



Review article

Recent progress in dispersion of palygorskite crystal bundles for nanocomposites



Wenbo Wang, Aiqin Wang*

^a State Key Laboratory of Solid Lubrication, Center of Eco-materials and Green Chemistry, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China^b Center of Xuyi Palygorskite Applied Technology, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Xuyi 211700, PR China

ARTICLE INFO

Article history:

Received 25 January 2015

Received in revised form 2 June 2015

Accepted 4 June 2015

Available online 29 June 2015

Keywords:

Palygorskite

Disaggregation

Nanocomposites

Dispersion

Nanorods

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.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Palygorskite (Pal, also called as attapulgite) is a naturally available hydrated magnesium aluminum silicate clay mineral with the theoretical formula of $\text{Si}_8\text{Mg}_8\text{O}_{20}(\text{OH})_2(\text{H}_2\text{O})_4 \cdot 4\text{H}_2\text{O}$ (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 $0.37 \text{ nm} \times 0.64 \text{ nm}$ (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; Chrissykos 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).

* Corresponding author.

E-mail address: aqwang@licp.cas.cn (A. Wang).

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, slurring, 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

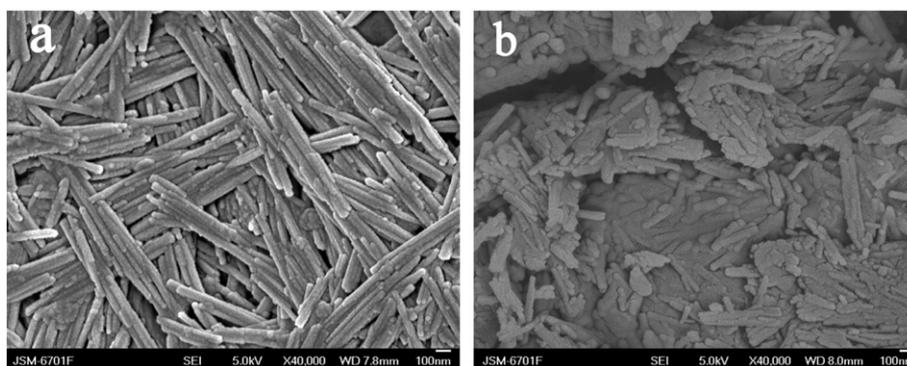


Fig. 1. Typical crystal bundles and aggregates of (a) raw Pal with longer rod crystal from Guanshan Mine located at Mingguang city of Anhui province, China; (b) raw Pal with shorter rod crystal from Gaojiawa Mine located at Xuyi county of Jiangsu province, China.

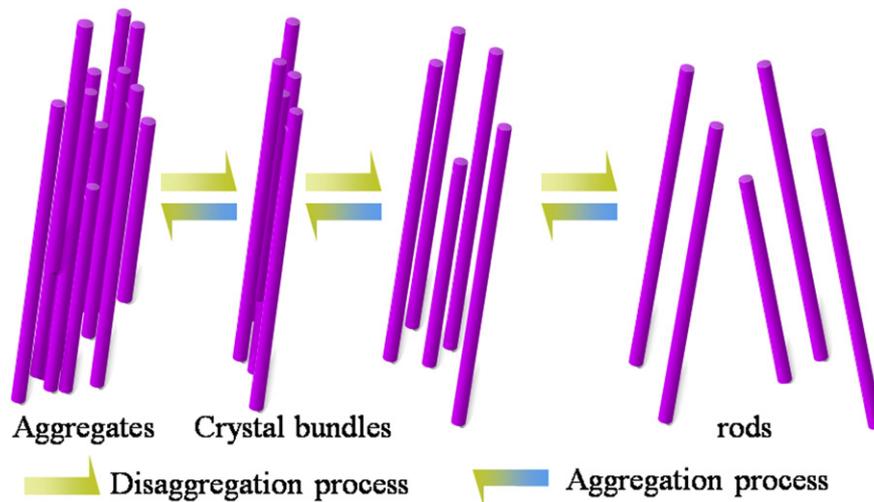


Fig. 2. Aggregation and disaggregation model of Pal rods.

composition, crystalline form and especially the content of water in the minerals may affect the change degree of crystals. After being grinded, the most prominent change of Pal is that the longer rods were broken as shorter rods or particles. Jin et al. (2004) studied the effect of the variable-frequency planet ultrafine ball grinding on the crystal structure and morphology of Pal. It was found that the grinding treatment for 1 h may decrease the particle size, but the crystalline structure was transformed as amorphous state. The further increase of grinding time to 2–4 h does not further reduce the particle size, but the amorphous degree further increased. When the ball-grinding time exceeds 5 h, the particles were seriously re-aggregated, and the crystal structure of rods was greatly damaged. Boudriche et al. (2014) compared the effect of different grinding types, e.g., batching ball milling, ultrafine airflow smashing, vibration ball milling, on the surface properties of Pal. Comparatively, the vibration ball grinding has relatively greater damage to the crystal structure than airflow smashing and vibration milling. The ball grinding technology was widely used for the processing of clay minerals, and mainly for the ultra-fine smash of minerals. However, ball grinding is not suitable for the disaggregation of Pal crystal bundles because it may seriously break the rod crystals, reduce the length of rods, and damage the crystal structure of Pal.

2.1.2. Stone milling

The stone milling may generate shearing and hoop stress during the milling process, and then tear up the crystal bundles as smaller bundles or rods. Our group (Liu et al., 2012) adopted stone milling treatment to disperse the crystal bundles of Pal. It was found that the crystal bundles and aggregates may be moderately disassociated under the action of mechanical forces, but the length of rods evidently reduces and even becomes as small particles when excessive milling times were applied, and the milling treatment for 10 times may induce the transformation of Pal crystals into an amorphous state, which indicates that the stone milling treatment may seriously damage the rod crystals. Although the stone milling treatment may improve the adsorption properties of Pal to some degree, the severe damage of rod crystals during milling process limits its application for the disaggregation of Pal crystal bundles.

2.1.3. Extrusion

Extrusion, as a traditional but important method, was widely applied for processing of clay mineral. It can tear up the bulk mineral as small particles and make these particles become fluffy. The moderate extrusion treatment may enhance the usage properties of Pal because the crystal bundles may be partially disaggregated as nanorods. Duke and Greene (1963) confirms that the extrusion treatment may enhance

the drainage properties of Pal. Haden and Schwint (1967) found that the decoloring capability of Pal could be evidently enhanced after extrusion treatment. Wang (2005) systematically studied the effect of extrusion times on the structure and dispersion of Pal. It was confirmed that the weaker extrusion can only partially disaggregate the crystal bundles. After extrusion treatment, clay minerals could be dispersed in the dispersion medium well because the “fluffy” particles could be hydrated and expanded more easily than raw mineral. However, the excessive extrusion treatment can't further improve the disaggregation degree of crystal bundles as expected; on the contrary, the rod crystals may be broken by the excessive mechanical treatment. The main reason is that the mechanical force generated by extrusion treatment mainly acts from the exterior to the interior of crystal bundles, and greater pressure was acted on the rods to break the rods. In fact, the disaggregation efficiency of crystal bundles and the damage of rod crystal are two opposites for the extrusion disaggregation methods. Up to now, the extrusion is still used as the pre-treatment process of Pal clay minerals before the disaggregation and dispersion of crystal bundles by wet-method.

2.1.4. Irradiation

Irradiation is a newly adopted method to modify or disperse the materials (Chowdhury and Sabharwal, 2011; S. Zhang et al., 2014). The high-energy radiation may initiate atoms, break the bonds or damage the texture of a matter. Zhang et al. (2013) found that some aggregates were broken up after ion-irradiation treatment, and the dispersion degree of Pal rods improved. However, the dispersed rods become bending, and connect with each other to form a network structure under the action of the instantly generated heat on the contact site of rods. The Pal treated by ion-irradiation shows improved adsorption properties for Methylene blue (Xiang et al., 2014). Although the dispersion of Pal rods was improved, the surface properties of Pal were also altered due to the irradiation treatment. In addition, the apparatus required for generating irradiation is expensive and is hardly to be popularized. So, the irradiation method is only suitable to be used in some special areas, and can't be used as a conventional method to disaggregate the crystal bundles of Pal.

2.2. Wet method

As described above, dry method is advantageous in the following several aspects: (i) the process is simple and low cost; (ii) it could be used for large-scale treatment; (iii) it has low requirement for apparatus; and (iv) it avoids the use of solvents. However, the mechanical force generated in the practical dry-method process may break up the nanorods, which reduce the length of rods, and even damage the

backbone structure of crystal because the rigid Pal nanorods are more easily to be broken at dry state. As a 1D nanomaterial, the properties of Pal are highly dependent on the aspect ratio of rod crystal, so the dry method, with greater damage to rod crystal, does not meet the practical usage requirement in many areas. Compared with mechanical treatment at dry state, the treatment at wet state obviously reduced the damage to the length and crystal structure of Pal rods. The US patent (Sampson et al., 1998) reports a representative wet method process to disperse Pal rods using poly(sodium acrylate) as the dispersants (Parker et al., 2000). In this process, water molecules may penetrate into the gap inside the crystal bundles or aggregates to dissolve the soluble matters, swell the rods and alter the state of ions around rod, and then promote the disaggregation of crystal bundles or aggregates under the action of external mechanical shearing or stirring. Although the wet method process required much water, the higher disaggregation efficiency and lower damage to rod crystals of this method make it still be the highly effective methods to produce nanoscale Pal (Chen et al., 2014).

2.2.1. High-speed shearing

High-speed shearing may impose shearing, impact and dispersion forces on the slurry suspension along the tangent line direction of the rotor, and then make the materials being dispersed (Tabata et al., 1986). This method was frequently used to disperse and mix the precursor for preparing various coating, pigment, adhesive and organic–inorganic nanocomposites (Yasmin et al., 2003; Wang and Sheng, 2006). As to the processing of clay minerals, the high-speed stirring was usually used for the production of colloidal clay. Viseras et al. (1999) confirms that the higher shearing rate and longer shearing time can disperse the suspension of Pal well, and can evidently enhance the viscosity of suspension. In the practice, high-speed stirring was used as the conventional method to disperse Pal into water for slurring and purification or to disperse Pal powder into other medium.

2.2.2. Ultrasonication

Ultrasonication treatment may disperse materials by its power characteristic and cavitation that may change some physico-chemical feature or dispersion state of materials (Peters, 1996). After ultrasonication process, dense materials become looser, and thus the constitutional unit of aggregates could be disassociated. Darvishi and Morsali (2011) prepared nanoscale Pal by ultrasonication technology. It was confirmed that the size of nanoscale Pal could be adjusted by altering the ultrasonication parameter. The bulk aggregates of Pal may be broken under the action of ultrasonication and then dispersed as small bundles or rods. Ultrasonication was frequently used for the pre-dispersion of various materials, but it is difficult to be applied for large-scale industrial production.

2.2.3. High-pressure homogenization

Different from the conventional treatment methods, high-pressure homogenization is a technology designed on basis of “Bernoulli principle”, and has been used for large-scale industrial refinement and dispersion process (Schultz et al., 2004). The high-pressure homogenization equipment could deliver the pressure up to 100 MPa, and even up to 350 MPa (Floury et al., 2002). In the process of homogenization, the materials rapidly flowed into the homogenization valve by a positive displacement pump, and accelerated into the channel between the valve rod and the seat. The suspension emerged from this channel as a radial jet that stagnated on an impact ring before leaving the homogenizer. The instant loading/release process of pressure may generate three effects: (i) shearing effect: when the high-speed flow suspension enter into a narrow region, the resulting greater velocity gradient may generate stronger shearing force; (ii) impact effect: the materials may impact the homogenization valve to generate stronger impact force (Lander et al., 2000); and (iii) cavitation effect: the great pressure drop generate when the materials flow through the gap of homogenization valve, and the bubbles filled with gas or vapor generate along with

the decrease of pressure (Freudig et al., 2003). The sudden collapse of bubbles induced higher pressure gradients and high local velocities of liquid layers in their vicinity, which produce intense shear force and cavitation effect on the particles in the liquid (Mohr, 1987).

The cavitation effect may form many “micro bomb” inside the crystal bundles, and generate force oriented from the interior to the exterior of crystal bundles. This force may overcome the electrostatic and Van der Waals’ force among the rods, and instantly disperse bundles as individual rods. Different from other methods, the mechanical force from high pressure homogenization process is mainly generated inside the crystal bundles, which may overcome the interaction between rods and make the rod disperse well. More importantly, this method is feasible in large-scale industrial processing.

Our groups firstly employed high pressure homogenization technology to disaggregate the crystal bundles of Pal, and systematic researches were done (Xu and Wang, 2012; Xu et al., 2012, 2013a, 2013b, 2013c, 2013d, 2014c). It was found that the crystal bundles could be disaggregated even at the lower pressure of 10 MPa (Xu et al., 2011). After being homogenized at 30 MPa, the crystal bundles could be disaggregated almost completely, but the length and crystal structure of rods do not obviously change (Fig. 3). The specific surface area, colloidal viscosity and suspension volume of Pal evidently increased after disaggregation. The disaggregation of crystal bundles and surface modification could be simultaneously achieved by the one-step high-pressure homogenization process, and the “cavitation effect” may also promote the interaction of modifiers with Pal. This is very favorable to the large-scale industrial production. As a new disaggregation technology, high pressure homogenization could also effectively combine with other process to achieve a better disaggregation efficiency (Xu et al., 2014a, 2014b).

2.3. Combination of dry and wet methods

Either of dry method or wet method can't meet the need of practical application on the disaggregation of crystal bundles or aggregates. The combination of dry and wet methods is recognized to be an effective way to disaggregate the crystal bundles of Pal, which is becoming the development tendency in future. The commonly used dry method treatment may break the bulk mineral particles of Pal into small particles or plate, or tear up the bulk crystal bundles to small bundles, which make Pal mineral more easily to be dispersed in the dispersion medium. Our works (Xu et al., 2014a, 2014b) confirm that the combination of extrusion, freezing, and high pressure homogenization can disaggregate the crystal bundles more effectively than the single one.

The effect of extrusion associated high-pressure homogenization on the disaggregation of crystal bundles and rheological properties were intensively studied (Xu et al., 2014b). With the increase of extrusion times, the dispersion degree of Pal rods initially increased and then decreased (Fig. 4). When Pal was rolled for 3 times, the dispersion degree of rods is the best. The particle size distribution of Pal becomes narrow after rolled for 3 times, and obviously reduced after rolled for 5 times. The further increase of rolling times does not improve the dispersion degree further. Inversely, the rods were broken and the length of rods reduced after excessive mechanical extrusion.

Freezing process is a green technology to change the aggregation state of materials. When water was transformed as ice, the volume may expand by about 10% (Chen et al., 2007). Generally, Pal contains four types of water molecules: the physical water adsorbed on external surface, the zeolitic water in the channels, the coordination water bonded to Mg^{2+} ions at the edge of structural ribbons, and the structural water coordinated to Mg^{2+} ions at the center of octahedral sheet (Bradley, 1940). In addition, there is much interstitial space filled by water between agglomerated crystal bundles. Therefore, it is reasonable to suggest that the increase of volume of ice during the freezing process can induce the disassociation of tightly bound Pal aggregates into weakly bound bundles, with no damage to the rod crystals of Pal.

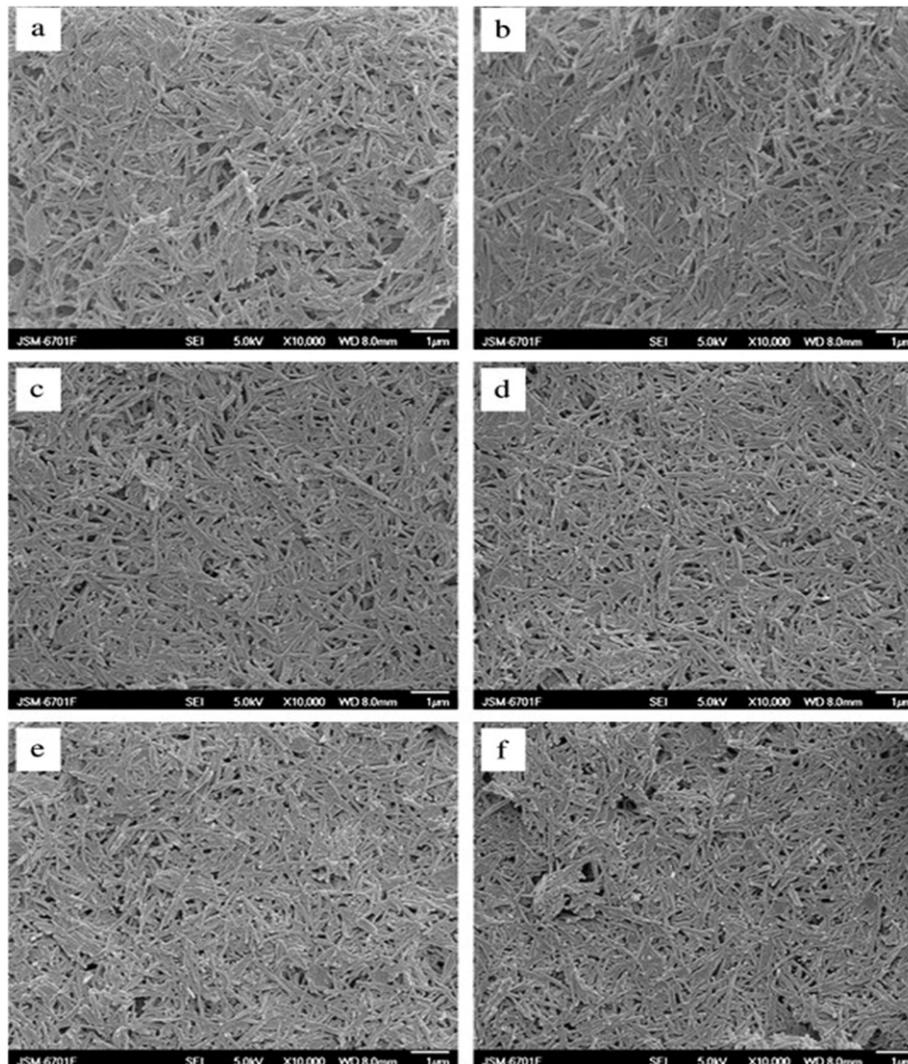


Fig. 3. FESEM images of homogenized Pal at (a) 0, (b) 10 MPa, (c) 30 MPa, (d) 50 MPa, (e) 70 MPa, and (f) 90 MPa. Adapted from Xu et al., 2011 – reproduced by permission of Copyright 2011 Elsevier.

Chen et al. (2010) and Q. Wang et al. (2014) demonstrate that freezing process and freezing drying treatment have positive action on the disaggregation of crystal bundles. Xu et al. (2013d) developed a novel approach to disperse aggregates of Pal into nanorods *via* adding freezing process into extrusion and homogenization treatment. It was found that the dispersion of Pal is dependent on the freezing time, and the highly dispersed Pal nanorods can be obtained after freezing for 4 h, followed by homogenization at 10 MPa. The dispersed Pal retains its original crystal structure, and the rod crystals were rarely disrupted. The rotary viscosity increased from 152 mPa s (for raw Pal) to 2682 mPa s, which is about 2.0 folds of the sample without freezing treatment. The effect of squeeze, homogenization, and freezing treatments on particle diameter and rheological properties of Pal was also studied (Xu et al., 2014a). The results indicated that highly dispersed nanorods without structural degradation are obtained after extrusion for 2 times, freezing for 4 h, and homogenization at 10 MPa (Fig. 5).

2.4. Chemical methods

The aggregation of Pal rods is mainly due to the existence of electrostatic, hydrogen-bonding, and Van der Waals' force among rods. The moderate mechanical treatment may overcome the force among rods and disperse the Pal crystal bundles. Various chemical methods, *e.g.*, acid treatment (R.N. Oliveira et al., 2013), electrolyte treatment (Jacobs

and Hamill, 1970), and organification (Liu et al., 2008; Chen et al., 2011; Sarkar, et al., 2012; F. Wang et al., 2013; C.S. Wang et al., 2014) have been employed to disperse Pal rod crystals or restrain the re-aggregation of dispersed rods. The main principles are, (i) to alter the interaction among rods by introducing different chemical molecules or ions; (ii) to dissolve the impurities inside the crystal bundles and then break up the bundles; and (iii) to increase the steric hindrance of rods by introducing larger molecular chains and then increase the repulsion among rods. The chemical modification was used in both dry method and wet method. For example, the introduction of sodium hexametaphosphate, sodium pyrophosphate, and stearic acid during ball-grinding may contribute to disperse rod crystals and reduce the damage of crystals (Jin et al., 2004); the surface chemical modification of Pal with quaternary ammonium salts, organosilanes or polymer chains may improve the dispersion of Pal rods and enhance their compatibility with the matrix (Tang et al., 2014); the acidification treatment of raw Pal may remove the impurities inside the crystal bundles to enhance the dispersion of Pal rods (R.N. Oliveira et al., 2013); the introduction of oxide may enhance the dispersion of Pal in the rubber matrix (Zhao et al., 2012). For a long time, the chemical methods have usually been adopted when the single physical method fails to attain desirable dispersion efficiency. Although the added chemicals may promote the dispersion of particles, but the surface features of Pal rods (*i.e.*, charges, activity, polarity and hydrophilic–hydrophobic

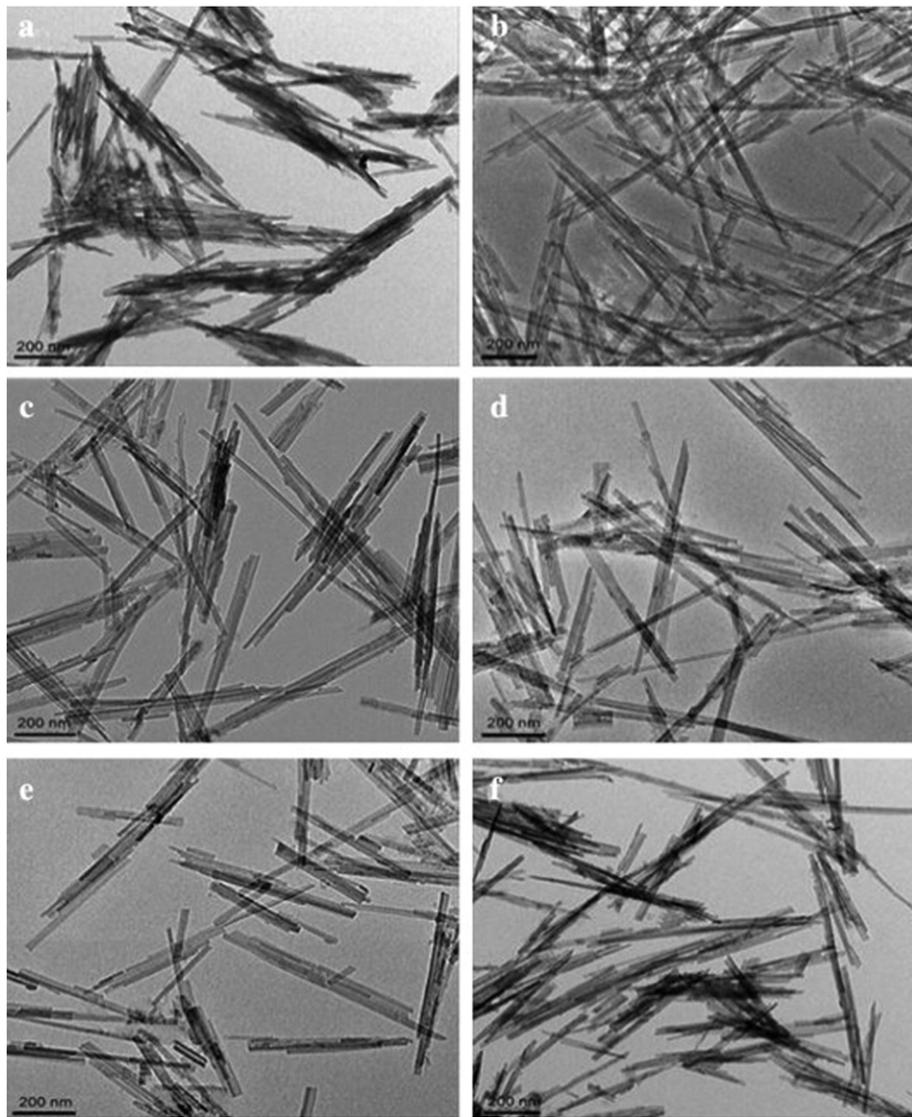


Fig. 4. HRTEM images of (a) raw Pal, and Pal treated by extrusion-homogenization: (b) 1 times, 30 MPa, (c) 3 times, 30 MPa, (d) 4 times, 30 MPa, (e) 5 times, 30 MPa, and (f) 3 times, 0 MPa. Adapted from Xu et al., 2014b – reproduced by permission of Copyright 2014 Elsevier.

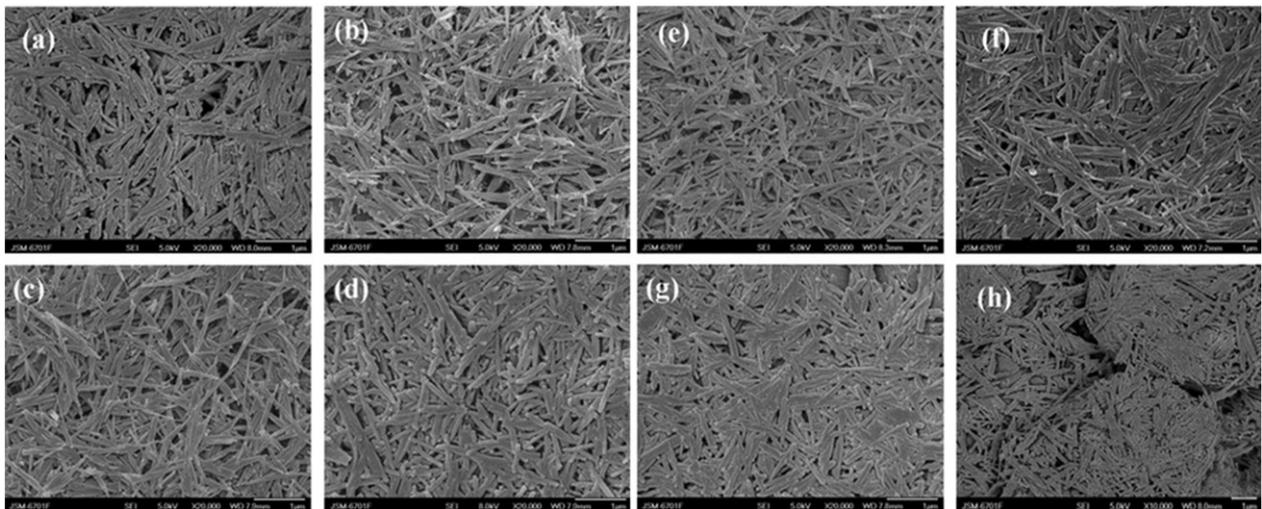


Fig. 5. FESEM images of treated Pal. (a) Pal 30, (b) Pal 70, (c) Pal 3-30, (d) Pal 5-30, (e) Pal 2-4-10, (f) Pal 2-8-10, (g) Pal 2-24-10, and (h) Pal 0. (Samples were marked as Pal x, Pal y-x and Pal y-z-x. x denotes homogenization pressure; y denotes extrusion times; z denotes freezing time). Adapted from Xu et al., 2014a – reproduced by permission of Copyright 2014 Elsevier.

features) were also changed by the chemicals. Thus, to choose moderate chemicals according to the practical usage requirement is necessary, and the associated physical and chemical method is recognized to be more effective to disaggregate the crystal bundles of Pal.

2.5. Integration disaggregation process

Generally, the desirable nanoscale Pal, produced from natural Pal clay minerals, has the following features: higher purity, excellent dispersion, and greater aspect ratio of nanorods. The single disaggregation method can't meet the above requirements. Thus, we carried out systematic researches on the development of "integration process" in order to achieve the large-scale production of high-quality nanoscale Pal for extending its industrial application in some high-end fields. Through the "extrusion/slurring/surface modification/high pressure homogenization" integration process, the high-efficient disaggregation of Pal crystal bundles, with no damage to the length of nanorods, was achieved on an industrial scale by our groups. In this process, the different cations (Xu et al., 2012; Xu et al., 2012), anions (Xu et al., 2013c), organic salts (Y. Liu et al., 2014), and organic solvents (Xu et al., 2014c) have been introduced to improve the dispersion of crystal bundles further. In addition, the high pressure homogenization technology is favorable to the interaction of modifiers with Pal. After introducing organic molecules phytic acid, the crystal bundles could be disaggregated well, and the rotary viscosity (7% aqueous suspension) reaches 3636 mPa s (Wang et al., 2015b), which is favorable to extend the application of nanoscale Pal as colloidal agents in fine chemicals.

3. Dispersion of Pal crystal bundles in various medium

The reaggregation of the dispersed nanorods during drying is inevitable due to their higher surface energy and greater surface area. Thus far, many chemical dispersants such as sodium hexametaphosphate, poly(sodium acrylate) and surfactants, have been used to improve the dispersion and prevent the reaggregation of nanorods (Chen et al., 2014). Polyelectrolyte ions may attach onto the surface of Pal rod, alter the surface charge, and increase the repulsion among rods, which may restrain the aggregation of rods. Although the introduction of ions is helpful to disperse the nanorods, the surface properties of Pal rods may also be altered, which is undesirable in many applications of Pal.

Like the ionic dispersants, organic solvents may also interact with Pal rods by dipolar or hydrogen bonding interaction. Currently, the dispersion of Pal in aqueous suspension is mainly focused, but little attention

was paid on the effect of organic solvents. Therefore, our groups (Xu et al., 2013a, 2013b, 2014c) systematically studied the effect of organic solvents or solvent/water mixture on the dispersion of Pal rods. It was revealed that the introduction of organic solvents contributes to improve the dispersion of Pal rods (Fig. 6) and enhance the colloidal properties. The combination of organic solvents with high pressure homogenization process forms synergistic effect to intensify the interaction between solvent molecules and Pal rods. The disaggregation of crystal bundles and the inhibition of re-aggregation were simultaneously achieved by the one-step process. The dimethyl sulfoxide (DMSO) treated Pal shows the best dispersion and colloidal stability. In order to reveal the interaction mechanism of solvent molecules with Pal, we firstly proposed that the polar solvents may form "Maya blue-like" structure with Pal, which is responsible for the superior dispersion and colloidal properties (Xu et al., 2013a). Comparatively, the polar DMSO and dimethylformamide molecules are easily to enter into the tunnels of Pal and form a strong hydrogen-bonding network with the zeolite water or bonding water molecules, which was confirmed by the superior thermal stability of DMSO after interacted with Pal. After dispersion with organic solvents, the surface energy of Pal decreased, and the solvent molecules may attach on the surface of Pal to form steric hindrance that is beneficial to restrain the aggregation of Pal rods. The solvents with weak polarity and low boil point may attach on the surface of Pal rods to improve the dispersion.

The homogenization process plays an important role to improve the dispersion of Pal rods and intensify the interaction of organic solvents with Pal. According to the cavitation theory, the cavitation effect is closely related to the viscosity, surface tension, and vapor pressure of the dispersion medium (Shah et al., 1999). Generally, in the solvents with low vapor pressure, more energy is required to generate cavitation, and consequently more energy could be released upon bubble collapse. The more released energy may generate greater force to promote the dispersion of Pal aggregates. The solvents with larger surface tension may increase the threshold of cavitation, and so the energy resulting from cavitation collapse in viscous liquids is also stronger than that in low-viscous liquid, which is favorable to the disaggregation of Pal crystal bundles or aggregates (Cheng et al., 2010). Therefore, compared with the vapor pressure, viscosity, and surface tension of the other solvents (Dean, 1999), DMSO has the lowest vapor pressure (0.056 kPa), higher viscosity (2.0 mPa s) and surface tension (0.0429 N m⁻¹). This means that more energy could be released after cavitation collapse, resulting in more efficient dispersion of Pal aggregates (Fig. 6). In addition, the shearing and cavitation force produced during homogenization process

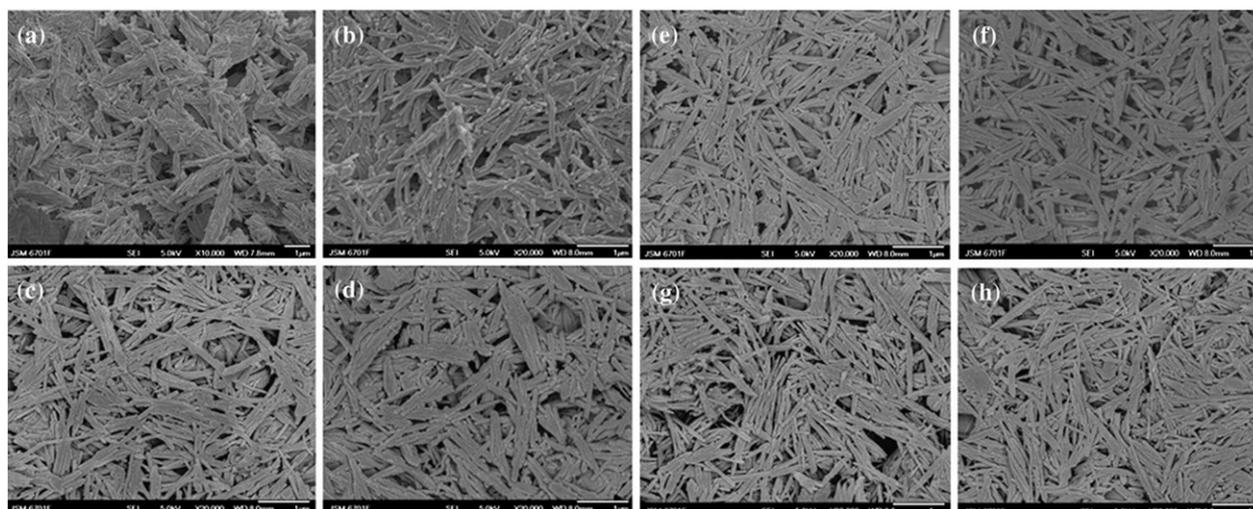


Fig. 6. FESEM images of raw Pal (a), unhomogenized (b) and homogenized Pal dispersed in (c) water, (d) methanol, (e) ethanol, (f) isopropanol, (g) dimethylformamide, and (h) DMSO. Adapted from Xu et al., 2013b – reproduced by permission of Copyright 2013 Elsevier.

provides the driving force to promote the organic molecules into the tunnels or attaching on the surface of Pal rod, which is favorable to the dispersion of Pal rods.

The effect of ethanol/water ratio on the dispersion of crystal bundles was investigated in order to explore an economical and feasible industrial approach to disperse Pal (Xu et al., 2014c). It is encouraging that ethanol may promote the dispersion of Pal rods, and the ethanol/water ratio of 6:4 corresponds to the best dispersion (Fig. 7). The Pal dispersed by ethanol/water mixture solvents gives a higher specific surface area in contrast to the raw Pal, which confirms that ethanol molecules are mainly attached on the surface of Pal, without entering the tunnels of Pal. The ethanol molecules on the surface of Pal may be easily removed during drying, and so it does not induce the adverse change of surface properties of Pal. This provides an industrially available route to disperse the Pal rods and restrain the reaggregation of nanorods.

4. Applications in nanocomposites

Recently, the processing and modifying of clay minerals as nanomaterials have been especially concerned in the field of nanoscience and nanotechnology, and such materials will play important roles in future sustainable energy, catalysis, green chemicals, and human health

areas (Zhou and Keeling, 2013). Silicate clay minerals, as a type of representative natural nanomaterials, have been widely applied in nanocomposites, and the relevant researches become the current hot spot (Sinha Ray and Okamoto, 2003; Pavlidou and Papaspyrides, 2008; Choudalakis and Gotsis, 2009; Garcia-Lopez et al., 2013; Sadeghipour et al., 2013; Barzegar et al., 2014; Faraz et al., 2014; Giannakas et al., 2014). The silicate-based nanocomposites have been honored as the promising materials of “greening 21st century material world” by virtue of the excellent performance and unique eco-friendly feature (Sinha Ray and Bousmina, 2005; Muller et al., 2014; Yang et al., 2014). Recently, the natural 1D nanoscale silicate clay minerals have attracted more attention owing to their special rod-like or tube-like crystal morphology and ideal surface activity. Ruiz-Hitzky et al. (2013) summarized the fibrous clay minerals and their bionanocomposites for potential applications in many fields. The intrinsic structure feature of Pal make it available for fabricating various functional materials as a substitution for expensive or environment-hazardous nanomaterials. However, most of researches concern how to enhance the compatibility of Pal with other matrix, or how to improve the homogeneity of the precursor used for preparing the nanocomposites; while the disaggregation and dispersion of crystal bundles does not arouse enough attention. Until recently, the disaggregation of Pal crystal bundles as individual nanoscale rods gradually highlight its advantages

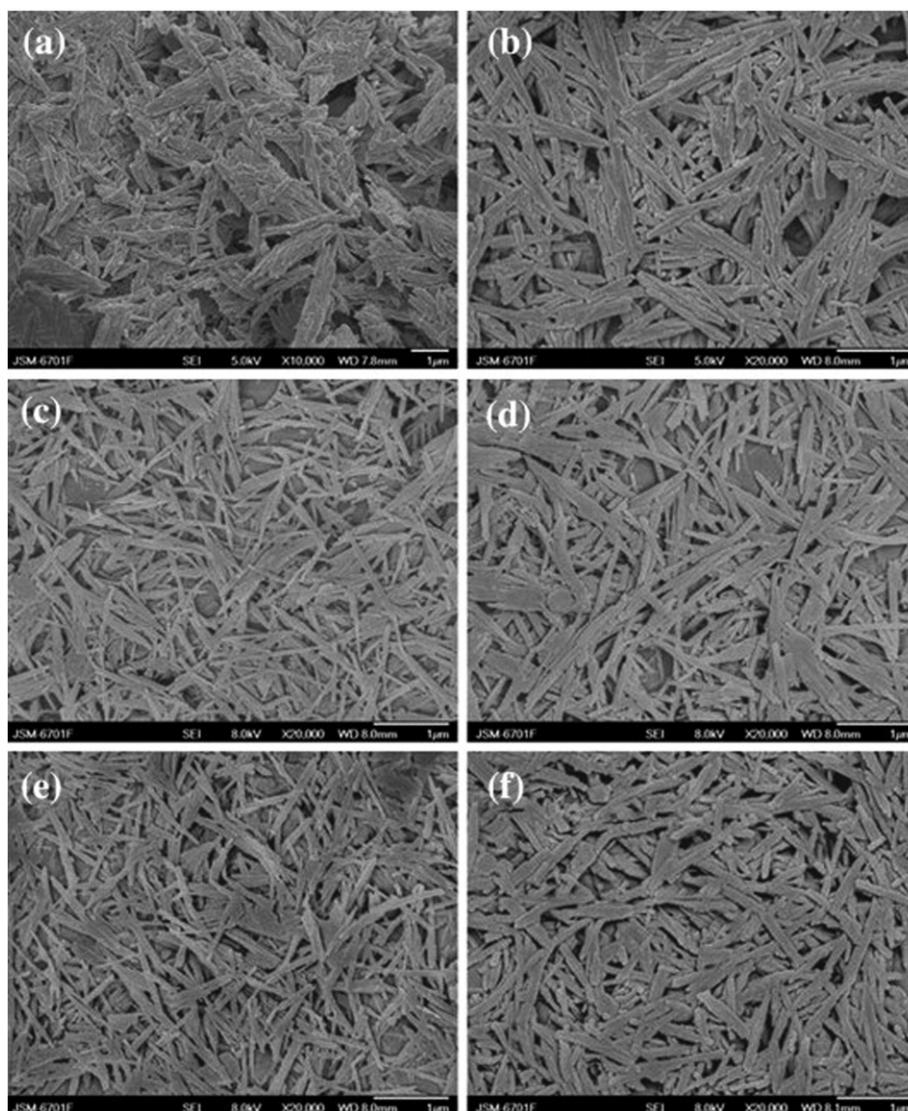


Fig. 7. FESEM of (a) raw Pal, (b) the unhomogenized Pal dispersed in water, and the homogenized Pal dispersed by ethanol–water mixture with the ratio of (c) 0:10, (d) 4:6, (e) 6:4, (f) 10:0. Adapted from Xu et al., 2014c – reproduced by permission of Copyright 2014 Elsevier.

of performance in each application aspect, and thus the dispersion of crystal bundles and the application of nanoscale Pal for fabricating nanocomposites are causing increasing attention.

Our groups demonstrate that the fully disaggregated Pal rods show better dispersion, surface activity, colloidal, adsorptive, and reinforcing properties that are greatly superior to the raw Pal. It is obvious that the nanometer effect of disaggregated Pal make it more effective to fabricate nanocomposites with improved performance.

4.1. Adsorption materials

The highly dispersed Pal nanorods are obviously advantageous to be used as the ideal carrier of magnetic particles by virtue of the relatively greater surface area and higher surface activity. Our group adopted highly dispersed nanoscale Pal to fabricate magnetic $\text{Fe}_3\text{O}_4/\text{Pal}@\text{(CS/Cys-}\beta\text{-CD)}_8$ (Mu et al., 2013) and $\text{Pal}/\text{Fe}_3\text{O}_4/\text{polyaniline}$ (Mu and Wang, 2015) adsorbents, which shows superior adsorption capability to noble metal ions and dyes. H. Lu et al. (2014) used the nanoscale Pal to prepare Pal/zero-valent iron nanocomposite, which shows excellent adsorption properties for Cr(VI). The highly dispersed Pal will be potential as ideal matrix to develop new hybrid adsorbents.

The nanocomposite of Pal with polymers may attain new type of adsorbent with three-dimensional (3D) network structure and plentiful functional groups. 3D network adsorbent has higher adsorption capacity, fast adsorption rate, and better regeneration properties. The conventional adsorbent prepared by solution polymerization is a bulk gel product, which requires much energy to be dried or prilled. Our groups synthesized granular 3D network adsorbent using solution polymerization (Zheng and Wang, 2012; Wang et al., 2013b, 2013c; Zheng et al., 2013), which can be directly used in practice with no need of prilling. It has been proved that the disaggregation of Pal crystal bundles is extremely important to fabricate a uniform granular 3D network adsorbent. Zheng et al. (2014) synthesized a granular chitosan-g-poly(acrylic acid-co-itaconic acid)/Pal adsorbent by one-step solution polymerization at room temperature and air atmosphere. The introduction of Pal nanorods may increase the adsorption rate and improve the network strength of the as-prepared adsorbent. The nanocomposite adsorbent shows extremely higher adsorption capacity for the dye malachite green (2433 mg/g) and excellent adsorption selectivity to cationic dyes in the binary mixture solution of dyes.

4.2. Superabsorbent materials

In order to develop new type of superabsorbent materials with better salt-resistant and ideal gel strength, the organic-inorganic nanocomposites attracted more attention (Wang and Wang, 2009; Kabiri et al., 2011; Feng et al., 2014; Rashidzadeh and Olad, 2014). The use of Pal for producing superabsorbent nanocomposite has been especially concerned due to its excellent salt-resistant properties (Wang et al., 2008; Wang and Wang, 2010; Shi et al., 2013; Wang et al., 2013e). Various modification methods including acid treatment, salt-exchange, thermal treatment, and organification have been employed to modify Pal for improving the water absorbency of superabsorbent nanocomposites (Wang and Zhang, 2006). In addition, it can also be found that the natural Pal is usually existed as bundles or aggregates, which can't be well dispersed in the matrix. The crystal bundles are physically filled in the matrix, and fail to fully react with the monomers. Thus, the disaggregation of crystal bundles is important to attain a well dispersion in the polymer matrix.

The dispersion of Pal by stone milling may partially disaggregate the crystal bundles, and can enhance the water absorbency of the superabsorbent (Liu et al., 2012). The grinding of Pal for 7 times can enhance the water absorbency by 86% than raw Pal. Compared with stone milling at dry state, the high-pressure homogenization treatment is a typical wet method process. As shown by our research (Wang et al., 2013f), the high-pressure homogenization treatment of Pal at different ethanol/water ratio has greater influence on the swelling properties of the

superabsorbent (NaAlg-g-P(NaA-co-St)/Pal). It was found that the crystal bundles were effectively disaggregated in the solution with the $m(\text{ethanol}):m(\text{water}) = 5:5$ after homogenized at 50 MPa, which clearly improved the gel strength (from 1300 to 1410 Pa, $\omega = 100$ rad/s), swelling capacity (from 442 to 521 g/g), swelling rate (from 3.3303 to 4.5736 g/g/s), and reswelling ability of the resultant superabsorbent nanocomposite. This confirms that the disaggregation of Pal crystal bundles is favorable to enhance the properties of the superabsorbent.

4.3. Reinforcing fillers for polymer nanocomposites

Polymer/clay minerals nanocomposites are the more promising application areas of clay minerals (Choudalakis and Gotsis, 2009; Lvov and Abdullayev, 2013). The intrinsic nanometer character of Pal makes it available as the reinforcing materials of polymer materials (Zhao et al., 2012; Ruiz-Hitzky et al., 2013), but the aggregation of rods usually discount on the reinforcing effect. Raw Pal can't be uniformly dispersed in the polymer matrix, and fails to play its "rebar"-like reinforcing role in the polymer/clay mineral nanocomposites.

In previous studies, the surface chemical modification of Pal via introducing different organic groups was mainly studied (Carrado, 2000; Liu, 2007) in order to improve the compatibility of clay minerals with polymer. Comparatively, the disaggregation of crystal bundles for fabricating polymer nanocomposite is rarely concerned. The effect of Pal disassociated by high pressure homogenization process on the structure and mechanical performance of poly(vinyl alcohol)/chitosan (PVA/CS) film was explored (Huang et al., 2012). As discussed above, the high-pressure homogenization process can not only disperse Pal nanorods well, but also can retain the original length of rod, which obviously affected the performance of the nanocomposite film. Compared with raw Pal, the homogenized Pal can enhance the mechanical properties more obviously. The film added only 3 wt.% of Pal may achieve the elongation at break of 133% and tensile strength of 58.54 MPa. The water resistance of the film was clearly enhanced after introducing the dispersed Pal by homogenization process in contrast to the raw Pal (Fig. 8). More importantly, the transparency of the film prepared from the dispersed Pal in the visible light regions (400–800 nm) is obviously higher than the film prepared from raw Pal, which confirms that the highly disaggregated Pal may disperse in the polymer matrix more uniformly.

Although the polymer nanocomposites have received considerable attention, and much research works have been published, it deserves to be pointed out that the "polymer/clay nanocomposite" was wrongly used in material science. According to the International Association for the Study of Clays, "clay mineral" is more accurate and scientific than

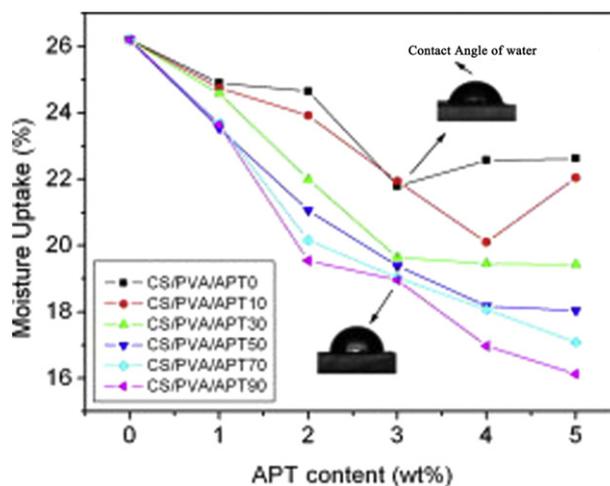


Fig. 8. Moisture uptake at equilibrium of the nanocomposite films with adding the Pal homogenized at different pressures (0, 10, 30, 50, 70, 90 MPa). Adapted from Huang et al., 2012 – reproduced by permission of Copyright 2012 Elsevier.

“clay”, and so the “polymer/clay mineral nanocomposite” was highly emphasized and suggested to be used to indicate such materials.

4.4. Catalysis materials

The immobilization of active components onto natural clay minerals opens a new avenue to fabricate new eco-friendly catalysts. The existence of carrier may restrain the aggregation of active particles. The special 1D nanoscale crystal structure of Pal makes it advantageous to be used as a carrier of catalyst. Many active components, e.g., noble metals, transition metals, semiconductor, and solid acid, have been loaded on Pal to prepare a variety of catalysts (H.R. Zhang et al., 2014; He and Yang, 2014; Jiang et al., 2014). However, the aggregation of Pal rods may limit the stability and activity of the resultant materials. After disaggregated the crystal bundles, the active components can be uniformly loaded on the surface of Pal rod more easily, and also the hybrid materials have better dispersion on a bulk scale. The disaggregated Pal was adopted to prepare the Pal/Fe₃O₄/AuNP catalyst (Wang et al., 2013d) and Pal/AgNPs (W.B. Wang et al., 2014) nanocomposite catalyst by a facile *in-situ* reaction approach. The nanocomposite shows higher catalytic activity for decoloration of Congo red. The Pal shows better dispersion and the AgNPs have a uniform distribution on the surface of Pal. Mu and Wang (2015) prepared the Pal/Fe₃O₄/polyaniline nanocomposite using high-pressure homogenized Pal and used as a carrier to fabricate Pal/Fe₃O₄/polyaniline/AuNP nanocomposite catalyst, and the desirable catalytic activity for reduction of 4-nitrophenol was obtained. With the increasing industrial requirement for highly active and eco-friendly catalyst, the nanoscale Pal will show a great prospect to fabricate new-type nanocomposite catalysts.

4.5. Hybrid materials

Maya blue, an organic–inorganic hybrid pigment, has bright color and superior stability, which does not fade even though it was exposed to external environment for more than thousands of years (Sanz et al., 2012). Numerous researches confirm that Pal is the irreplaceable carrier to prepare a stable Maya blue hybrid pigment. In the preparation procedure, the grinding process is fundamental to achieve a uniform dispersion of dye and better stability (Doménech et al., 2009; Giustetto and Wahyudi, 2011; Leitão and Seixas de Melo, 2013). The grinding process may disperse the crystal bundles, release more pores, and intensify the interaction between dye and Pal, which may promote dye molecules to enter the tunnel, and thus the dispersion of the hybrid materials was improved. The contribution of grinding to the dispersion of crystal bundles causes the increase of specific surface area and the change of surface activity, which are all favorable to the loading of dyes. We have studied the effect of grinding time and the water content during grinding on the stability of the methylene blue/palygorskite (MB/Pal) hybrid (Zhang et al., 2015). It was confirmed that grinding time plays a key role for the formation of a stable hybrid structure, because it greatly influenced the dispersion of Pal crystal bundles and the interaction between MB molecules and Pal. The aggregates of Pal rods were highly dispersed as individual nanorods after being ground for 30 min, and the MB molecules are more easily to be adsorbed on the Pal nanorods or encapsulated in their tunnels, so the thermal stability, acid, and UV-light resistance of the nanocomposites were enhanced, which is consistent with previous report (Reinen et al., 2004). The optimal water content during grinding is 36.9%. These researches confirm that the nanoscale dispersion of Pal will be helpful to fabricate a stable inorganic “host” framework that is suitable for holding a “guest” molecule into the cages or channels.

5. Concluding remarks and perspectives

Natural 1D nanomaterial has received growing attention in both academic and industrial areas. The nanoscale dispersion of Pal rods for

nanocomposites represents the future development direction in the field of materials because the highly dispersed Pal nanorods may contribute a lot to the performance of materials. The efficiency of many traditional disaggregation methods is limited, and some rod crystals may also be broken in the disaggregation process, which restricts the high-value application of Pal minerals.

The high-pressure homogenization technology was adopted by our groups to efficiently disaggregate the crystal bundles, without damage to the length of rods. This overcomes the drawbacks of traditional techniques and resolves the problems mentioned above. Also, the “extrusion/slurring/surface modification/high pressure homogenization” integration disaggregation process was also developed and used for the large-scale industrial production of nanoscale Pal. The resultant nanoscale Pal shows satisfactory usage properties superior to the raw ones. However, the utilization of disaggregated Pal for nanocomposites is rarely focused previously, and has gradually drawn attention until recent years, especially in the fields of nanotechnology.

We have conducted exploratory works about the utilization of disaggregated Pal for nanocomposites, and a satisfactory result was attained. Undoubtedly, the contribution of bulk crystal bundles to performance is far away lower than that of individual nanorods. The nanoscale Pal is potential to be applied to develop lubricant additive (Nan et al., 2014), smart materials (Peng et al., 2011; Jin et al., 2014), biomaterials (S. Han et al., 2014), plastic (An et al., 2008), rubber (Wang and Chen, 2013), tissue engineering materials (Gao et al., 2014), superhydrophobic coating (Li et al., 2013), and so on. The special 1D nanoscale feature, excellent surface compatibility, and mechanical/thermal stability of Pal render it advantageous as a filler of polymer materials. In the future, the applications of Pal for polymer nanocomposite are the primary development direction as confirmed by numerous researches. The disaggregation of Pal crystal bundles may disperse bulk particles as individual nanorods, which may be dispersed in polymer matrix more easily. The better dispersion of Pal rods in polymer matrix brings possibility to attain desirable hybrid properties, e.g., mechanical strength, thermal stability, bioactivity, light-resistance, and anti-aging performance. “From nature, for nature, and into nature” will be the sustainable subject in the future, and the disaggregation of Pal crystal bundles as individual nanorods will ignite their future applications for nanocomposites.

Abbreviations

1D	one-dimensional
3D	three-dimensional
Pal	palygorskite
Pal/Fe ₃ O ₄ /AuNPs	palygorskite/ferroferric oxide/gold nanoparticles
Pal/AgNPs	palygorskite/silver nanoparticles
Pal/Fe ₃ O ₄ /polyaniline/AuNPs	palygorskite/ferroferric oxide/polyaniline/gold nanoparticles
DMSO	dimethyl sulfoxide
Fe ₃ O ₄ /Pal@(CS/Cys-β-CD) ₈	ferroferric oxide/palygorskite@(chitosan/ L-cysteine-β-cyclodextrin) ₈
MB/Pal	methylene blue/palygorskite
PVA/CS	poly(vinyl alcohol)/chitosan
NaAlg-g-P(NaA-co-St)/Pal	sodium alginate-graft-poly(sodium acrylate-co-styrene)/palygorskite

Acknowledgment

The authors would like to thank the “863” Project of the Ministry of Science and Technology, PR China (No. 2013AA032003) and the National Natural Science Foundation of China (No. 21377135, U1407114 and 51403221) for financial support of this research.

References

- Abdo, J., 2014. Nano-attapulgite for improved tribological properties of drilling fluids. *Surf. Interface Anal.* 46, 882–887.
- Abdo, J., Haneef, M.D., 2013. Clay nanoparticles modified drilling fluids for drilling of deep hydrocarbon wells. *Appl. Clay Sci.* 86, 76–82.
- Aguzzi, C., Cerezo, P., Vieras, C., Caramella, C., 2007. Use of clays as drug delivery systems: possibilities and limitations. *Appl. Clay Sci.* 36, 22–36.
- Alcántara, A.C.S., Darder, M., Aranda, P., Ruiz-Hitzky, E., 2014. Polysaccharide–fibrous clay bionanocomposites. *Appl. Clay Sci.* 96, 2–8.
- Al-Futaisi, A., Jamrah, A., Al-Hanai, R., 2007. Aspects of cationic dye molecule adsorption to palygorskite. *Desalination* 214, 327–342.
- An, L., Pan, Y.Z., Shen, X.W., Lu, H.B., Yang, Y.L., 2008. Rod-like attapulgite/polyimide nanocomposites with simultaneously improved strength, toughness, thermal stability and related mechanisms. *J. Mater. Chem.* 18, 4928–4941.
- Baltar, C.A.M., Benvindo da Luz, A., Baltar, L.M., de Oliveira, C.H., Bezerra, F.J., 2009. Influence of morphology and surface charge on the suitability of palygorskite as drilling fluid. *Appl. Clay Sci.* 42, 597–600.
- Barrios, M.S., Gonzhlez, L.V.F., Rodriguez, M.A.V., Pozas, J.M.M., 1995. Acid activation of a palygorskite with HCl: development of physico-chemical, textural and surface properties. *Appl. Clay Sci.* 10, 247–258.
- Barzegar, H., Azizi, M.H., Barzegar, M., Hamidi-Esfahani, Z., 2014. Effect of potassium sorbate on antimicrobial and physical properties of starch–clay nanocomposite films. *Carbohydr. Polym.* 110, 26–31.
- Bergaya, F., Lagaly, G. (Eds.), 2013. *Handbook of Clay Science, 2nd ed Developments in Clay Science vol. 5*. Elsevier, Amsterdam.
- Boudriche, L., Calvet, R., Hamdi, B., Balard, H., 2012. Surface properties evolution of attapulgite by IGC analysis as a function of thermal treatment. *Colloids Surf. A* 399, 1–10.
- Boudriche, L., Chamayou, A., Calvet, R., Hamdi, B., Balard, H., 2014. Influence of different dry milling processes on the properties of an attapulgite clay, contribution of inverse gas chromatography. *Powder Technol.* 254, 352–363.
- Bradley, W.F., 1940. The structure scheme of attapulgite. *Am. Mineral.* 25, 405–410.
- Cai, X., Zhang, J., Ouyang, Y., Ma, D., Tan, S., Peng, Y., 2013. Bacteria-adsorbed palygorskite stabilizes the quaternary phosphonium salt with specific-targeting capability, long-term antibacterial activity, and lower cytotoxicity. *Langmuir* 29, 5279–5285.
- Cao, E., Bryant, R., Williams, D.J.A., 1996. Electrochemical properties of Na-attapulgite. *J. Colloid Interface Sci.* 179, 143–150.
- Carrado, K.A., 2000. Synthetic organo- and polymer-clays: preparation, characterization, and materials applications. *Appl. Clay Sci.* 17, 1–23.
- Chae, H.S., Zhang, W.L., Piao, S.H., Choi, H.J., 2015. Synthesized palygorskite/polyaniline nanocomposite particles by oxidative polymerization and their electrorheology. *Appl. Clay Sci.* 107, 165–172.
- Chemedá, Y.C., Christidis, G.E., Khan, N.M.T., Koutsopoulou, E., Hatzistamou, V., Kelesidis, V.C., 2014. Rheological properties of palygorskite–bentonite and sepiolite–bentonite mixed clay suspensions. *Appl. Clay Sci.* 90, 165–174.
- Chen, R.F., Wang, C.A., Huang, Y., Ma, L.G., Lin, W.Y., 2007. Ceramics with special porous structures fabricated by freeze-gelcasting: using tert-butyl alcohol as a template. *J. Am. Ceram. Soc.* 90, 3478–3484.
- Chen, J., Jin, Y.L., Qian, Y.H., Hu, T., 2010. New approach to efficiently disperse aggregated palygorskite into single crystals via adding freeze process into traditional extrusion treatment. *IEEE Trans. Nanotechnol.* 9, 6–10.
- Chen, F., Lou, D., Yang, J.T., Zhong, M.Q., 2011. Mechanical and thermal properties of attapulgite clay reinforced polymethylmethacrylate nanocomposites. *Polym. Adv. Technol.* 22, 1912–1918.
- Chen, L., Liu, K., Jin, T.X., Chen, F., Fu, Q., 2012. Rod like attapulgite/poly(ethylene terephthalate) nanocomposites with chemical bonding between the polymer chain and the filler. *Express Polym. Lett.* 6, 629–638.
- Chen, Q., Jin, Y.L., Lu, Q.M., Ding, S.J., Jiang, J.L., Chen, J., 2014. Nano-dispersion behavior and crystal-bundles dissociation of palygorskite under water. *J. China Univ. Min. Technol. (Chin.)* 43, 521–525.
- Cheng, Q.H., Debnath, S., Gregan, E., Byrne, H.J., 2010. Ultrasound-assisted SWNTs dispersion: effects of sonication parameters and solvent properties. *J. Phys. Chem. C* 114, 8821–8827.
- Chisholm, J.E., 1990. An X-ray diffraction study of palygorskite. *Can. Mineral.* 28, 329–339.
- Chisholm, J.E., 1992. Powder diffraction patterns and structural models of palygorskite. *Can. Mineral.* 30, 61–73.
- Choudalakis, G., Gotsis, A.D., 2009. Permeability of polymer/clay nanocomposites: a review. *Eur. Polym. J.* 45, 967–984.
- Chowdhury, S.R., Sabharwal, S., 2011. Molecular-scale design of a high performance organic–inorganic hybrid with the help of gamma radiation. *J. Mater. Chem.* 21, 6999–7006.
- Chrysoskos, G.D., Gionis, V., Kacandes, G.H., Stathopoulou, E.T., Suarez, M., Garcia-Romero, E., del Rio, M.S., 2009. Octahedral cation distribution in palygorskite. *Am. Mineral.* 94, 200–203.
- Corma, A., Mifsud, A., Sanz, E., 1987. Influence of the chemical composition and textural characteristics of palygorskite on the acid leaching of octahedral cations. *Clay Miner.* 22, 225–232.
- Darvishi, Z., Morsali, A., 2011. Sonochemical preparation of palygorskite nanoparticles. *Appl. Clay Sci.* 51, 51–53.
- Dean, J.A., 1999. *Lange's Handbook of Chemistry*. 15th edition. McGraw-Hill Inc., New York.
- Doménech, A., Doménech-Carbó, M.T., del Río, M.S., de Agredos Pascual, M.L.V., 2009. Comparative study of different indigo-clay Maya Blue-like systems using the voltammetry of microparticles approach. *J. Solid State Electrochem.* 13, 869–878.
- Drits, V.A., Sokolova, G.V., 1971. Structure of palygorskite. *Sov. Phys. Crystallogr.* 16, 183–185.
- Duke, J.B., Greene, E.W., 1963. Attapulgite Clay Filter Aid Product and Method of Making Same (US, 3080214A).
- Faraz, M.I., Besseling, N.A.M., Korobko, A.V., Picken, S.J., 2014. Structure–property relationships and modeling of the mechanical properties of a high-temperature resistant thermoset nanocomposite. *Compos. Part B Eng.* 56, 9–14.
- Feng, E.K., Ma, G.F., Wu, Y.J., Wang, H.P., Lei, Z.Q., 2014. Preparation and properties of organic–inorganic composite superabsorbent based on xanthan gum and loess. *Carbohydr. Polym.* 111, 463–468.
- Floury, J., Desrumaux, A., Legrand, J., 2002. Effect of ultra-high-pressure homogenization on structure and on rheological properties of soy protein-stabilized emulsions. *J. Food Sci.* 67, 3388–3395.
- Freudig, B., Tesch, S., Schubert, H., 2003. Production of emulsions in high pressure homogenizers—Part II: influence of cavitation on droplet breakup. *Eng. Life Sci.* 3, 266–270.
- Galán, E., 1996. Properties and applications of palygorskite–sepiolite. *Clay Clay Miner.* 31, 443–454.
- Galán, E., Carretero, M.L., 1999. A new approach to compositional limits for sepiolite and palygorskite. *Clay Clay Miner.* 47, 399–409.
- Galán, E., Aparicio, P., Miras, A., 2011. Sepiolite and palygorskite as sealing materials for the geological storage of carbon dioxide. In: Galán, E., Singer, A. (Eds.), *Developments in Palygorskite–Sepiolite Research*. Elsevier, Amsterdam, The Netherlands, pp. 375–392 (Chapter 16).
- Gao, G.R., Du, G.L., Cheng, Y.J., Fu, J., 2014. Tough nanocomposite double network hydrogels reinforced with clay nanorods through covalent bonding and reversible chain adsorption. *J. Mater. Chem. B* 2, 1539–1548.
- García-Lopez, D., Fernandez, J.F., Merino, J.C., Pastor, J.M., 2013. Influence of organic modifier characteristic on the mechanical properties of polyamide 6/organosepiolite nanocomposites. *Compos. Part B Eng.* 45, 459–465.
- García-Romero, E., Suárez, M., 2013. Sepiolite–palygorskite: textural study and genetic considerations. *Appl. Clay Sci.* 86, 129–144.
- García-Romero, E., Suárez, M., 2014. Sepiolite–palygorskite polysomatic series: oriented aggregation as a crystal growth mechanism in natural environments. *Am. Mineral.* 99, 1653–1661.
- Giannakas, A., Grigoriadi, K., Leontiou, A., Barkoula, N.M., Ladavos, A., 2014. Preparation, characterization, mechanical and barrier properties investigation of chitosan-clay nanocomposites. *Carbohydr. Polym.* 108, 103–111.
- Giustetto, R., Chiari, G., 2004. Crystal structure refinements of palygorskite and Maya Blue from molecular modeling and powder synchrotron diffraction. *Eur. J. Mineral.* 16, 521–532.
- Giustetto, R., Wahyudi, O., 2011. Sorption of red dyes on palygorskite: synthesis and stability of red/purple Mayan nanocomposites. *Microporous Mesoporous Mater.* 142, 221–235.
- Giustetto, R., Vitillo, J.G., Corazzari, I., Turci, F., 2014. Evolution and reversibility of host/guest interactions with temperature changes in a Methyl Red@palygorskite polyfunctional hybrid nanocomposite. *J. Phys. Chem. C* 118, 19322–19337.
- Gonzalez, F., Pesquera, C., Blanco, C., Benito, I., Mendioroz, S., Pajares, J.A., 1989. Structural and textural evolution of Al- and Mg-rich palygorskites, I. Under acid treatment. *Appl. Clay Sci.* 4, 373–388.
- Güven, N., 1992. The coordination of aluminium ions in the palygorskite structure. *Clay Clay Miner.* 40, 457–461.
- Haden Jr., W.L., 1963. Palygorskite: properties and uses. *Clay Clay Miner.* 284–290.
- Haden, W.L., Schwint, I.A., 1967. Attapulgite: its properties and applications. *Ind. Eng. Chem.* 59, 58–69.
- Han, S., Liu, F., Wu, J., Zhang, Y., Xie, Y.J., Wu, W.Y., Liu, W.S., Wang, Q., Tang, Y., 2014a. Targeting of fluorescent palygorskite polyethyleneimine nanocomposite to cancer cells. *Appl. Clay Sci.* 101, 567–573.
- Han, J., Xu, Y.M., Liang, X.F., Xu, Y.J., 2014b. Sorption stability and mechanism exploration of palygorskite as immobilization agent for Cd in polluted soil. *Water Air Soil Pollut.* 225, 2160.
- He, X., Yang, H.M., 2014. A novel strategy to the synthesis of Na₃YSi₂O₇ from natural palygorskite. *Appl. Clay Sci.* 101, 339–344.
- Huang, D.J., Wang, W.B., Xu, J.X., Wang, A.Q., 2012. Mechanical and water resistance properties of chitosan/poly (vinyl alcohol) films reinforced with attapulgite dispersed by high-pressure homogenization. *Chem. Eng. J.* 210, 166–172.
- Huo, C.L., Yang, H.M., 2013. Preparation and enhanced photocatalytic activity of Pd–CuO/palygorskite nanocomposites. *Appl. Clay Sci.* 74, 87–94.
- Jacobs, D.A., Hamill, H.R., 1970. Attapulgite clay dispersions and preparation thereof. US patent, 3509066DA.
- Jiang, J.L., Xu, Y., Duanmu, C.S., Gu, X., Chen, J., 2014. Preparation and catalytic properties of sulfonated carbon–palygorskite solid acid catalyst. *Appl. Clay Sci.* 95, 260–264.
- Jin, Y.L., Qian, Y.H., Zhu, H.F., Yao, H.Q., Zhao, Y.P., 2004. Effect of ultrafine grinding on the crystal structure and morphology of attapulgite clay. *Non-Met. Mines (Chin.)* 27 (3), 14–15 (27).
- Jin, T., Cheng, Y.C., He, R., Luo, Y.X., Jiang, M., Chen, C., Xu, G.J., 2014. Electric-field-induced structure and optical properties of electrorheological fluids with attapulgite nanorods. *Smart Mater. Struct.* 23, 075005.
- Jones, B.F., Galan, E., 1988. Palygorskite and sepiolite. In: Bailey, S.W. (Ed.), *Hydrous Phyllosilicates—Reviews in Mineralogy* 19. Mineralogical Society of America, Washington, pp. 631–674.
- Kabiri, K., Omidian, H., Zohuriaan-Mehr, M.J., Doroudiani, S., 2011. Superabsorbent hydrogel composites and nanocomposites: a review. *Polym. Compos.* 32, 277–289.
- Kasai, E., Mimura, H., Sugiyama, K., Saito, F., Akiba, K., Waseda, Y., 1994. Mechanochemical changes in natural and synthetic zeolites by dry grinding using a planetary ball mill. *Adv. Powder Technol.* 5, 189–203.

- Kong, Y., Ge, H.L., Xiong, J.X., Zuo, S.X., Wei, Y., Yao, Chao, Deng, L.D., 2014. Palygorskite polypyrrole nanocomposite: a new platform for electrically tunable drug delivery. *Appl. Clay Sci.* 99, 119–124.
- Krause, B., Villmow, T., Boldt, R., Mende, M., Petzold, G., Pötschke, P., 2011. Influence of dry grinding in a ball mill on the length of multiwalled carbon nanotubes and their dispersion and percolation behaviour in melt mixed polycarbonate composites. *Compos. Sci. Technol.* 71, 1145–1153.
- Krekeler, M.P.S., Guggenheim, S., 2008. Defects in microstructure in palygorskite–sepiolite minerals: a transmission electron microscopy (TEM) study. *Appl. Clay Sci.* 39, 98–105.
- Lander, R., Manger, W., Scouloudis, M., Ku, A., Davis, C., Lee, A., 2000. Gaulin homogenization: a mechanistic study. *Biotechnol. Prog.* 16, 80–85.
- Leitão, I.M., Seixas de Melo, J.S., 2013. Maya Blue, an ancient guest–host pigment: synthesis and models. *J. Chem. Educ.* 90, 1493–1497.
- Li, B.C., Zhang, J.P., Wu, L., Wang, A.Q., 2013. Durable superhydrophobic surfaces prepared via spray coating of polymerized organosilanes/attapulgite nanocomposites. *ChemPlusChem* 78, 1503–1509.
- Li, Z.H., Liu, F.H., Xu, G.J., Zhang, J.L., Chu, C.Y., 2014. A kinetics-controlled coating method to construct 1D attapulgite @ amorphous titanium oxide nanocomposite with high electrorheological activity. *Colloid Polym. Sci.* 292, 3327–3335.
- Liang, X.F., Xu, Y.M., Tan, X., Wang, L., Sun, Y.B., Lin, D.S., Sun, Y., Qin, X., Wang, Q., 2013. Heavy metal adsorbents mercapto and amino functionalized palygorskite: preparation and characterization. *Colloids Surf. A* 426, 98–105.
- Liu, P., 2007. Polymer modified clay minerals: a review. *Appl. Clay Sci.* 38, 64–76.
- Liu, Y.S., Liu, P., Su, Z.X., 2008. Thermal stabilities of attapulgite/polystyrene (ATP/PS) nanocomposites via microwave-assisted bulk polymerization. *J. Dispersion Sci. Technol.* 29, 478–481.
- Liu, Y., Wang, W.B., Wang, A.Q., 2012. Effect of dry grinding on the microstructure of palygorskite and adsorption efficiency for methylene blue. *Powder Technol.* 225, 124–129.
- Liu, H.B., Chen, T.H., Chang, D.Y., Chen, D., He, H.P., Yuan, P., Xie, J.J., Frost, R.L., 2013. Characterization and catalytic performance of Fe₃Ni₈/palygorskite for catalytic cracking of benzene. *Appl. Clay Sci.* 74, 135–140.
- Liu, P., Jiang, L.P., Zhu, L.X., Wang, A.Q., 2014a. Novel approach for attapulgite/poly(acrylic acid) (ATP/PAA) nanocomposite microgels as selective adsorbent for Pb(II) ion. *React. Funct. Polym.* 74, 72–80.
- Liu, P., Zhu, L.X., Guo, J.S., Wang, A.Q., Zhao, Y., Wang, Z.R., 2014b. Palygorskite/polystyrene nanocomposites via facile *in-situ* bulk polymerization: gelation and thermal properties. *Appl. Clay Sci.* 100, 95–101.
- Liu, Y., Xu, J.X., Wang, W.B., Wang, A.Q., 2014c. Effects of sodium salts organic acids modification on the microstructure and dispersion behavior of palygorskite nano-powder via high-pressure homogenization process. *J. Dispersion Sci. Technol.* 35, 840–847.
- Lopez-Galindo, A., Viseras, C., Cerezo, P., 2007. Compositional, technical and safety specifications of clays to be used as pharmaceutical and cosmetic products. *Appl. Clay Sci.* 36, 51–63.
- Lu, H., Xu, H., Chen, Y., Zhang, J., Zhuang, J., 2014a. ZVI/PANI/ATP composite by static polymerization as adsorbent for removal of Cr (VI). *RSC Adv.* 4, 5873–5879.
- Lu, J., Tian, X.X., Jin, Y.L., Chen, J., Walters, K.B., Ding, S.J., 2014b. A pH responsive pickering emulsion stabilized by fibrous palygorskite particles. *Appl. Clay Sci.* 102, 113–120.
- Luo, S.P., Chen, Y., Zhou, M., Yao, C., Xi, H.T., Kong, Y., Deng, L.H., 2013. Palygorskite-poly(o-phenylenediamine) nanocomposite: an enhanced electrochemical platform for glucose biosensing. *Appl. Clay Sci.* 86, 59–63.
- Lvov, Y., Abdullayev, E., 2013. Functional polymer-clay nanotube composites with sustained release of chemical agents. *Prog. Polym. Sci.* 38, 1690–1719.
- Mckeown, D.A., Post, J.E., Etz, E.S., 2002. Vibrational analysis of palygorskite and sepiolite. *Clay Miner.* 50, 667–680.
- Mohr, K.H., 1987. High-pressure homogenization. Part I. Liquid–liquid dispersion in turbulence fields of high energy density. *J. Food Eng.* 6, 177–186.
- Mu, B., Wang, A.Q., 2015. One-pot fabrication of multifunctional superparamagnetic attapulgite/Fe₃O₄/polyaniline nanocomposites served as adsorbent and catalyst support. *J. Mater. Chem. A* 3, 281–289.
- Mu, B., Kang, Y.R., Wang, A.Q., 2013. Preparation of a polyelectrolyte-coated magnetic attapulgite composite for the adsorption of precious metals. *J. Mater. Chem. A* 1, 4804–4811.
- Muller, P., Kapin, E., Fekete, E., 2014. Effects of preparation methods on the structure and mechanical properties of wet conditioned starch/montmorillonite nanocomposite films. *Carbohydr. Polym.* 113, 569–576.
- Murray, H.H., 2000. Traditional and new applications for kaolin, smectite, and palygorskite: a general overview. *Appl. Clay Sci.* 17, 207–221.
- Nan, F., Xu, Y., Xu, B.S., Gao, F., Wu, Y.X., Tang, X.H., 2014. Effect of natural attapulgite powders as lubrication additive on the friction and wear performance of a steel tribo-pair. *Appl. Surf. Sci.* 307, 86–91.
- Oliveira, R.N., Acchar, W., Soares, G.D.A., Barreto, L.S., 2013a. The increase of surface area of a Brazilian palygorskite clay activated with sulfuric acid solutions using a factorial design. *Mater. Res.* 16, 924–928.
- Oliveira, A.M.B.M., Coelho, L.F.O., Gomes, S.S.S., Costa, I.F., Fonseca, M.G., de Sousa, K.S., Espinola, J.G.P., da Silva, E.C., 2013b. Brazilian palygorskite as adsorbent for metal ions from aqueous solution-kinetic and equilibrium studies. *Water Air Soil Pollut.* 224, 1687.
- Papoulis, D., Komarneni, S., Panagiotaras, D., Nikolopoulou, A., Li, H.H., Shu, Y., Tsugio, S., Katsuki, H., 2013. Palygorskite–TiO₂ nanocomposites: Part 1. Synthesis and characterization. *Appl. Clay Sci.* 83–84, 191–197.
- Paquet, H., Duplay, J., Valleron-blanc, M.M., Millot, G., 1987. Octahedral composition of individual particles in smectite–palygorskite and smectite–sepiolite assemblages. *Proc. Int. Clay Conf. Denver*, pp. 73–77.
- Parker, D., Ruff, D., Sampson, P., 2000. U.S. Patent No. 6,130,179. Washington, DC: U.S. Patent and Trademark Office.
- Pavlidou, S., Papispyrides, C.D., 2008. A review on polymer-layered silicate nanocomposites. *Prog. Polym. Sci.* 33, 1119–1198.
- Peng, L.Q., Zhou, L.C., Li, Y.F., Pan, F., Zhang, S.D., 2011. Synthesis and properties of water-borne polyurethane/attapulgite nanocomposites. *Compos. Sci. Technol.* 71, 1280–1285.
- Peters, D., 1996. Ultrasound in materials chemistry. *J. Mater. Chem.* 6, 1605–1618.
- Quan, G.X., Zhang, J., Guo, J., Lan, Y.Q., 2014. Removal of Cr(VI) from aqueous solution by nanoscale zero-valent iron grafted on acid-activated attapulgite. *Water Air Soil Pollut.* 225, 1979.
- Rashidzadeh, A., Olad, A., 2014. Slow-released NPK fertilizer encapsulated by NaAlg-g-poly(AA-co-AAm)/MMT superabsorbent nanocomposite. *Carbohydr. Polym.* 114, 269–278.
- Reinen, D., Köhl, P., Müller, C., 2004. Colour centres in 'Maya Blue'—the incorporation of organic pigment molecules into the palygorskite lattice. *Z. Anorg. Allg. Chem.* 630, 97–103.
- Ruiz-Hitzky, E., Darder, M., Fernandes, F.M., Wicklein, B., Alcântara, A.C.S., Aranda, P., 2013. Fibrous clays based bionanocomposites. *Prog. Polym. Sci.* 38, 1392–1414.
- Sadeghipour, H., Ebadi-Dehaghani, H., Ashouri, D., Mousavian, S., Hashemi-Fesharaki, M., Gahrouei, M.S., 2013. Effects of modified and non-modified clay on the rheological behavior of high density polyethylene. *Compos. Part B Eng.* 52, 164–171.
- Sampson, P., Parker, D., Ruff, D., 1998. Purified attapulgite clay. US patent, 6130179.
- Sánchez-Soto, P.J., Jiménez, Carmen, de Haro, M., Pérez-Maqueada, L.A., Varona, I., Pérez-Rodríguez, J.L., 2000. Effects of dry grinding on the structural changes of kaolinite powders. *J. Am. Ceram. Soc.* 83, 1649–1657.
- Sanz, E., Arteaga, A., García, M.A., Cámara, C., Dietz, C., 2012. Chromatographic analysis of indigo from Maya Blue by LC–DAD–QTOF. *J. Archaeol. Sci.* 39, 3516–3523.
- Sarkar, B., Megharaj, M., Xi, Y.F., Naidu, R., 2012. Surface charge characteristics of organo-palygorskites and adsorption of p-nitrophenol in flow-through reactor system. *Chem. Eng. J.* 185, 35–43.
- Schultz, S., Wagner, G., Urban, K., Ulrich, J., 2004. High-pressure homogenization as a process for emulsion formation. *Chem. Eng. Technol.* 27, 361–368.
- Shah, Y.T., Pandit, A.B., Moholkar, V.S., 1999. Cavitation Reaction Engineering. Kluwer Academic/Plenum Publishers, New York.
- Shi, X.N., Wang, W.B., Wang, A.Q., 2013. pH-responsive sodium alginate-based superporous hydrogel generated by an anionic surfactant micelle templating. *Carbohydr. Polym.* 94, 449–455.
- Sinha Ray, S., Bousmina, M., 2005. Biodegradable polymers and their layered silicate nanocomposites: in greening the 21st Century materials world. *Prog. Mater. Sci.* 50, 962–1079.
- Sinha Ray, S., Okamoto, M., 2003. Polymer/layered silicate nanocomposites: a review from preparation to processing. *Prog. Polym. Sci.* 28, 1539–1641.
- Su, D.H., Wang, C.H., Cai, S.M., Mu, C.D., Li, D.F., Lin, W., 2012. Influence of palygorskite on the structure and thermal stability of collagen. *Appl. Clay Sci.* 62–63, 41–46.
- Suárez, M., García-Romero, E., del Río, M.S., Martinetto, P., Dooryhée, E., 2007. The effect of octahedral cations on the dimensions of the palygorskite cell. *Clay Miner.* 42, 287–297.
- Tabata, M., Hosokawa, Y., Watanabe, O., Sohma, J., 1986. Direct evidence for main chain scissions of polymers in solution caused by high speed stirring. *Polym. J.* 18, 699–712.
- Tang, A., Su, L., Li, C., 2012. Effect of dry grinding on the physicochemical properties of silica materials prepared from kaolin residue. *Powder Technol.* 218, 86–89.
- Tang, Q.G., Yang, Y., Wang, F., Liang, X.H., Zhang, F.Q., Liang, J.S., 2014. Effect of acid on surface properties of modified attapulgite and performance of styrene butadiene rubber filled by modified attapulgite. *Nanosci. Nanotechnol. Lett.* 6, 231–237.
- Tang, Q.G., Wang, F., Guo, H., Yang, Y., Du, Y.L., Liang, J.S., Zhang, F.Q., 2015. Effect of coupling agent on surface free energy of organic modified attapulgite (OAT) powders and tensile strength of OAT/ethylene-propylene-diene monomer rubber nanocomposites. *Powder Technol.* 270, 92–97 (Part A).
- Viseras, C., Meeten, G.H., Lopez-Galindo, A., 1999. Pharmaceutical grade phyllosilicate dispersions: the influence of shear history on floc structure. *Int. J. Pharm.* 182, 7–20.
- Viseras, C., Aguzzi, C., Cerezo, P., Lopez-Galindo, A., 2007. Uses of clay minerals in semisolid health care and therapeutic products. *Appl. Clay Sci.* 36, 37–50.
- Wang, S., 2005. Effect of extrusion on the bond behavior of attapulgite clay. *China Non-Met. Min. Ind. Her. (Chin.)* 3, 23–24.
- Wang, J.H., Chen, D.J., 2013. Mechanical properties of natural rubber nanocomposites filled with thermally treated attapulgite. *J. Nanomater.* 496584.
- Wang, L., Sheng, J., 2006. A kinetic study on the thermal degradation of polypropylene/attapulgite nanocomposites. *J. Macromol. Sci. B* 45, 1–11.
- Wang, W.B., Wang, A.Q., 2009. Preparation, characterization and properties of superabsorbent nanocomposites based on natural guar gum and modified rectorite. *Carbohydr. Polym.* 77, 891–897.
- Wang, W.B., Wang, A.Q., 2010. Nanocomposite of carboxymethyl cellulose and attapulgite as a novel pH-sensitive superabsorbent: synthesis, characterization and properties. *Carbohydr. Polym.* 82, 83–91.
- Wang, A.Q., Zhang, J.P., 2006. Organic-Inorganic Superabsorbent Composites (Chinese). Science Press, Beijing, China.
- Wang, W.B., Zheng, Y.A., Wang, A.Q., 2008. Syntheses and properties of superabsorbent composites based on natural guar gum and attapulgite. *Polym. Adv. Technol.* 19, 1852–1859.
- Wang, F., Feng, L., Tang, Q.G., Liu, H.F., Liu, H.M., 2013a. Preparation and performance of cis-polybutadiene rubber composite materials reinforced by organic modified palygorskite nanomaterials. *J. Nanomater.* 936838.
- Wang, W.B., Huang, D.J., Kang, Y.R., Wang, A.Q., 2013b. One-step *in-situ* fabrication of a granular semi-IPN hydrogel based on chitosan and gelatin for fast and efficient adsorption of Cu²⁺ ion. *Colloids Surf. B* 106, 51–59.
- Wang, W.B., Kang, Y.R., Wang, A.Q., 2013c. One-step fabrication in aqueous solution of a granular alginate-based hydrogel for fast and efficient removal of heavy metal ions. *J. Polym. Res.* 20, 101 (10 pp.).

- Wang, W.B., Wang, F.F., Kang, Y.R., Wang, A.Q., 2013d. Facile self-assembly of Au nanoparticles on a magnetic attapulgite/Fe₃O₄ composite for fast catalytic decoloration of dye. *RSC Adv.* 3, 11515–11520.
- Wang, Y.Z., Wang, W.B., Shi, X.N., Wang, A.Q., 2013e. Enhanced swelling and responsive properties of an alginate-based superabsorbent hydrogel by sodium p-styrenesulfonate and attapulgite nanorods. *Polym. Bull.* 70, 1181–1193.
- Wang, Y.Z., Shi, X.N., Wang, W.B., Wang, A.Q., 2013f. Ethanol-assisted dispersion of attapulgite and its effect on improving properties of alginate-based superabsorbent nanocomposite. *J. Appl. Polym. Sci.* 129, 1080–1088.
- Wang, X.G., Lü, S.Y., Gao, C.M., Xu, X.B., Zhang, X.J., Bai, X., Liu, M.Z., Wu, L., 2014a. Highly efficient adsorption of ammonium onto palygorskite nanocomposite and evaluation of its recovery as a multifunctional slow-release fertilizer. *Chem. Eng. J.* 252, 404–414.
- Wang, W.B., Kang, Y.R., Wang, A.Q., 2014b. In-situ fabrication of Ag nanoparticles/attapulgite nanocomposites: green synthesis and catalytic application. *J. Nanopart. Res.* 16, 2281 (8 pp.).
- Wang, Q., Zhang, J.P., Wang, A.Q., 2014c. Freeze-drying: a versatile method to overcome re-aggregation and improve dispersion stability of palygorskite for sustained release of ofloxacin. *Appl. Clay Sci.* 87, 7–13.
- Wang, C.S., Wu, Q.S., Liu, F., An, J., Lu, R., Xie, H.F., Cheng, R.S., 2014d. Synthesis and characterization of soy polyol-based polyurethane nanocomposites reinforced with silylated palygorskite. *Appl. Clay Sci.* 101, 246–252.
- Wang, W.B., Tian, G.Y., Zhang, Z.F., Wang, A.Q., 2015a. A simple hydrothermal approach to modify palygorskite for high-efficient adsorption of methylene blue and Cu(II) ions. *Chem. Eng. J.* 265, 228–238.
- Wang, W.B., Wang, F.F., Kang, Y.R., Wang, A.Q., 2015b. Nanoscale dispersion crystal bundles of palygorskite by associated modification with phytic acid and high-pressure homogenization for enhanced colloidal properties. *Powder Technol.* 269, 85–92.
- Windsor, S.A., Tinker, M.H., 1999. Electro-fluorescence polarization studies of the interaction of fluorescent dyes with clay minerals in suspensions. *Colloids Surf. A* 148, 61–73.
- Xiang, Y., Wang, M., Sun, X., Cai, D., Wu, Z., 2014. Controlling pesticide loss through nano-networks. *ACS Sustain. Chem. Eng.* 2, 918–924.
- Xu, J.X., Wang, A.Q., 2012. Electrokinetic and colloidal properties of homogenized and unhomogenized palygorskite in the presence of electrolytes. *J. Chem. Eng. Data* 57, 1586–1593.
- Xu, J.X., Zhang, J.P., Wang, Q., Wang, A.Q., 2011. Disaggregation of palygorskite crystal bundles via high-pressure homogenization. *Appl. Clay Sci.* 54, 118–123.
- Xu, J.X., Wang, W.B., Mu, B., Wang, A.Q., 2012. Effects of inorganic sulfates on the microstructure and properties of ion-exchange treated palygorskite clay. *Colloids Surf. A* 45, 59–64.
- Xu, J.X., Wang, W.B., Wang, A.Q., 2013a. Superior dispersion properties of palygorskite in dimethyl sulfoxide via high-pressure homogenization process. *Appl. Clay Sci.* 86, 174–178.
- Xu, J.X., Wang, W.B., Wang, A.Q., 2013b. Effects of solvent treatment and high-pressure homogenization process on dispersion properties of palygorskite. *Powder Technol.* 235, 652–660.
- Xu, J.X., Wang, W.B., Wang, A.Q., 2013c. Influence of anions on the electrokinetic and colloidal properties of palygorskite clay via high-pressure homogenization. *J. Chem. Eng. Data* 58, 764–772.
- Xu, J.X., Wang, W.B., Wang, A.Q., 2013d. A novel approach for dispersion palygorskite aggregates into nanorods via adding freezing process into extrusion and homogenization treatment. *Powder Technol.* 249, 157–162.
- Xu, J.X., Wang, W.B., Wang, A.Q., 2014a. Effect of squeeze, homogenization, and freezing treatments on particle diameter and rheological properties of palygorskite. *Adv. Powder Technol.* 25, 968–977.
- Xu, J.X., Wang, W.B., Wang, A.Q., 2014b. Enhanced microscopic structure and properties of palygorskite by associated extrusion and high-pressure homogenization process. *Appl. Clay Sci.* 95, 365–370.
- Xu, J.X., Wang, W.B., Wang, A.Q., Zheng, M.S., 2014c. Dispersion of palygorskite in ethanol–water mixtures via high-pressure homogenization: microstructure and colloidal properties. *Powder Technol.* 261, 98–104.
- Yang, Q.L., Wu, C.N., Saito, T., Isogai, A., 2014. Cellulose-clay layered nanocomposite films fabricated from aqueous cellulose/LiOH/urea solution. *Carbohydr. Polym.* 100, 179–184.
- Yasmin, A., Abot, J.L., Daniel, I.M., 2003. Processing of clay/epoxy nanocomposites by shear mixing. *Scr. Mater.* 49, 81–86.
- Zha, F., Huang, W.Y., Wang, J.Y., Chang, Y., Ding, J., Ma, J., 2013. Kinetic and thermodynamic aspects of arsenate adsorption on aluminum oxide modified palygorskite nanocomposites. *Chem. Eng. J.* 215–216, 579–585.
- Zhang, J., Cai, D.Q., Zhang, G.L., Cai, C.J., Zhang, C.L., Qiu, G.N., Zheng, K., Wu, Z.Y., 2013. Adsorption of methylene blue from aqueous solution onto multiporous palygorskite modified by ion beam bombardment: effect of contact time, temperature, pH and ionic strength. *Appl. Clay Sci.* 83–84, 137–143.
- Zhang, S., Wang, W., Wang, H., Qi, W., Yue, L., Ye, Q., 2014a. Synthesis and characterisation of starch grafted superabsorbent via 10 MeV electron-beam irradiation. *Carbohydr. Polym.* 101, 798–803.
- Zhang, H.R., Yang, H.J., Guo, H.J., Yang, J., Xiong, L., Huang, C., Chen, X.D., Ma, L.L., Chen, Y., 2014b. Solvent-free selective epoxidation of soybean oil catalyzed by peroxophosphotungstate supported on palygorskite. *Appl. Clay Sci.* 90, 175–180.
- Zhang, Y., Wang, W.B., Mu, B., Wang, Q., Wang, A.Q., 2015. Effect of grinding time on fabricating a stable methylene blue/palygorskite hybrid nanocomposites. *Powder Technol.* 280, 173–179.
- Zhao, G.Z., Shi, L.Y., Feng, X., Yu, W.J., Zhang, D.S., Fu, J.F., 2012. Palygorskite-cerium oxide filled rubber nanocomposites. *Appl. Clay Sci.* 67–68, 44–49.
- Zheng, Y.A., Wang, A.Q., 2012. Granular hydrogel initiated by Fenton's reagent and their performance on Cu(II) and Ni(II) removal. *Chem. Eng. J.* 200–202, 601–610.
- Zheng, Y.A., Wang, W.B., Zhu, G., Wang, A.Q., 2013. Enhanced selectivity for heavy metals using polyaniline modified hydrogel. *Ind. Eng. Chem. Res.* 52, 4957–4961.
- Zheng, Y.A., Zhu, Y.F., Wang, A.Q., 2014. Highly efficient and selective adsorption of malachite green onto granular composite hydrogel. *Chem. Eng. J.* 257, 66–73.
- Zhou, C.H., Keeling, J., 2013. Fundamental and applied research on clay minerals: from climate and environment to nanotechnology. *Appl. Clay Sci.* 74, 3–9.