

Research Article

Fabrication of Mechanical Durable Polysiloxane Superhydrophobic Materials

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A mechanical durable polysiloxane superhydrophobic surface was successfully prepared by means of polymerization of silanes blending with particles. The as-prepared polysiloxane surface showed stable superhydrophobicity even after the surface underwent a long distance friction. The superhydrophobicity of the polysiloxane materials can be even slightly enhanced by the surface abrasion. The scanning electron microscopy demonstrated that the micro- and nanometer structures distributed through the whole materials thickness are responsible for the mechanical durable superhydrophobicity.

1. Introduction

The wettability of solid surface is one of the most important aspects in both theoretical and industrial applications [1]. One of the extreme cases of wettability, superhydrophobicity, has aroused considerable interests for many researchers inspired by the water-repellent nature of lotus leaves in recent years [2]. Heretofore, numerous methods were presented to fabricate the superhydrophobic surfaces with various materials by mimicking the surface of lotus leaves [3–10]. Due to its novel and important properties, the superhydrophobic surfaces were greatly anticipated to be used in applications such as self-cleaning coatings [11], anti-icing and fogging surfaces [12–14], nonwetting fabrics [15, 16], and buoyancy and flow enhancement [17, 18]. However, there are still quite few real applications with superhydrophobic materials so far.

Durability is of great importance in many applications of superhydrophobic surface. The micro- and nanoscale surface topography, which is essential for superhydrophobicity, can be very easily destroyed by even a slight friction on the surface. Up to date, studies have begun to address the mechanical durability and methods were developed to enhance the durability of superhydrophobic surface [19], such as fabricating self-healing surfaces, enhancing the robustness

of the hierarchical structure, and fabricating with hydrophobic materials. Li et al. demonstrated a self-healing superhydrophobic coating fabricated by preserving healing agents of reacted fluoroalkylsilane in layered polymeric coatings [20]. When the top layer of fluoroalkyl chains decomposes or the coatings are scratched, the healing agents migrate to the surface to restore the superhydrophobicity. In this case, it takes special conditions and hour's time to restore the superhydrophobicity and the fluoroalkylsilane reagent is still required. It still remains a great challenge to fabricate superhydrophobic materials with excellent antiwear property.

In the current study, we presented a facile and cheap method to fabricate wear-durable superhydrophobic materials. Inspired by the ability that the lotus leaf can regenerate its microstructures, we have presented a strategy to fabricate the materials which are made up of the microstructures through the whole thickness of the materials to resist the surface abrasion. When the initial surface suffered abrasion, a new surface with new hierarchical roughness will appear. Herein, the micro- and nanoparticles were used to shape the hierarchical roughness and the organic silanes were used to fix these particles. The as-prepared polysiloxane superhydrophobic materials showed good antiwear property. From both theoretical and practical aspects, the present results and the fabrication strategy are of great significance

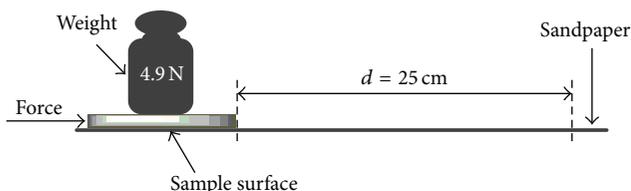


FIGURE 1: Schematic representation of abrasion measurement employed to evaluate wearability of the as-prepared material surface.

to fabricate superhydrophobic materials with stable antiwear property.

2. Experimental Section

2.1. Materials. The nanoscale silicon dioxide particles (50 nm) were purchased from Ross Technology Corporation. The microscale silicon dioxide particles (0.5–10 μm , approximately 80% between 1 and 5 μm), the triethoxymethylsilane, and the diethoxydimethylsilane were all purchased from Sigma-Aldrich. Hydrochloric acid (HCl, 37%), the isopropanol, acetone, and methanol were analytical and used as received without any purification. In all the process, deionized water was used.

2.2. Fabrication of the Antiwear Superhydrophobic Materials. The 0.12 g nanoscale silicon dioxide particles and 0.6 g microscale silicon dioxide particles were added to 8 mL mixed solution of isopropanol and water ($V:V = 2:1$). The mixture was ultrasonic and dispersed for 30 min. Then 0.4 mL hydrochloric acid, 3.0 mL triethoxymethylsilane (0.015 mmol), and 0.90 mL diethoxydimethylsilane (0.005 mmol) were added to the mixed solution. The reaction mixture was stirred for 3 hours at 60°C. After the mixture was cooled to room temperature, the mixture was then dropped onto the glass slide (2.5 cm \times 2.5 cm) surface until it spread all over the glass surface. A Petri dish cover was placed above the glass in order that the solvent evaporates slowly. After the mixture was dried overnight the samples were heat-treated at 160°C for 2 hours.

2.3. Characterization. The methodology illustrated in Figure 1 was invoked to evaluate the antiwear property. The grade of sandpapers adopted here is 180. The sample surfaces were blown by the N_2 and washed by large amounts of water to remove the abrasion dust after each abrasion test. Contact angles were measured at ambient temperature. The advancing contact angles were measured by advancing a small volume of water onto the surface using a syringe. The receding contact angle was measured by slowly removing water from a drop already on the surface. The water droplets were 5 μL for the contact angle measurement and 10 μL for the sliding angle for measurement. For each sample, a minimum of four different readings was recorded and the typical error in measurements was 1°. The thickness of the material was measured with an optical microscope by observing the sample's cross section, and three different

readings were recorded. The surfaces were observed by the scanning electron microscopy (SEM, XL-30, Philips) to characterize their morphology.

3. Results and Discussion

The applications of superhydrophobic surfaces have been greatly hampered by the poor mechanical durability of the microscopic surface topography. Furthermore, most of the artificial superhydrophobic surfaces fabricated with hydrophilic materials required a hydrophobic surface coating and it is obvious that the original hydrophilic materials would be exposed when the surface was mechanically damaged. Herein we adopted the strategy to fabricate the superhydrophobic materials which consist of the micro- and nanometer scale structures through the whole thickness of materials to resist the abrasion. Two kinds of particles were used for fabricating the micro- and nanometer scale structures which are essential for superhydrophobicity. The triethoxymethylsilane was adopted to polymerize to embed and fix the microparticles. The diethoxydimethylsilane was added to control the polymer with appropriate rigidity, flexibility, and hydrophobicity. After the polymers were cured in oven, the as-prepared particles combined polysiloxane surface has a static water contact angle (CA) of 133°, as shown in Figure 2(a), while the water CA can be greatly increased from 133° to 160° after the polysiloxane surface bore a 25 cm slide on the sandpaper surface.

Although there is no standardized test method to evaluate the mechanical durability of a superhydrophobic surface [19], the apparatus by rubbing the sample against the sandpaper illustrated in Figure 1 was adopted here. Figure 3(a) showed the relationship between the static water CA and the length of the sample surface sliding on sandpaper. The initial water CA of the as-prepared particles combined polysiloxane surface is only 133°, which shows hydrophobicity not superhydrophobicity. After a 25 cm length rubbing against the sandpaper with a 500 g weight on the back of the sample, the water contact angle has increased greatly to 160° and presented the good superhydrophobicity. After one more 25 cm length slide, there is 2° increment of water CA. After this the water CA shows little fluctuation and changed from about 162° to 163° when the surface bore 75 cm to 200 cm length slide abrasion. Figure 2(b) showed the water droplets have a static water CA of 163° on the polysiloxane surface which bore a 200 cm slide on the sandpaper surface. A superhydrophobic steel surface, which is prepared according to Zhang's procedure [21], also underwent the same abrasion test. The result showed that the superhydrophobic steel surface, which is fabricated with hydrophilic material and hydrophobic coatings, has a poor antiwear property. The water CA decreased dramatically from 159° to 72° after the superhydrophobic surface endured a 25 cm length rubbing against the sandpaper with a 500 g weight on the back of the sample, as shown in Figure 3(a). After one more 25 cm length slide, the initial superhydrophobic steel surface lost completely its superhydrophobicity and switched to a hydrophilic surface with a water CA of 15°. The thickness

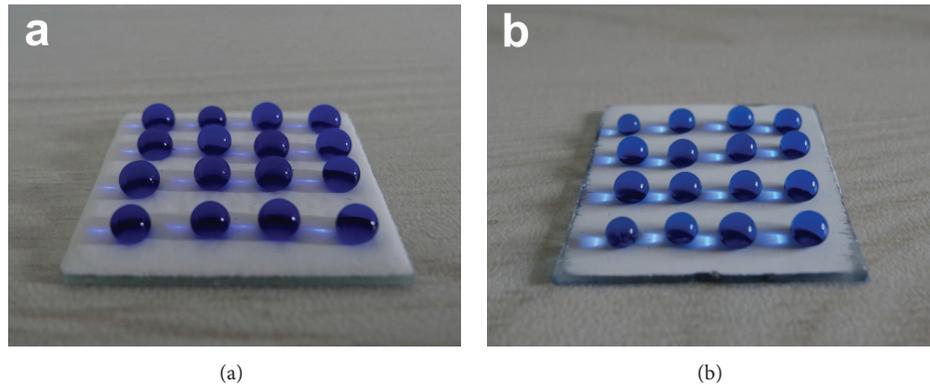


FIGURE 2: Images of water droplets dyed by methylene blue with different sizes on the particles combined polysiloxane surfaces of the same sample before (a) and after (b) the surface abrasion. The contact angles of the water droplets on the corresponding surfaces are 133° (a) and 163° (b), respectively.

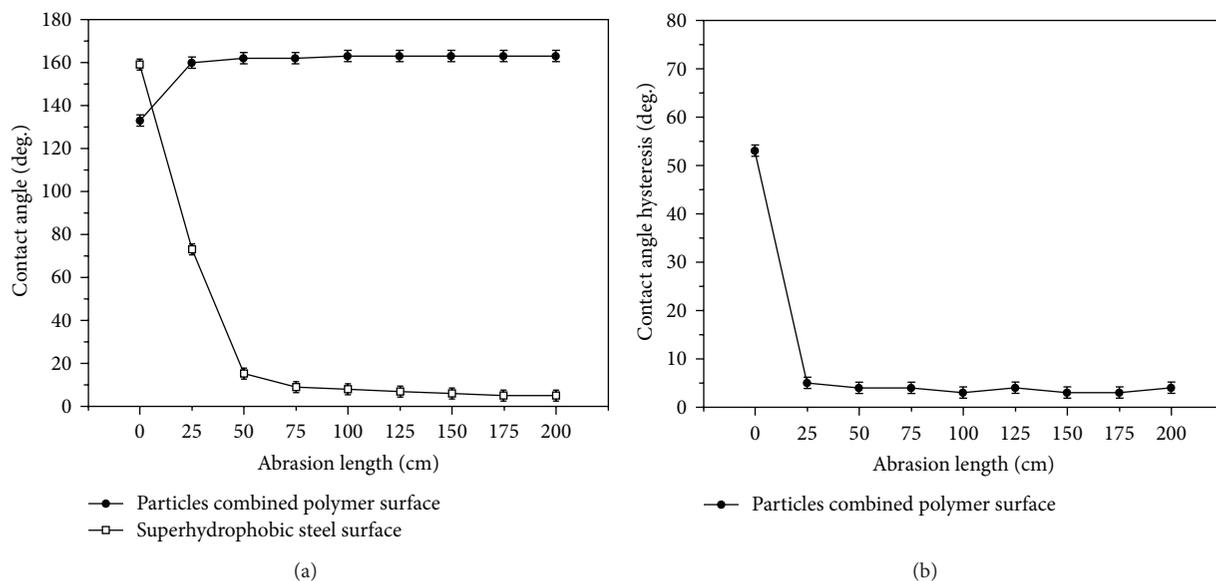


FIGURE 3: (a) The relationship between the static water contact angle and the lengths of the as-prepared polysiloxane surface (superhydrophobic steel surface) sliding on the sandpaper. (b) The relationship between the contact angle hysteresis and the lengths of the as-prepared polysiloxane surface sliding on the sandpaper.

measurements have also been carried out with an optical microscope before and after the abrasion test to investigate the thickness change of the polysiloxane film. It showed that the polysiloxane film of the as-prepared sample is 0.89 μm , while the thickness of the film decreased to 0.22 μm after the surface bore the 200 cm length slide abrasion. These results clearly revealed that the water repellency of the particles combined polysiloxane film not only has the mechanical durability but also can be enhanced with the increase of surface roughness by the surface abrasion.

In addition to a high static contact angle, a small contact angle hysteresis is also vital for a surface to be truly superhydrophobic because a small hysteresis leads to a water droplet being able to roll off of a surface easily. Thus, the contact angle hysteresis after the sample rubbed against the sandpaper should also be measured. Figure 3(b) showed

the CA hysteresis of the as-prepared particles combined polymers after each slide. Before the surface abrasion, the initial combined polysiloxane surface has a CA hysteresis of 53° , which is relatively high and implying a high roll-off angle. After a 25 cm slide against the sandpaper, the CA hysteresis has decreased greatly to 5° and the falling water droplet already can bounce from the surfaces and eventually roll off without ever coming to rest on the surface. The CA hysteresis shows little fluctuation when the surface bore 75 cm to 200 cm length slide abrasion. These results clearly proved that the as-prepared particles combined polymers have remained of the true superhydrophobicity even after a severe surface abrasion.

The initial as-prepared polysiloxane surface has a water CA of 133° , while the water CA is increased greatly to 162° after the surface abrasion. The great changes of the surfaces morphology before and after the surface abrasion have been

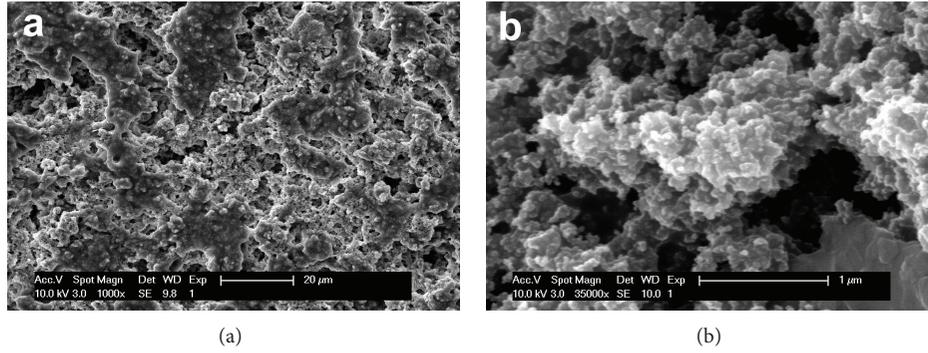


FIGURE 4: (a) SEM images of the as-prepared particles combined polysiloxane surface before the abrasion. (b) The porous and rough structures with micro- and nanometer scale exist below the outmost surface. The scale bars represent $20\ \mu\text{m}$ (a) and $1\ \mu\text{m}$ (b), respectively.

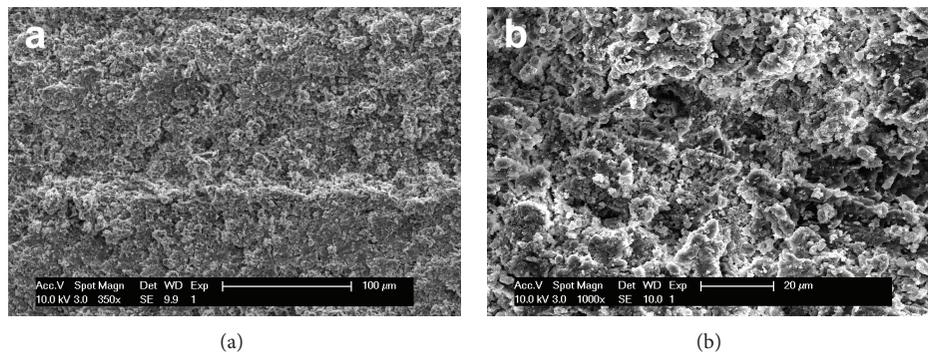


FIGURE 5: SEM images at different magnifications of the particles combined polysiloxane surface after the abrasion. The scale bars represent $100\ \mu\text{m}$ (a) and $20\ \mu\text{m}$ (b), respectively.

observed carefully by the scanning electron microscopy. Figure 4 is the SEM images before the surface abrasion test. There is a porous and rough structure which made up the materials. However, many-large-island structure with diameters of about $20\text{--}50\ \mu\text{m}$ is distributed randomly across the upper surface, as shown in Figure 4(a). Figure 4(a) also revealed that the top of the island structure is relatively flat and there is no porous structure on the island surfaces. This relative flat surface probably formed during the process of the solvent evaporate process has decreased the surface roughness to a certain extent and lowered the water CA as a result. According to the Cassie equation [22],

$$\cos \theta_r = f_1 \cos \theta - f_2, \quad (1)$$

which is generally valid for heterogeneous surfaces, composed of air and a solid with superhydrophobicity. Here, θ_r (132°) is the CA of the initial particles combined polysiloxane surface. θ (107°) is the CA of the smooth polysiloxane surface without particles and f_1 and f_2 are the fractional interfacial areas of the microstructures and of the air in the interspaces among the microstructures, respectively (i.e., $f_1 + f_2 = 1$). According to the equation, the f_2 value of the rough surface with the microstructures is estimated to be 0.53. This means that air occupies only 53% of contact area between the water droplet and the microstructures. Figure 4(b) is a magnified image of the porous and rough

structures with micrometer scale existing below this flat island. Figure 4(b) showed that the nanoscale particles are distributed across the rough structure surface. These micro- and nanometer scale structures inside the surface have the certain superhydrophobicity and it was exposed after the top flat islands were gotten rid of.

Figure 5(a) is the low-magnification image of the new surface produced by the surface abrasion. Compared with Figure 4(a), the main difference is that there are no more island structures on the top of surface and the remarkable scratches appeared across the surface. Figure 5(b) showed that a furrow-like structure with width of $20\text{--}50\ \mu\text{m}$ micrometer was parallel distributed on the surface. These scratches which are produced by the sandpaper during sample sliding on sandpaper surface are vital to the superhydrophobicity since this behavior has gotten rid of the flat-top island and greatly increased the surface roughness. These images clearly revealed that a new surface appeared after the surface abrasion just like the natural superhydrophobic plant leaves regenerating their hydrophobic wax coating. The existence of the nanometer particles is also important to the superhydrophobicity for forming the nanometer scale structure and bestowing the synergistic binary geometric structures on the surfaces. These images demonstrated that the particles combined polymers surface after the surface abrasion has the structures at the micro- and nanometer scale, and such synergistic binary geometric structures made the surface

roughness increase and the air fraction of the interfacial areas high enough. The binary micro- and nanometer scale structures have already trapped enough amount of air to prevent the penetration of the water droplet into the holes, which bestowed the superhydrophobicity on the surfaces. According to the Cassie equation, the f_2 value of the rough surface with the hierarchical rough structures is estimated to be 0.93. This means that air already occupies 93% of contact area, which is responsible for the enhancement of superhydrophobicity after the surface abrasion.

4. Conclusions

In summary, we fabricated the mechanically durable superhydrophobic surfaces with organic silane and particles by polymerizing silane and embedding the particles. The as-prepared particles combined polysiloxane surface showed stable superhydrophobicity even after the surface underwent a long distance friction. Furthermore, the superhydrophobicity of the polymer materials can be enhanced or restored. These properties will greatly accelerate and broaden the applications of superhydrophobic surfaces. We expect this strategy will open a new avenue in the preparation of mechanically durable superhydrophobic surface.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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