

Synthesis of LDHs and Rheological Properties of Laponite/LDHs Dispersions

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Abstract: The chemical composition, morphology of the particles of positively charged layered double hydroxides (LDHs) were studied by ICP, Mastersizer, TEM. The preliminary results indicated that with adding LDHs to 1% laponite dispersion the yield stress of laponite/LDHs mixed dispersions increased at first, then decreased dramatically to a minimum, and the yield stress rose again when LDHs increased further.

Keyword: Laponite, layered double hydroxide, rheological properties.

Aqueous dispersions of anisotropic species show remarkable rheological properties, which have been the focus of current researches. Many materials, such as clay, LDHs are good examples of anisotropic particles as they occur in different geometries like rods (boehmites) and platelets (montmorillonite and LDHs)¹. Because of the isomorphous substitutions, most clay minerals like montmorillonite and laponite carry a positive charge, whereas easily synthetic LDHs have a negative charge. When clays or LDHs are dispersed in water different equilibrium states can be obtained like free flowing suspensions, gels, and phase separated flocs. Consequently extensive rheological behavior for clay or LDHs dispersions has been studied like thixotropic and viscoelastic properties¹⁻³.

Particle-size distribution and polydispersity are two decisive aspects of rheological properties of clay and LDHs dispersions. Model colloids are used to investigate the mechanism of complicated rheological properties. Due to the large polydispersity in both shape and size for natural clay samples, most recent fundamental studies on clay dispersions have been carried out with synthetic Hectorite laponite that can be considered as mono-disperse disks of about 25 nm in diameter and about 1 nm in height². LDHs particles with narrow size distribution and regular shape could be obtained iteratively in experiments.

In the early reports, rheological properties of dispersions with increasing ionic strength were studied in montmorillonite dispersions¹ on sol-gel transitions. With increasing the clay concentrations, dispersions can form repulsive gel due to electrostatic repulsive

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forces of diffuse layers of counter-ions. When adding small amount of salt to dispersions, storage modulus decreased dramatically to a minimum due to the attenuation of the electroviscous effect, where the linear viscoelastic behavior was not observed. With further addition of salt the yield stress rose slowly to a higher value.

Both clay and LDHs dispersions have been researched separately, the rheological properties and structure of clay/LDHs mixed dispersion have received little attention^{4,5}. In this paper, we used laponite and LDHs to investigate the mechanism of rheological properties and structure of mixed dispersions and the preliminary results were reported.

Aqueous suspensions of Laponite RD (Laporte Ltd.), a gift from Southern Clay Products (Gonzales, Texas), were prepared by adding required clay powder (2% w/w) to de-ionized water⁶, then stirred vigorously for 20 min (until clarification), resulting in solutions with $\text{pH} \approx 9.8$ and ionic strength $I \approx 10^{-4}$ mol/L. The acquired dispersion evolved into homogeneous, charge-stabilized glassy phases after a sufficient induction period^{6,7}. Samples for rheological measurement were stored in sealed vials under nitrogen to prevent sample acidification due to dissolved CO_2 .

LDHs were synthesized by a non-steady coprecipitation method⁸. A mixed solution of magnesium and aluminium chlorides was prepared in a molar ratio of 1:1 with total metal concentration of 0.5 mol/L. Then the mixed solution was added to diluted aqueous ammonia solution [5:1(v/v)] with vigorously stirring, and the final pH of the suspension was 9.50. The precipitate was aged for 5 h at room temperature and then washed with deionized water. The filter cake was peptized at 70°C to form the positive sol. Finally, the acquired LDHs sol was filtered through filter paper to remove the large particles.

The laponite/LDHs dispersions in experiments were prepared by mixed required laponite and LDHs dispersions, and treated in an ultrasonic bath for 15 min, then stored for 24 h to assure the data recurrence.

Chemical analysis for metal content were carried out by ICP using the solution of the powder samples in 20% HNO_3 . Transmission electron microscopy (TEM) analysis was performed using a JEM-100CX II electron microscope. The particle-size distribution was determined using Zetasizer3000 (Malvern company). Rheological measurements were performed on a RS75 rheometer (HAAKE company, Germany) affixed with a concentric cylinder Z41 geometry. Each suspension was exposed to an equivalent preshear in order to prevent the effect of shear history. The run temperature was 15°C .

According to chemical analysis of ICP, the molar ratio of Mg /Al of LDHs sol was about 1:1 equal to the molar ratio in the raw material. Particle-size distribution results showed that the particles have an average diameter of 80.5 nm, of which 81.1%(volume fraction) arranges between 45.3 nm and 113.8 nm. **Figure 1** shows the LDHs morphology in TEM photo, and particles are in platelike.

Figure 2 shows rheological curves of LDHs and laponite dispersions at different concentrations. LDHs dispersions show analogical properties with laponite dispersions, namely with increasing LDHs concentration, the dispersions develop a yielding type of behavior from a Newtonian fluid.

Figure 1 TEM microphoto of LDHs (72k multiple)

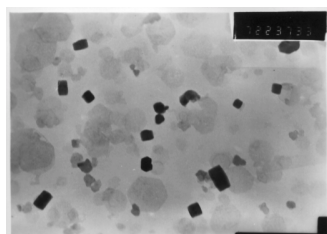
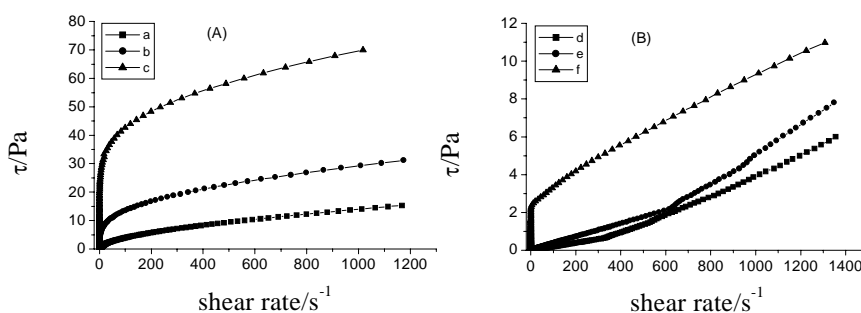


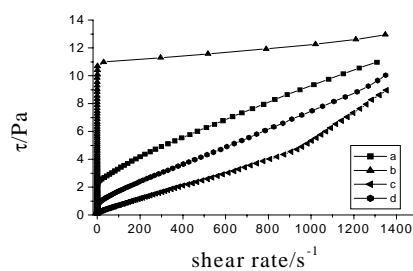
Figure 2 Rheological curves of LDHs (A) and laponite (B) dispersions at different concentrations



(A): a=20%, b=23.64%, c=26%;

(B): d=0.5%, e=0.75%, f=1%

Figure 3 Rheological curves of dispersions of 1% laponite and different LDHs concentrations



a: LDHs; b:0.2% LDHs; c:1% LDHs

Figure 3 shows rheological curves of laponite/LDHs mixed dispersions at 1% laponite and different LDHs concentrations. It can be seen that when increasing the concentration of LDHs, the yield stress increased at first, then decreased sharply to a minimum, where the mixed dispersion almost became a Newtonian fluid. After that, the yield stress increased slowly again when the concentration of LDHs increased further.

Macroscopic rheological properties of the dispersions are determined by their microstructure. The structure of pure laponite dispersion forms nematic order where face to face mutual orientation is favored because of indirect and loose contact between particles⁷. Adding few positively charged LDHs enhanced electrostatic attractive forces

between oppositely charged particles, and a bridge conformation⁹ of three-dimension linked structure was formed gradually, so the yield stress increased little by little. When LDHs particles increase to an optimal ratio, the strongest structure can be formed. Adding LDHs particles more than the optimal ratio, the dispersion showed almost Newtonian response, because the interactions of the oppositely charged particles were similar to stabilizing effects of polymers. When the concentration of LDHs particles are increased further, on account of bridging effect of LDHs and laponite particles, the linked net structure, namely gel structure, is formed again.

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