mixture of OMt

744 and OSep. The gel structure was proposed based on the XRD results of OC/oil gels
745 (Zhuang et al., 2018c, 2019c). At normal temperature, OMt firstly swelled in oil by
746 adsorbing oil molecules while OPal or OSep showed stable dispersion due to its
747 nanoscale fibers, laths and bundles. Aged at high temperature, the basal reflection of
748 OMt disappeared while the (100) reflection remained, indicating that thermal motion
749 promoted the exfoliation of OMt into nanolayers. The interweave of nanofibers (laths
750 and bundles) of nanolayers enhanced the network structure, resulting in improvement
751 of rheological properties. According to the XRD results, a graphical summary was
752 presented in Fig. 19. The mutual support between OMt nanolayers and nanofibers
753 protected this network structure from being damaged by high temperatures.

754

755 5. Conclusions and perspectives

756 The study of organoclays and the application in oil-based drilling fluids are a large
757 field and shows an immense potential to be explored. OMt is mostly used as the
758 rheological additive in oil-based drilling fluids. More attention should be paid to the
759 application of OPal and OSep in oil-based drilling fluids. OC are usually modified
760 with quaternary ammonium salts. Large basal spacing, good lipophilicity and
761 exfoliation are significant for the gel formation ability and rheological properties of
762 OMt in oil. Organic modifiers with longer and/or more alkyl chains are suggested to
763 be employed to prepare OMt for oil-based drilling fluids. OPal and OSep are easy to
764 disperse in oil due to the nanosized fibrous morphology. Organic modifiers cannot

765 intercalate into the interlayer space like OMT. Hence, penetration of surfactants into
766 the channels and tunnels is very important for the stability of oil-based drilling fluids,
767 especially at high temperatures. When choosing a modifier for OPal and OSep, the
768 molecular size and compatibility with oil should be considered. Synergetic use of
769 OMT and fibrous OC is a promising method to enhance the rheological properties and
770 thermal stability of oil-based drilling fluids.

771 In order to develop suitable rheological additives for oil-based drilling fluids,
772 more issues are still necessary to be investigated. (i) The present work mostly
773 concerned about the rheological properties of OC in oil-based drilling fluids.
774 Filtration loss, another important property for drilling fluids, is also need to be
775 checked. (ii) Compatibility between OC and other agents should be paid more
776 attention. In practice, an oil-based drilling fluid is a complex system which contains
777 many agents, such as salty water, emulsifier, barite, etc. The compatibility between
778 OC and other agents would affect the properties of the final drilling fluids. (iii)
779 Temperature and pressure are two important factors which influence the rheological
780 properties a lot. (iv) Last but not least, the interactions between clay minerals and
781 organic surfactants, and the structure of OC in oil need more detailed investigations.
782 But the present work mostly ignored the influence of pressure.

783 Although oil and gas are not renewable, they are the most important energy
784 resources on the earth in the next 30 years. The new energies cannot completely
785 replace these fossil energies in a short time. Seeking and exploring more oil and gas
786 from the difficult locations is an economic and simple way. Studying on the

787 application of OC in oil-based drilling fluids will promote the development of
788 petroleum industry and our daily life.

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1310

1311 Figure captions:

1312 Fig. 1 The crystal structure of Mt and corresponding SEM and TEM images (Mt

1313 obtained from Liaoning, China).

1314 Fig. 2 Experimental viscous flow curves, and Sisko–Barus' model fitting, for the
1315 different OMT/oil dispersions studied, as a function of pressure, at 40 °C (Hermoso et
1316 al., 2014).

1317 Fig. 3 Evolution of the experimental density with pressure, at three different
1318 temperatures for the OMT/oil fluids (Hermoso et al., 2017).

1319 Fig. 4 Dynamic rheological curves of OMT/oil fluids aged at different temperatures
1320 (Zhuang et al., 2017b).

1321 Fig. 5 Left: digital pictures of 1.0 g dispersion of Mt and OMT in 50mL white oil after
1322 16 h (from left to right); right: API filtration loss results for Mt and OMT (Fan et al.,
1323 2015).

1324 Fig. 6 The structures of Mt in water (drawing based on Luckham et al., 1999)

1325 Fig. 7 XRD patterns of selected OMT/oil fluids aged at different temperatures (Zhuang
1326 et al., 2017d). Exfoliation of DC18-Mt in oil occurred at 150-200°C.

1327 Fig. 8 A summary of the structural changes of OMT in oil (summarized from Zhuang
1328 et al., 2017b, 2019a, b).

1329 Fig. 9 (A) Different network structures of OMT in oil and (B) Structural changes of
1330 OMT in oil at different shear rate.

1331 Fig. 10 Thermal degradation and desorption of organic surfactants in OMT (Zhuang et
1332 al., 2019a).

1333 Fig. 11 Crystal structures of Pal and Sep, and their TEM images (Pal was from Hebei,
1334 China, and Sep was obtained from Spain).

1335 Fig. 12 Hypothesized surfactant ad micelles on fibrous clay mineral surfaces such as
1336 sepiolite (Li et al., 2003)

1337 Fig. 13 Dynamic rheological curves of OSep/oil aged at (A) 66°C, (B) 150°C, (C)
1338 180°C and (D) 200°C for 16 h (Zhuang et al., 2018b).

1339 Fig. 14 TEM images of (A) Sep, (B) C18-A-Sep, (C) C18-B-Sep and (D) DC18-Sep
1340 (Zhuang et al., 2018b).

1341 Fig. 15 (A) the structures of OPal or OSep in oil and (B) Different aggregations of
1342 OPal and OSep.

1343 Fig. 16 The structure of sepiolite and possibilities of the positions of organic
1344 surfactants (drawing based on Zhuang et al., 2018b).

1345 Fig. 17 Interpretive diagram of the states of organic surfactant on the surface of
1346 sepiolite (Zhuang et al., 2018b).

1347 Fig. 18 Dynamic rheological curves of OC/oil fluids aged at (A) 66°C, (B) 150°C, (C)
1348 180°C and (D) 200°C for 16 h (Zhuang et al., 2018c).

1349 Fig. 19 Interpretive diagram of the network structure of the mixed OMt and OSep in
1350 oil (Zhuang et al., 2018c).

1351