Studies on Synthesis of MMH and Rheological Properties of Concentrated MMH Dispersions

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A positively charged mixed metal hydroxides (MMH) was synthesized by a non-steady method. The chemical composition and morphology of the positive MMH nanoparticles were studied by ICP, Mastersizer and TEM. Preliminary rheological measurements indicated that when adding NaCl to exhaustively deionized MMH dispersion, the yield stress, G′ and G″ first decreased to a minimum, and then rose again.

Clays are very versatile materials and widespread in nature. In addition to their applications in catalysts or catalyst supports, inorganic precursors, adsorbents, ceramics, clays are also used in drilling muds, paper coatings and fillings, pharmaceuticals, etc.[1,2] Clays can be divided into two broad groups; cationic clays and anionic clays. Because of the isomorphous substitutions, cationic clays such as montmorillonite and laponite have negatively charged silicate layers, which have cations in the interlayer space to balance the charge, while the anionic clays, which are rare in nature but relatively easy and inexpensive to synthesize[3,4] such as MMH, have positively charged metal hydroxide layers with balancing anions and water molecules located interstitially. When dispersing them in water, different equilibrium states can be obtained like Newtonian liquids, viscoelastic gels, and phase separated dispersions.[5] Therefore extensive rheological behavior for clays or MMH dispersions has been studied on their colloidal and rheological properties.[2,6,7]

Recently, keen attention has been paid to the rheological properties of dispersions of cationic clays like montmorillonite under exhaustively deionized conditions.[7–9] Because of the electrostatic repulsive interactions of electric double layers, montmorillonite dispersions in relatively high concentrations form three-dimension network, namely repulsive gel. When adding salt to dispersions, both the elastic storage moduli (G′) and viscous loss moduli (G″) decrease sharply in frequency sweep curves and G′ is only slightly higher than G″ at relative high salt concentration, but the variations of G′ and G″ under much higher ionic strength have not been investigated and the similar studies of MMH dispersions have not hitherto been studied. This letter will report the preliminary results about synthesis of MMH and rheological properties of concentrated MMH dispersions with increasing ionic strength.

MMH, or the so-called layered double hydroxides, is a large group of compounds with the chemical formula $[M(II)_{(1-X)}M(III)_X(OH)_2]^{x+}(A^{m-}{}_{x/m})\cdot mH_2O$, where M(II) are the cations of double-charged metals, M(III) are the cations of triple-charged metals, A^{m-} are interlayer anions.[3] In this study MMH was synthesized by a non-steady coprecipitation method.[10] 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/dm^3. Then the mixed solution was slowly added to diluted ammonia water [5:1(v/v)] with vigorous stirring, and the final pH of the suspension was 9.50. The precipitate was aged for 5 h at room temperature and then washed thoroughly with deionized water. The filter cake was peptized at 70 °C for at least 8 h to form the positively charged MMH sol. Finally, the acquired MMH sol was filtered through filter paper to remove the large particles. Then some of them was distilled under vacuum until the concentration of the dispersion was up to 26%(w/w). Samples for rheological measurements were stored in sealed vials under nitrogen to prevent samples from acidification due to dissolved CO_2.[11] And MMH can be synthesized repeatedly with the same size and morphology.

The MMH dispersions in experiments were prepared by mixing required salt solutions and MMH dispersions, then treated in an ultrasonic bath for 15 min, finally stored for 24 h to assure the data repetition.

The Mg and Al contents were obtained using ICP to analyze MMH solutions dissolved in 20% HNO_3. The particle-size distribution was determined using Zetasizer3000 (Malvern company). Transmission electron microscopy (TEM) analysis was performed using a JEM-100CX II electron microscope. Rheological measurements were performed on a RS75 rheometer (HAAKE company, Germany) affixed with a concentric cylinder Z41 Ti geometry. Each suspension was exposed to an equivalent preshear in order to prevent the effect of shear history. The run temperature was 15 °C.

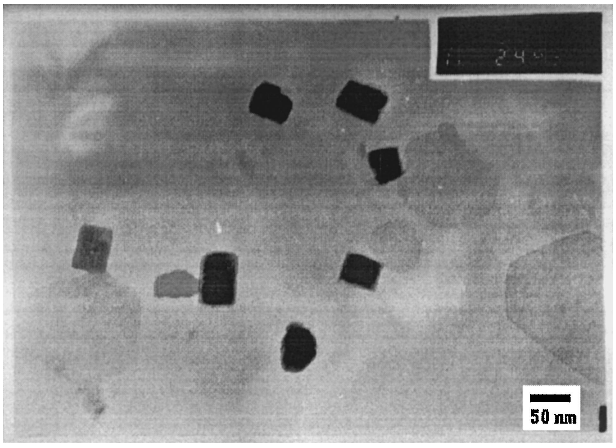

Figure 1. TEM micrograph of MMH (100 k multiple).

According to the analytical results of ICP, the Mg/Al ratio of MMH sol was about 1:1 equal to that in the raw material. Particle-size distribution showed that the mean equivalent diameter was 79.4 nm with 99.4% (volume fraction) in the width of 90.6 nm by Zetasizer3000. Figure 1 shows the MMH morphology in TEM micrograph, and particles are platelike.

Figure 2 is flow curves of different MMH dispersions. It can be seen that when the concentration is higher than 20%, the dispersions show a yield stress, indicating that MMH dispersions

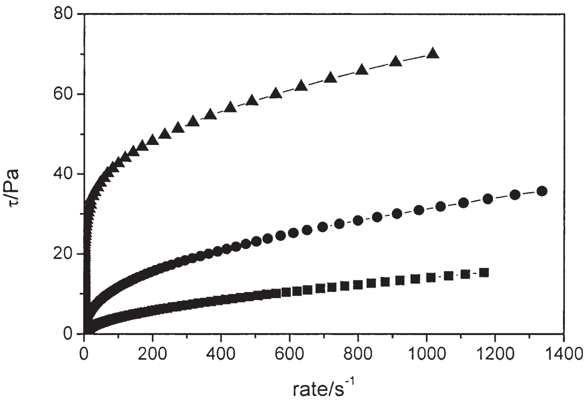

Figure 2. Flow-curves of different MMH dispersions (■: 20%; ●: 22%; ▲: 26%).

form gel structure. Figure 3 is frequency sweep curves of dispersions of 26% MMH and different NaCl concentrations. When increasing ionic strength, the rheological parameters such as yield stress, G′ and G″ first decrease to a minimum, then increase slowly to a higher value than that without NaCl.

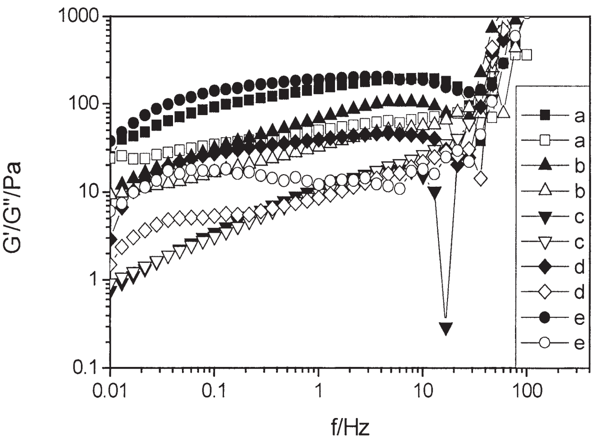

Figure 3. Frequency sweep curves of dispersions of 26% MMH and different salt concentrations. Salt concentrations are 0 (a), 10^{-4} M (b), 10^{-3} M (c), 5×10^{-3} M (d), 10^{-2} M (e). Full symbols: G′, and open symbols: G″.

Table 1. Yield stresses of dispersions of 26% MMH and different salt concentrations

NaCl/M	0	10^{-4}	10^{-3}	0.005	10^{-2}
Yield stress/Pa	9.18	5.07	0.17	0.65	12.90

Table 1 shows that the yield stresses of different dispersions change in a similar way with Figure 3. These results indicate that the finally obtained MMH gel dispersion has very low ionic strength. It takes only 8 h to get the exhaustively deionized MMH dispersions in our experiments, while it takes 8 years to obtain the completely deionized state for montmorillonite suspensions[8] with ion-exchange resins.

In Figure 2, at low MMH concentration the repulsive interactions among electric double layers of MMH particles were relatively weak, thereafter the dispersions show almost Newtonian response. With increasing MMH concentration, the distances of particles decrease gradually, and there is a sol-gel transition due to the electrostatic repulsive forces of diffuse double layers of counterions preventing the direct contact between particles. The dispersion with a concentration of 26% has a yield stress of 9.18 Pa indicating the existence of strong repulsive interactions among particles. In MMH dispersions the effective radii of particles are equal to the sum of radius (r) and thickness of electric double layer of counterion. In Eq (1), F is Faraday constant and R is gas constant, ε is dielectric

$$1/\kappa = \left(\frac{\varepsilon\varepsilon_0 RT}{2F^2 I}\right)^{1/2} \quad (1)$$

constant of the medium, ε_0 is the dielectric constant for vacuum. Thus, $1/\kappa$ only depends on the ionic strength (I).[2] When adding very small amount of NaCl to MMH dispersions, the effective radii decrease because of the compression of electric double layers, therefore the repulsive forces are weakened. So the yield stress decreases as well as G' and G''. With further increasing the ionic strength, a minimum can be obtained (seen in Figure 3) due to the attenuation of the thickness ($1/\kappa$). But if the ionic strength rises much higher, the repulsive double layer potential is almost screened and van der Waals attractive forces dominate the whole dispersion. The higher the ionic strength, the stronger the van der Waals attractive forces. Ultimately when the NaCl concentration is 0.01 mol/dm^3 in 26% MMH dispersion, the gel structural strength is higher than that without salt and strong enough to withstand gravitational stresses and can bear their own weight, indicating that the structure of dispersion changed from repulsive gel to attractive gel under very high ionic strength.

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