# Structural analysis of clay particles in water under shear and the effect of additives

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## 1. Introduction

Clay minerals have a high affinity with organic molecules and these minerals can be a good adsorbent of toxic molecules in water. The toxic molecules adsorbed on clay minerals are recovered by filtration, however, small clay nanoparticles make a clogging problem. Improving the water permeability in filtration can be realized by forming microparticles of clay minerals. The morphology of microparticles alters the water permeability and therefore the control of the morphology can improve the permeability. Clay microparticles have been fabricated by spray drying method. We found that “Doughnut”-like clay microparticles can be fabricated by adding tetrasodium pyrophosphate in the clay dispersion, while spherical microparticles are formed without the additive [1]. The mechanism of morphological alteration is, however, unclear. The network structure of clay particles in water before spray drying may be a clue for understanding the reason why the morphology of microparticles changed by the presence of additives.

The network structure of clay (Laponite RD, LRD) dispersion without any additives was studied by small angle neutron scattering (SANS) coupled with rheological measurements (Rheo-SANS) and scanning electron-assisted dielectric microscopy (SE-ADM) [2]. The SE-ADM revealed that 100-300 nm scale periodic structure which can be interpreted by the periodic aggregation of clay particles. No significant difference of SANS profiles was observed under high shear rate of 1000 $s^{-1}$, indicating that structure from 10 to 100-nm scale was preserved under the shear rate. These properties of clay dispersion may be altered by the presence of additive. In this study, the structure of hectorite dispersion with tetrasodium pyrophosphate was analyzed by the Rheo-SANS method to reveal the difference of network and microscopic structure of clay dispersed in water with or without the additive.

## 2. Experiment

The network structure of clay dispersion was studied by Rheo-SANS installed on BL15 (TAIKAN) at Materials and Life Science Experimental Facility (MLF) in Japan Proton Accelerator Research Complex (J-PARC). Commercially available synthetic hectorite with additive of sodium pyrophosphate, Laponite-RDS® (LRDS), was dispersed in deuterated water ($D_2O$) using a magnetic stirrer over 24 hours. The SANS profiles of 2 and 11 wt% LRDS dispersions were measured under shear. The experimental apparatus and conditions were the same as our previous experiments [2].

## 3. Results

*Rheology of LRDS dispersions*: The flow curves of 2 and 11 wt% LRDS dispersions were shown in Fig. 1. No yield point was observed for both curves. The viscosity of 11 wt% dispersion slightly decreased at high shear rate. The curve of 2 wt% LRDS dispersion was similar to that of Newtonian fluid. The viscosity of 11 wt% LRDS was larger than that of 2 wt% LRDS; however, the clay particles in both dispersions seem not to form aggregations.

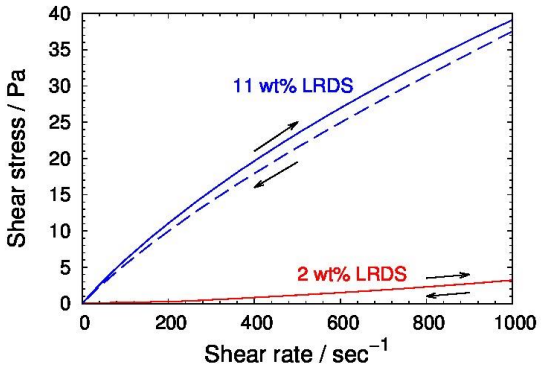


Fig. 1. Shear stress as a function of shear rate for 2 and 11 wt% LRDS dispersion. The arrows indicate the direction of shear rate.

*Effects of shear rate and shear direction*: The SANS profiles

of 11 wt% LRDS dispersion were plotted in Fig. 2. No significant difference was observed among shear rates, shear directions, and sector-averaged two-dimensional (2D) SANS profiles for horizontal (Ix) and vertical (Iy) directions. The difference at high $Q > 0.1$ Å$^{-1}$ depending on the shear directions is ascribed to the low S/N ratio of tangential measurements owing to the small beam size (0.5 mm × 10 mm) compared with that of radial measurements (10 mmΦ).

*Effects of clay concentrations*: The SANS profiles depending on the clay concentrations were plotted in Fig. 3. To compare the shape of the SANS profiles between 2 and 11 wt%, the intensities were normalized by the clay concentrations. No significant difference was observed for the gradient at $Q > 0.03$ Å$^{-1}$. The well-fitted theoretical curve to the profile of 2 wt% dispersion indicates that the presence of monodispersed circular plate of 125 Å in radius and 10 Å in thickness which are similar with that of LRD dispersion [2]. The difference at low $Q$ (<0.03 Å$^{-1}$) would reflect the strong excluded volume effect in 11 wt% dispersion due to the clay particle-particle interaction. Further analysis is required for revealing the precise interparticle interactions.

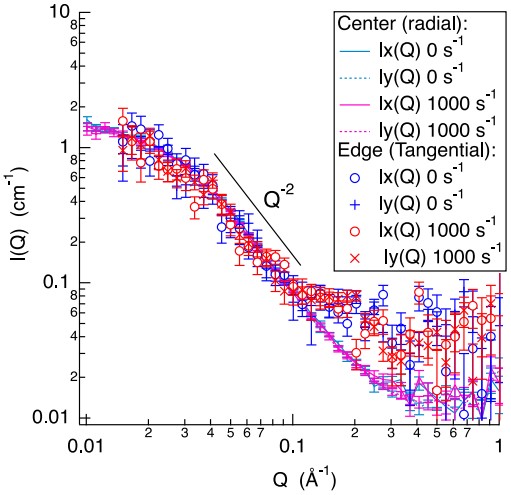


Fig. 2. SANS profiles of 11 wt% LRDS depending on the shear rates (0 and 1000 s$^{-1}$), shear directions (lines: radial; symbols: tangential), and sector-averaged 2D profiles (horizontal: Ix, vertical: Iy).

## 4. Conclusion

The profiles at low $Q$ would reflect the interparticle interactions depending on the concentration. These profiles seem to be different from the highly concentrated LRD dispersion reported by our previous study [2]. In future works, the SANS profiles of LRDS dispersion as a function of clay concentrations would be useful for understanding the difference of interparticle interactions in water depending on the clay species.

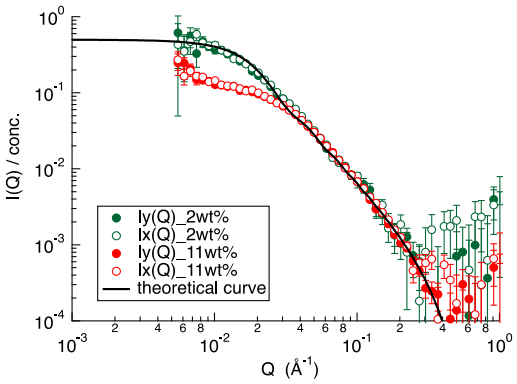


Fig. 3. SANS profiles of LRDS depending on the concentrations (2 and 11 wt%) at the radial shear direction. The effect of incoherent scattering from hydrogen included in the clays were excluded from the experimental SANS profiles.

## 5. References


[1] H. Sakuma, K. Tamura, K. Minagawa, "Doughnut"-like clay microparticles fabricated using a hybrid method of spray drying and centrifugal disc atomization, *Chemistry Letters*, **47** (2018) 68-70.

[2] H. Iwase, T. Ogura, H. Sakuma, K. Tamura, Y. Fukushima, Structural investigation of hectorite aqueous suspensions by dielectric microscopy and small-angle neutron scattering coupling with rheological measurement, *Applied Clay Science*, **157** (2018) 24-30.