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Effect of polycarboxylate ether comb-type polymer on viscosity and interfacial properties of kaolinite clay suspensions

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ABSTRACT

The interactions between kaolinite clay particles and a comb-type polymer (polycarboxylate ether or PCE), so-called PCE super-plasticizer, were investigated through viscosity and surface forces measurements by a rheometer and a Surface Forces Apparatus (SFA). The addition of PCE shows a strong impact on the viscosity of concentrated kaolinite suspensions in alkaline solutions (pH = 8.3) but a weak effect under acidic conditions (pH = 3.4). In acidic solutions, the high viscosity measured is attributed to the strong electrostatic interaction between negatively charged basal planes and positively charged edge surfaces of clay particles. Under the alkaline condition, the suspension viscosity was found to first increase significantly and then decrease with increasing PCE dosages. The results from surface forces measurement show that PCE molecules at low dosages can bridge the kaolinite particles in the concentrated suspensions via hydrogen bonding, leading to the formation of a kaolinite-PCE "network" and hence an increased suspension viscosity. At high PCE dosages, clay particles are fully covered by PCE molecules, leading to a more dispersed kaolinite suspensions and hence lower suspension viscosity due to steric repulsion between the adsorbed PCE molecules. The insights derived from measuring viscosity and interfacial properties of kaolinite suspensions containing varying amount of comb-type super-plasticizer PCE at different pH provide the foundation for many engineering applications and optimizing industrial processes.

1. Introduction

The viscosity and interfacial properties of clay mineral suspensions are important for many engineering and industrial applications including processing of ceramics, manufacture of cements, formulation of inks and paints, production of pulp and paper, transportation of coal [1] and flotation of minerals [2,3]. For instance, industrial waste residues known as tailings contain a large amount of clay particles. The treatment for such waste residues has been a major challenge for decades in coal, mineral processing and oil sands industry. Extensive research has been conducted to understand the interfacial properties and interactions between flocculants and clay particles in the context of investigating the flocculation of clay suspensions for tailings treatment [4–8]. On one hand, fine clay particles disperse well and will retard the settling performance of mineral tailings. On the other hand, clay can also self-aggregate in pigment for paper coating and in cementitious system. In paper coatings, the pigment content can be as high as 60–70% and efficient dispersants are normally needed to stabilize the pigment suspension [9]. In cement, clay particles have a significant impact on its rheological properties, reducing the fluidity of cement and leading to higher water consumption in order to maintain appropriate workability of cement. Therefore, a polymeric modifier is often used to reduce the water content of cement and to retain its workability when large quantities of industrial wastes such as slag and fly ash were present in the concrete mixture [10–12].

Polymer additives have been widely used in various colloidal suspensions to either stabilize or flocculate the colloidal particles, depending on the purpose of applications. Comb-type polymers have been shown to be effective additives in stabilizing different colloidal systems [4,13–22]. In cement industry, for example, the comb-type polymer, polycarboxylate ethers (PCEs), has been commonly used to control the stability and rheology of process streams and known as super-plasticizers or water-reducing admixtures. The addition of this comb-type polymer PCE to fresh concrete can impact the interfacial properties between particles and liquid medium, controlling the bulk physical properties (i.e., viscosity) of suspensions and reducing water-to-cement ratio of the hardened paste [22–25]. The dispersing effect of PCE is suggested to be mainly due to the adsorption of these polymers on particle surfaces, which induces electrostatic and/or steric repulsive forces among the particles [26]. The comb-type polymer PCE consists of a negatively charged backbone and neutral polyethylene-oxide

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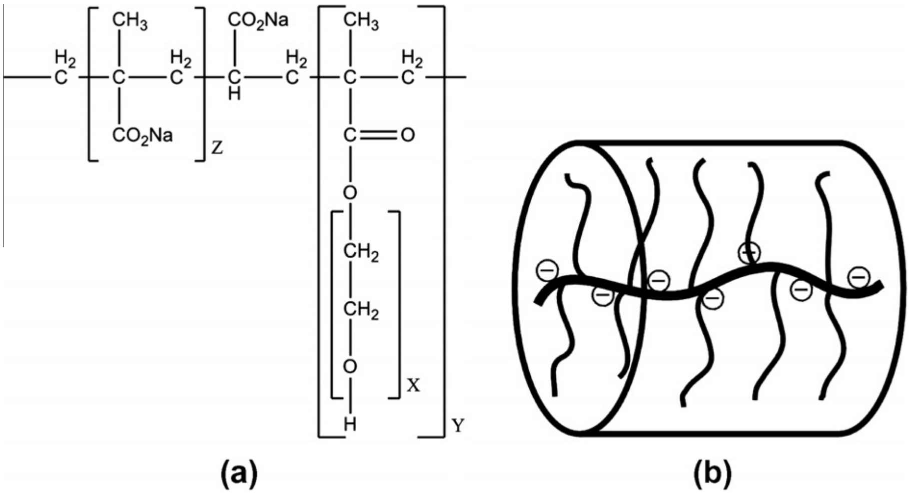

Fig. 1. (a) Chemical structure and (b) schematic structure (brush conformation) of a super-plasticizer, PCE used in this work.

(PEO) side chains, as illustrated in Fig. 1. Both the length and number of side chains can be varied to manipulate the adsorption behavior of PCEs and their ability to control the stability of dispersions. Although great efforts have been devoted to investigating the interaction mechanisms between various polymer surfaces, brushes and thin films using different techniques including atomic force microscope (AFM) and Surface Forces Apparatus (SFA) [27–35], few study is available on the interactions in clay suspensions containing comb-type polymers.

In this work, kaolinite clay particles were chosen as a model system, due to its wide range of applications in many industrial processes and products, to investigate the effects of PCE on the viscosity and interfacial properties of the kaolinite suspensions. Combined with settling tests, various fundamental measurements including viscosity, zeta potential and surface forces provide complementary information regarding the interactions between PCE and kaolinite particles, and their consequences on stability of kaolinite suspensions. The results obtained in this study provide an insight into the basic interaction mechanisms between clay particles and polymer additives in many colloidal suspensions, which is of both practical and fundamental importance.

2. Materials

The kaolinite clay used in this project was purchased from Kentucky Tennessee Clay Co. The particle size distribution was determined with a MasterSizer 2000 to be D90 = 19.38 μm, D50 = 4.69 μm and D10 = 0.16 μm. D90 = 19.38 μm means that the mean diameter of 90 wt.% particles are below 19.38 μm. D50 = 4.69 μm and D10 = 0.16 μm suggest that the mean diameter of 50 wt.% and 10 wt.% of particles are below 4.69 μm and 0.16 μm, respectively. Aqueous solutions were prepared in 18.2 MΩ cm deionized water (Millipore, Mississauga, ON, Canada). PCE Melflux 2651F provided by BASF (Germany) was used as received. The chemical structure and schematic conformation of PCE are shown in Fig. 1.

3. Experimental methods

3.1. Sample preparation

Clay suspension was prepared by mixing kaolinite particles with the DI water. A given amount of clay particles were added slowly into the DI water under constant stirring until a desired solid concentration was reached. PCE solutions of different concentrations were then added by following the same procedure. In this work, the "PCE dosage" refers to the mass percent of PCE to kaolinite, that is, the same as "polymer/kaolinite mass ratio."

3.2. Viscosity measurement

Viscosity was measured using a concentric cylinder with the standard vane rotor on a TA Instruments AR G2 rheometer. A thermal jacket was used to control the temperature of suspension samples at 25 °C. About 25 ml clay suspension was required for each measurement. During the measurement, each sample was presheared for 2 min at a shear rate of 10 s^{-1} and then the measurement was conducted at 10–1000 s^{-1}. The viscosity of kaolinite suspensions (μ) was determined as a function of shear rate ($\dot{\gamma}$) at pH = 3.4 and pH = 8.3. The pH of the suspension was adjusted by sodium hydroxide stock solutions.

3.3. Zeta potential measurement

Zeta potential of kaolinite suspension was measured using a ZetaPALS instrument (Brookhaven Instrument Corporation, USA). Kaolinite suspensions of 2 wt.% solids with different PCE dosages were prepared at both pH = 3.4 and pH = 8.3, in which the PCE dosages were kept the same as that used in the viscosity measurement. The clay suspension was allowed to settle for 24 h before the supernatant was taken for zeta potential measurement. All the measurements were conducted at 25 °C.

3.4. Settling tests

Kaolinite suspension of 2 wt.% solids was prepared and mixed for 24 h to ensure that the kaolinite suspension was well dispersed. The prepared suspensions were then transferred to 100 ml-graduated cylinders for settling tests. Time required for the mud line (the solid–liquid interface) to descend by every 10 ml was recorded. The settling curve was constructed by plotting the normalized mud-line height (h/H) as a function of time, where H and h were the initial height of suspension and the height of the mud line at specified time, respectively. The initial settling rate (ISR) was obtained from the initial slope of the settling curve.

3.5. Measurement of interaction force using Surface Forces Apparatus

Interaction forces as a function of separation distance (D) between two mica surfaces (model clay surfaces) in PCE solutions were determined using a Surface Forces Apparatus (SFA). The detailed setup for SFA experiments has been reported elsewhere