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Jin Yang[ab]; Zhao-Zhu Zhang[a]; Xue-Hu Men[ab]; Xiang-Hui Xu[ab]
[a] Chinese Academy of Sciences, State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Lanzhou, P. R. China [b] Chinese Academy of Sciences, Graduate School, Beijing, P. R. China

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Fabrication of Stable Superhydrophobic Coatings with Furfural Acetone Resin/PTFE Composites

JIN YANG[1,2], ZHAO-ZHU ZHANG[1,*], XUE-HU MEN[1,2] and XIANG-HUI XU[1,2]

[1] *State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, P. R. China*
[2] *Graduate School, Chinese Academy of Sciences, Beijing 100039, P. R. China*

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We describe a simple and inexpensive technique to fabricate superhydrophobic coatings with furfural acetone resin/poly (tetrafluoroethylene) (FAR/PTFE) composites. An interesting hierarchical structure with dispersed cavities and protuberances in microscale was achieved. The water contact angle (CA) of the superhydrophobic surface is 157° and the sliding angle is about 5°. The coatings can be applied to large substrates by spray coating with ease and possess high cohesional strength with the substrates. Meanwhile, the superhydrophobic coatings show long-term stability in pure water and acidic solutions with higher concentration.

Keywords: Superhydrophobic coating, FAR/PTFE, stability, hierarchical structure

1 Introduction

Superhydrophobicity situated at the hydrophobic extreme of the wettability has attracted tremendous attention from both academia and industry due to its wide application involving water-repellent and stainless coatings, self-cleaning and antifouling surface designs, and laboratory-on-a-chip devices (1–4). Therefore, a wide variety of methods to mimic this effect have been discovered by combining rough surface morphology and low-surface-energy coatings (5–9). However, these methods can be used for fabricating superhydrophobic surfaces with their limitations in the practical applications such as expensive low-surface-energy materials, severe conditions, the low cohesional strength and no long-term stability. Stability is the important issue we need to be concerned with in view of practical applications. Superhydrophobic coatings cannot find practical use without sufficient stability including mechanical, thermal and chemical stability (3). Recently, stable superhydrophobic surfaces that can be used over a wide pH range have aroused great interest for their resistance to corrosive liquids (10–15). However, they only measured the CA using the corrosive liquids instead of water, or immersed in corrosive solutions over the pH range to investigate the stability of the superhydrophobic surfaces.

Herein, the superhydrophobic surfaces of the FAR/PTFE composite coating were prepared using conventional simple spray and curing processes on various substrates such as stainless steel, copper, aluminum, glass, etc. The coating shows an interesting hierarchical structure with dispersed cavities and protuberances in microscale. Importantly, the superhydrophobic coating exhibits high cohesional strength with the substrate and excellent superhydrophobic properties, and remains stable, not only in pure water, but also in acidic solutions with higher concentration. It is expected that this technique will make it possible to prepare acid-resistant superhydrophobic coatings with new potential applications in industry in the future.

2 Experimental

FAR was synthesized by mixing acetone and furfural with equi-molar quantities, and using sodium hydroxide for catalysis. Appropriate amounts of the pure FAR and PTFE powder were ultrasonically mixed in chloroform for 1 h to obtain homogenous suspension. By spraying the suspensions with 0.2 MPa nitrogen gas onto clean stainless steel blocks, evaporating chloroform at room temperature, and then curing (at temperature of 180°C for 1 h and 300°C for 2 h), the FAR/PTFE composite coating was obtained. Furthermore, the pure FAR coating without PTFE was

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*Address correspondence to: Zhao-Zhu Zhang, State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, P. R. China. Tel./Fax: +86 931 4968098; E-mail: zzzhang@lzb.ac.cn

also prepared. The thickness of all prepared coatings was about 50 μm.

The topographical microstructures of the FAR/PTFE composite coating were observed by field emission scanning electron microscopy (FESEM). X-ray photoelectron spectroscopy (XPS) was employed to evaluate the chemical composition of the coatings prepared. The water CA measurements were carried out by the sessile drop method using a KRÜSS DSA 100 (KRÜSS) apparatus and distilled water.

3 Results and Discussion

We prepared composite coatings with 10, 20, 30, 40 wt% PTFE particles on stainless steel blocks. Figure 1 shows the effect of the weight fraction of PTFE on FAR coatings on water CA to the superhydrophobic surfaces. Profiles of water droplets on corresponding surfaces are also shown in the Figure 1 insets, respectively. The data suggest that CA increases sharply with PTFE concentration; this is true for PTFE concentration lower than 20 wt%. Above this "critical" point, CA values are almost constant and are not affected by PTFE concentration. Overall, CA increases from 73° for pure FAR to 157° for FAR with 40 wt% PTFE. However, the cohesional strength between the coating and substrate became relatively weak with PTFE concentration above 20 wt%. It is possible that PTFE particles restrained the curing and cross-linking of FAR. Therefore, 20 wt% is the optimum proportion; the superhydrophobic coating surface has the water CA of 157° and high cohesional strength with the substrate.

Figure 2 shows the field emission scanning electron microscope (FESEM) images of prepared samples and the shapes of water droplets on the surface are inserted. It is clear that no obvious micrometer-scale or nanometer-scale structure is observed on the pure FAR coating surface (Figure 2a, b), and the water CA on the surface is about 73° (Figure 2a inset). From the surface morphology of the no curing FAR/PTFE coating (Figure 2c), we can see the surface with the dense pure FAR coating and the embedded PTFE particles. More detailed morphology is shown in Figure 2d. Smooth areas of continuous polymer film are clearly visible; the PTFE particles disperse well in the polymer which induces the water CA increase to 93° (Figure 2c inset). After curing at 300°C, the morphology of the as-formed surface was much different (Figure 2e). The coating shows an interesting hierarchical structure with dispersed cavities and protuberances in microscale. The size of the micro-protuberances ranges from approximately 1 μm to 10 μm. On the top of the micro-protuberances, some nanoparticles ($\sim$ 100 nm) can be obviously observed in the magnified image of the Figure 2f. In addition, the surface exhibits micro-cavities on the order of 1–10 μm (Figure 2e). These results indicate that the curing process dramatically influences the structures of the FAR/PTFE composite coating. The reason is that the volume of FAR shrank and some low molecular weight substance such as H_2O, CO, CH_4 and CO_2 volatilized at the process of curing (16). In this case, the prepared coatings possess double-scale structure (micro and nanostructures) and exhibit superhydrophobic properties. Air can be adequately trapped among the hierarchical structure and the water CA on the surface reaches to 157° (Figure 2e inset). Further evidence for the superhydrophobicity of the surface is given by the low sliding angle (about 5°). The free rolling of the water droplets on the surface illustrates the self-cleaning effect, similar to the lotus leaf.

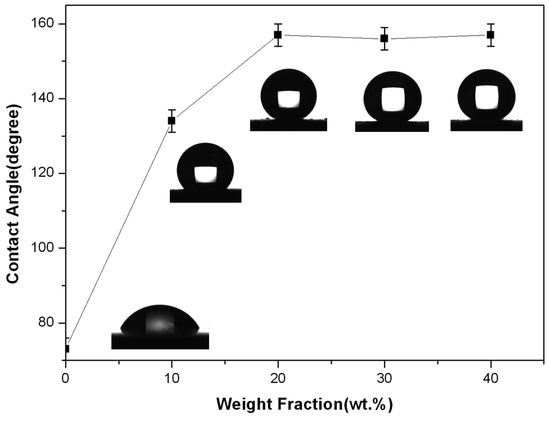

Fig. 1. Relationship between the weight frication of PTFE in the FAR coating and the water CA on the surfaces of a stainless steel substrate. Inset: Water drop profile in CA measurement (5 μL droplet size) on corresponding surfaces with different concentration PTFE.

The surface chemical composition is another important influencing factor for fabricating superhydrophobic surface. XPS (Figure 3) demonstrates that the elements of the prepared coatings are C, O, and F. The peaks of O1s and F1s located at 533eV and 690eV are attributed to the oxygen element of FAR molecular chain and the fluorine element of PTFE molecular chain, respectively. In addition, the XPS spectrum of curing coating displays stronger intensity of fluorine peak than the no curing coating. The ratio of C, O and F further clarifies the change of surface component in the curing process. It was found that the ratio of C/O/F was 51.2/17.3/31.5% when the coating dried at the room temperature (Figure 3a), but the ratio changed to 25.8/2.8/71.4% after curing at 300°C (Figure 3b), and the atom concentration of fluorine increased from 31.5 to 71.4%, which can be owed to the volume of FAR shrank and fluorine was enriched at the top surface at high temperature. Meanwhile, owing to more fluorine element covering the surface, the oxygen element content on the surface was relatively decreasing, which is also crucial to obtain the superhydrophobic surface.

We used hydrochloric acid to investigate the stability and durability of the superhydrophobic coating in the acidic solutions. Figure 4 shows the effect of immersion time

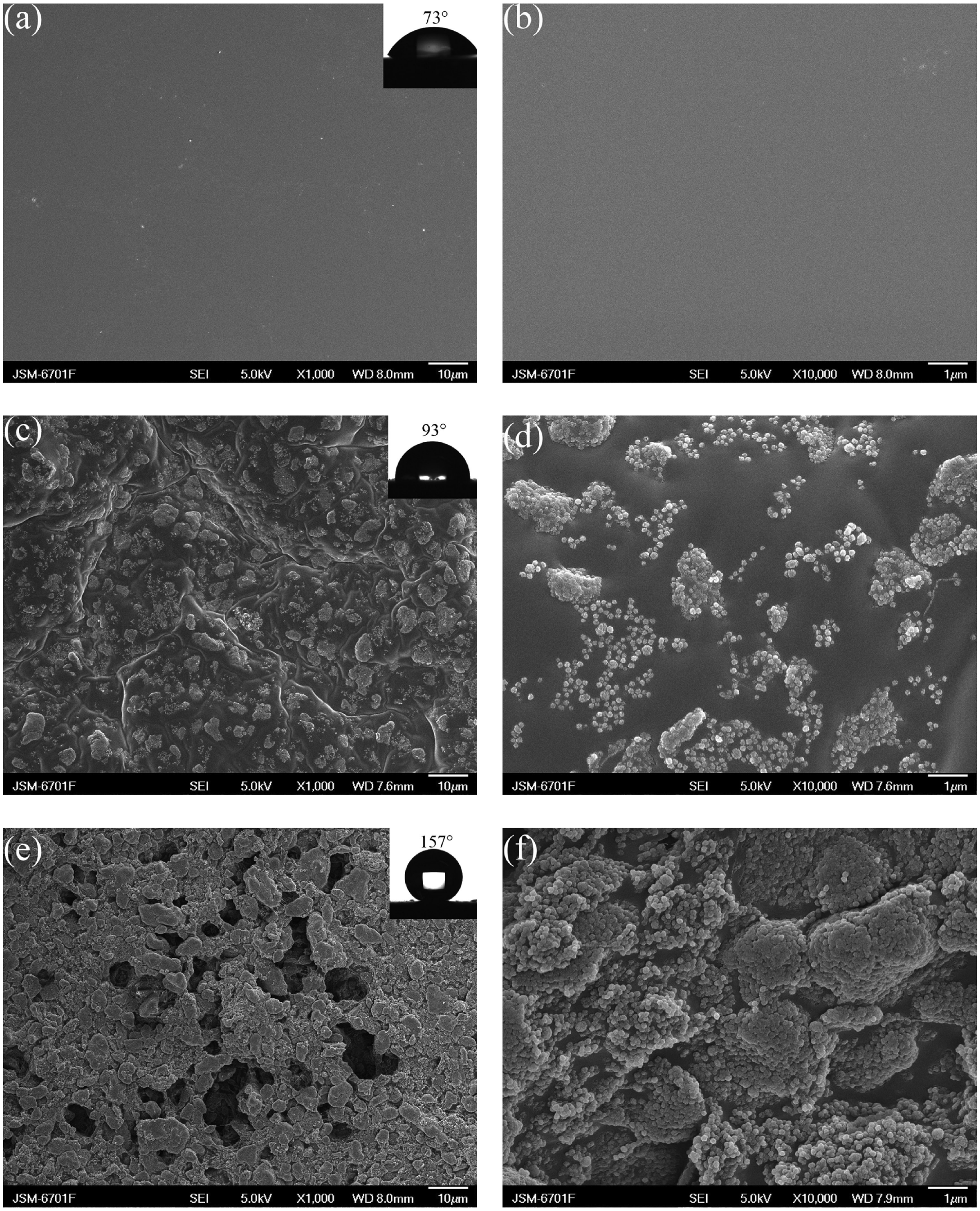

Fig. 2. FESEM images of the surfaces of pure FAR (a and b), no curing FAR/PTFE(c and d) and curing FAR/PTFE (e and f). Inset images indicate the CA of a 5 μL water drop on the corresponding surfaces.

on the water CA of the coating with 20 wt% PTFE in pure water and hydrochloric acid solutions. The water CAs only decreased about 10°, 11° and 15° in the hydrochloric acid solutions of 10, 15 and 20 wt% when the immersion time increased from 0 to 12 h. One reason for the good stability of the coating can be found when regarding the wetting process. In the Cassie-Baxter model, only a small fraction of the surface area is wetted by the solutions when the samples are immersed in aqueous media (17), which is evident by total reflectance of the light being observed at the liquid/solid interface upon immersion (18), and the wetted surface area is the crosslinking FAR and PTFE with intrinsic chemical and environmental resistances. These effectively retard deterioration of the coating and lead to the observed stability of the superhydrophobic properties. Meanwhile, there is no obvious fluctuation of the water CAs on the superhydrophobic surface within experimental error when immersed in pure water, indicating

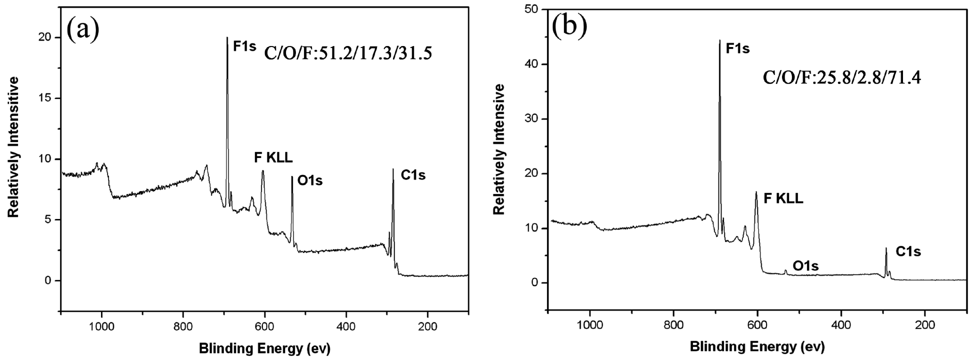

Fig. 3. XPS spectra of the FAR/PTFE composite coating surfaces (a) without curing (dried at room temperature) and (b) curing at 300°C.

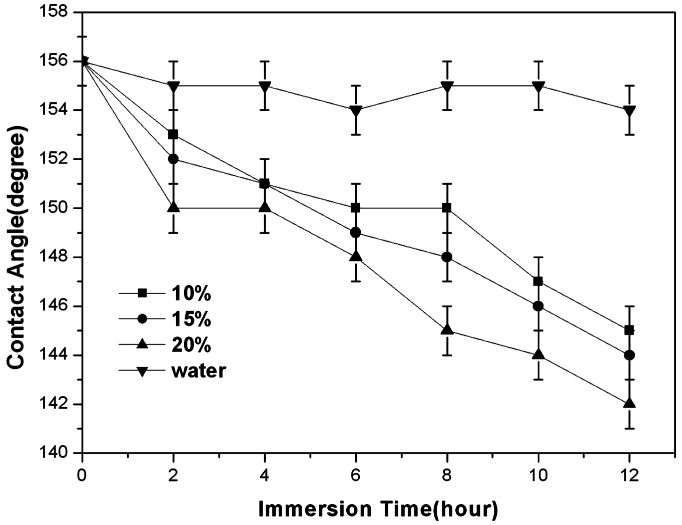

Fig. 4. The effect of immersion time on the water CA of the superhydrophobic coating in pure water and hydrochloric acid solutions of 10, 15 and 20 wt%.

that the immersion time has little effect on the water CAs.

4 Conclusions

In summary, we have successfully fabricated superhydrophobic surfaces on various substrates by conventional simple spray and curing processes. The superhydrophobic surfaces possess an interesting hierarchical structure with dispersed cavities and protuberances in microscale, and some nanoparticles (~ 100 nm) can be obviously observed on the top of the micro-protuberances. Moreover, the superhydrophobic surfaces show high cohesional strength with the substrate and long-term stability in pure water and hydrochloric acid solutions. This research had made a further step toward producing a larger-scale of superhydrophobic engineering materials and improving the self-cleaning and anticorrosive properties of engineering materials for the practical industrial applications.

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