Disaggregation of palygorskite crystal bundles via high-pressure homogenization

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1. Introduction

Palygorskite is a hydrous layered Al-Mg silicate mineral with a fibrous structure and a theoretical formula \((\text{Al}_2\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2)\cdot 4\text{H}_2\text{O}\) (Drits and Sokolova, 1971). Palygorskite has larger specific surface area, higher mechanical strength and aspect ratio, and so it has been applied as effective reinforce filler of nanocomposites (An et al., 2008; Lu et al., 2005; Xue et al., 2006), adsorbents (Xue et al., 2010) and carrier of catalyst (Bounia et al., 2011). However, the fibrous crystals of natural palygorskite prefer to exist as aggregates or crystal bundles under the action of electrostatic and van der Waals' interactions. Thus, the unique nanometer characteristics of palygorskite cannot be fully developed and its extensive application was limited, and the high-efficient disaggregation of palygorskite aggregates into individual fibers becomes a key to utilize the nanometer properties and develop the related product.

Thus far, two methods have been employed to dispense palygorskite aggregates and crystal bundles: chemical modification and physical approach. Chemical modification is focused on improving the compatibility and interfacial interaction of palygorskite with polymeric matrices (Liu, 2007; Lu et al., 2005; Xue et al., 2006). However, this approach is limited to a few polymers and is difficult for industrial scale processing. Different physical approaches such as high-shear mixing, extrusion, grinding and ultrasonication (Chen et al., 2010; Mendelovici, 2001; Neeman and Singer, 2000) are more effective and frequently employed to disaggregate crystal bundles of palygorskite, improve its specific surface area, porosity and dispersibility. On most cases, the extrusion and grinding techniques only slightly improve the properties of palygorskite and are not as effective as expected. Moreover, it is not feasible to achieve better dispersion of palygorskite fibers by simply increasing the number and intensity of grinding or extrusion. For ultrasonication and high-shear mixing techniques, the processing procedure requires high-energy consuming and the strong mechanical action may disrupt the fibrous crystal structure of palygorskite.

In current work, we adopted a new, facile and efficient high-pressure homogenization technology to disperse palygorskite crystal bundles. The high-pressure homogenization equipment could deliver pressure in the order of 100 MPa, and the homogenizer studied in Stansted, U.K., in 1997 even achieved pressure up to 350 MPa (Floury et al., 2002). During the homogenization process, the strong forces (shear and impact) could overwhelm the interactions among the fibrous crystals (electrostatic and van der Waals' forces) and instantly disperse the bundles into individual crystals. More importantly, this method is feasible for industrial scale processing. In this paper, the effects of homogenizing pressure on the morphology, pore structure, surface area and sedimentation properties of palygorskite were investigated in detail.

2. Materials and methods

2.1. Materials

Palygorskite mineral, obtained from Juchuan 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 by X-ray Fluorescence (XRF).

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2.2. High-pressure homogenization

50 kg of polygorskite mineral treated with a three-rolling grinder was dispersed in 350 kg of tap water and stirred for 60 min to obtain a homogeneous dispersion. The dispersion was filtered through a vibration sieve to remove quartz and other impurities. Subsequently, the collected polygorskite dispersion was homogenized with a high-pressure homogenizer (GJB-20, Changzhou Homogenizer Machinery Co., Ltd., Jiangsu, China) at different pressures (0, 10, 30, 50, 70 and 90 MPa). Then, the treated polygorskite was separated from water by a filter. The filter mass was dried at 110 °C for 12 h, ground and passed through a 75 μm sieve, and the filtrate was discharged. The samples were denoted as APT0, APT10, APT30, APT50, APT70 and APT90 according to the homogenizing pressure.

2.3. Measurements and characterization

The sedimentation experiments were carried out as follows. 2.0 g of the sample was dispersed in 120 mL of deionized water with a high-speed mixer (model GJB-B12K, Qingdao Haitongda Factory). The dispersion was transferred to 100 mL measuring cylinders and allowed to settle. The position of the solid/liquid interface was recorded at fixed time intervals.

The rheological measurements were made using an Anton Paar Physica MCR301 Rheometer (Germany), with the steady shear rate range from 0.1 to 200 s⁻¹. The frequency sweep at a given stress of 0.1% and frequency range varying from 0.1 to 100 rad/s were performed to obtain the dynamic shear modulus. The IR spectra of the samples were obtained on a Thermo Nicolet NEXUS TM spectrophotometer in the range of 4000–400 cm⁻¹ using KBr pellets. The XRD patterns of the samples were performed on an X′Pert PRO diffractometer equipped with a Cu Kα radiation source (40 kV, 40 mA). The specific surface area (SSA) of the samples was determined by using the BET method (Micromeritics, ASAP 2010) at 77 K. The micropore surface area (Smic), external surface area (Sext), and the micropore volume (Vmic) were obtained by the t-plot method. The total pore volume (Vt) was estimated from the volume of liquid N₂ (P/P₀ = 0.95). The average pore size (a) was calculated from P2−4 V/A, where V is the total volume of pores and A is the BET surface area.

The morphology of the polygorskite samples was observed by using FESEM (JSM-6701F, JEOL, Ltd.) and HRTEM (TECANI–G2–F30, FEI).

The particle size distribution (PSD) of homogenized polygorskite was determined using a laser light scattering analyzer (SFC-106, OMEC Technology Corporation, Ltd., Zhuhai, China).

3. Results and discussion

3.1. FESEM and HRTEM

According to FESEM images the polygorskite used (Fig. 1) is composed of many large crystal bundles and few single needle-like crystals (Fig. 1a). The size of polygorskite agglomerates decreased after homogenization even at 10 MPa. This fact is confirmed by the median particle size (D50) which decreases from 2.17 to 0.96 μm (Table 1). Compared to the APT0, the stacking degree of the crystal bundles evidently decreased. The polygorskite crystal bundles were further disaggregated with increasing the pressure to 30 and 50 MPa, and the length of polygorskite fibers is about 1 μm (Fig. 1c and d). After homogenized at 70 and 90 MPa, single needle-like crystals with the lengths below 0.5 μm appeared (Fig. 1e and f). The disruption of polygorskite fibers became serious with further increasing the shear and impact forces. These results indicate that the crystal bundles of polygorskite can be effectively disaggregated while keeping the aspect ratio of the fibrous crystals simply by controlling the homogenizing pressure.

HRTEM images were also used to verify the extent of disaggregation and disruption of polygorskite fibers after homogenized at different pressures (Fig. 2). After homogenized at 30 MPa (Fig. 2b), the polygorskite crystal bundles (Fig. 2a) were effectively disaggregated. The individual fibers with a diameter of 20–40 nm and a length of 1–2 μm corresponding to the single crystals of polygorskite were obtained. However, shorter individual fibers (200–500 nm) appeared after homogenized at 90 MPa (Fig. 2c), which indicates the breakage of the polygorskite fibers.

3.2. IR analysis

The IR spectra of the natural and homogenized polygorskite samples were studied to clarify the structural changes during high-pressure treatment (Fig. 3). The changes in IR spectra could be obviously observed in the range of 400–1600 cm⁻¹ where lattice vibrations present. The intensity of the band at 430 cm⁻¹ corresponding to Si–O–Mg and Si–O bending vibrations remained unchanged at 10 MPa. However, the increase of this band for APT30, especially for APT70 and APT90, was observed, which is attributed to the break of connected tetrahedral-octahedral sheets and then the exposure of Si–O groups. The bands at 1196 and 640 cm⁻¹ correspond to the asymmetric and symmetric stretching of the Si–O–Si bridges linking the aluminosilicate ribbons of polygorskite. The bands at 1089, 1027, and 982 cm⁻¹ are attributed to the asymmetric stretching modes of the tetrahedral silicate sheet (Augsburger et al., 1998). Most of them decreased after high-pressure homogenization, especially at 70 and 90 MPa, implying the structural degradation in the tetrahedral sheet (Cornejo and Hermosin, 1988). The band at 790–785 cm⁻¹ is attributed to silicean phases (quartz and/or chalcedony) and some weak –OH deformation vibrations, such as Fe-Mg-OH and Mg-OH (Farmer, 1974). This absorption band increased with increasing the homogenizing pressure, indicating the exposure of M–OH (Fe or Mg) at broken edges.

3.3. XRD analysis

The structure changes of polygorskite after homogenized at different pressures were also studied by XRD (Fig. 4). A slight increase in the intensity of the (110) characteristic diffraction peak of polygorskite and a decrease in intensity of the diffraction peak of quartz is observed after homogenization. In addition, the homogenized samples show XRD patterns similar to that of APT0, and the polygorskite homogenized at 90 MPa still displayed rather well defined (110) characteristic reflections. This suggests that the homogenized polygorskite retained its crystallinity without any amorphization. This result does not accord with the reported effects of grinding on the structure of clay mineral such as montmorillonite, sepiolite and talc (Cornejo and Hermosin, 1988; Filo et al., 1994; Hrachová et al., 2007), which have undergone amorphization and structural degradation after increasing treatment time. Therefore, it is considered that high-pressure homogenization is a very effective method of obtaining highly disaggregated polygorskite without serious disruption on the crystal structure of polygorskite.

3.4. BET analysis

The influences of disaggregation of polygorskite on its structure parameters including specific surface area and pore volume were summarized in Table 1. The SSA increased gradually with increasing homogenizing pressure and reached the maximum of 246 m²/g in sample APT50, and then decreases slightly to 237 m²/g with further increasing the pressure to 90 MPa. Whereas for talc (Aglietti, 1994), pyrophyllite (Wiewióra et al., 1993) and sepiolite (Cornejo and Hermosin, 1988) which were ground for different times, their specific
surface area suddenly decreased after a certain time. This difference may be associated with the corresponding structure changes of clay after mechanical treatment by different approaches. The similar tendency was also observed for $S_{\text{micro}}$, $S_{\text{ext}}$, and $V_{\text{micro}}$. This result is consistent with the FESEM and HRTEM results. The $S_{\text{ext}}$ increases with increasing the pressure from 10 to 90 MPa and the average pore size and the median particle size (D50) of polygorskite decrease after homogenization.

Table 1

Physical properties deduced from N$_2$ adsorption–desorption experiments of homogenized polygorskite samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>API10</th>
<th>API10</th>
<th>API30</th>
<th>API50</th>
<th>API70</th>
<th>API90</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{\text{reg}}$/m$^2$/g</td>
<td>192</td>
<td>205</td>
<td>241</td>
<td>246</td>
<td>238</td>
<td>237</td>
</tr>
<tr>
<td>$S_{\text{max}}$/m$^2$/g</td>
<td>72</td>
<td>89</td>
<td>107</td>
<td>110</td>
<td>103</td>
<td>96</td>
</tr>
<tr>
<td>$S_{\text{at}}$/m$^2$/g</td>
<td>120</td>
<td>116</td>
<td>134</td>
<td>135</td>
<td>135</td>
<td>136</td>
</tr>
<tr>
<td>$V_{\text{at}}$/cm$^3$/g</td>
<td>0.033</td>
<td>0.041</td>
<td>0.049</td>
<td>0.051</td>
<td>0.047</td>
<td>0.045</td>
</tr>
<tr>
<td>$V_{\text{total}}$/cm$^3$/g</td>
<td>0.33</td>
<td>0.33</td>
<td>0.42</td>
<td>0.39</td>
<td>0.44</td>
<td>0.40</td>
</tr>
<tr>
<td>P2/100m</td>
<td>7.96</td>
<td>6.37</td>
<td>6.95</td>
<td>6.27</td>
<td>7.33</td>
<td>6.68</td>
</tr>
<tr>
<td>D50</td>
<td>7.17</td>
<td>6.96</td>
<td>6.53</td>
<td>6.57</td>
<td>6.9</td>
<td>6.57</td>
</tr>
</tbody>
</table>

3.5. Sedimentation behavior

Polygorskite samples in a poorly dispersed or flocs form settle rapidly and the sedimentation volumes are small, whereas the well dispersed polygorskite samples settle slowly and have higher sedimentation volumes (Zeng et al., 2008). In addition, the increased viscosity of the continuous phase for the well dispersed polygorskite samples also contributes to the slow sedimentation (Eriksson et al., 2010). Fig. 5a shows the effect of homogenization on the sedimentation behavior of.
Fig. 2. HRTEM images of homogenized palygorskite. (a) APT0, (b) APT50, and (c) APT70.

Fig. 3. IR spectra of homogenized palygorskite.

Fig. 4. XRD patterns of palygorskite homogenized at different pressures (P = palygorskite; Q = quartz).

Palygorskite dispersion. The suspension of APT0 settled rapidly, indicating a poor dispersion and lower viscosity of the dispersion. High-pressure homogenization resulted in a sharp increase in the sedimentation volume and the sample homogenized at 30 MPa gives a sedimentation volume of 90 mL after incubation for 96 h. After homogenized at 50 and 70 MPa, the sedimentation volumes decreased to 75 and 72 mL, respectively. For the sample APT50, a highly stable dispersion was observed until 6 h of incubation, after which the position of the interface rapidly fell to the equilibrium position. A perfect dispersion with sedimentation volume of 98 mL after 96 h was obtained at 90 MPa. Similar tendency of viscosity, storage modulus and loss modulus of palygorskite with increasing the pressure were also observed (Fig. 5b and c).

At low pressure (10 and 30 MPa), the improved sedimentation volume is associated with the disaggregated small palygorskite bundles and individual fibers which can be entangled with each other and form stable flocculated suspension. For the palygorskite homogenized at 50 MPa (Fig. 1d), they contain no large bundles, but have more individual fibers with large aspect ratio. So that the sedimentation volume, viscosity and modulus would be higher since more individual particles have more surface area and the intimacy of association would increase due to an increase in the contact area. However, this is not the case. It is likely that the interactions between the bundles and the dispersed individual fibers are so strong that they overrule the effects from the increase of the surface area (Xu et al., 2005). Therefore, the larger sedimentation volume of sample APT50 before 6 h is due to the well dispersion of bundles, after which the rapid fall of solid/liquid interface can be explained in terms of the lower suspension viscosity. The reason for the minimum of sedimentation volume, viscosity and modulus of sample APT70 is that the shortening of fibers caused by high shear and impact interactions, which decreased the strength of network structure.

Interestingly, the highest sedimentation volume was obtained when palygorskite was homogenized at 90 MPa although the disruption of palygorskite needles is also presented. The viscosity and modulus also reach the maximum. A possible explanation for this behavior is that high-pressure treatment leads to the disruption of fibers (Fig. 1e and f).
more negative charge presents on the particle surface and the zeta potential of sample APT90 is measured to be $-262 \text{ mV}$ (obtained by ZEN3600, Malvern), but sample homogenized at 10 MPa only has a value of $-13.4 \text{ mV}$. This indicates that strong electrostatic repulsive forces exist in the sample homogenized at 90 MPa. These strong repulsive forces can provide a better dispersion of fibers and is favorable to the formation of cluster with larger size. It was confirmed that while keeping constant solid volume fraction and shear rate imposed, the viscosity of suspension increases with the increase of the clusters size (Shen et al., 2004). On the other hand, the temperature of the system obviously rises after homogenization at 90 MPa. The rise of temperature will result in an increase of the intensity of Brownian motion. In addition, the Brownian effects also become more important when the particle size is less than 500 nm (Xu et al., 2005). It is reasonable to suggest that the Brownian motion tends to make the short fibers move freely. Therefore, the strongly entangled structure of APT90 may be likely that these short fibers act as path to fill the gap of cluster and cause the association of cluster much stronger.

4. Conclusions

A simple and effective method for the disaggregation of polygorskite crystal bundles was found. High-pressure homogenization has evident influences on the micro-morphologies and properties of polygorskite. The disaggregation of polygorskite agglomerates is pressure-dependent and individual fibrous crystals of polygorskite can be obtained after homogenized at proper pressure. However, too high pressure (70 MPa or more) would inevitably result in the disruption of the fibrous crystals. In addition, the surface area, micropore surface area and micropore volume of the treated samples were obviously enhanced after homogenization treatment compared to the natural polygorskite. Moreover, a perfect dispersion with a stable network structure was obtained by homogenizing the dispersion at 90 MPa.

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References


