



Full Length Article

Fabrication of recyclable and durable superhydrophobic materials with wear/corrosion-resistance properties from kaolin and polyvinylchloride



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ABSTRACT

In this study, mechanically stable and recyclable superhydrophobic materials were prepared from polyvinylchloride (PVC) and kaolin nanoparticles modified by stearic acid using a simple and low-cost drop-coating. The obtained materials displayed liquid-repellent toward water and several other liquids of daily life (such as orange juice, coffee, milk, coca cola and ink). These superhydrophobic materials showed remarkable robustness against sandpaper abrasion, UV-irradiation and ultrasonication test, while retaining its superhydrophobicity even after 60 abrasion cycles loaded of 500 g with sandpaper, 7 days UV-irradiation or 120 min ultrasonication test. The excellent durability against complex conditions was attributed to the hierarchical structure and strong interfacial adhesion of the materials. More significantly, the materials used in the coating could be recycled and reconstructed without losing its superhydrophobicity. The current superhydrophobic materials tolerate rigorous environment, opening a new avenue to a variety of practical applications.

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1. Introduction

Learning from nature is an important source of new techniques and advanced materials. A typical example of the superhydrophobic phenomenon, where a surface shows a contact angle of water greater than 150° , is an amazing occurrence in nature [1–3] which can be found on the leaves of plants [4,5], the legs of water strider [6], etc. Mimicking the lotus leaves surface morphology has led to the development of a number of artificial superhydrophobic surfaces using vapor deposition [7], sol-gel processing [8], chemical etching [9], electrospinning [10], laser etching [11], layer-by-layer self-assembly [12], and so on [13–15]. Due to the interesting and important properties, the superhydrophobic surfaces have been greatly anticipated to be used in applications such as drag reduction [16], anti-corrosion [17–20], anti-icing [21,22], anti-fogging [23], oil-water separation [24,25], and self-cleaning [26]. It is well known that two critical factors should be simultaneously satisfied for the preparation of superhydrophobic surfaces: (a) creation of a suitable roughness on hydrophobic surfaces, and (b) chemical modification

of rough surfaces with low surface energy substances [27]. The situation is, however, the practical applications of superhydrophobic surfaces have been hindered by unavoidable abrasion and corrosion [28]. Although many superhydrophobic coatings have been reported [29,30], the superhydrophobicity of these coatings cannot even withstand slight finger touch and friction [31]. Therefore, it is still a great challenge to prepare robust superhydrophobic surfaces for especially under the rigorous real application environment [3].

Surface roughness, the structure on the surface, is a key point in achieving surface superhydrophobicity regardless of how low the surface free energy is. Most of functional surfaces currently available can be easily damaged by routine use, resulting in the immediate loss of the chemical functionalities, surface-structure and related chemical/physical properties. The natural superhydrophobic plant leaves, however, have the ability to repair the surface structure and renew their hydrophobic layer. Up to date, the mechanical durability and many methods have been developed to enhance the durability of superhydrophobic surface [32–38], such as fabricating self-healing surfaces, enhancing the robustness of the hierarchical structure and fabricating with hydrophobic materials, have attracted the attention of many researchers. To improve the mechanical stability of these surface-coated layers, various strategies have been developed to enhance the mechanical prop-

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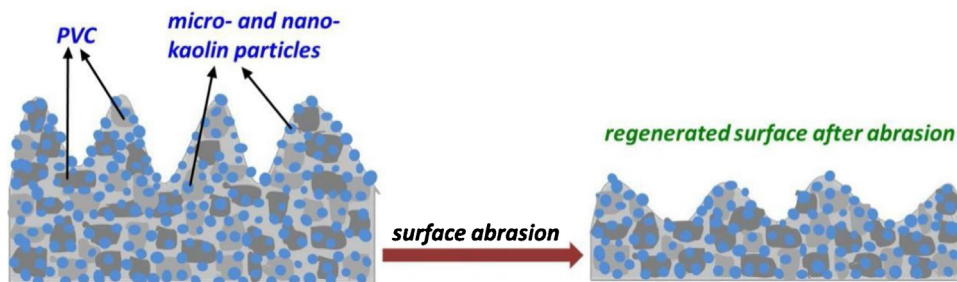


Fig. 1. Schematic representation of the anti-wear mechanism of the modified kaolin/PVC composite superhydrophobic material.

erties by introducing polymer or building a multi-level structure, which could weaken external force to the surface damage [39–41]. Furthermore, the formation of covalent bonds between low surface energy nano-particles and the modifier is considered to be an important method and has resulted in good improvement [42,43]. Different approaches have been described up to now in the literature for the fabrication of durable superhydrophobic surfaces. Xu et al. fabricated superhydrophobic polymer surfaces with excellent abrasion resistance by a simple lamination templating method [44]. The surfaces remained superhydrophobic after more than 5500 abrasion cycles at a pressure of 32.0 kPa. Chen and his co-workers reported a simple and cost-effective technical route for constructing superhydrophobic surfaces with excellent abrasion resistance on various substrates [45]. However, the poor mechanical stability and durability of these artificial superhydrophobic surfaces have also severely hindered their practical applications.

In this study, we adopted two strategies that inspired by the natural superhydrophobic plant leaves which can self-repair their micro- and nano-structures and can also recover the wax coating to simulate the key abilities of lotus leaves. The first strategy is to fabricate superhydrophobic material consisting of micro- and nano-scale structures through the whole material thickness which would expose and the new rough structures were regenerated after the surface abrasion. The second strategy is that the hydrophobic polyvinylchloride (PVC) are adopted and the newly exposed rough surface with PVC can be regarded as the new wax layer of the lotus leaf. The schematic representation of this mechanism is shown in Fig. 1. Kaolin is a natural nanomaterial frequently used for the reinforcement of polymers because of its high performance and low cost, but rarely used for designing multifunctional superhydrophobic materials [46,47]. This research opens a new window for versatile applications of superhydrophobic engineered materials.

2. Materials and methods

2.1. Materials

Kaolin particles of size 100–400 nm were purchased from Sinopharm Chemical Reagent Co., Ltd. And before used, they were dried at 120 °C for 5 h to remove water. Stearic acid purchased from Nanjing Daoning Chemical Co., Ltd. was used as received. All other reagents were AR grade and used as received. The polyvinylchloride (PVC) was purchased from Shaanxi North Yuan Chemical Group Co., Ltd. Ethanol and tetrahydrofuran (THF) were analytical and used as received without any purification.

2.2. Fabrication of the wear-resistance superhydrophobic materials

The first step, 0.32 g stearic acid was dissolved in 11 mL anhydrous ethanol at 40 °C for 20 min, and then 5.0 g kaolin particles were ultrasonically dispersed in the mixture. After 20 min, they

were heated at 106 °C for 2 h with magnetic stirring. Then the particles were collected by suction filtration using a sand core funnel. Finally, they were dried at 120 °C for 2 h to obtain the superhydrophobic kaolin particles.

The second step, 0.5 g PVC was dissolved in 10 mL THF at room temperature and 0.5 g modified kaolin particles were ultrasonically dispersed in 3 mL the mixture at least 20 min. Afterwards, this mixture was sealed and allowed to react for 6 h at 40 °C under magnetic stirring, and then drop-coated onto glass substrates (2.5 cm × 2.5 cm) carefully. The samples were dried under ambient conditions for one night covered with a suitably dish to slow down THF evaporation. Finally, the samples were cured for 2 h at 80 °C. After the samples cooling to room temperature, the surfaces were rubbed with 600 grit sandpaper.

2.3. Characterization

Water contact angle (WCA) and slide angle (SA) measurements were performed with an instrument (JC2000DM, China) at ambient temperature with a 5 μL deionized water droplet as the indicator. Water droplets less than 4 μL could not to be placed onto the surface because the adhesion force between the micro syringe tip and the water droplet. Each water contact angle value was an average value of at least five measurements on different locations of the surface. The sample surface morphology in top-view or in cross-sections was characterized with a scanning electron microscopy (SEM, JEOL JSM-6460LV). Before the SEM investigations, all the samples were coated with gold cluster. Nanostructure of the materials was visualized by bright-field images with a transmission electron microscope (TEM, JEOL JEM-3010). The chemical compositions of the samples were investigated with a Fourier-transform infrared spectrophotometer (FTIR, Perkin Elmer FTIR System 2000) and X-ray photoelectron spectrometer (XPS, K-Alpha of Thermo Electron Corporation). To investigate the mechanical stability of the fabricated samples using friction test was conducted by the sandpaper surface with varying applied pressure and distance with a speed of 10 mm/s. The pencil hardness tests for the coatings were carried out according to the standard of Wolff-Wilborn. It uses pencil to lead different hardness grades (6B–6H). UV-Durability was conducted by irradiation using an artificial light source (UV lamp) emitting a Gaussian-shaped spectrum which peaked at 370 nm with a cut off at 290 nm. The ultrasonication test was obtained by an ultrasonic cleaner (KQ5200, China). Samples to be tested were placed in a beaker filled with distilled water and then the beaker was placed in the ultrasonic cleaner.

3. Results and discussion

One of the greatest problems hindering the large-scale use of superhydrophobic surfaces is their poor mechanical durability. To obtain a durable superhydrophobic material, it is essential to imitate the lotus leaf completely and deeply by fabricating the material

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