Effects of solvent treatment and high-pressure homogenization process on dispersion properties of palygorskite

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Abstract

Dispersion of natural palygorskite in distilled water, methanol, ethanol, isopropanol, dimethyl formamide, and dimethyl sulfoxide was carried out using high-pressure homogenization. The effects of solvent parameters on the microstructure, morphology and colloidal properties of palygorskite were investigated in detail. Elemental analysis, infrared spectroscopy (IR) and thermogravimetric analysis (TGA) confirmed that some solvent molecules were encapsulated within the tunnels of palygorskite. The efficiency of the homogenization process to disperse palygorskite aggregates was closely correlated to the solvent parameters, particularly soluble vapor pressure and viscosity. A well disaggregated palygorskite was obtained after dispersing in dimethyl sulfoxide. It was also confirmed that colloidal stability and suspension viscosity were affected by the solvent nature. A more stable suspension with higher viscosity of 2364 mPa s was obtained by dispersing palygorskite in isopropanol.

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1. Introduction

Palygorskite is a crystalline hydrated magnesium aluminum silicate with rod-like morphology. Because of its natural abundance, the nanometric dimension of the single rod-like crystal, the excellent thermal/mechanical stability, and the silanol-based chemistry of the surface, palygorskite is a good candidate for an inorganic constituent in many nanotechnological applications such as photocatalysis [1], dye adsorption [2,3], metallic nanoparticle support [4], polymer nanocomposites [5,6]. Most of these applications would profit from the availability of highly dispersed or individualized palygorskite rods. However, due to the interparticle van der Waals and hydrogen bonding interactions, the naturally presented palygorskite is in the form of micrometric aggregates which is not readily dispersible in either water or common organic solvents like swelling bentonites [7]. It becomes a significant obstacle in the application of palygorskite, and the disaggregation of the crystal bundles of palygorskite becomes a key to expand the application of palygorskite.

Until now, improved dispersion of palygorskite has been achieved by introduction of a second component to the palygorskite surface such as noncovalent or covalent adsorption of quaternary ammonium salts in water, organosilanes or polymer chains with special reactive group in organic solvent [8–10]. Surfactant coating and polymer wrapping of palygorskite rods are considered to be the mechanism of dispersion. Physical methods including high shear mixing and ultrasonication in aqueous media were frequently employed as simple approaches to disperse palygorskite aggregates [11,12]. These methods disaggregate palygorskite by strong shear action and the shear strength decides on the efficiency of disaggregation and the degree of disruption of rod-like crystal.

Recently, we proposed an interesting method that use high-pressure homogenization process to disperse the aggregates of palygorskite [13]. The main mechanism by which the homogenization process accomplished this dispersion came from the turbulent flow and cavitation of the liquid, which produced intense shear forces on the particles presented in the liquid, thus breaking the aggregates into smaller units [14]. Whereas, homogenization process is dependent on many factors including: (1) the nature of the liquid media, namely the vapor pressure, viscosity, and surface tension. These parameters can govern the threshold of the cavitation and the energy resulting from bubble collapse, which will then influence the dispersion of palygorskite. Most of the available results in the literature, however, were mainly focused on aqueous suspensions [15,16], and relatively little attention was paid on organic suspensions; (2) Homogenizing pressure. The level of homogenizing pressure influences the strength of particle collision, the size of cavitation and the probability of cavitation events per unit volume; (3) The nature of gas solubilized in the suspension, which can influence the number of cavitation events and gas content; (4) Ambient suspension temperature and pressure. Because many of the solvent parameters are temperature dependent, a change of temperature will affect the suspension properties and the gas solubility.
For these reasons, it is necessary to examine how these factors influence the dispersion of aggregates during homogenizing process. In a previous work, we have studied the effects of homogenizing pressure on the morphology of palygorskite and found that the crystal bundles were perfectly disaggregated without disrupting the rod-like crystals after homogenization the suspension at 30 MPa [13].

In this study, the influences of dispersed media on the homogenization process were considered. The dispersion of palygorskite aggregates in a series of common solvents including distilled water, methanol, ethanol, isopropanol, dimethyl formamide, and dimethyl sulfoxide were carried out with the aid of high-pressure homogenization technology. The effects of solvent parameters on microstructure, morphology of resultant palygorskite were investigated systematically via elemental analysis, infrared spectroscopy (IR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), field emission scanning electron microscopy (FESEM) techniques. Sedimentation volume and viscosity measurements were also performed to study the colloidal properties of suspensions.

2. Experimental

2.1. Materials

Palygorskite mineral, obtained from Jiuchuan technology Co., Jiangsu, China, is composed of 1.29% CaO, 10.47% Al2O3, 1.52% Na2O, 20.41% MgO, 64.31% SiO2, 0.13% K2O and 0.87% Fe2O3 as determined via elemental analysis, infrared spectroscopy (IR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), field emission scanning electron microscopy (FESEM) techniques. Sedimentation volume and viscosity measurements were also performed to study the colloidal properties of suspensions.

2.2. Dispersion of palygorskite

50.0 g of palygorskite was dispersed in 500 mL of various dispersed media (distilled water, methanol, ethanol, isopropanol, dimethyl formamide, and dimethyl sulfoxide, respectively) and stirred at 800 rpm for 120 min by mechanical stirring to obtain a homogeneous suspension. The obtained suspension was filtered through a vibrating sieve to remove quartz and other impurities. Subsequently, the collected palygorskite suspension was homogenized with a high-pressure homogenizer (GYB-3004, Shanghai Donghua High Pressure Homogenizer Factory, Shanghai, China) at 30 MPa. The homogenized suspensions were centrifuged at 5000 rpm for 20 min, and the solid products were dried at 105 °C for 4 h. Finally, the dry products were grinded and passed through a 200 mesh screen. The sample dispersed by water and prepared according to the similar procedure but without homogenization treatment was also obtained to compare the effect of homogenization process on microstructure and dispersion properties of palygorskite. All palygorskite samples with a particle size smaller than 74 μm were used for further experiments.

2.3. Colloidal properties measurements

The colloidal stability of the palygorskite suspension was evaluated using the conventional sedimentation technique in a graduated cylinder. 2.0 g of obtained palygorskite was dispersed in 120 mL of distilled water and stirred intensively at 11,000 rpm for 10 min with a high-speed mixer (JGB-B12K, Qingdao Haitongda Factory) and then transferred to 100 mL graduated cylinder, where it was allowed to stand undisturbed for some time. The sedimentation volume was read directly from the graduated cylinder at fixed time intervals.

The apparent viscosity of the suspension was measured using a rotational viscosimeter (ZNN-D6, Qingdao Camera Factory) at different time and constant shear rate. Typically, 3.75 g of obtained palygorskite was dispersed in 50 mL of distilled water and stirred with a high-speed mixer as in colloidal stability measurements, and then the viscosity was measured under the constant shear rate of 30 rpm using spindle 3 at ambient temperature.

2.4. Characterization

The elemental analyses were performed using an Elementar Vario EL Elemental Analyzer. The IR spectra of the obtained samples were measured using a Thermo Nicolet NEXUS TM spectrophotometer. The KBr pressed-disk technique was used. The XRD was performed on an X’ Pert PRO diffractometer equipped with a Cu Kα radiation source (40 kV, 40 mA), and the diffraction data were collected from 3 to 50° in a fixed time mode. The morphology of the samples was observed using FESEM (JSM-6701F, JEOL, Ltd.). Before the FESEM observation, all samples were fixed on copper stubs and coated with gold. N2 adsorption-desorption isotherm was recorded using a Micromeritics ASAP 2010 apparatus at 77 K (Micromeritics, Norcross, GA, USA). Before measurements, all the samples were preheated at 90 °C under N2 for 10 h to remove moisture. The TGA were performed on a Diamond TG-DTA 6300 thermoanalyzer under a nitrogen atmosphere from ambient temperature to 800 °C at a heating rate of 10 °C min⁻¹. Before analysis, the samples were dried at 105 °C for 8 h.

3. Results and discussion

3.1. Elemental analysis

In order to determine if there were organic solvents presented in the obtained palygorskite samples (Table 1), the elemental analysis was performed and the percentages of carbon in the results of elemental analysis were chosen for this determination. Because no additive was added into the suspension, the increased content of carbon in obtained samples was only from the used dispersed medium. As listed in Table 1, the percentages of carbon of the unhomogenized and homogenized palygorskite dispersed by water are 0.91% and 1.28%, respectively, which increased to 3.97%, 1.59%, 3.97%, 3.41%, and 4.14% for palygorskite dispersed by methanol, ethanol, isopropanol, dimethyl sulfoxide, and dimethyl formamide solvents, respectively. It meant that some organic solvents were presented in the palygorskite after homogenization, but the amount of ethanol molecules contained in the palygorskite was less than other organic solvents molecules.

3.2. IR analysis

Palygorskite can be regarded as a “magnesium-based clay” having tunnels with a cross section of 3.7 × 6.0 Å. The tunnels are filled with water molecules at ambient temperature, which can be replaced by small polar molecules, such as ammonia, methanol, ethanol, acetone, and other molecular species [17]. Because the discontinuity of the silica sheets of palygorskite, silanol groups (Si – OH) are presented on the surface of the rods and make the surface of palygorskite hydrophilic. Therefore, in the process of preparing palygorskite suspension,

<table>
<thead>
<tr>
<th>Liquid media</th>
<th>C (%)</th>
<th>H (%)</th>
</tr>
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<tbody>
<tr>
<td>Water</td>
<td>0.91</td>
<td>1.64</td>
</tr>
<tr>
<td>Water</td>
<td>1.28</td>
<td>1.26</td>
</tr>
<tr>
<td>Ethanol</td>
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<td>Isopropanol</td>
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<td>Dimethyl sulfoxide</td>
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<td>1.58</td>
</tr>
<tr>
<td>Dimethyl formamide</td>
<td>4.14</td>
<td>1.63</td>
</tr>
</tbody>
</table>

* Unhomogenization.
the solvent molecules could be attached onto palygorskite in two different manners: solvent molecules adsorbed on the external surface and solvent molecules incorporated into the tunnels of palygorskite. To demonstrate this adsorption behavior, a systematic study of the IR spectra and thermal decomposition behavior of the obtained palygorskite was carried out.

The IR spectra of obtained palygorskite samples dispersed by various liquid media are shown in Fig. 1. No obvious changes in the characteristic peaks of palygorskite dispersed by water followed by homogenized at 30 MPa or not are observed. However, compared to the IR spectrum of homogenized sample dispersed by water, a new band at about 1393 cm\(^{-1}\), which is related to the C–H symmetric bending vibration of CH\(_3\), appears in the IR spectra of palygorskite dispersed by methanol, isopropanol, and dimethyl formamide, while the band at about 1318 cm\(^{-1}\) which can be assigned to the C–H bending vibration of S–CH\(_3\) is found in IR spectrum of dimethyl sulfoxide-dispersed palygorskite. Unfortunately, the characteristic peak of CH\(_3\) is not observed in the spectrum of ethanol-dispersed palygorskite. Because the C=O stretching vibration (1650 cm\(^{-1}\)) of the dimethyl formamide was overlapped with the bend vibration of water (1654 cm\(^{-1}\)), the O–H stretching vibration (1050 cm\(^{-1}\)) of the alcohols and the S=O stretching vibration (1050 cm\(^{-1}\)) of the dimethyl sulfoxide were hidden below the strong peak related to the asymmetric stretching band of the palygorskite tetrahedral silicate sheet (1089 cm\(^{-1}\)), the C=O, O–H and S=O characteristic peaks are not clearly found in the IR spectra of palygorskite dispersed in organic solvents.

In previous study, Kuang et al. have discussed the incorporation behavior of ethanol and methanol molecules in the tunnels of palygorskite by submitting the palygorskite in the alcohol vapors. It was found that the alcohol molecules entrapped in the tunnels of palygorskite were released at 130 °C (ethanol) and 80 °C (methanol), while the alcohol molecules coordinated with structural water through hydrogen bonding were removed at higher temperature [18]. Therefore, to further corroborate if there were interactions between the organic solvent molecules and the palygorskite, the homogenized palygorskite samples were heated at 200 and 380 °C, and the changes of IR characteristic peaks of CH\(_3\) group of solvents molecules were discussed. Heating of the homogenized samples at 200 °C had no substantial effect on the characteristic peak of CH\(_3\) group as shown in the IR spectra of palygorskite dispersed in methanol, isopropanol, dimethyl formamide, and dimethyl sulfoxide solvents (Fig. 2). Further heating of the homogenized samples at 380 °C caused the intensities of methanol, isopropanol and dimethyl formamide related C–H bending vibration to sensibly decrease, but not to completely disappear (Fig. 2). It indicated that a portion of the solvents molecules were released at this temperature. The still presence of such band after heating at higher temperature might be suggested that specific interactions were likely to form between solvents molecules and the palygorskite framework. Whereas, the C–H bending vibration of S–CH\(_3\) group at 1318 cm\(^{-1}\) was almost disappeared after palygorskite heated at 380 °C (Fig. 2f). Such disappearance was due to the combustion of dimethyl sulfoxide molecules which had a low ignition temperature of about 300 °C.

It can be also seen from Fig. 1 that another new band located at 1620 cm\(^{-1}\) is presented in the IR spectra of palygorskite dispersed in methanol, isopropanol, dimethyl formamide, and dimethyl sulfoxide solvents. Heating of corresponding palygorskite samples at 200 and 380 °C also caused no substantial modification in this band except for dimethyl sulfoxide-dispersed sample (Fig. 2). This band could not be related to the bend vibration of coordinated and zeolitic water at 1620 cm\(^{-1}\) [19], because no counterpart band was found in the spectrum of water-dispersed palygorskite. Furthermore, this band was also disappeared when heated the dimethyl sulfoxide-dispersed palygorskite at 380 °C. So such band might be related to the vibrational mode of organic solvent molecules entrapped in the tunnels of palygorskite.

3.3. Thermogravimetric analysis

TGA and derivative thermogravimetric (DTG) curves of obtained palygorskite dispersed by various liquid media are presented in Fig. 3. The TGA curve of the unhomogenized palygorskite displayed four mass losses in the studied range of temperature. The first step occurred at 103 °C with a mass loss of 4.15% (\(<\)130 °C) was assigned to the release of physically adsorbed water and partial zeolitic water. The second mass loss of 3.41% (130–270 °C) with the maximum rate at 227 °C was observed. According to the dehydration process of palygorskite reported in the literatures, Cheng et al. suggested that the dehydration of rest part of zeolitic water was occurred between 125 and 180 °C with the maximum rate at 160 °C [20], while Kuang et al. thought that the second mass loss was originated from the release of first structural water (130–270 °C) [21]. Because the chemical composition and origin of mineral could influence the thermal decomposition properties of palygorskite, it was likely that the residual zeolitic water and partial

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**Fig. 1.** IR spectra of unhomogenized and homogenized palygorskite dispersed by various liquid media.
first structural water of palygorskite was removed from 130 to 270 °C. The third step was observed at 447 °C with mass losses of 5.44% (270–560 °C), which was related to the loss of the residual first and the second structural water [22]. The last step was occurred at 635 °C with mass losses of 2.27% (560–680 °C). In general, the dehydroxylation was occurred between 580 and 950 °C with the maximum rate of 860 °C for palygorskite [21]. The IR spectra (1450 cm$^{-1}$) indicated that the used palygorskite contained traces of calcite (Fig. 1). Therefore, the fourth mass loss might be corresponded to the calcination of the calcite and the partial dehydroxylation of the Mg–OH groups [20,23]. In comparison with unhomogenized palygorskite, the mass losses occurred at lower temperature of 100, 219, 446, and 624 °C were observed for homogenized palygorskite dispersed by water (Fig. 3). The decrease of dehydroxylation (the second step) and dehydroxylation or calcination (the fourth step) temperature might be related to the weakness of the hydrogen bonding between the zeolitic water and structural water [24], and decoherence of carbonate from palygorskite, respectively due to the produced strong shear forces during homogenization process.

The TGA and DTG curves of the homogenized palygorskite obtained by dispersing in liquid media are also shown in Fig. 3. Similar thermal decomposition behavior (four mass losses) were found for ethanol-dispersed palygorskite compared with water-dispersed sample, while five mass losses were occurred for palygorskite dispersed by methanol, isopropanol, dimethyl formamide, and dimethyl sulfoxide solvents. The mass loss resulted from the release of the physically adsorbed water and partial zeolitic water was smaller than that measured from water-dispersed sample, which decreased to 1.52%, 2.51%, 1.23%, and 1.26%, respectively over the same temperature range for methanol-, ethanol-, isopropanol-, and dimethyl sulfoxide-dispersed palygorskite. In addition, a reduction of mass losses (130–270 °C) was also observed for palygorskite dispersed by methanol, isopropanol, and dimethyl formamide solvents. These results indicated that few water molecules adsorbed on the external surface, and the zeolitic water filled in the tunnels of palygorskite was replaced by the organic solvent molecules. The boiling points of dimethyl formamide and dimethyl sulfoxide are 153 and 189 °C, respectively, the adsorbed dimethyl formamide and dimethyl sulfoxide molecules on external surfaces of palygorskite cannot be completely removed after drying at 105 °C. So these dimethyl formamide and dimethyl sulfoxide molecules were released together with the zeolitic and partial the first structural water molecules upon thermal treatment, resulting in the mass losses at 55–175 and 110–265 °C were 3.03% and 5.05%, respectively.

As can be also seen from Fig. 3, both TGA and DTG curves showed small but significant differences between water-dispersed palygorskite and the samples dispersed by methanol, isopropanol, dimethyl formamide, and dimethyl sulfoxide solvents, respectively in the 270–550 °C temperature interval. The loss of structural water was occurred in two distinct steps for water-dispersed palygorskite, whereas, an almost continuous mass loss was observed for samples dispersed by organic solvents. Moreover, the mass loss of third step increased to 8.27%, 8.17%, 9.72%, and 8.09% for palygorskite samples dispersed by methanol, isopropanol, dimethyl formamide, and dimethyl sulfoxide solvents, respectively. It was likely that the loss of structural water between 270 and 560 °C was accompanied by the loss of residual methanol, isopropanol, dimethyl formamide, and dimethyl sulfoxide molecules.

Combined with the results of elemental analysis, IR and TGA results, it is reasonable to conclude that the methanol, isopropanol, dimethyl formamide, and dimethyl sulfoxide molecules were encapsulated inside the tunnels of palygorskite, and the host/guest interactions were formed between solvents molecules and the palygorskite framework increasing the stability of solvent molecules and preventing these molecules from disappearance at lower temperature. The dehydration temperature (second step) started at a lower temperature compared with that of palygorskite dispersed in water. This may be related to the breaking of the hydrogen bonding among the zeolitic water, structural water and the tetrahedral sheet owing to the incorporation of organic molecules into the tunnels of palygorskite. The dehydroxylation of the Mg–OH groups and the calcination of the calcite were still observed in the TGA curves of palygorskite dispersed by organic solvents.

### 3.4. XRD analysis

Fig. 4 shows the XRD patterns of obtained palygorskite dispersed by various liquid media. The strong diffraction peaks at 2θ values of 8.34°, 13.74°, 16.34°, 19.83°, 27.54°, and 34.38° were assigned to the characteristic peaks of palygorskite. The peaks at 2θ values of 20.85° and 26.63° could be ascribed to the characteristic peaks of quartz impurity, and the peak at 2θ value of 30.97° was corresponded to the characteristic peak of carbonate impurity. Direct comparison showed that the intensity and position of (110) diffraction peak (2θ = 8.34°) remained nearly invariable when palygorskite samples were dispersed by methanol, ethanol, isopropanol, and dimethyl formamide solvents followed by homogenized at 30 MPa. However, the position of (110) diffraction peak negatively shifted to 8.28° for dimethyl sulfoxide-dispersed palygorskite (Fig. 4). The polarity of these organic solvents follows the sequence of dimethyl sulfoxide > methanol > dimethyl formamide > isopropanol > ethanol. Moreover, the polarity rather than molecular dimension governed the incorporation of small molecules inside the tunnels of palygorskite [17]. So the shift in (110) diffraction peak of dimethyl sulfoxide-dispersed palygorskite was attributed to the incorporation of more dimethyl sulfoxide into the tunnels (Table 1) and occupying the volume that was previously filled by zeolitic water. The molecular dimension of dimethyl sulfoxide was larger than that of water and therefore led to slight expansion of the tunnels. In addition, weakness in the intensities of (110) diffraction peak of dimethyl sulfoxide-dispersed palygorskite might be due to the structure factor contribution of the incorporated dimethyl sulfoxide atoms [3].
3.5. Microstructure analysis

Table 2 lists the textural parameters obtained from the N₂ adsorption–desorption isotherms of homogenized palygorskite dispersed by various liquid media. The values of specific surface area (SBET) were calculated by the BET method. The total pore volume (Vtotal) was obtained from the volume of N₂ held at the relative pressure P/P₀ = 0.95. The micropore volume (Vmicro) was estimated by the t-plot method. The SBET of homogenized palygorskite dispersed by water was 234 m² g⁻¹ with a Vmicro of 0.048 cm³ g⁻¹ and a Vtotal of 0.39 cm³ g⁻¹. Such high surface area was due to the porous structure of palygorskite [25]. A decrease of SBET and Vtotal was observed for samples dispersed by organic solvents. Correspondingly, the microporosity of these samples was wholly lost except for ethanol-dispersed palygorskite. Because the molecular dimensions of organic solvents are larger than that of water, the decrease in textural parameters for samples dispersed in organic solvents was due to the presence of solvents molecules in the tunnels of palygorskite, which can decrease the N₂ adsorption. The polarity of ethanol was small by comparison with other organic solvents, the chance of ethanol molecules incorporated into the tunnels of palygorskite decreased, so the ethanol-dispersed palygorskite still has a micropore volume of 0.004 cm³ g⁻¹. This was also the reason that the percentage of carbon in ethanol-dispersed palygorskite was less and the C–H adsorption band of CH₃ group was not presented in IR spectrum of corresponding sample.

3.6. Morphological characterization

The morphology of obtained palygorskite samples dispersed by various liquid media are shown in Fig. 5. The natural palygorskite appeared as bundles of parallel aggregates with large size (Fig. 5a). Many crystal bundles which still bound together were presented in the palygorskite obtained by dispersing in water using mechanical stirring (Fig. 5b). The homogenization treatment had not affected...
the fibrous morphology of palygorskite, but the number and size of crystal bundles decreased when palygorskite was dispersed by water followed by homogenized at 30 MPa. Whereas, the homogenized palygorskite dispersed by methanol (Fig. 5d) still contained some crystal bundles with a diameter of about 300–500 nm, but no large agglomerates. Some single rods and small crystal bundles with a diameter of 100–200 nm can be found in ethanol- and isopropanol-dispersed palygorskite (Fig. 5e and f). Many of single rod-like crystals with a length of 1–2 μm were observed after palygorskite dispersing in dimethyl formamide and dimethyl sulfoxide (Fig. 5g and h). It can be seen from the FESEM results that with no surface modification or the introduction of a second component to the system, the dispersion of palygorskite can be controlled by dispersing in proper liquid medium and homogenization at 30 MPa.

3.7. Sedimentation behavior

The sedimentation behavior of obtained palygorskite samples dispersed by various solvents was discussed (Fig. 6). Palygorskite sample in a poorly dispersed or aggregated form settles rapidly, whereas the well dispersed palygorskite sample settles slowly and has higher colloidal stability. Because natural palygorskite existed as aggregates or bundles (Fig. 5a), it was difficult to get well-dispersed palygorskite rods through simple mechanical stirring of its aqueous suspension (Fig. 5b). The aggregates were led to poor colloidal stability of palygorskite suspension due to gravitational forces. Therefore, the sedimentation volume of unhomogenized palygorskite was smaller than the homogenized sample (Fig. 6). The homogenized palygorskite dispersed by dimethyl sulfoxide gave a sedimentation volume of 90.5 mL after incubation for 72 h. The colloidal stability of suspensions gradually decreased when palygorskite was dispersed by isopropanol, dimethyl formamide, ethanol, and water, and a sedimentation volume of 69.5 mL was observed for water-dispersed palygorskite after incubation for 72 h. A relatively fast settlement at the range of studied sedimentation time was occurred for suspension based on methanol-dispersed palygorskite.

3.8. Apparent viscosity

In palygorskite suspension, the single rods and small crystal bundles presented in a random fashion and associated with each other to form flocculated clusters. A lot of water molecules were entrapped inside these clusters, resulting in an increase of the effective solid volume fraction of suspension and a higher viscosity. However, the colloidal properties of palygorskite were not apparent until the crystal bundles were separated into single rods [7]. As discussed above, the debundling of palygorskite during homogenization process was critically dependent on the dispersed media, and certainly showed different influences on the viscosity of suspension. As shown in Fig. 7, an increase in apparent viscosity was observed for homogenized palygorskite. Compared to the viscosity of suspension based on water-dispersed palygorskite, the viscosity increased after palygorskite dispersed by ethanol and isopropanol solvents. Specifically, suspension with viscosity of 2364 mPa s at 30 s was obtained by dispersing palygorskite in isopropanol. The sample dispersed by ethanol gave a viscosity of 2248 mPa s. However, the suspensions based on methanol-, dimethyl formamide-, and dimethyl sulfoxide-dispersed palygorskite have lower viscosities than that water-dispersed palygorskite system. In addition, a gradual decrease of equilibrium viscosity of all the suspensions with prolonging the shearing time was found. This was due to the formation of dense particles and clusters with increasing shearing time [26].

High-pressure homogenization, where high pressure is experienced over very short time, was commonly employed in chemical, pharmaceutical, and food applications to form emulsions with small drops and narrow size distributions. The homogenizer valve geometry was shown in Fig. 8. The suspension was fed axially into the homogenizer valve using a positive displacement pump and accelerated into the channel between the valve rod and the seat, referred to as the gap space. The suspension emerged from this channel as a radial jet that stagnated on an impact ring before leaving the homogenizer. Because the inlet flow rate was typically fixed by the associated feed pump and the impact ring was fixed in the valve, the channel gap space between the valve rod and the seat was the only operating variable that could be varied by a flywheel attached to the valve rod to control the inlet or operating pressure, which was typically indicated on the homogenizer [27]. The shorter of the gap space the higher homogenizing pressure will be.

In the process of homogenization, the high-speed jet emerged from the valve gap into the impingement section and spread out into the surrounding suspension. High stress and turbulence existed in the mixing region immediately adjacent to the jet where the surrounding suspension was accelerated. This led to local pressure loss and the inception of cavitation by bubble formation [28]. Cavitation was the formation of cavities filled with gas or vapor as pressure decreased, and they collapse as soon as the pressure increased again [29]. The sudden collapse of cavitation bubbles induced high pressure gradients and high local velocities of liquid layers in their vicinity. These in turn produced shear forces that were capable of breaking the aggregates into smaller particles. This was the mechanochemical action of homogenization on aggregates. On the other hand, when palygorskite suspension homogenized at 30 MPa, the produced shear and cavitational forces provided the driving forces for the organic molecules incorporation into the tunnels of palygorskite, which would substitute the zeolitic water molecules to fill the tunnels of palygorskite. Because the structural water molecules were still presented in the tunnels, and the intrinsic charge of palygorskite was very low (few exchangeable cations), one can hypothesize that

<table>
<thead>
<tr>
<th>Liquid media</th>
<th>$S_{BET}$ (m$^2$ g$^{-1}$)</th>
<th>$V_{mirc}$ (cm$^3$ g$^{-1}$)</th>
<th>$V_{total}$ (cm$^3$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>234</td>
<td>0.048</td>
<td>0.39</td>
</tr>
<tr>
<td>Methanol</td>
<td>113</td>
<td>–</td>
<td>0.28</td>
</tr>
<tr>
<td>Ethanol</td>
<td>121</td>
<td>0.004</td>
<td>0.27</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>108</td>
<td>–</td>
<td>0.25</td>
</tr>
<tr>
<td>Dimethyl sulfoxide</td>
<td>108</td>
<td>–</td>
<td>0.28</td>
</tr>
<tr>
<td>Dimethyl formamide</td>
<td>110</td>
<td>–</td>
<td>0.26</td>
</tr>
</tbody>
</table>
the incorporated organic molecules did not protonate but were linked to the palygorskite structure through hydrogen bondings to the structural water molecules.

The forces that could disperse palygorskite aggregates during homogenization came from cavitation process, which were similar to the sonication-driven dispersion mechanism. According to the theory of cavitation process, the cavitation effect was strongly dependent on the vapor pressure, viscosity, and surface tension of solvent [30]. So the variations in colloidal properties of homogenized palygorskite might be attributed to the variations of solvent parameters [31] (Table 3). Generally, in solvents with low vapor pressure, more energy was required to induce cavitation, and consequently more energy was released upon bubble collapse. This energy was then available to aid in the dispersion of palygorskite aggregates. In addition, although

Fig. 5. FESEM images of natural palygorskite (a), unhomogenized (b) and homogenized palygorskite dispersed in (c) water, (d) methanol, (e) ethanol, (f) isopropanol, (g) dimethyl formamide, and (h) dimethyl sulfoxide.
viscous solvents with larger surface tension were known to increase the threshold of cavitation, the energy resulting from cavitation collapse in viscous liquids was also stronger than that in less viscous liquid, which will result in more efficient debundling of palygorskite aggregates [32]. Therefore, compared to the vapor pressure, viscosity, and surface tension of used dispersed media (Table 3), the dimethyl sulfoxide had the lowest vapor pressure (0.056 KPa), higher viscosity (2.0 mPa s), and surface tension (0.0429 N m⁻¹). This meant that more energy was released from cavitation collapse, resulting in more efficient dispersion of the palygorskite aggregates (Fig. 5). So the higher sedimentation volume of dimethyl sulfoxide-dispersed suspension was due to the well dispersion of palygorskite aggregates (Fig. 6).

For the samples which were dispersed in alcohol solvents with similar surface tension (Table 3), the nuance of surface tension for these alcohol solvents was not critical to influence the dispersion of aggregates. Instead, the most important factors affecting the disaggregation of palygorskite were the vapor pressure and viscosity. The isopropanol had larger vapor pressure and viscosity than the methanol and ethanol solvents, the energy resulted from bubble collapse in isopropanol-dispersed suspension was stronger than that in methanol- and ethanol-dispersed suspensions, and then leading to more efficient dispersion of palygorskite aggregates. So a stable suspension was obtained when palygorskite was dispersed in isopropanol. In case where palygorskite dispersed in water, some crystal bundles were found in obtained sample (Fig. 5c) and the colloidal stability of corresponding suspension was poor (Fig. 6). This might be due to the presence of particle bridging produced by hydrogen bonding of water to two terminal silanol groups of palygorskite [33]. As drying of the products, the “bridging” water molecules of interparticle were gradually removed, and the rods were close enough that formation of hydrogen bonding between terminal silanol groups of different rods, leading to reaggregation of dispersed rods. Whereas, in cases where palygorskite was dispersed in alcohol solvents with lower surface tension than that of water, excess organic solvents cannot form hydrogen bonding between alkoxy groups and the surface of rods, leading to the reaggregation of rods although alcohol molecules were also adsorbed onto the hydrophilic surface of palygorskite. Even though the surface tension of methanol was also small (0.0227 N m⁻¹), many crystal bundles with large diameter were observed in methanol-dispersed palygorskite (Fig. 5d), and the colloidal stability of corresponding suspension was worst (Fig. 6). It can be seen from Table 3 that the methanol had the lowest viscosity (0.6 mPa s) and highest vapor pressure (13.33 KPa). This indicated that energy released from cavitation collapse during homogenization was weaker compared to other solvents dispersed systems and not strong enough to disperse efficiently palygorskite aggregates. It also suggested that the homogenization process, rather than drying process, governed the dispersion of palygorskite aggregates.

Finally, it can be seen from Figs. 6 and 7 that there was no clearly correlation between the colloidal stability and the viscosity of suspension. The isopropanol-dispersed palygorskite had a maximum viscosity value after homogenization at 30 MPa, but the highly disaggregated palygorskite dispersed by dimethyl sulfoxide gave the lowest viscosity of suspension. The results indicated that introducing better dispersion does not necessarily increase the viscosity of suspension. Because the special colloidal nature of palygorskite suspension was originated from the association of single rods and small crystal bundles, the viscosity of the palygorskite suspensions was affected by the flocculated network structure, which was related to the palygorskite morphologies such as the degree of aggregation and aspect ratios of the rods [34]. It was likely that the association between small crystal bundles and single rod-like crystals in isopropanol-dispersed sample was so strong that it offset

<table>
<thead>
<tr>
<th>Liquid media</th>
<th>$\eta$ (mPa·s)</th>
<th>P (KPa)</th>
<th>$\sigma$ (10⁻² N·m⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>1.0</td>
<td>2.34</td>
<td>72.7</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.6</td>
<td>13.33 (21 °C)</td>
<td>22.7</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.2</td>
<td>5.33 (19 °C)</td>
<td>22.3</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>2.4</td>
<td>4.40 (20 °C)</td>
<td>21.7</td>
</tr>
<tr>
<td>Dimethyl sulfoxide</td>
<td>2.0</td>
<td>0.056 (20 °C)</td>
<td>42.9</td>
</tr>
<tr>
<td>Dimethyl formamide</td>
<td>0.9</td>
<td>0.36 (25 °C)</td>
<td>36.4</td>
</tr>
</tbody>
</table>
the effects from improvement of dispersion and generated higher viscosity [35].

4. Conclusions
Dispersion of natural palygorskite in distilled water, methanol, ethanol, isopropanol, dimethyl formamide, and dimethyl sulfoxide was conducted with the aid of sonication treatment. The elemental analysis, IR spectra, and TGA results showed that partial organic solvent molecules incorporated and were bound within the tunnels of palygorskite, resulting in low surface areas and pore volumes. Dimethyl sulfoxide molecules could enter into tunnels more easily and cause slight expansion of basal spacing. The morphology and colloidal properties of obtained palygorskite were critically dependent on the homogenization process, which was closely related to the nature of dispersed media such as vapor pressure, viscosity, surface tension. Palygorskite aggregates were efficiently debundled by dispersing in dimethyl sulfoxide and dimethyl formamide solvents. The stability and viscosity of suspension was obviously enhanced when palygorskite was dispersed by isopropanol. Homogenization treatment palygorskite suspensions dispersed in common solvent was a very effective method for preparing highly dispersed palygorskite while prevented serious reaggregation of palygorskite rods. Given it does not need special conditions, such as high temperature, special surfactants, long time, this method will help to expand the application of palygorskite.

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