Applied Clay Science 157 (2018) 24–30

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

Structural investigation of hectorite aqueous suspensions by dielectric microscopy and small-angle neutron scattering coupling with rheological measurement

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ARTICLE INFO

Keywords:
Synthetic hectorite
Aqueous suspension
SE-ADM
Rheo-SANS
Non-contact card house
Thixotropy
Molecular motion

ABSTRACT

The microstructure of synthetic hectorite aqueous suspensions was investigated by scanning electron-assisted dielectric microscopy (SE-ADM) and small angle neutron scattering (SANS) coupled with rheological measurements (Rheo-SANS). The direct observations of the aqueous suspensions by SE-ADM confirmed the array structure of the hectorite discs with ~100–300 nm scale periodic length. The suspensions demonstrated a typical thixotropic flow curve with hysteresis. No change in the SANS profiles at high shear rate (1000 s^{-1}) was observed by the Rheo-SANS. These results suggested that the array was destroyed by the shear rate but the microstructure in the arrays was preserved in flow condition.

1. Introduction

A clay, considered as a nanocomposite made of water and clay minerals, has been widely used for porcelain productions since ancient times. Understanding the structure of silicate layers in aqueous suspensions is one of the key information that allow for a suitable control of the industrial processes using clays (Tadros, 1993). Their macroscopic properties were analyzed by rheological measurements (van Olphen, 1964; Suzuki et al., 2017) whereas the microstructure in a liquid matrix was studied by techniques that provide a more detailed and in-depth analysis such as light scattering and small-angle X-ray/neutron scattering (SAXS/SANS) (Pignon et al., 1997). Transmission electron microscopy (TEM) (Vryzas et al., 2016; Mouzon et al., 2016; Jatav and Joshi, 2017) or scanning electron microscopy (SEM) (Mouzon et al., 2016) was undertaken to investigate morphological properties of dried or frozen samples. However, the transition from microscopic to mesoscale structure is still not well understood due to the high number of control parameters, such as lateral size of silicate layers, concentration, salt concentration, pH, temperature, mixing procedure, aging time, etc.

Using static and dynamic light scattering, neutron spin echo, X-ray photon correlation spectroscopy, SAXS, rheological measurements and dilution experiments with simulations (Ruzicka et al., 2008, 2010; Angelini et al., 2014; Marques et al., 2015), Laponite suspensions in absence of salts form different states depending on the volume fraction of clay (C_w); equilibrium gel ($C_w < 2$ vol%), Wigner glass ($2 < C_w < 4$ vol%), and disconnected house of cards glass ($C_w > 4$ vol%). Although an interesting model was proposed for the microstructure in the glassy states, more information is necessary to understand the macroscopic rheological behavior of the aqueous suspension with lower concentrations. It is expected that the direct observation of aqueous gels and glassy states as well as the microstructure of re-dispersed structure under shear flow field to bring more light into this important issue with industrial implications.

A recently developed scanning electron-assisted dielectric microscopy (SE-ADM) (Ogura, 2014) proves to be an interesting technique that produces high-resolution images offering in-depth knowledge on the structural features of the silicate layers into an aqueous environment. SAXS and SANS techniques give information on a length scale of 1–100 nm that is correlated with colloid systems (Tudisca et al., 2014). In addition, to combine the structural information provided using neutrons that highly penetrate materials with measurement of the rheological parameters, simultaneous SANS and rheological measurements, so-called “Rheo-SANS” was developed. This technique was previously applied to deeply characterize hydrogels, polymer melts, emulsions, micelles and polymer/nano clays (Loizou et al., 2010; Matsunaga et al., 2010; Eberle and Porcar, 2012). However, the focus was put only on the effect of the organic polymer on the structure of suspensions under static state and flow field.

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https://doi.org/10.1016/j.clay.2018.02.016
Received 8 August 2017; Received in revised form 17 January 2018; Accepted 9 February 2018

In this study, the Rheo-SANS of an aqueous suspension containing synthesized hectorite was comparatively analyzed with a direct observation by SE-ADM to get a clearer image on the microscopic to mesoscale structure of the aqueous suspensions or glassy state.

2. Experimental

2.1. Sample preparation

Synthetic hectorite, Laponite-RD®, was used without purification and dispersed in deuterated water (D_2O). The dried powdered hectorite was dispersed in D_2O in glass bottles using magnetic stirrer for approximately 24 h. The prepared 1, 1.5, 2, and 4 wt% of synthetic hectorite suspensions were aged for approximately one month in sealed glass bottles. The samples of 1, 1.5, 2, and 4 wt% correspond approximately to 0.5, 0.8, 1.1, and 2.2 vol%. The estimation was performed using a tentative hectorite density (2.8 g/cm^3) and D_2O (1.11 g/cm^3). The 2 wt% hectorite aqueous suspensions were aged for one more month. Purified natural montmorillonite from Yamagata, Japan, Kunipia-F® suspensions (2 and 4 wt%), were also prepared for the SE-ADM observations.

2.2. Scanning electron-assisted dielectric microscopy (SE-ADM)

SE-ADM was carried out to directly observe silicate layers in water with approximately 10 nm of spatial resolution (Ogura, 2015). An aqueous suspension sample holder (4 mm × 4 mm × 10 μmt) shown in Fig. 1 was mounted on a pre-amplifier attached stage installed into the specimen chamber of FE-SEM system (JSM-7000F, JEOL, Tokyo, Japan). A scanning electron beam was applied to the W-coated SiN film (thickness of 20 nm) at 3–4 kV of the acceleration voltage. Irradiated electrons were absorbed in a tungsten layer on the SiN thin film to arise a negative electric-field (Ogura, 2014), which was detected at the bottom measurement terminal through the specimen in water. A large difference in the dielectric constant of silicate layers with that of liquid water gave a high-contrast image of the aqueous suspensions. The electrical signal from the pre-amplifier was fed into the AD converter after low-pass filtering. The electron beam-scan signals were logged by a PC through an AD converter at a sampling frequency of 50 kHz. SEM images (1280 × 1020 pixels) were captured at 20,000–80,000 magnification with a scanning time of 80 s.

2.3. Simultaneous SANS and rheological measurements (Rheo-SANS)

A rheometer (Anton Paar MCR302) was set up at the small- and wide-angle neutron scattering instrument (TAIKAN) installed on the BL15 beamline at Materials and Life Science Experimental Facility (MLF) in Japan Proton Accelerator Research Complex (J-PARC) (Takata et al., 2015). A double-cylinder-type cell of quartz glass inner rotor with 48 mmΦ and quartz glass outer status cylinder with 50 mmΦ of inner diameter were employed, as shown in Fig. 2. Information of SANS both radial, using 10 mmΦ neutron beam, and tangential, using a 0.5 mm × 10 mm beam, were collected under shear rate of 0–1000 s^{-1} at 30 °C. Using the white neutrons in the wide range of wavelength (λ = 0.1–0.78 nm) based on time-of-flight method and the four area detector banks, TAIKAN can cover a wide Q-range from 5×10^{-2} to 150 nm^{-1} simultaneously, where the magnitude of the scattering vector Q is defined by $Q = 4\pi\sin(\theta/2)/\lambda$ (λ and θ represent the wavelength and the scattering angle, respectively). This Q-range correspond to 0.1 nm $< r <$ 125 nm in real space. The observed Q range was limited to 1×10^{-1} nm^{-1} $< Q <$ 10 nm^{-1}, corresponding to 0.6 nm $< r <$ 60 nm in real space, due to an increasing background level by incoherent scattering from hydrogen atoms in higher Q range. The SANS data were collected from the aqueous suspensions in the rheometer under the shear rate at 0 s^{-1} (static) and 1000 s^{-1} by the radial or tangential geometry (Fig. 2). The radial and tangential geometry observations offer us the structural information parallel and perpendicular to the flow direction, respectively.

3. Results

3.1. Scanning electron-assisted dielectric microscopy (SE-ADM) images

The SE-ADM images for the aqueous suspensions containing 2 and 4 wt% synthetic hectorite are shown in Fig. 3. As the lateral size of a silicate layer (25 nm) is comparable with the current resolution (10 nm) of the SE-ADM technique, the images are not clear. In addition, the images display isolated particle of 10–30 nm diameter, along with aggregations formed in suspensions for both concentrations. Concentrated and dilute parts as well as their ~100–300 nm scale periodic structures are observed. To note, the periodic structure did not change with concentration. However, although the correlation length of the aggregate structure was not altered, the size of the aggregates was increased with the concentration. A periodic aggregation with longer correlation length compared to the size of the layer was also observed for the natural montmorillonite aqueous gels (Bihannic et al., 2001).

The image corresponding to the 2 wt% hectorite suspension aged for another additional one month (i.e., total two months) are shown in Fig. 4. Accordingly, insignificant change was observed for the sample aged for two months. The aggregates with size of approximately 100 nm can still be observed in Fig. 4.

Two SE-ADM pictures of the aqueous suspensions of 2 and 4 wt% natural montmorillonite are shown in Fig. 5. As the resolution of the equipment is appropriate, clear images of the isolated silicate layers

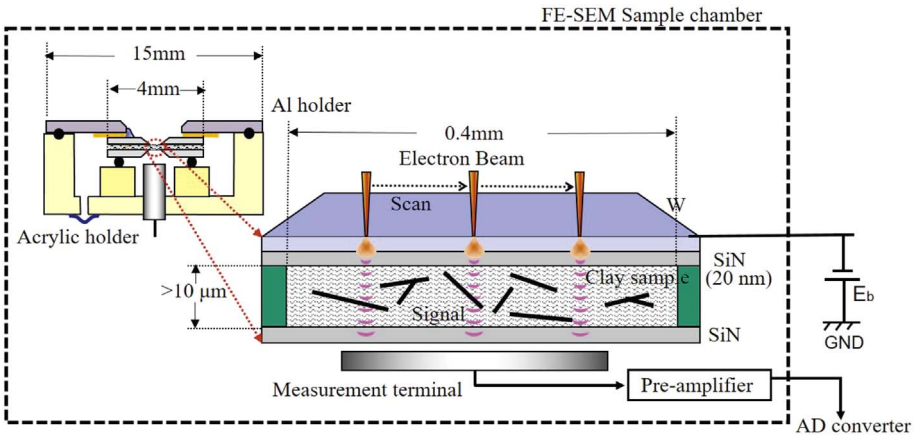

Fig. 1. Schematic diagram of scanning-electron assisted dielectric microscopy (SE-ADM).