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

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Abstract

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

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

Contents

1. Introduction

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

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

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

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

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

Drilling fluids are classified according to their continuous phases: water-based drilling fluids, oil-based drilling fluids and gas. Gas is used limitedly in practice. Thus, only water-based drilling fluids and oil-based drilling fluids are discussed in this work. Water-based drilling fluids were firstly developed and wildly used due to the low cost (Caenn and Chillingar, 1996; Meng et al., 2012; Sadeghalvaad and Sabbaghi, 2015). However, water-based drilling fluids are limited in difficult drilling operations, such as offshore, high-temperature, high-angle wells, because of the sensitivity to salts and poor shale inhabitation (Zhuang et al., 2015a). On the contrary, oil-based drilling fluids exhibit excellent thermal stability and drilling performance by producing low frictions, high rate of penetration, excellent shale inhabitation, wellbore stability, good lubricity and prominent salt resistance (Khodja et al., 2010) to overcome some undesirable characteristics of water-drilling fluids. Thus, oil-based drilling fluids are more popular in the difficult drilling operations (e.g., offshore drilling, high-temperature and high-angle wells).

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

The rheological properties (especially under high temperatures) of a drilling fluid are always concerned, because the functions of drilling fluids are basically supported by appropriate rheological properties. A drilling fluid is a thixotropic system; it exhibits low viscosity when sheared, such as on agitation or circulation (as by pumping) but, when such shearing action is halted, the fluid thickens to hold cuttings in place. The fluid must become thick rapidly, reaching a sufficient gel strength before suspended materials fall any significant distance. This behavior must be totally reversible at all temperatures encountered. In addition, when a free-flowing liquid, the fluid must retain a sufficiently high viscosity to carry all unwanted particulate matter from the bottom of the hole back up to the surface. Moreover, the increasing geothermal gradient may damage the fluids. Thus, a drilling fluid must accomplish a number of these interrelated functions over a wide range of temperatures to satisfy the requirements to be a commercial drilling fluid.

Hence, greater emphasis is placed on the rheological properties provided by the colloidal and rheological additives. Clay minerals, such as montmorillonite (Caenn and Chillingar, 1996; Abu-Jdayil, 2011; Caenn et al., 2011; Abdo and Haneef, 2013a), palygorskite (Guven et al., 1988; Dahab and Jarjarah, 1989; Dahab, 1991; Galan, 1996; Murray, 2000; Neaman and Singer, 2004; Baltar et al., 2009) and sepiolite (Guven, 1981; Guven et al., 1988; Galan, 1996; Altun and Serpen, 2005; Osgouei, 2010; Razali and Zafirah, 2011; Altun et al., 2014; Abdo et al., 2016; Al-Malki et al., 2016) are widely used as colloidal and rheological additives in water-based drilling fluids, due to their formation of network structure in water. Inspired by the use of clay minerals in water-based drilling fluids, organoclays (OC), which are obtained by reacting clay minerals with organic compounds, are developed to be used in oil-based drilling fluids as rheological additives for many years. It has been admitted that OC can be used to thicken organic compositions and particularly oil-based drilling fluids. Organic modification results in appropriate colloidal and rheological properties of OC in oil-based system. Addition of OC in the continuous phase enables to achieve suitable properties of the fluid during the different well drilling phases. Consequently, OC promotes a thixotropic behavior combining a low viscosity under shear i.e. during the drilling process, and also the ability to form rapidly a gel retaining suspended materials when the shear is halted. Hence, they have to maintain the rheological properties of the oil-base drilling fluids at different depth i.e. over a wide temperature range. Furthermore, OC has to minimize interaction of oil-base drilling fluids with the bearing rocks by forming a low permeability protective cake on the bore wall and developing adequate physicochemical characteristics to avoid the swelling of drilled shale rocks.

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

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

2. Organo-montmorillonite

2.1 Montmorillonite

Montmorillonite (Mt), the main component of bentonite, belongs to the general family of clay minerals. An ideal Mt layer is composed of two continuous [SiO_4] tetrahedral sheets (T) and a [AlO_6] octahedral sheet (O) (Fig. 1). Thus, the structure of Mt is described as TOT type (Bergaya et al., 2012; Brigatti et al., 2013). Due to isomorphism, Mt layers are often negatively charged. A negative charge layer arises from the substitution of Mg^{2+} and other lower charge cations for Al^{3+} in octahedral sites (Brigatti et al., 2013; Jaber et al., 2014). Consequently, some exchangeable cations, such as Na^+ and Ca^{2+} present in the interlayer space counterbalance the deficit of positive charges (Murray, 1991; Chiou, 1997; Bergaya and Lagaly, 2001; Brigatti et al., 2013). Thus, Mt exhibits high cation exchange capacity (CEC). Murray (1999) reported that the CEC of Mt generally lied in the range of 60-100 cmol/kg. Some recent papers demonstrated higher CEC values which were more than 100 cmol/kg (He et al., 2010; Karaca et al., 2012; Sun et al., 2013; Fernández et al., 2014; Luo et al., 2015). An extremely high CEC of Mt was reported as 174 cmol/kg by Fernández et al. (2014). Mt occurs normally as thin flakes of small particles. The special structure and features result in large specific surface area, swelling properties in polar solvents, adsorptive property and rheological properties of Mt. When mixed with water, the high charge and fine particle size give the fluid a very high viscosity. These basic properties of Mt are related to many industrial uses such as rheological additives in drilling fluids, as foundry bond clays, for pelletizing iron ores, and as sealants in irrigation ditches, farm ponds, earthen dams, landfill liners, etc. (Murray, 1991, 1999). Particularly, raw Mt is widely used in water-based drilling fluids and OMt is also extensively used in oil-based drilling fluids.

2.2 Synthesis of OMt

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

Generally, OMt can be prepared by aqueous solution and solid-state reaction. Reacting in aqueous solution is the most common method to prepare OMt in laboratory or even at the industrial scale. OMt is easily obtained by contact with surfactants in aqueous solutions. In aqueous solution thanks to the osmotic pressure, intercalation of organic cations occurs quickly at room temperature. Heating to 50-80°C was also employed in some reports. Usually, OMt prepared by aqueous solution exhibits ordered interlayer arrangement, especially at a high surfactant's loading level.

Reacting in aqueous solution was criticized because the use of large amount of water. Hence, solid-state methods, including grinding, ball milling and heating the mixtures, were tried to prepare OMt. At first, heating the mixture of Mt and organic compounds was applied. Organic molecules such as acrylamide, methacrylamide, and urea (Ogawa et al., 1989) and bipyridine or hydroxyquinolines (Ogawa et al., 1991; Khaorapapong and Ogawa, 2007). However, in these examples, the driving force for intercalation of the organic molecule was the formation of a coordination complex with the preexisting interlayer cations. A mechanochemical route to the interlayer polymerization of polyaniline and polypyrrole in montmorillonite has also been proposed (Yoshimoto et al., 2004a,b, 2005a, b, c), but there are few data regarding non-polymerizing solid-state intercalation of surfactants. OMt was prepared by heating the mixture of Mt, cetyl trimethyl ammonium bromide (CTAB) and silane coupling agent with vigorous stirring (Ge and Jia, 2008, 2009). Recently, grinding and ball milling attracted much attention when preparing OMt (Hrachová et al., 2007). Ball milling method had been employed to modify Mt with nonionic surfactants and accompanying with anionic surfactants (Zhuang et al., 2015b). Nonionic and anionic surfactants successfully intercalated into the interlayer space and increased the basal spacing. Afterwards, Xie et al. (2014) compared the structures of OMt prepared with Mt and CTAB in aqueous solution and ball milling method. They found that ball milling method is a promising way to produce OMt and the basal spacing of the corresponding OMt was as large as 4.55 nm.

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

Different organic modifiers were used with Mt via different interaction mechanisms. Displacement reactions occur when water molecules in the interlayer space of Mt. Polar molecules enter the interlayer space by replacing water molecules. Neutral organic compounds can form complexes with the interlayer cations. The adsorption of neutral molecules is driven by various chemical interactions: hydrogen bonds, ion-dipole interaction, co-ordination bonds, acid base reactions, charge transfer, and van der Waals forces (Lagaly et al., 2013). Anionic surfactants are difficult to intercalate into the interlayer space due to the negative charges. However, they can also enter the interlayer space by accompanying with cations (Zhang et al., 2010b; Fu et al., 2016).

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

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

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

2.3 Rheological properties of OMt in oil-based drilling fluids

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

A recent study by Hermoso et al. (2014) showed that viscous flow behaviors of oil-based drilling fluids with two commercial OMt samples (B34 and B128) as additives at different pressure are strongly influenced by OMt nature and concentration (Fig. 2). Higher concentration of OMt in oil resulted in larger viscosity. The viscosity of OMt/oil fluids increased with the increase of pressure. This phenomenon might be due to the compression of base oil under high pressure, which led to the increase of concentration of OMt. They also observed that shear-thinning behavior of the OMt/oil fluids at different concentrations is related to the development of various microstructures, which depend on the type of surfactants. Hermoso et al. (2015) investigated the rheological properties of OMt in invert-emulsion oil-based drilling fluids with the influences of concentration and pressure, and they found the similar phenomenon. In addition, the water fraction also positively affected the viscosity of the fluids. Afterwards, Hermoso et al. (2017) jointly researched the influence of aqueous phase volume fraction, OMt concentration, pressure and temperature on density of oil-based drilling fluids. They studied the pressure-temperature-density behavior of the OMt/oil fluids by Tait equation, with a maximum relative error lower than 0.21%. The density of the OMt/oil fluids decreased as temperature increased while the density increased as pressure augmented (Fig. 3).

Moreover, Zhuang et al. (2016) investigated the structure of OMt/oil fluids and their viscous flow behaviors under different temperatures. They observed that swelling and gel formation of organoclay dispersion were positively affected by compatibility between base oil and OMt, basal spacing and surfactant loading level. Temperature rising promoted the viscosity and thixotropy before 150°C and continuous increase of temperature resulted in damage to the rheological properties, due to the loss of surfactants within organoclay interlayers. But they just investigated the OMt modified by CTAB. Later, Zhuang et al. (2017b) investigated the structures and rheological properties of OMt modified by different quaternary ammonium salts in oil-based drilling fluids. The selected surfactants included dodecyl trimethyl ammonium chloride (C12), octadecyl trimethyl ammonium chloride (C18-A), benzyl dimethyl octadecyl ammonium chloride (C18-B) and dimethyl dioctadecyl ammonium chloride (DC18). The results demonstrated that longer or more long alkyl chains gave rise to greater gel formation (Table 1). Accordingly, they evaluate the rheological properties using dynamic rheological test (Fig. 4). Usually, the rheological properties of a drilling fluid, such as apparent viscosity (AV), plastic viscosity (PV) and yield point (YP), are determined by a Fann type viscometer, which assumes the flow behavior conforms to Bingham model. The dynamic rheological curves indicated three models, i.e., Newtonian for OMt modified with badly lipophilic surfactants, power law model for OMt modified with moderately lipophilic surfactants and very good shear thinning behavior with critical points for OMt modified with highly lipophilic surfactants. The temperature significantly influenced the rheological properties of OMt modified with highly lipophilic modifiers. Temperature rising before 180°C improved the viscosity and thixotropy while continuous rising led to decline. Surfactants with longer and/or more long alkyl chains are advised to prepare OMt, aiming to provide greater viscosity, thixotropy and thermal stability for oil-based drilling fluids.

Table 1 Gel volume of different OMt/oil fluids aged at different temperatures (Zhuang 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

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

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

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

2.4 Rheological mechanism of OMt in oil

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

However, it is quite different for OMt in oil. Schmidt et al. (1987) reported that the interaction between OMt and water in base oil contributed to the viscosity of oil-based drilling fluids. Recent researches also demonstrated that more water percentages increased the viscosity of oil-based drilling fluids (Hermoso et al., 2015; Zhuang et al., 2015a). But this point of view ignored the interaction between OMt and base oil. In all-oil-based drilling fluids, OMt may present excellent rheological properties even without any water. Silva et al. (2014a, b) found the positive relationship between the swelling ability of OMt in oil and the viscosity of oil-based drilling fluids. Generally, the excellent swelling ability of OMt caused great viscosity while poor swelling resulted in inferior viscosity. This phenomenon was also testified by Zhuang et al. (2015a). Zhuang et al. (2016, 2017b, d) studied the structures of OMt/oil gels aged at different temperatures by X-ray diffraction and noticed the exfoliation behavior of DC18-Mt at high temperature (Fig. 7). The rheological properties of OMt in oil are influenced by the basal spacing and ability of swelling and exfoliation, which are deeply affected by the surfactants' nature. According to the previous investigation (Zhuang et al., 2017d, 2019a,b), the structural changes of different OMt in oil are summarized in Fig. 8. Surfactants with a single short alkyl chain (< 12 C atoms), showing poor lipophilicity, led to small basal spacing and poor compatibility with oil, and finally resulted in inferior swelling and even shrinking. Organic surfactants with a single long alkyl chain (> 16 C atoms) resulted in good swelling at normal temperature but shrinking at high temperature. Most important, surfactants with double long alkyl chains, exhibiting excellent lipophilicity, contributed to large basal spacing and appropriate compatibility with base oil, which brought about the easier intercalation of oil molecules and consequently resulted in exfoliation in oil. Although the use of OMt samples modified with more alkyl chains in oil-based drilling fluids has never been reported, these OMt samples may present considerable rheological properties. Moreover, the surfactants' loading level also affects the rheological properties of OMt in oil-based drilling fluids. Generally, more surfactants should promote the rheological properties of oil-based drilling fluids by increasing the basal spacing and compatibility of OMt with oil. But the occupation of organic surfactants in the interlayer space is limited.

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

Geothermal high temperature is another challenge for drilling fluids. Thermal stability of OMt in oil should be considered. Two possible changes of the organic modifiers in OMt can be proposed: (i) thermal degradation and (ii) dissolving into the base oil. Xie et al. (2001) proved that the initial degradation of the quaternary ammonium cations in OMt followed a Hoffmann elimination reaction by TG-FTIR-MS and pyrolysis/GC-MS analysis. Zhuang et al. (2019a) investigated the thermal stability of different OMt samples in oil by XRD, thermal analysis and N elemental analysis. The results demonstrated that both desorption and degradation influenced the thermal stability of OMt/oil fluids. Surfactants with short alkyl chains desorbed in oil even at low temperatures, while organic modifiers having long alkyl chains did not. Quaternary ammonium salts degraded into olefins and amines before 200°C, and continuous oxidation occurred at higher temperatures. The resulting olefins and amines first stayed in the interlayer space and then gradually dissolved into the base oil at higher temperatures (Fig. 10). Consequently, surfactants with two or three long alkyl chains were suggested to contribute to excellent thermal stability and rheological properties of OMt in oil-based drilling fluids. For example, OMt prepared with DC18 can suffer from thermal attack at 250°C for 16 h, while the viscosity at 100 s^{-1} decreased by only 12.8% and the gel volume remained 100.0% (Zhuang et al., 2019a).

3. Organo-palygorskite and organo-sepiolite

3.1 Palygorskite and sepiolite

Compared with the large deposit of Mt, palygorskite (Pal) and sepiolite (Sep) are less on the earth. But these two clay minerals attract more interests due to their special adsorptive, colloidal-rheological, and catalytic properties which are the basis for many technological applications. Pal and Sep are clay minerals inasmuch as they contain a continuous two-dimensional tetrahedral sheet; however, they differ from other layer silicates in that they lack continuous octahedral sheets. The apical oxygen atoms of the tetrahedra partially form the coordination unit of the octahedral sheet. Therefore, there is a region of the structure where a channel may form adjacent to the basal oxygen planes between two 2:1 layers (Fig. 11). Channels are 3.7 × 10.6 Å in sepiolite and 3.7 × 6.4 Å in palygorskite. As the octahedral sheet is discontinuous at each inversion of tetrahedra, oxygen atoms in the octahedra at the edge of the ribbons are coordinated to cations on the ribbon side only, and coordination and charge balance are completed along the channel by protons, coordinated water and a small number of exchangeable cations. Also, a variable amount of zeolitic water is contained in channels (Bradley, 1940; Alvarez, 1984; Krekeler and Guggenheim, 2008; Álvarez et al., 2011; Guggenheim and Krekeler, 2011; Suárez and García-Romero, 2011).

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

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

3.2 Synthesis of OPal and OSep.

Pal and Sep are usually used as adsorbents, rheological agents, catalytic carriers, and fillers for polymer nanocomposites. In some applications, organic modification is necessary before use due to the poor compatibility between these clay minerals and organic compounds. For example, the adsorption of organic compounds from waste water and polymer nanocomposites. The modifiers include cationic surfactants, amines, organosilanes and polymers. The synthesis of OPal and OSep are summarized in Table 2. Most of OPal and OSep were prepared using quaternary ammonium salts in aqueous solution. In some cases, heating was employed to help the reactions. Only a few examples were prepared in organic solvents. The interaction between modifiers and clay minerals not only occurred on the external surface, but also may penetrate into the structural channels. Maya blue, an ancient hybrid pigment, was proved as a hybrid, in which the natural indigo dye molecules penetrated into Pal channels, resulting in outstanding residence to acids, bases, solvents and light (Chiari et al., 2003; Río et al., 2011).

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

Table 2 A summary of the synthesis of OPal and OSep

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

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

Mt is the most used clay mineral for water-based drilling fluids, since it presents excellent viscosity and thixotropy in fresh water. However, when in contact with salts, Mt tends to coagulate reducing its viscosity and losing its thixotropic properties, because the network structure of Mt in water is affected by the electrolytes. Pal and Sep, in contrast, remains a viscous dispersion in the presence of dissolved salts (Galan, 1996; Baltar et al., 2009; Abdo and Haneef, 2013b). It is because these two clay minerals form a “haystack” structure by organizations of nanofibers and it is not sensitive to electrolytes. It is thus used as a component of drilling fluids for wells drilled off shore or those that cross layers of soluble salts. The desired rheological properties remain relatively constant even at high electrolyte concentrations over a wide pH (Neaman and Singer, 2000a).

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

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

Later, the use of OSep in oil-based drilling fluids were also studied. Zhuang et al. (2018d) modified Sep with benzyl dimethyl octadecyl ammonium chloride (C18-B) and investigated the rheological properties of OSep in oil. The optimized amount of surfactant equals to 35 wt.% of raw Sep. OSep showed excellent viscosity and thixotropy in oil. The temperature rising below 180°C promote the rheological properties. By calculating the size of organic modifier, surface area test and thermal analysis, a part of surfactants were testified to insert into the Sep channels. Later, Zhuang et al. (2018b) researched structures and rheological properties of three surfactant-modified OSep (Fig. 13). The pore width and micropore volume distribution demonstrated that C18-A and C18-B inserted into the Sep channels while DC18 cannot. Compared with the channel size, C18-A is much smaller, C18-B is a little smaller with one side almost identical, and DC18 is much larger. Consequently, C18-B can block the channels and fixed on the surface, resulting in the best rheological properties and thermal stability.

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

3.4 Rheological mechanism of OPal and OSep in oil

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

OPal/oil gels. They found that OPal kept the crystal structure in oil. This was very different from OMt which swelled and even exfoliated in oil. According to the fibrous morphologies (See Fig. 14), Pal and Sep form a “haystack” or “brush heap” structure in solvents. Hence, OPal and OSep were considered to form the similar “haystack” structure in oil. Due to the lipophilic surface, OPal and OSep fibers can disperse in oil and form a network structure by natural stack and connection. The rheological properties of OPal and OSep in oil were influenced by the compatibility between OC and oil. OPal and OSep presented three possible structures in oil (Fig. 15(A)), i.e., stack, network structure and dispersion. Surfactants of poor lipophilicity led to inferior compatibility between OC and oil, resulting in stack of nanofibers. Oppositely, OPal and OSep modified with surfactants of great lipophilicity usually led to excellent compatibility with oil, consequently causing fine dispersion in oil. Neither stack nor dispersion contributed to prominent rheological properties of oil-based drilling fluids, due to the weak interaction between nanofibers. The selection of appropriate surfactants is very important for enhance the rheological properties of oil-based drilling fluids containing these OC. According to the previous investigations (Zhuang et al., 2017a, 2018b), C18-A (mass 25% of Pal) was optimal for the rheological properties of OPal in oil while C18-B (mass 35% of Sep) improved most for OSep among the selected surfactants. In addition, the aggregations of OPal and OSep also influenced the rheological properties. OPal and OSep existed in the form of different aggregations, i.e., particles, aggregations, crystal bundles (including several fibers) and individual fibers (Fig. 15(B)). Except for organic modification, high temperature can also promote the disaggregation of crystal bundles and aggregates, resulting in more individual fibers and small aggregates. This disaggregation contributed to a stronger network structure. Extremely high temperature (usually > 180°C) would damage the rheological properties Thermal degradation and desorption of organic surfactants may be responsible, but more details need be specified.

Zhuang et al. (2017b, 2018b) studied the interactions between these two clay minerals and organic surfactants, and their influences on the rheological properties. Surfactant cations stayed in OPal and OSep at four possible locations (Fig. 16), i.e., (i) completely inserting into the channels and/or tunnels, (ii) partially inserting into the channels and/or tunnels, (iii) blocking the channels and/or tunnels and (iv) covering on the surface. Two possibilities were proposed for the thermal stability of OPal and OSep in oil: (i) thermal degradation of organic modifiers and (ii) dissolution of organic modifiers detached from OC and dissolution into oil. The insertion of surfactants into the channels is significant for the stability of OPal and OSep in oil. In the previous study (Zhuang et al., 2017b), DC18-Mt presented the best rheological properties and thermal stability in oil-based drilling fluids. But the optimized modifiers were C18-A for OPal and C18-B for OSep. This fact demonstrated that the decline of rheological properties of OPal and OSep in oil below 200°C is mostly due to the desorption of organic surfactants and accordingly resulted in poor compatibility between clay minerals and oil. Obviously, the insertion of modifiers enhanced the fixation of modifiers in oil, even under high temperatures. The insertion of organic modifiers was testified by pore volume distribution (Zhuang et al., 2018b). By comparing the molecular size, C18-A and C18-B were possible to insert into Sep channels while DC18 was not (Fig. 17). Because C18-A is much smaller than the channel size, it is not as stable as C18-B in the channels and tunnels of Sep. Accordingly, based on the molecular size, C18-A is possible to penetrate into Pal channels and tunnels while C18-B and DC18 are not.

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

4.1 Rheological properties of synergetic use of different OC.

Some literature reported about the joint use of two clay minerals to enhance the rheological properties of clay minerals in aqueous dispersion or water-based drilling fluids. Neaman and Singer (2000b) researched the rheological properties of mixed Mt and Pal in aqueous dispersion and they found that small montmorillonite additions (≤ 10 wt.%) increased the rheological parameters (plastic viscosity and Bingham yield value). Au and Leong (2013) found that the mixture of Mt and kaolinite in aqueous dispersion could adjust the optimized pH value and rheological properties by changing the amount of these two clay minerals. Aiming for using in water-based drilling fluids, İşçi and Turutoğlu (2011) researched the mixture of Mt and Sep in water. They found the mixture is not adequate for water-based drilling fluids and stabilizers were necessary. Afterwards, Chemeda et al. (2014) investigated the rheological properties of dispersions of fibrous clay minerals (Pal and Sep) mixed with Mt with different layer charge. The degree of interaction between Mt and fibrous clay particles and its effect on the apparent viscosity and yield point of the dispersions depend on the concentration, layer charge and charge localization of the Mt in the mixture. The physical and chemical properties of the fibers (fiber length, specific surface area and CEC) also affect the interaction of fibrous clays with smectite and consequently the rheological properties of the mixtures. The rheological properties were affected by layer charge of Mt and the proportion of fibrous clay minerals. An appropriate mixture of Mt and fibrous clay minerals enhanced the rheological properties by the interaction of particle-particle linkages. Al-Malki et al. (2016) found that bentonite-based drilling mud with Sep nanoparticles showed a great stability in plastic 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 OMt and OSep may also promote the rheological properties and thermal stability of oil-based drilling fluids. This is a promising way to sustain oil-based drilling fluids work in difficult wells. Zhuang et al. (2017d) comparatively studied the rheological properties of OMt and OPal in oil-based drilling fluids. Although OMt presented greater viscosity and thixotropy than OPal in oil, OPal exhibited better thermal stability and dispersity. Mainye and Teutsch (2015) researched the mixture of OMt and OPal (or OSep) as a rheological additive to improve the ultra-low shear rate viscosity and to increase the carrying capacity of oil-based drilling fluids. The clay minerals were modified with quaternary amines and/or quaternary ammonium salts. The mass percentage of OPal or OSep was 10%. They found the mixture of different organoclays significantly yielded stable gels that were non-progressive compared to each individual organoclay used separately. But this work didn’t systematically study the synergetic use of two organoclays in oil-based drilling fluids.

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

4.2 Rheological mechanism of mixed OC in oil

There is no microscopic evidence about the gel structure of the mixture of OMt and OSep. The gel structure was proposed based on the XRD results of OC/oil gels (Zhuang et al., 2018c, 2019c). At normal temperature, OMt firstly swelled in oil by adsorbing oil molecules while OPal or OSep showed stable dispersion due to its nanoscale fibers, laths and bundles. Aged at high temperature, the basal reflection of OMt disappeared while the (100) reflection remained, indicating that 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. According to the XRD results, a graphical summary was presented in Fig. 19. The mutual support between OMt nanolayers and nanofibers protected this network structure from being damaged by high temperatures.

5. Conclusions and perspectives

The study of organoclays and the application in oil-based drilling fluids are a large field and shows an immense potential to be explored. OMt is mostly used as the rheological additive in oil-based drilling fluids. More attention should be paid to the application of OPal and OSep in oil-based drilling fluids. OC are usually modified with quaternary ammonium salts. Large basal spacing, good lipophilicity and exfoliation are significant for the gel formation ability and rheological properties of OMt in oil. Organic modifiers with longer and/or more alkyl chains are suggested to be employed to prepare OMt for oil-based drilling fluids. OPal and OSep are easy to disperse in oil due to the nanosized fibrous morphology. Organic modifiers cannot intercalate into the interlayer space like OMt. Hence, penetration of surfactants into the channels and tunnels is very important for the stability of oil-based drilling fluids, especially at high temperatures. When choosing a modifier for OPal and OSep, the molecular size and compatibility with oil should be considered. Synergetic use of OMt and fibrous OC is a promising method to enhance the rheological properties and thermal stability of oil-based drilling fluids.

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

Although oil and gas are not renewable, they are the most important energy resources on the earth in the next 30 years. The new energies cannot completely replace these fossil energies in a short time. Seeking and exploring more oil and gas from the difficult locations is an economic and simple way. Studying on the application of OC in oil-based drilling fluids will promote the development of petroleum industry and our daily life.

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Figure captions:

Fig. 1 The crystal structure of Mt and corresponding SEM and TEM images (Mt obtained from Liaoning, China).

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Fig. 18 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 (Zhuang et al., 2018c).

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