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Durable, self-cleaning and anti-fouling superhydrophobic coating based on double epoxy layer

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Abstract

The practical application of superhydrophobic coatings has been greatly restricted due to the complicated preparation and fragile hierarchical structures on the surface. In this study, we prepared a robust superhydrophobic coating with a double-layer structure via a low-cost and facile method, adhering the non-wettability layer composed of silica nanoparticles and fluorine-modified epoxy resin to a binder resin layer on aluminum. The fluorine-modified epoxy resin with low surface energy can fix the silica nanoparticles after curing and cross-link with the adhesive layer. When the SiO₂ content in the surface layer is 40%, the water contact angle (WCA) of the coating is 162°, and the sliding angle (SA) is 2°. In the mechanical performance test, the durable coating can remain superhydrophobic even after 260 cycles of friction or 160 cycles of tape peeling. In addition, the superhydrophobic coating with self-cleaning and anti-fouling properties also has the performance of acid-base solution resistance. Hence, the combination of the rough layer and the adhesive layer makes the practical application of artificial superhydrophobic coatings possible.

1. Introduction

Superhydrophobic coating with a water contact angle (WCA) greater than 150° and a sliding angle (SA) less than 10° has attracted significant attention due to its many valuable properties, such as self-cleaning [1], anti-icing [2], oil-water separation [3–6] and anti-fouling [7]. Inspired by the rough micro-nano scale protrusions and low surface energy substances on the surface of the lotus leaf, researchers have prepared many superhydrophobic coatings through various methods, such as sol-gel [8], chemical vapor deposition [9], dip-coating [10] and self-assembly [11]. However, the micro-nano scale structures that are crucial for superhydrophobicity can be easily destroyed, which greatly hinders the application of superhydrophobic coatings [12].

To date, introducing of adhesive resin like polyurethane and polydimethylsiloxane (PDMS) into the coating to protect the hierarchical structure has been proven to be an effective method to improve the mechanical properties of the coating [13–21]. Fu et al prepared a fluorine-modified polyurethane through a two-step thiol click reaction, and blended it with silica nanoparticles to prepare a superhydrophobic coating with high mechanical stability. This coating maintained superhydrophobicity after 30 m of sandpaper friction and 450 times of tape peeling [22]. Masood et al used high-impact polystyrene to improve the adhesion of the coating to the substrate. Compared with standard polystyrene, high-impact polystyrene is more resistant to friction, which can resist 35 Taber (R) abrasion cycles [23]. Long et al fabricated a coating composed of polydimethylsiloxane and ZnSn(OH)₆. The coating can not only be applied to various substrates, but also maintain a WCA of more than 150° after chemical corrosion and mechanical friction [24].

At the same time, the attention of superhydrophobic coating researchers has been attracted to epoxy due to its strong adhesion and dense network structure [25–28]. Zeng et al applied low surface energy epoxy resin to aircraft coatings, which have good adhesion, wear-resistance, corrosion resistance and anti-ageing properties. In addition, the polymer particles dispersed in the epoxy resin provide rough micro-nano structures, making the coating also superhydrophobic and anti-icing [29]. Si et al manufactured a mechanically robust
superhydrophobic coating containing epoxy resin and Stearic Acid-Mg(OH)$_2$ through a simple and non-toxic method [30].

On the other hand, in addition to introducing a resin with hydrophobicity and good adhesion, the mechanical properties of the coating can be further improved by changing the structure of the coating. Guo et al sprayed silicone-modified polyurethane and nano-silica particles respectively on the substrate to prepare a superhydrophobic coating, which can resist 30 cycles of friction on 1000-mesh sandpaper. This method is simpler and greatly reduces the number of nanoparticles [31]. Shao et al introduced polydimethylsiloxane as a bonding layer to fix the superhydrophobic layer composed of polydimethylsiloxane and SiO$_2$ on the substrate. This double-layer coating exhibited higher resistance to tape peeling than a superhydrophobic coating without a bonding layer [32]. Wu et al sprayed the mixture of epoxy resin and nano alumina particles onto the pre-cured base resin to form a robust superhydrophobic coating [33].

In this study, a low-cost adhesive resin layer composed of diglycidyl ether of bis phenol A (E51) was formed on the substrate by dip-coating, so as to strengthen the adhesion between the rough layer and the substrate. Then, the hydrophobic layer composed of fluoro-modified epoxy resin and SiO$_2$ was fabricated on the pre-cured adhesive layer by spray-coating. A mechanically robust superhydrophobic coating was fabricated after the coating was completely cured. In addition, the preparation process of this chemically stable, anti-fouling and self-cleaning superhydrophobic coating is inexpensive and facile, which is conducive to large-scale application.

2. Experimental

2.1. Materials

N,N,N',N'-Tetrakis(oxiranylmethyl)-1,3-benzenedimethanamine (AG-601) and diglycidyl ether of bis phenol A (E51) were provided by Shanghai Sino Polymer Co., Ltd (China). Silica nanoparticles with average diameters of 15 nm (R202) were purchased from Evonik Degussa Co., Ltd (China). Maleic anhydride (MAH), methyl tetrahydrophthalic anhydride (MeTHPA), and 3, 3, 4, 4, 5, 5, 6, 6, 7, 7, 8, 8, 8-tridecafluoro-1-octano (F13-OH) were supplied by Aladdin Biochemical Technology Co., Ltd (China).

2.2. Synthesis of F13OH modified epoxy resin (F13EP)

To improve the hydrophobicity of epoxy resin, we introduced fluorne elements into the molecular skeleton of AG-601. As shown in figure 1, F13-OH and MAH (in a molar ratio of 1:1) were reacted at 90 °C for 3 h to prepare maleic acid monoester (F13C). Then, the F13C was added dropwise to AG-601 in a molar ratio of epoxy group: COOH = 4:1 at 75 °C. After 3 h, low surface energy epoxy F13EP was obtained.

2.3. Preparation of superhydrophobic coating

The preparation process is shown in figure 2. First, E51, MeTHPA and 1-methylimidazole were mixed in a ratio of 10:8:0.08. Then, the mixture was dip-coated on the cleaned aluminum substrate to form an adhesive layer. The binder layer was precured at 80 °C for 1 h before the next step. Second, the rough hydrophobic layer was formed by spraying dispersions of F13EP and SiO$_2$ in different proportions on the adhesive layer (The mass fraction of silica in the surface layer ranged from 0 ∼ 100). Finally, the coatings were cured at 80 °C, 100 °C and...
120 °C for 1 h each to ensure that the hydrophobic layer was bonded to the adhesive layer and the SiO$_2$ on the surface were firmly fixed.

### 2.4. Characterization

The chemical composition of modified epoxy was analyzed using the fourier infrared spectrometer (FT-IR) (Nicolet IS5, America). Meanwhile, the time-of-flight mass spectrometer (4800plus, Singapore) was used to verify the relative molecular mass of the modified epoxy resin. The coating hydrophobicity was evaluated by WCA and SA, which was measured by optical contact angle goniometer (JC2000D, China). For each coating, five measurements were required at different locations. The field emission scanning electron microscope (S-4800, Japan) with a scanning range of 20 to 800,000 times was used to observe the surface morphology of the coating.

In the wear-resistance test of the coating, the coated side of the aluminum sheet was in contact with 400-mesh sandpaper. The 5 cm $\times$ 5 cm sample moved 20 cm on the sandpaper as a cycle under a load of 100 g. In the tape peel test, the adhesion of the coating was measured by the number of times the tape peels off before the coating loses superhydrophobicity. The process of wear-resistance test and tape peeling test is shown in figure 6 (a) and figure 7 (a).

### 3. Results and discussion

The infrared spectra of MAH, F13C and F13EP are shown in figure 3(a). In the spectrum of F13C and F13EP, the peaks assigned to vibration of C=C and $\text{–C}$ are observed at 1652 cm$^{-1}$ and 1172 cm$^{-1}$. Furthermore, the coupling peaks at 1780 cm$^{-1}$ and 1855 cm$^{-1}$ correspond to the anhydride group is not observed. Compared with the double peaks at 1748 cm$^{-1}$ and 1717 cm$^{-1}$ embodied the vibration of ester C=O and carboxy C=O in the spectrum of F13C, F13EP exhibits only one single peak corresponding to the ester C=O at 1722 cm$^{-1}$.

Meanwhile, the strong peak at 3440 cm$^{-1}$ is the stretching vibration peak of $\text{–OH}$. The above peaks prove the successful synthesis of F13EP. As shown in figure 3(b), the mass spectrum also further verified the structure of fluorine modified epoxy. In addition, the surface energy of the F13EP coating was calculated to be 27.13 mJ/m$^2$ based on Young’s equation, which means low liquid adhesion to the resin.

Compared to covering the surface with low surface energy epoxy, constructing micro-nano scale rough structure on the surface by adding silica nanoparticles is a more efficient way to enhance the non-wettability of the coating [34–36]. Figure 4 shows the effect of increasing the SiO$_2$ content on the coating wettability. Although the low surface energy epoxy F13EP on the surface enhances the hydrophobicity of the coating, the WCA of the
coating is only $108^\circ$ when there is no silica in the surface layer. The WCA of the coating rose to $116^\circ$ after adding 10% silica into the surface layer. The improvement of the hydrophobicity of the coating is attributed to the introduction of nanoparticles, which increased the surface roughness. The WCA of the coating increased with the increase of the surface silica content. When the SiO$_2$ content is 40%, the WCA of the coating is as high as $162^\circ$, and the SA is $2^\circ$. This change is attributed to the increase in surface roughness, resulting in more air being trapped on the coating surface, which improves the water repellency of the coating. The WCA and SA of the coating will not change significantly until the silica content reaches 80%. Excessive silica in the surface layer caused the decrease of hydrophobicity of the coating, which may be related to the F13EP cannot cover the surface of the coating. The surface morphology of coatings is shown in figure 5. Only a small amount of silica nanoparticles is dispersed on the surface of the coating when the mass fraction of silica in the surface layer is 10%. In contrast, there are many cavities and protrusions formed by the accumulation of silica on the coating with 40% SiO$_2$ on the surface layer, which can hold air between coating and waterdrop.

Enhancing the mechanical durability of the coating may realize the practical application of superhydrophobic coating [37]. Coatings with a silica content of 40 ~ 80% in the surface layer were examined in the abrasion test. As shown in figure 6(b), the WCA of the coatings all decreased significantly after the friction of 400-mesh paper under a load of 100 g, which means the fragile hierarchical structures were all damaged. However, the higher the content of F13EP in the rough surface layer, the more times the coating can resist friction before losing superhydrophobicity. The coating containing F13EP and silica with a mass ratio of 2:8 can only withstand 30 frictions, but the coating with 60% F13EP on the top layer maintained superhydrophobicity after 260 cycles of friction. The rigid network structure formed by the curing of F13EP played a significant role in fixing the silica nanoparticles on the surface, preventing the shedding of the micro-nano structures formed by the agglomeration of silica during the friction process. At the same time, the rough structure became stronger as the content of F13EP in the surface layer increased. Subsequent tests continued on the group with the best abrasion resistance.

Adhesion is also an important factor in evaluating the mechanical properties of the coating. Good coating adhesion can greatly extend the lifespan of the coating [38]. Compared to single-layer superhydrophobic

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**Figure 4.** The WCA and SA of coatings with a silica content of 0%–100% in the surface layer.

**Figure 5.** Surface morphology of coatings with 10% and 40% silica content in the surface layer.
coatings, which are prone to cracking, double-layer superhydrophobic coatings with a resin bonding layer have stronger adhesion to the substrate. The tape-peeling test was performed, as shown in figure 7(a). The tape tightly adhered to the surface of the coating can take away the coating or the fragile structure on the surface when it is peeled off. The adhesion can be judged by the number of times the coating can withstand the peeling. Benefit from the adsorption of the polar groups in E51 to the substrate as well as the interfacial cross-linking of E51 and F13EP, the adhesion of the hierarchical structure to the substrate had been enhanced. After the coating was stripped 160 times by 3M 610 tape, the WCA of the coating remained above 150° (figure 7(b)). Meanwhile, the double-layer coating achieved a 5B level in the cross-cut test according to ASTM D3359. Although the coating was cut by the knife, there was no peeling of the coating. It can be seen from figure 8 that the edges of the scratches were very neat and clean. Furthermore, the introduction of a resin bonding layer ensured the coating could be applied to a variety of substrates, including wood, glass and iron (figure 9), which greatly expands the application fields of superhydrophobic coatings.

Surprisingly, the double-layer superhydrophobic coating exhibited good environmental stability. As shown in figure 10(a), the WCA of the coated aluminum remain 162° when placed in the air. Even if the coating was immersed in water for 24 h, the WCA only slightly dropped to 160°. In addition, in order to further test the chemical stability of the coating, we put the coatings into an aqueous hydrochloric acid solution and an aqueous...
sodium hydroxide solution. After 24 h of immersion, there is a great reduction in the WCA of the coating, but the coating still maintained superhydrophobicity, which was mainly ascribed to the epoxy resin matrix. The dense and closed structure formed by curing of E51 and F13EP prevented the corrosive aqueous solution from entering and destroying the coating. It can also maintain non-wettability for droplets of different pH (figure 10(b)). The above tests show that the superhydrophobic coating has good performance in harsh environments.

Figure 9. Superhydrophobic coatings applied on different substrates.

Figure 10. (a) The WCA of coatings that were placed in solutions with different pH for 48 h. (b) WCA of droplets with different pH on the superhydrophobic coating.

Figure 11. (a) The schematic of superhydrophobic coating self-cleaning. (b) The self-cleaning test.
Potential applications in the fields of building, clothing and photovoltaic device have made self-cleaning properties one of the most discussed topics [39–41]. The self-cleaning test is shown in figure 11(b). The carbon powder evenly dispersed on the coating was easily taken away by water droplets that are similar to balls, indicating the excellent self-cleaning performance of the coating. In contrast, the water droplets on the uncoated aluminum cannot even roll off, let alone remove the contaminants on the surface. This phenomenon that cleans the surface without any external force is mainly ascribed to the hierarchical structure and low surface energy surface, leading to the low adhesion of water droplets and contaminants to coatings (figure 11(a)). Meanwhile, we found that the coating is also resistant to liquid pollutants. As shown in figure 12(a), droplets of milk, coffee and juice remained spherical on the superhydrophobic coating. The anti-fouling performance were also investigated by putting coated aluminum into milk, juice and coffee. The coated aluminum was maintained clean and dry after being whipped out vertically from the liquid (figure 12(b)). The air cushion between the hierarchical rough surface and the liquid contaminant plays a great role in avoiding the contamination of the coating. The excellent self-cleaning and anti-fouling properties of the coating further expand the application field of this double-layer coating.

4. Conclusions

According to the ‘Adhesive + Paint’ method, we fabricated a mechanically robust superhydrophobic coating with a double-layer structure. The rough layer on the surface composed of F13EP and SiO2 endows the coating with great water repellency. When the content of SiO2 in the rough layer is 40%, the WCA of the coating is 162°, and the SA is 2°. Meanwhile, the adhesive layer and F13EP ensure the coating remained non-wettability after 260 cycles of friction and has a WCA of 150° after 160 cycles of tape peeling. Furthermore, the robust superhydrophobic coating with chemical stability, anti-fouling and self-cleaning properties can be applied to various substrates, which greatly expands the application areas of coatings.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).
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