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Review article

Recent progress in dispersion of palygorskite crystal bundles for nanocomposites

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ABSTRACT

Palygorskite (Pal), as a valuable naturally available one-dimensional (1D) nanomaterial, has received greater attention in both academic and industrial areas. However, the rod crystals of Pal are usually existed as crystal bundles or aggregates in natural Pal owing to the stronger hydrogen-bonding and Van der Waals' interaction among rods, which limit the dispersion of Pal into water or other medium. Thus, the unique nanometer characteristics of Pal cannot be fully developed and its extensive application was limited, and so the high-efficient disaggregation of Pal aggregates into individual nanorods becomes a key to utilize the nanometer properties and develop the related product. In this review, the scattered information on the dispersion of crystal bundles or aggregates of natural Pal for application in nanocomposites was organized, and the high-pressure homogenization technology and integration disaggregation process proposed by our groups were especially introduced. The crystal bundles could be disaggregated by the "shearing, impact and cavitation" effects generated during high pressure homogenization process, without damaging the crystal structure and length of nanorods. The resultant nanoscale rods of Pal exhibit remarkable improvement of the colloidal, adsorptive, mechanical, thermal, and surface properties. These results reflect a scientific technical contribution to the nanocrystallization of the aggregated Pal rod crystals and its key role to develop various functional nanocomposites.

1. Introduction

Palygorskite (Pal, also called as attapulgite) is a naturally available hydrated magnesium aluminum silicate clay mineral with the theoretical formula of $Si_8Mg_8O_{20}(OH)_2(H_2O)_4 \cdot 4H_2O$ (Bradley, 1940; Galán, 1996; Giustetto and Chiari, 2004; Bergaya and Lagaly, 2013). Pal is assigned as the family of sepiolite in mineralogy because the microscopic structure and morphology of Pal is similar to sepiolite (Drits and Sokolova, 1971). Pal is composed of ribbons of 2:1 phyllosilicate units. Each ribbon is connected to the next by the inversion of SiO_4 tetrahedron along a set of Si–O–Si bonds, forming zeolite-like channels with the size of 0.37 nm × 0.64 nm (Chisholm, 1990, 1992; Mckeown et al., 2002). The perfect Pal crystal should be a trioctahedral mineral in which the octahedral sites are all occupied by Mg^{2+} ions. However, some trivalent cations, *e.g.*, Al^{3+} and Fe^{3+} ions, may replace the Mg^{2+} ions in octahedral sites due to the isomorphism effect, which lead to the formation of dioctahedral or intermediate structure (Paquet et al., 1987; Güven, 1992; Galán, 1996; Galán and Carretero, 1999; Suárez et al., 2007; Chryssikos et al., 2009). As a result, the crystallographic defects could be found in the octahedral sheets of natural Pal, and the structural negative charges are usually compensated by considerable amounts of exchangeable cations (Krekeler and Guggenheim, 2008).

The special crystal structure, stacking mode and nanometric dimension of the rod crystals of Pal endow it with plentiful pores, higher aspect ratio, better ion-exchange capacity (about 30 to 40 meq/100 g), and affluent surface groups (Haden, 1963; Gonzalez et al., 1989; Cao et al., 1996; Windsor and Tinker, 1999; Murray, 2000). So, Pal shows excellent colloidal, adsorption, reinforcing properties, and thermal/mechanical stability (Jones and Galan, 1988), and has been applied as ideal candidates in many fields of nanotechnology such as colloidal or stabilizing agents (Abdo and Haneef, 2013; Abdo, 2014; Chemeda et al., 2014; J. Lu et al., 2014), adsorbents (Al-Futaisi et al., 2007; A.M.B.M. Oliveira et al., 2013; Zha et al., 2013; H. Lu et al., 2014; J. Han et al., 2014; X.G. Wang et al., 2014; Quan et al., 2014; Wang et al., 2015a), carrier of catalysts (Huo and Yang, 2013; Liu et al., 2013; Papoulis et al., 2013; W.B. Wang et al., 2014), polymer nanocomposites (Ruiz-Hitzky, et al., 2013; Alcântara et al., 2014; Kong et al., 2014; Liu et al., 2014a; Chae et al., 2015; Tang et al., 2015), organic–inorganic hybrid pigments (Giustetto et al., 2014), drug delivery carriers (Aguzzi, et al., 2007; Q. Wang et al., 2014), biosensing materials (Luo et al., 2013), antibacterial material (Cai et al., 2013), health care and therapeutic products (Viseras et al., 2007), pharmaceutical product (Lopez-Galindo et al., 2007), electrorheological materials (Li et al., 2014), and sealing materials (Galán et al., 2011).

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In fact, most of the applications mentioned above would desire the highly dispersed or individualized Pal nanorods. However, the rods are usually existed as bulk crystal bundles or aggregates in natural Pal (Fig. 1), which is not readily dispersible in either water or common organic solvents. About the definition of the main microcosmic building units in natural Pal clay mineral, there is still no uniform statement. García-Romero and Suárez (2013, 2014) demonstrate that natural Pal clay mineral is mainly composed of the laths (the smallest structure units), the rods (the oriented association of laths), and the bundles (the association of rods). In many other researches, fibers (Corma et al., 1987; Barrios et al., 1995; Baltar et al., 2009; Boudriche, et al., 2012; Liang et al., 2013) or rods (Chen et al., 2012; Su et al., 2012; Liu et al., 2014b) were frequently adopted to describe the smallest crystal units. In this review, "rod" was used to denote the smallest crystal units (Fig. 2), and correspondingly the association of rods was described as crystal bundles, and the association of crystal bundles was described as aggregates. The single rod crystal of Pal can be recognized as nanomaterial, but the crystal bundles or aggregates with bulk size can't play the best performance of Pal as a 1D nanomaterial. The bulk crystal bundles in natural Pal clay mineral are difficult to be dispersed in other medium or matrix, which certainly limited the role of Pal to fabricate a variety of high-performance nanocomposites.

In order to improve the dispersion of Pal nanorod and extend its application, many physical (*i.e.*, ball milling, extrusion, ultrasonication, and high-speed shearing) or chemical modification (*i.e.*, acid treatment, salt treatment, and organification) methods have been investigated (Carrado, 2000; Liu, 2007; Darvishi and Morsali, 2011; Liu et al., 2012; R.N. Oliveira, et al., 2013; Boudriche et al., 2014). Although these traditional methods are still be widely used to process clay minerals up to now, the disaggregation efficiency of these methods is not enough, and the rod crystals may be broken during disaggregation process by the strong mechanical action. Thus, the disaggregation and dispersion of crystal bundles, with no damage to the length of rods, have long been the key bottle-neck problem that restricts the high-value application of Pal. With the unceasing expansion of application of Pal in functional materials, the high-level dispersion of Pal rods are required, and so the disaggregation of crystal bundles as small single rod crystals (Fig. 2) becomes extremely important.

In this review, we summarized the recent progress on the disaggregation of Pal crystal bundles by employing various physical or chemical methods. Based on this, the effect of stone milling, freezing, extrusion, slurring and purification, high-pressure homogenization, and surface modification on the microstructure and properties of Pal was intensively introduced. Our groups proposed the "extrusion/slurring/surface modification/high pressure homogenization" integration process based on a lot of researches, and have successfully achieved the large-scale industrial production of nanoscale Pal. The obtained nanoscale Pal shows remarkable superiority of properties in contrast to the raw one, which will open a new avenue for extending the applications of Pal in nanocomposites.

2. Disaggregation of Pal crystal bundles

As discussed above, the efficient disaggregation of Pal crystal bundles as individual nanorods is essential to extend the application of Pal in the field of functional materials. The principle of disaggregation process is to overcome the electrostatic, hydrogen-bonding and Van der Waals' forces among rods by imposing external forces. The mechanical treatment and chemical modification have been frequently used to disaggregate the crystal bundles of Pal and enhance the dispersion of Pal rods. The mechanical treatment may impose extrusion, shearing and knead forces on the crystal bundles and then tear up the bulk bundles as smaller bundles or single rods, while chemical modification may alter the surface charges of Pal rods and then weaken the interaction among rods. According to different practical usage requirement, the disaggregation methods could be selected to attain the required dispersion efficiency of crystal bundles and the desirable physicochemical properties of the product. The commonly used methods to disaggregate crystal bundles are classified as dry method, wet method, and dry-wet combination method.

2.1. Dry methods

Dry method is a low cost ultra-fine dispersion process of clay minerals because it does not require use of liquid dispersion medium. The original treatment process of Pal clay minerals is a typical dry method. In this process, raw minerals were crushed and grinded as powder, and the partial dispersion of minerals may improve the specific surface area and surface activity of particles and thus enhance the adsorption, slurrying, and reinforcing properties. The main principle of dry method is to shred the larger particles as small-size particles by stronger mechanical forces, and the dispersion degree is dependent on the mechanical strength and treatment time. The commonly used dry methods mainly include ball grinding, stone milling, extrusion and irradiation.

2.1.1. Ball grinding

Ball grinding treatment may crush and mix the materials by the impact and collision action of the rapidly dropped grinding body, such as steel ball, or cobble. When the grinding bodies rotated rapidly, the wear action between the grinding body and the interior wall of jar may continuously grind the materials to achieve a better dispersion (Krause et al., 2011; Tang et al., 2012). In the process of dispersion, the crystal structure, pores, and surface properties of minerals were usually changed, and even the amorphous product may be formed when imposing excessive grinding (increasing grinding strength or prolonging grinding time) (Kasai et al., 1994; Sánchez-Soto et al., 2000). The chemical

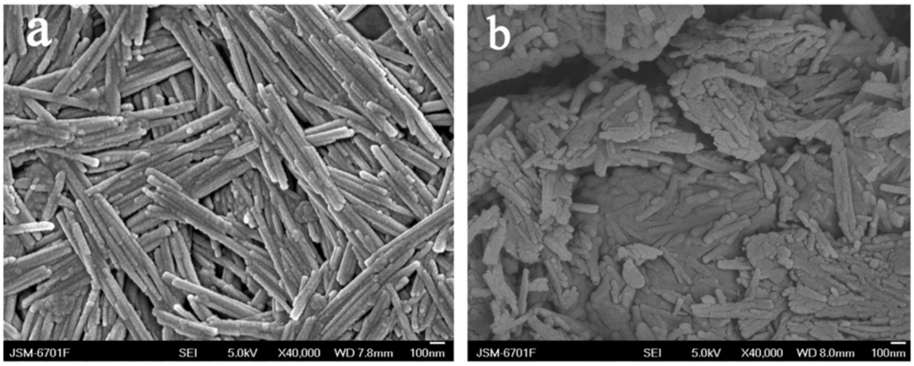

Fig. 1. Typical crystal bundles and aggregates of (a) raw Pal with longer rod crystal from Guanshan Mine located at Mingguang city of Anhui province, China; (b) raw Pal with shorter rod crystal from Gaojiawa Mine located at Xuyi county of Jiangsu province, China.