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Research paper

The structure and rheology of organo-montmorillonite in oil-based system aged under different temperatures

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ABSTRACT

This work aims to study the structure of organo-montmorillonite (OMt), structure of OMt/oil gels and the rheology of OMt/oil fluids aged under different temperatures. Most important, we focused on the relationship among OMt, OMt/oil and temperatures. The results of XRD and contact angle test demonstrated that surfactants loading deeply influenced the structure and surface properties of OMt. The results of XRD, optical microscope and gel volume of OMt/oil indicated that the structure of OMt in oil went through three stages with the temperature rising: swelling → continuous swelling → exfoliation → shrinking. The enwinding, absorption and other attraction among absorbed surfactants bridged individual OMt sheets, particles and aggregates, forming the gel structure. The swelling and gel formation of OMt/oil were influenced by the surface/interface properties, basal spacing, surfactants loadings and temperature. Dynamic rheological curves demonstrated that OMt/oil followed the Bingham plastic model at high shear rate (often ≧20 s^{-1}) while deviation emerged at low shear rate range. The viscosity, gel strength and thixotropy of OMt/oil were relevant to the structure which was influenced by multiple elements, such as surface/interface properties, basal spacing, surfactants loadings, temperature, etc. The best performance of individual element did not automatically lead to the greatest rheological properties. Higher surfactants loading, higher d_{001} without very ordered internal lattice and moderate polarity of surface/interface of OMt were expected. For oil-based drilling fluids containing OMt prepared with cetyl trimethyl ammonium bromide (CTAB), the operating temperature was advised below 150 °C.

1. Introduction

Organo-montmorillonite (OMt) is a kind of hydrophobic material which obtained by modifying montmorillonite (Mt) with various organic compounds through intercalation process and surface grafting (Bergaya and Lagaly, 2001; Bergaya et al., 2011; de Paiva et al., 2008; He et al., 2014). OMt is known for its ability for swelling and thixotropic gel formation in organic media (Lagaly and Malberg, 1990; Moraru, 2001; Slabaugh and Hiltner, 1968). Thus OMt is widely used as a rheological additive in industrial applications such as paints, inks, adhesives, greases, and varnishes, cosmetics and medicines (de Paiva et al., 2008; He et al., 2010). Particularly, OMt is also widely used in oil-based drilling fluids (Fan et al., 2015; Hermoso et al., 2015; Silva et al., 2014; Zhang et al., 2012; Zhuang et al., 2015).

Generally, oil-based drilling fluids have high thermal stability and drilling performance by producing low frictions, high rate of penetration, shale inhibition, wellbore stability, high lubricity and salt resistance to overcome certain undesirable characteristics of water-based drilling fluids (Amani et al., 2012; Caenn and Chillingar, 1996; Khodja et al., 2010). Greater emphasis is placed on rheological properties of drilling fluids because the rheological behavior of drilling fluids is a critical issue in the success of drilling operations, particularly in drill cuttings removal. OMt increases the viscosity and thixotropy of oil-based drilling fluids. The viscous flow behavior of oil-based drilling fluids is strongly influenced by OMt nature and concentration (Hermoso et al., 2014). In addition, as a drilling fluid mostly works at high temperatures, the temperature also influences the rheological properties by affecting the structure of OMt/oil. Thus, the relationship of OMt-OMt/oil-temperature needs to be revealed for guiding the oil-based drilling fluids' use in practice.

Much important work about the above issue was done by scientists and engineers, but some problems still exist. Much literature (Amani, 2012; Coussot et al., 2004; Hermoso et al., 2014; Hermoso et al., 2015; Lee et al., 2012; Saasen and Løklingholm, 2002; Zhuang et al., 2015; Silva et al., 2014) reported the rheological properties and other applied properties of oil-based drilling fluids under high temperatures. But the structure of organoclay/oil was lacking of more discussion, and how the organoclay and temperature influence the rheological properties is still unknown. Several studies on the structure and rheology of OMt in organic solvents at normal temperatures had been reported (Bhatt et al., 2013; Burgentzlé et al., 2004; Minase et al., 2008; Moraru, 2001; Okamoto et al., 2000; Zhong and Wang, 2003). However, the influence

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of temperature on the structure and rheological properties of OMt/oil is still unsettled. No research on the relationship of OMt-OMt/oil-temperature is reported at present. Aiming to solve the above issues, we studied the structure of OMt, structure of OMt/oil and the rheological properties of OMt/oil (such as rheological model, gel strength, viscosity and thixotropy) aged at different temperatures. The influence of temperature on the structure and rheological properties of OMt/oil fluids was revealed.

2. Materials and methods

2.1. Materials

Raw Mt, which was milled and sieved with a 200-mesh sieve, was obtained from Kazuo Shuanglong Mining co., Ltd., Liaoning Province, China. The cation exchange capacity (CEC) of Mt was 125 mmol/100 g and the given purity was ≥95%. Cationic surfactant cetyl trimethyl ammonium bromide (CTAB) (purity of 99.9%) was bought from Shantou Xilong Chemical Co., Ltd., China. The diesel oil was bought from China National Petroleum Corporation.

2.2. Preparation of OMt

OMt were prepared in aqueous solution as the following steps: 100 g Mt was added into 3000 mL distilled water, stirring for 10 min; then a certain amount of CTAB was added into the previous dispersion, stirring for 1 h; at last, by centrifugation, drying at 60 °C for 24 h, milling and sieving with a 200-mesh sieve, OMt was prepared. OMt prepared with 0.5 CEC, 1.0 CEC, 1.5 CEC and 2.0 CEC CTAB were named C(0.5)-Mt, C(1.0)-Mt, C(1.5)-Mt and C(2.0)-Mt, respectively.

2.3. Preparation of oil-based fluids (OMt/oil gels)

12 g OMt was added into 400 mL diesel oil (concentration of 30 kg/m^3) and blended for 20 min. The resulting fluid was placed in a rotary oven heated to 66 °C, 150 °C, 180 °C and 200 °C where it was aged for 16 h. The oil-based fluids were named OMt/oil-temperature. For example, C(0.5)-Mt dispersed in diesel oil and aged at 66 °C for 16 h was named C(0.5)-Mt/oil-66.

2.4. Characterization

The X-ray diffraction (XRD) analysis was conducted on a Rigaku D/max-rA (12 kW) X-ray powder diffractometer operating at Cu Kα radiation, 40 kV, 100 mA and a scan speed of 4.0°(2θ)/min. Powders and OMt/oil gels were packed in vertical aluminum holders. Contact angle tests were conducted on a contact angle measurement JC200D and the measurement was performed with distilled water. OMt samples for contact angle test were pressed to tablets under the pressure of 15 MPa for 1 min. Then a drop of distilled water dript on the surface of OMt tablet. The gel volume results were obtained by adding 100 mL aged fluid into a graduated cylinder with a stopper and standing for 24 h. Optical microscopy observations were carried out by using an Olympus BX52 microscope, equipped with an Olympus C5050Z camera. Optical micrographs were obtained for all the different OMt/oil samples manufactured, using the incident light mode. The samples were carefully poured into a sample holder and spread under the glass cover slip, at room temperature, before the observations. The dynamic rheological behavior of oil-based fluids was tested by a Thermo Scientific HAAKE Roto Visco 1 rotational viscometer. The tested program was: the shear rate linearly increased from 0 s^{-1} to 100 s^{-1} in 5 min, and then linearly decreased from 100 s^{-1} to 0 s^{-1} in 5 min.

3. Results and discussion

3.1. Structure of OMt

The XRD patterns of Mt and OMt samples are given in Fig. 1. The (001) reflection of Mt emerged at 2θ = 6.9°, corresponding to basal spacing of 1.28 nm. With the increase of CTAB loading, the basal spacing of OMt increased. The basal spacing of C(0.5)-Mt, C(1.0)-Mt, C(1.5)-Mt and C(2.0)-Mt were 1.48 nm, 1.98 nm, 4.06 nm and 4.00 nm, which were identical to previous reports (He et al., 2006; Zhu et al., 2003). The XRD results indicated that CTAB intercalated into the interlayer of Mt and expanded the interlayer space.

The results of contact angle test which were presented in Fig. 2(A) indicated the detailed arrangements of the external CTAB. With the increase of CTAB, the contact angles firstly increased, but finally decreased, in accord with our previous report (Zhuang et al., 2015). Why did not the contact angles of OMt always increase with the increase of CTAB? Previous studies (He et al., 2005; Hedley et al., 2007; Juang et al., 2002; Ma et al., 2015; Zhou et al., 2007; Zhu et al., 2011) had demonstrated that surfactants did not only enter into the Mt interlayer space, but also occupied the surface of Mt. The arrangements of CTAB on the surface of OMt varied with the concentration of CTAB. Based on the previous reports and contact angle test, the arrangements of CTAB were graphically presented in Fig. 2(B). At low loadings of CTAB (e.g. below 1.0 CEC), most CTAB intercalated into the interlayer space of Mt, and the rest were absorbed on the surface by electrostatic attraction (the first layer of CTAB), resulting in the exposure of alkyl chains of CTAB and hydrophobicity of OMt. At an appropriate coating, i.e. 1.0 CEC, the surface of Mt was fully coated and the corresponding OMt showed the best hydrophobicity. While at higher loading levels (e.g. above 1.0 CEC), excess CTAB cations were absorbed on the first layer of CTAB

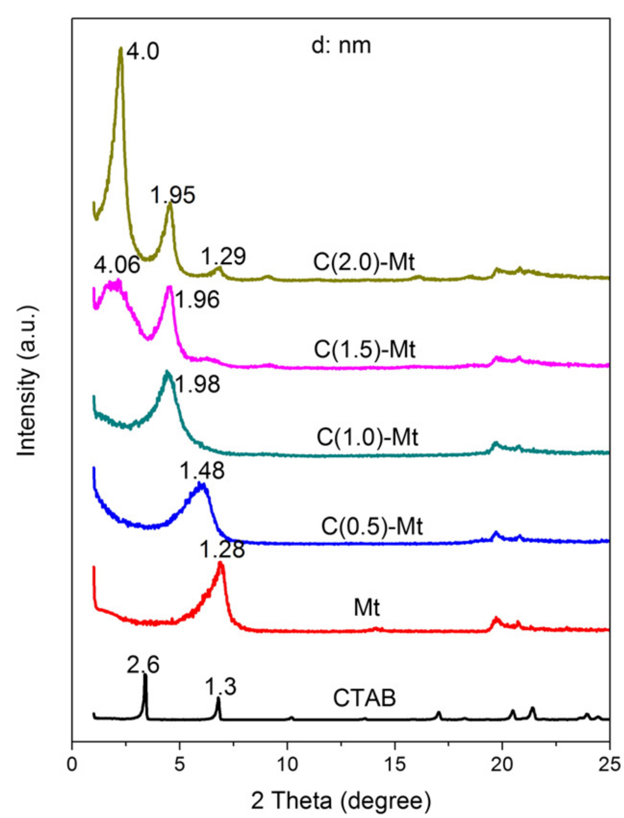

Fig. 1. XRD patterns of Mt and OMt samples.