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Original Research Paper

Effect of squeeze, homogenization, and freezing treatments on particle diameter and rheological properties of palygorskite

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ABSTRACT

The natural palygorskite exist as aggregates or bundles via weak electrostatic and van der Waals interactions. A new method for effective disaggregation of bundles was developed via freezing combined with squeeze and homogenization processes. In this work, the effects of squeeze, homogenization, and freezing treatments on particle size and rheological properties of palygorskite were investigated systematically by particle diameter distribution, steady shear, and linear oscillatory measurements. The influences of squeezing times, homogenization pressure, and freezing time on shear stress and shear modulus were studied in detail. The association capacity of rods in the obtained suspensions was discussed according to a power law of the form $Y = k_y C^n$. The correlation among the dispersion of palygorskite, the aspect ratio of the rods, and the rheological properties was discussed. The diameter distribution changed from 4.3 to 3.0 μm of natural palygorskite to 1.8 μm of sample squeezed for two times, frozen at −18 °C for 4 h, and homogenized at 10 MPa. The suspension with higher shear stress and shear modulus was obtained after squeezed for three times and homogenized at 30 MPa.

1. Introduction

The colloid chemistry of clay minerals (i.e., bentonite, laponite, sepiolite, palygorskite, and kaolin) is industrially relevant and academically interesting. Their rheological properties are very important in many fields such as painting, pharmaceutical, ceramic, food, coating, and drilling fluids [1]. Among all the clays used, palygorskite is one of the most important gel-forming minerals. Palygorskite is a nanorod-like silicate mineral with the diameter of about 20–70 nm and the length of 1–2 μm. The exchangeable cations, the fibrous morphology, and the large aspect ratios of palygorskite render it with excellent colloidal properties. Moreover, the naturally available palygorskite is in the form of micrometric aggregates due to the van der Waals and hydrogen bonding interactions among rods [2].

Generally, the colloidal nature of palygorskite is different from bentonite which depends on the swelling of unit layers caused by the penetration of water [3]. In palygorskite suspension, the rods and bundles are present in a random fashion and associated with each other to form clusters. A lot of water molecules are entrapped inside these clusters, which lead to the increase of the effective solid volume fraction in suspension and yield a high viscosity. In theory, palygorskite can form more stable suspension with high viscosity at relatively lower concentration compared with other clays. However, the rheological properties of palygorskite are not prominent before the aggregates are separated into rods [3]. Hence, the direct development and usage of natural palygorskite is limited because of its poor dispersion in both water and common organic solvents.

To data, various electrolytes, polymers, and surfactants have been introduced to disperse clays and improve the rheological properties of suspensions because they can alter the surface charge of particles and control the interparticle forces [4–10]. Moreover, the rheological properties of clay suspensions in the presence of these additives were discussed in detail. On the other hand, many mechanical activation methods including high-shear mixing, milling, and squeeze were also used to disperse the aggregates. As reported previously, mechanical activation could reduce the size of the agglomerates and disaggregate the larger bundles into small units. Mechanical activation also had considerable influences on the specific surface area and the aspect ratio of particle [11–18]. All the decreased agglomerate size, improved dispersion of bundles, increased specific surface area, and structural defects induced by mechanical activation would certainly influence the association

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of the particles, and then the rheological properties of suspension. However, few efforts have been done to study systematically the influences of mechanical activation on the rheological properties of palygorskite suspensions.

In previous work, it was found that homogenizing palygorskite suspension at 30 MPa could effectively disaggregate its bundles [11]. In addition, the cooperative effects of squeeze, high-pressure homogenization, and freezing treatment on the morphology and structure of palygorskite were also discussed [19]. Whereas, the effects of homogenization with or without squeeze and freezing treatments on the rheological properties of palygorskite suspension was not studied. Hence, as a part of efforts to further discuss the influences of mechanical treatment on the properties of palygorskite, the rheological behavior of corresponding suspensions were compared and evaluated by steady shear and oscillatory measurements. The particle diameter distribution of palygorskite treated under various conditions was also discussed.

2. Experimental section

2.1. Materials

Palygorskite, with a chemical composition of 64.31% SiO_2, 10.47% Al_2O_3, 0.87% Fe_2O_3, 20.41% MgO, 1.52% Na_2O, 0.13% K_2O, 1.29% CaO as determined by a MiniPal 4 X-ray fluorescence spectrometer (PANalytical Co.), was obtained from Jiuchuan Technology Co. (Jiangsu, China).

2.2. Preparation of mechanical-activated palygorskite

50 g of palygorskite was first squeezed with a three-roll grinder, and then dispersed in 660 mL of water. The mixture was stirred at 800 r min^{-1} for 120 min at ambient temperature. The obtained suspension was filtered through a 74 μm (200 mesh) screen to remove quartz (1.0 wt.%, based on the weight of palygorskite). Subsequently, the filtered suspension was homogenized with the high-pressure homogenizer (GJB 8-20, Changzhou Homogenizer Machinery Corporation Ltd., Jiangsu, China). The homogenized suspensions were centrifuged at 5000 r min^{-1} for 10 min, and the solid products were dried at 105 °C for 4 h. Finally, the dry products were ground and passed through a 74 μm screen. All samples with the particle size smaller than 74 μm were used for further experiments.

In order to discuss the effects of homogenization pressure on rheological properties of palygorskite, five homogenized samples at different pressures (0, 10, 30, 50, and 70 MPa, respectively) were prepared and denoted as PAL0, PAL10, PAL30, PAL50, and PAL70. To investigate the effects of associated squeeze and homogenization process on rheological properties of palygorskite, five samples squeezed for one, two, three, four, and five times, respectively and homogenized at 30 MPa were prepared and denoted as PAL1–30, PAL2–30, PAL3–30, PAL4–30, and PAL5–30. To discuss the synergetic effects of freezing process on rheological properties of palygorskite, a pre-freezing treatment was carried out and four frozen palygorskite samples were obtained by the following method. Palygorskite squeezed by a three-roll grinder for two times was directly frozen at −18 °C for different time (0, 4, 8, 16, and 24 h, respectively), and then dispersed with water. The purification and the following treatments were carried out as described above except that the homogenization pressure is 10 MPa. These frozen samples were denoted as PAL2–0-10, PAL2–4-10, PAL2–8-10, PAL2–16-10, and PAL2–24-10.

2.3. Measurement of particle diameter distribution

The particle diameter distribution of palygorskite samples treated under various conditions was determined using a dynamic light scattering analyzer (BI-200SM, BIC) at 25 °C. Before measurements, 0.01 g of obtained samples were dispersed in 10 mL of distilled water and sonicated for 5 min.

2.4. Measurement of rheological properties

Shear rheological measurements of palygorskite suspension were conducted on an Physica MCR301 Rheometer (Anton Paar, Germany) using a cone-plate sample cell at 25 °C. For steady shear measurements, the shear rate was ranged from 0.1 to 200 s^{-1}. For small amplitude oscillatory shear, the strain sweep was done first to determine the linear viscoelastic region. The frequency sweep at a given stress of 0.1% (chosen in the linear viscoelastic region where the amplitude of the deformations is very low) and frequency range varying from 0.1 to 100 rad s^{-1} was performed to obtain the shear modulus. Before measurements, 5.0 g of the obtained palygorskite was fully dispersed in 45 mL of distilled water under high-speed stirring at 11,000 r min^{-1} for 20 min.

2.5. Characterization

The morphology of the samples was observed using a JSM-6701F Field emission scanning electronic microscope (JEOL, Ltd., Japan) after all samples were fixed on copper stubs and coated with gold.

3. Results and discussion

3.1. Particle diameter distribution

The high-pressure homogenization process may generate moderate shear, turbulent, and cavitational forces, which may break the bulk particles into small units. It is more efficient in disaggregating crystal bundles on an industrial scale, but the higher homogenization pressure could disrupt the rods [11]. Squeeze can partially tear apart the agglomerates of palygorskite by the strong mechanical shear action resulting from two rollers, and the shear strength determines the disaggregation efficiency and the disruption degree of rods. Therefore, the change of homogenization pressure and squeezing times could give rise to two effects: the first one is the disaggregation effect on the bundles of palygorskite; another is the disruption effect on rods. The former can raise but the latter weaken the association of the rods and then affect the rheological properties of the suspensions. Palygorskite contains four kinds of water (physically adsorbed water, zeolitic water, coordination water, and structural water) in its crystal structure [20] and has filled water in the interstitial spaces of agglomerates. Generally, the physically absorbed water and filled water could turn into ice in accompany with volumetric expansion when palygorskite was frozen at temperature below zero. Thus, the agglomerates would burst into weakly bound bundles with the aid of expansion forces of water turning into ice. For these reasons, the particle diameter distributions of obtained palygorskite were discussed to compare the effects of various treatment conditions on the dispersion of bundles, and the results were shown in Fig. 1.

The single rod of palygorskite is about 1–2 μm in length and 20–70 nm in diameter [3]. The diameter distribution of palygorskite without homogenization (Fig. 1, PAL0) is relatively broad (4.3–3.0 μm), which indicate that the sample contained some larger agglomerates and bundles. The appearance of some agglomerates with larger size in the SEM micrograph of untreated palygorskite