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RHEOLOGY OF MIXED PALYGORSKITE-MONTMORILLONITE SUSPENSIONS

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INTRODUCTION

The rheological parameters of a clay suspension can be used to evaluate particle-particle interactions. Although there have been many studies of the rheological behavior of suspensions of reference clays, only few studies were performed with suspensions of mixed clays, and the rheological properties of these suspensions are not yet fully understood. The length-to-width ratio of some soil clays was evaluated by Egashira and Matsumoto (1981) based on viscosity measurements of very dilute suspensions of these clays. The influence of montmorillonite additions on the rheological behavior of kaolinite suspensions was determined by Keren (1989, 1991). The particle arrangement in three soil-clay suspensions was studied by Zhao *et al.* (1991) based on rheological measurements. The effects of mineralogical composition and particle size on the rheological behavior of concentrated suspensions of lateritic soil clays were investigated by Cerpa *et al.* (1999).

The rheological properties of suspensions of reference palygorskite clays were investigated in a previous study (Neaman and Singer, 2000). To determine if the rheology of palygorskite suspension is affected by the addition of montmorillonite, we investigated the rheological properties of palygorskite-montmorillonite suspensions.

MATERIALS AND METHODS

Three palygorskite samples were used for this study: clays from Mt. Flinders (Queensland, Australia), Mt. Grainger (South Australia), and Yucatan (Sacalum, Mexico). Wyoming montmorillonite (SWy-1, Crook Country, USA) was used for preparation of palygorskite-montmorillonite mixtures.

The clays were ultrasonically dispersed in water and the <2-μm size fraction was separated by sedimentation under gravity. The clays were then lightly treated by 0.1 N HCl (sample:solution ratio of 1:10) for the removal of carbonates. The samples were rapidly heated in the acid to boiling and the pH values of the suspensions were immediately adjusted to pH 7 by addition of 0.1 N NaOH. The sample from Mt. Grainger contains considerable amounts of free iron oxides which were extracted by the dithionite-citrate-bicarbonate method (Kunze and Dixon, 1986). Na-clays were prepared by washing and centrifuging the clay-size fraction three times with 1 N NaCl solution and then by washing and centrifuging with ethyl alcohol until the electrical conductivity of the equilibrium solution was <10 dS/m. The clays were then freeze-dried.

Oriented specimens of Na-saturated clays were prepared for X-ray diffraction (XRD) analysis by sedimentation of a clay suspension onto a glass slide. XRD data were obtained using a Rigaku diffractometer with CuKα radiation. According to the XRD analyses, palygorskite samples from the Mt. Flinders, Mt. Grainger, and Yucatan do not contain any other phases.

Rheological properties of aqueous suspensions were determined at 25°C using a Haake viscometer (model CV 20) of the Couette type with a rotating outer cylinder and a stationary inner cylinder. The gap between the two cylinders was 0.32 mm (sensor system ZB 30). Suspensions of palygorskite-montmorillonite mixtures were prepared by suspending these minerals in distilled water in appropriate amounts, giving montmorillonite contents of 0, 5, 10, 20, 40, 60, 80, and 100 wt. % and a total clay concentration in suspension of 3% weight per volume (w/v). The samples were ultrasonified to obtain homogeneous suspensions. The pH of the suspensions was adjusted to 7 by addition of dilute HCl or NaOH. The samples were shaken 1 h and the pH adjustment was repeated several times until pH 7 was obtained. Samples were shaken 24 h before rheological measurements were initiated. Measurements were performed in two replications.

RESULTS AND DISCUSSION

Figure 1 shows plots of shear rate against shear stress of 3% w/v suspensions of Na-saturated clays at pH 7. The Mt. Grainger and Mt. Flinders palygorskite samples exhibit a nearly Newtonian flow; for Yucatan-palygorskite and Wyoming-montmorillonite samples the flow curves are typical of clay materials with a pseudoplastic behavior (van Olphen, 1977). Differences in flow curves between the palygorskite samples were discussed in detail in Neaman and Singer (2000).

Pseudoplastic rheology of colloid suspensions may be described by the Bingham model (Güven, 1992).

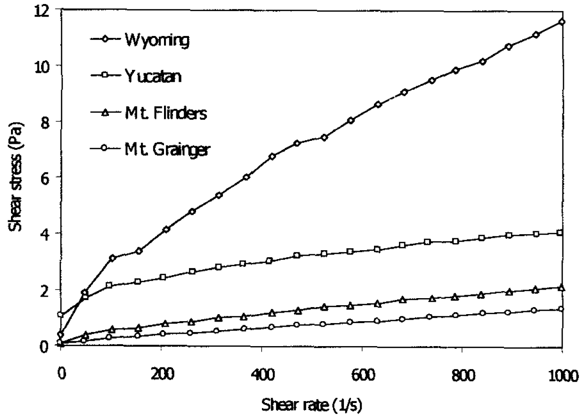

Figure 1. Flow curves of 3% w/v suspensions of Na-saturated clays at pH 7.

At low rates of shear, such systems exhibit non-Newtonian flow, which is characterized by a progressive decline in viscosity as shear rate increases. Above a certain value of shear rate, the flow curve becomes linear. According to the Bingham model, the slope of the linear part of the flow curve is referred to as the plastic viscosity, the intercept of the linear portion of the curve with the stress axis is referred to as the Bingham yield (stress) value. For all samples, the flow curves become linear at shearing rates of 250–1000 s^{-1}. Plastic viscosities and Bingham yield values of each reference clay suspension are shown in Table 1.

Table 1. Plastic viscosity (PV) and Bingham yield value (BYV) of 3% w/v suspensions of Na-saturated clays at pH 7.

Clay mineral	Sample	PV, mPa s	BYV, Pa
Palygorskite	Mt. Grainger	1.29	0.13
	Mt. Flinders	1.71	0.49
	Yucatan	1.93	2.27
Montmorillonite	Wyoming	9.03	2.78

The individual clay particles in suspension are associated into micro-aggregates. The micro-aggregates progressively diminish in size as the rate of shear increases, leading to an overall decrease in viscosity. There is a certain value of shear rate at which structural disruption is complete, and above which the viscosity remains constant. Viscosity is a measure of the resistance to the flow of the individual clay particles, whereas the yield stress represents the degree of association between the clay particles and the work required to reduce the micro-aggregates in size.

Plots of plastic viscosity and Bingham yield value of mixed palygorskite-montmorillonite suspensions *vs.* percentage of montmorillonite in the mixture are shown in Figure 2. Small (≤10 wt. %) montmorillonite additions to the Yucatan and Mt. Flinders suspensions increase the rheological parameters (plastic viscosity and Bingham yield value). Further additions (10–20 wt. %) of montmorillonite, however, decrease both plastic viscosity and Bingham yield value of the suspension. In the case of plastic viscosity, the decrease was related to the initial value of the pure palygorskite suspension. In the case of Bingham yield, the decrease was more evident, and Bingham yield became significantly lower than its initial value for the pure palygorskite suspension. Further montmorillonite additions in the range of 20–40 wt. % to the Yucatan and Mt. Flinders suspensions do not change the rheological parameters significantly, and the suspensions showed nearly Newtonian flow with plastic viscosity equal to its initial value of pure palygorskite suspension. In contrast to suspensions of the above samples, Mt. Grainger suspensions do not show an increase in rheological parameters with small (≤10 wt. %) montmorillonite additions. Plastic viscosity and Bingham yield value increased monotonously to 40 wt. % montmorillonite addition. Additions of montmorillonite over 40 wt. % increase sharply the rheological parameters of all suspensions, and no significant differences between the samples were obtained.

Neaman and Singer (2000) reported that the Florida and Georgia palygorskite samples contain 2.8 and 3.1

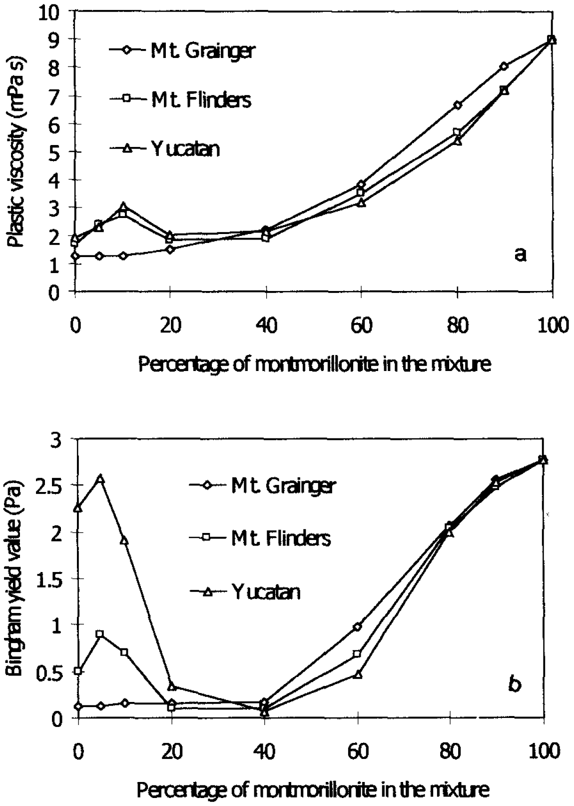

Figure 2. Effect of montmorillonite concentration on plastic viscosity (a) and Bingham yield value (b) of mixed suspensions of Na-saturated palygorskite and montmorillonite at a total clay concentration of 3% w/v and pH 7.

wt. % of smectite impurities, respectively. They suggested that the relatively high rheological parameters of the Florida and Georgia suspensions are related to smectite impurities. Results of the present study, showing an increase of rheological parameters of the Yucatan and Mt. Flinders suspensions with small (≤10 wt. %) montmorillonite additions, support this suggestion. The Mt. Grainger suspension, however, does not show this phenomenon.

Keren (1989, 1991) studied the rheology of mixed kaolinite-montmorillonite suspensions. The addition of Na-saturated montmorillonite to Na-saturated kaolinite suspensions at pH 7 was found to change the flow of suspension from Newtonian to non-Newtonian and the suspension increased in viscosity. Thus, the interaction between montmorillonite and kaolinite particles occurs in the suspension, which in turn, causes the increase of yield value of the suspension. In the above mentioned studies, ≤10 wt. % montmorillonite was added to the kaolinite suspension, and no data were reported for further additions. Results of the present study, showing increase of both plastic viscosity and Bingham yield value of palygorskite suspensions with small (≤10 wt. %) additions of montmorillonite are consistent with Keren (1989, 1991) regarding the effect of montmorillonite addition on the rheology of kaolinite suspensions.

Particle arrangement in palygorskite suspensions at pH 7 deviates considerably from that of montmorillonite suspensions. Loose-packed domains of fibers are formed by face-to-face contacts in palygorskite suspensions at pH 7 (Neaman and Singer, 2000), to produce a three-dimensional network structure or so-called "scaffolding structure" (van Olphen, 1977). In contrast to palygorskite suspensions, mainly edge-to-edge interaction exists in the montmorillonite suspension at neutral pH values (Keren, 1988).

Nearly Newtonian rheology of the Yucatan and Mt. Flinders suspensions with 20–40 wt. % montmorillonite addition and of the Mt. Grainger suspension with montmorillonite addition of ≤40 wt. % indicates that the interactions between palygorskite and montmorillonite particles are negligible at these montmorillonite concentrations. Thus, montmorillonite addition to palygorskite suspensions prevents forming of a "scaffolding structure" of palygorskite fibers, probably because of the high negative surface charge of montmorillonite. The edge-to-edge structure of montmorillonite particles also can not be formed in suspension, probably because of the fiber morphology of palygorskite.

CONCLUSIONS

Addition of montmorillonite to palygorskite suspensions does affect the rheological behavior of the system. In the case of two palygorskite samples, small (≤10 wt. %) montmorillonite additions increase the rheological parameters (plastic viscosity and Bingham yield value). Larger additions (10–20 wt. %) of montmorillonite, however, decrease the rheological parameters. At even larger montmorillonite additions, in the range of 20–40 wt. %, the rheological parameters remain almost constant. The suspensions showed nearly Newtonian flow, with a plastic viscosity equal to the initial value of the pure palygorskite suspension. With a third palygorskite sample, plastic viscosities and Bingham yield values increased slowly and monotonously to 40 wt. % montmorillonite addition. Additions of montmorillonite over 40 wt. % increase sharply the rheological parameters of all suspensions without significant differences between the samples. Thus, the degree of interaction between palygorskite and montmorillonite particles depends on the montmorillonite concentration in the mixture.

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