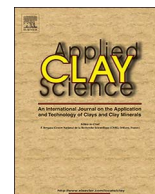




Contents lists available at ScienceDirect

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## Research paper

# Effects of modification of palygorskite on superamphiphobicity and microstructure of palygorskite@fluorinated polysiloxane superamphiphobic coatings

Penglin Zhang<sup>a</sup>, Ning Tian<sup>a,b,c</sup>, Junping Zhang<sup>b,c,\*</sup>, Aiqin Wang<sup>b,c</sup><sup>a</sup> College of Material Science and Engineering, Lanzhou University of Technology, Lanzhou 730050, PR China<sup>b</sup> Key Laboratory of Clay Mineral Applied Research of Gansu Province, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China<sup>c</sup> State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China

## ARTICLE INFO

## Keywords:

Attapulgite  
Superhydrophobic  
Superoleophobic  
Contact angle  
Wettability

## ABSTRACT

Palygorskite (PAL) is a promising natural clay mineral for the preparation of bionic super anti-wetting coatings, a new application field of PAL. Here, the effects of modification of PAL on superamphiphobicity and microstructure of the PAL@fluorinated polysiloxane (PAL@fluoroPOS) superamphiphobic coatings were systematically studied. First, PAL was modified via acid activation, solid-state grinding and heat activation. Then, the PAL@fluoroPOS coatings were prepared by hydrolytic condensation of 1H,1H,2H,2H-perfluorodecyltriethoxysilane and tetraethoxysilane onto the modified PAL, followed by spray-coating onto substrates. It was found that the microstructure of the coatings is controllable by acid activation and solid-state grinding. Acid activation with HCl at moderate conditions (2 M HCl, 15 °C) and grinding for a proper time (10 min) are helpful to improve superamphiphobicity of the coatings by forming smaller protrusions and micropores on the surface of the coatings. On the contrary, heat activation results in decline of the superamphiphobicity, especially at high temperature. The achieved coatings show excellent superamphiphobicity, and are mechanically robust and thermally stable, which can withstand intensive water jetting at 100 kPa for 20 min and 350 °C for 1 h. Moreover, the coatings can be applied onto various substrates like aluminum foil, PTFE plate, wood plate and polyester textile. We believe that the findings will promote the development of novel clay-based super anti-wetting coatings.

## 1. Introduction

Inspired by natural objects like lotus leaves (Neinhuis and Barthlott, 1997) and water strider legs (Gao and Jiang, 2004), superhydrophobic coatings with extremely high repellency to water are of great interests (Li et al., 2011; Chu and Seeger, 2015). Superhydrophobic coatings have a lot of potential applications, e.g., self-cleaning, corrosion resistance and oil/water separation, etc. However, superhydrophobic coatings can be easily contaminated by organic liquids of low surface tension, which seriously hinders their applications because there are different kinds of organic compounds in real-world surroundings. However, this problem can be solved if the coating could repel both water and organic liquids of low surface tension, i.e., superamphiphobic coatings. Obviously, superamphiphobic coatings have much more potential applications, but are more difficult to prepare theoretically and technically compared with superhydrophobic coatings

(Li and Zhang, 2016). This is because organic liquids often have much lower surface tension compared with water (Steele et al., 2008; Chu and Seeger, 2014). For example, the surface tension of *n*-decane and *n*-dodecane are 23.8 mN m<sup>-1</sup> and 28.4 mN m<sup>-1</sup>, respectively, whereas that of water is 72.8 mN m<sup>-1</sup>. When the surface tension of a liquid goes lower, a drop of the liquid tends to wet or even spread on a solid surface (Chen et al., 2015). As is well known, the combination of appropriate surface microstructures and materials of low surface tension is effective in preparing superhydrophobic coatings (Zhang et al., 2016). However, such simple combination is in most cases ineffective for preparing superamphiphobic coatings. The as-prepared superamphiphobic coatings often have high contact angles (CA) for organic liquids, but the liquids adhere stably on the coatings and cannot roll off. However, a low sliding angle (SA) is important for a superamphiphobic coating as this is closely related to its unique self-cleaning property and other representative applications. For the preparation of superamphiphobic

\* Corresponding author at: Key Laboratory of Clay Mineral Applied Research of Gansu Province, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China.

E-mail address: [jpzhang@licp.cas.cn](mailto:jpzhang@licp.cas.cn) (J. Zhang).

<https://doi.org/10.1016/j.clay.2018.01.015>

Received 26 September 2017; Received in revised form 11 January 2018; Accepted 17 January 2018  
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coatings with low SAs, some special micro-/nanostructures and materials of very low surface tension have been invented (Tuteja et al., 2007; Xu et al., 2011a; Liu and Kim, 2014). Zhang and Seeger fabricated transparent superamphiphobic coatings with low SAs even to *n*-decane based on silicone nanofilaments (Zhang and Seeger, 2011). Wong et al. prepared superamphiphobic coatings with re-entrant structure and trichlorosilane (Wong et al., 2017). In addition, low mechanical stability is a crucial issue for superamphiphobic coatings, which limits their widespread applications (Tian et al., 2016). Also, the preparation of superamphiphobic coatings is often complicated and expensive (Chu and Seeger, 2014).

In order to solve the issues in the field of superamphiphobic coatings and to obtain superamphiphobic coatings with excellent properties, we reported the first clay-based superamphiphobic coating. Durable and self-healing superamphiphobic coatings with high repellency to both cool and hot liquids have been successfully prepared by the combination of nanorod-like palygorskite (PAL) and organosilanes via spray-coating (Li and Zhang, 2016). The method can also be used to prepare magnetic liquid marbles (Li et al., 2016) and colorful superamphiphobic coatings (Dong et al., 2017). The PAL-based superamphiphobic coatings showed very low SAs even for *n*-decane and had high stability. Also, the coatings can be applied onto various substrates via simple spray-coating. These merits have paved the way for real-world applications of the PAL-based superamphiphobic coatings. We found that PAL has great influences on properties of the coatings because of its unique nanorod-like microstructure in comparison with other clay minerals (Lima et al., 2012). On the other hand, we know that the physicochemical properties and microstructure of PAL can be tailored by various approaches such as ultrasonication (Darvishi and Morsali, 2011; Yuan et al., 2017), acid activation (Zhang et al., 2010; Oliveira et al., 2013; Rusmin et al., 2016; Zhu et al., 2017), heat activation (Chen et al., 2011; Qiao et al., 2015; Biswas et al., 2016; Zeng et al., 2017) and grinding (Krause et al., 2011; Xu et al., 2011b), etc. These treatments should have some influences on properties of the PAL-based superamphiphobic coatings, and should be helpful for us to understand deeply the role of PAL in forming the superamphiphobic coatings.

Here, we studied the effects of acid activation, grinding and heat activation of PAL on superamphiphobicity and microstructure of superamphiphobic coatings based on PAL and fluorinated polysiloxane. The PAL@fluorinated polysiloxane (PAL/fluoroPOS) superamphiphobic coatings were fabricated by hydrolytic condensation of 1H,1H,2H,2H-perfluorodecyltriethoxysilane (PFDTES) and tetraethoxysilane (TEOS) onto PAL to form the homogeneous PAL@fluoroPOS suspensions, which were then spray-coated onto the substrates. The coatings show high CAs and low SAs for water and various organic liquids of low surface tension, such as *n*-hexadecane and *n*-decane. We found that acid activation and grinding of PAL could improve superamphiphobicity of the coatings, which are mechanically robust and thermally stable.

## 2. Materials and methods

### 2.1. Materials

Natural PAL was obtained from Xuyi, Jiangsu, China. TEOS (99.9%) and PFDTES (97%) were purchased from Gelest. Glass slides (24 mm × 50 mm, Menzel, Braunschweig, Germany) were used as the main substrates. *n*-Dodecane, anhydrous ethanol, ammonia, diiodomethane, *n*-hexadecane and *n*-decane were bought from China National Medicines Co. Ltd. The reagents used were all of analytical grade.

### 2.2. Acid activation, grinding and heat activation of PAL

First, the mixture of 680 g of natural PAL and 6.12 L of deionized water were mechanically stirred at 400 rpm for 2 h to form a stable suspension. The suspension was centrifuged at 1000 rpm for 10 min,

and the precipitant was removed. The purified PAL suspension was further centrifuged at 5000 rpm for 10 min, and then the precipitant was collected and dried at 105 °C to a constant weight. The purified PAL was crushed for 15 s using a pulverizer.

For acid activation, 15 g of the purified PAL was suspended in 150 mL of HCl aqueous solutions of different concentrations ( $C_{\text{HCl}} = 1, 2, 4, 6$  or 12 M) at room temperature (winter, ~15 °C), and stirred at 650 rpm for 2 h. Besides room temperature, the effects of acid activation temperature ( $T_a = 25, 50, 60, 70, 80$  or 90 °C) were also studied. The acid activated PAL (A-PAL) was washed with deionized water until pH 6 of the decanted water, and then dried at 105 °C to a constant weight.

For solid-state grinding, the A-PAL ( $C_{\text{HCl}} = 2$  M,  $T_a = 15$  °C) was ground manually for 1, 5, 10, 20 or 30 min to form the acid activated and ground samples (A-G-PAL).

For heat activation, the above A-G-PAL ( $t_{\text{grinding}} = 10$  min) was treated in a muffle furnace for 1 h at 200, 300, 400, 500, 600, 700 or 800 °C (A-G-H-PAL).

### 2.3. Preparation of PAL-based superamphiphobic coatings

0.5 g of the activated PAL was added into 43 mL of anhydrous ethanol and 7 mL of ammonia solution in a 100 mL conical flask. The suspension was ultrasonicated (200 W) at room temperature for 30 min, and then 50  $\mu\text{L}$  of TEOS and 0.6 mL of PFDTES were added in turn into the suspension. After reaction at room temperature for 3 h, the homogeneous PAL@fluoroPOS suspension was formed. 10 mL of the suspension was spray-coated onto the vertically placed substrates using an airbrush (INFINITY 2 in 1, Harder & Steenbeck, Germany) with 0.2 MPa  $\text{N}_2$ . The substrates were adhered onto a hot plate (150 °C) with double side tapes. The substrates are glass slide, textile, wood plate and aluminum foil, etc. The substrates were sequentially cleaned with ethanol and deionized water, and then dried under  $\text{N}_2$  flow.

### 2.4. Characterization

The surface morphology was observed by a field-emission scanning electron microscope (SEM, JSM-1736701F, JEOL). For SEM observation, the samples were fixed on copper stubs and coated with a layer of gold (~7 nm). The Fourier transform infrared (FTIR) spectra were recorded using a Thermo Nicolet Nexus spectrometer (Thermo, Madison, USA) in the range of 4000–400  $\text{cm}^{-1}$  using KBr pellets. The surface chemical composition was explored by X-ray photoelectron spectroscopy (XPS) with a VG Escalab 250 Xi spectrometer equipped with a monochromated Al  $K\alpha$  X-ray radiation source and a hemispherical electron analyzer. The XPS spectra were recorded in the constant pass energy mode with a value of 100 eV, and all binding energies were calibrated using the C 1s peak at 284.6 eV as the reference. The CAs and SAs of liquids of different surface tension were measured using a Contact Angle System OCA20 (Dataphysics, Germany) equipped with a tilting table at room temperature. The syringe was positioned in a way that the liquid droplets (5  $\mu\text{L}$ ) could contact surface of the samples before leaving the needle. Tilting angle of the table was adjustable (0–70°) and allowed the subsequent measurement of the SAs at the same position. A minimum of six readings were recorded for each sample, and the average values with standard errors were reported.

## 3. Results and discussion

### 3.1. Preparation of PAL-based superamphiphobic coatings

The schematic illustration of preparation of superamphiphobic coatings based on PAL, A-PAL, A-G-PAL and A-G-H-PAL is shown in Fig. 1. PAL is a kind of unique one-dimensional nanorod-like silicate clay mineral, which is suitable to build micro-/nanostructures of bionic super anti-wetting coatings (Vuong et al., 2013; Zhang et al., 2016).

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