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A novel method to prepare a microflower-like superhydrophobic epoxy resin surface

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HIGHLIGHTS

► A novel microflower-like superhydrophobic epoxy resin surface was obtained by a novel method.
► The presented preparation method is very facile.
► The microflower-like epoxy resin surface shows superhydrophobicity in the pH range of 3–14.

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ABSTRACT

A novel microflower-like superhydrophobic epoxy resin surface was obtained using a novel method. The water contact angle and sliding angle of the superhydrophobic epoxy resin surface was $158 \pm 1.7°$ and 3°, respectively. The as-prepared microflower-like superhydrophobic epoxy resin surface also showed superhydrophobic property in the pH range of 3–14. After being stored in ambient environment for one month, no decrease in water contact angle was observed.

1. Introduction

Wettability is an important property for a solid surface [1,2]. Inspired by the natural lotus effect [3,4], superhydrophobic surfaces with water contact angle greater than 150° have attracted much attention due to their great potential industrial and biological applications [5–12]. According to the investigation on the natural superhydrophobic species [13–16], researchers recognize that the combinations of rough surface microstructures and hydrophobic low-surface-energy materials are necessary to obtain superhydrophobic surfaces. Based on the understanding on the natural superhydrophobic mechanism, many clever methods, such as the solution method [17], sol-gel method [18–20], plasma fluorination method [21–24], electrospinning method [25–29], template method [30–32], layer-by-layer self-assembly [33–35], and other methods [36–42] have been proposed to prepare superhydrophobic surfaces.

Epoxy resin is one of the known important materials, which has great potential applications. However, the water contact angle of the common epoxy resin is lower than 90°, which limits its wide applications to certain extent. Thus, it is necessary and important to study the preparations and properties of superhydrophobic epoxy resin surfaces. However, to the best of our knowledge, there are at present few paper to report the fabrication of superhydrophobic epoxy resin surfaces [43,44]. Herein, we present a novel method to prepare superhydrophobic epoxy resin surface with microflower-like surface microstructures by using the ZnO powder agglomerations as template. Compared with the most methods mentioned above, our method is simpler and easier to control, which has great potential to prepare large scale superhydrophobic surface.

2. Experimental

2.1. Materials

Commercial-grade liquid epoxy resin (E-51 type) was used without any further treatment. Diethylenetriamine was chosen as

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the curing agent. Acetone was chosen as the diluent. ZnO powders (0.3–1 μm) were used as fillers.

2.2. Preparation of superhydrophobic epoxy resin surface

First, 20 g epoxy resin and 15 g ZnO powder were added into 100 mL acetone and stirred for 30 min to form a uniform solution. Next, 2 g diethylenetriamine was added into the solution and stirred for 10 min. Then, the solution was coated onto a cleaned glass substrate. After solidifying the coating for 5 h at 80 °C, the sample was immersed into acetic acid solution with the concentration of 2 mol L^{-1} for 5 min. Finally, the sample was immersed in 1 wt.% stearic acid solution for 30 min and then dried at ambient environment for 10 h. As a result, a microflower-like superhydrophobic epoxy surface was obtained.

2.3. Preparation of smooth epoxy resin surface

The smooth epoxy resin surface was obtained by casting the mixture of liquid epoxy and diethylenetriamine on a cleaned smooth glass plate and drying for 5 h at 80 °C.

2.4. Surface morphology characterization

The surface morphologies of the epoxy resin coatings were observed on a FEI Quanta 200 Environmental Scanning Electron Microscope (SEM).

2.5. Contact angle and sliding angle measurements

The contact angles of the epoxy resin surfaces were measured on a dataphysics OCA20 contact-angle system by sessile drop method at ambient temperature with about 5 μL droplets. The sliding angles were measured by tilting the sample stage from 0 to higher angles and then putting a droplet on the sample using a micro-gauge. When the droplet rolled off the surface, the angle of the sample stage was the sliding angle. Each of the reported water contact angle and sliding angle values was obtained by averaging five measurement results on different areas of the samples.

3. Results and discussion

Fig. 1a shows the SEM image of the smooth epoxy resin surface. Fig. 1b shows that the water contact angle of the smooth epoxy resin surface is only 79 ± 2°, indicating that the epoxy resin surface is hydrophilic. According to the previous literatures [1,20,22,26,45], rough surface microstructure and modification with low-surface-energy materials are necessary to obtain a superhydrophobic surface on a hydrophilic substrate. Thus, we should first prepare rough surface microstructure on epoxy resin. To obtain a rough surface microstructure, we added 15 g ZnO powders into the epoxy resin and stirred them to form a uniform mixed solution, then the mixed solution was coated onto a clean glass substrate and solidified at 80 °C for 5 h, and the resulting surface was smooth composite comprised of ZnO powders and epoxy. Because the ZnO powders distributed on the surface layer of epoxy resin were very easy to be corrosive by acetic acid. However, the epoxy resin was hard to be corrosive by acetic acid. It suggested that removing the ZnO powders trapped in the epoxy resin surface layer by acetic acid solution was feasible to obtain a rough surface microstructure on epoxy resin. Thus, we immersed the composite comprised of epoxy resin and ZnO powders into an acetic acid solution with the concentration of 2 mol L^{-1} for 5 min. The resulting surface morphology is shown in Fig. 2a. Fig. 2b is the higher magnification of Fig. 2a. From Fig. 2a and b, we know that the resulting surface is very rough, and it is comprised of many microflowers with the average diameter of about 10 μm. Each microflower is comprised of many nanoscale petals. Many holes are formed on the surface. We tested the water contact angle of the microflower-like surface, and the water contact angle was 9 ± 1°, which can be explained by Wenzel model [46] shown in equation (1):

$$\cos\theta_r = r\cos\theta \quad (1)$$

Here, r is the roughness factor, and θ and θ_r are the equilibrium contact angles of a liquid on a smooth solid surface and a rough solid surface, respectively. According to equation (1), if the roughness is increased, the contact angle of a hydrophilic solid surface will decrease. Because the epoxy resin is an intrinsically hydrophilic material (shown in Fig. 1b), rough surface should become more hydrophilic than those of smooth according to Wenzel model. However, interestingly, after modification with stearic acid, the water contact angle of the microflower-like epoxy resin surface reached to 158 ± 1.7°(shown in Fig. 2c). The advancing and receding contact angles of water droplets on the modified microflower-like epoxy resin surface were 159 ± 1.8° and 156 ± 2°, respectively, with the small difference between them indicating low contact angle hysteresis. To know the effect of stearic acid on the superhydrophobic property, we observed the surface microstructure of the modified epoxy resin. Fig. 2d shows the SEM image of the modified epoxy resin. Compared with Fig. 2b and d, we know that there is no obvious difference before and after modification with stearic acid, indicating that stearic acid plays an important role in achieving superhydrophobicity. However, the water contact angle of a smooth epoxy resin modified with stearic acid was only

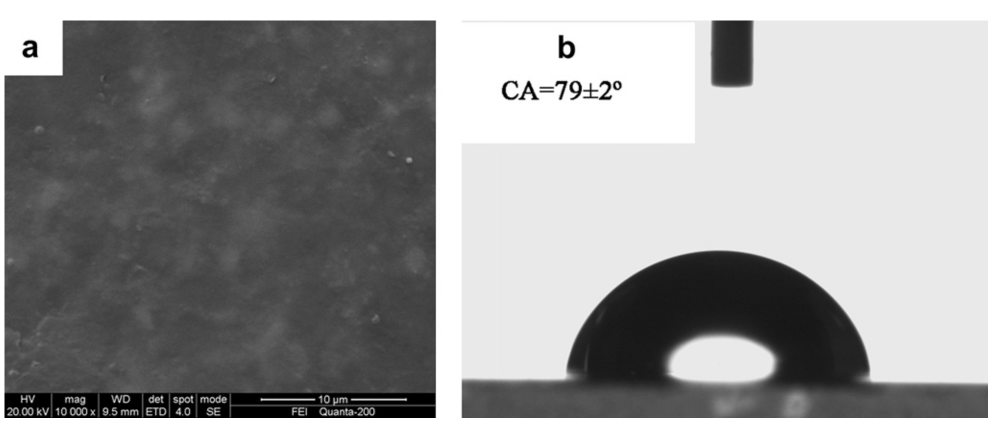

Fig. 1. (a) SEM image of smooth epoxy resin surface, (b) is the shape of water droplet on the smooth epoxy resin surface.

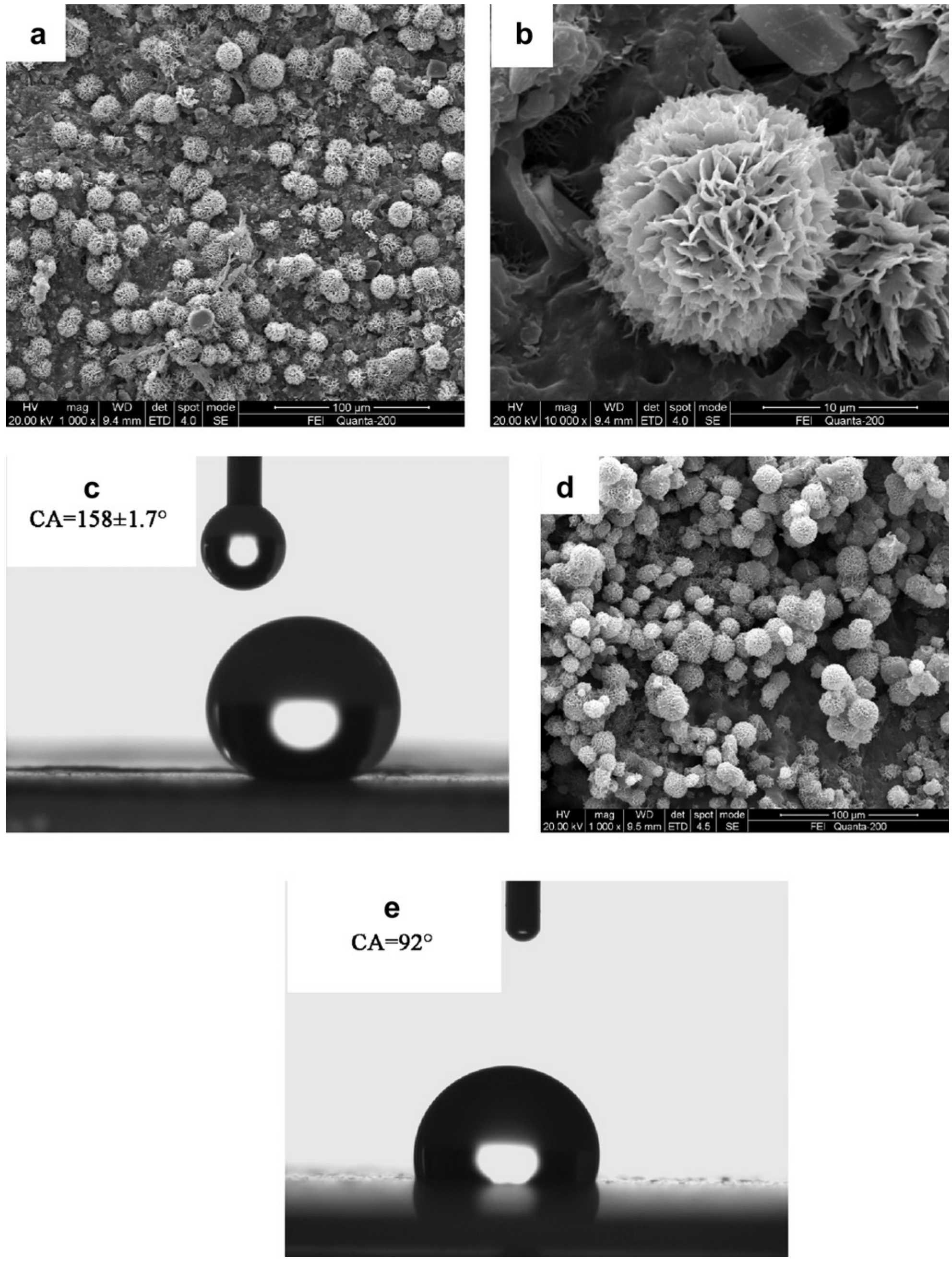

Fig. 2. (a) SEM image of the as-prepared microflower-like epoxy resin surface before modification with stearic acid, (b) is the higher magnification of (a), (c) The shape of water droplet on the as-prepared microflower-like epoxy resin surface after the modification of stearic acid, (d) SEM image of the microflower-like epoxy resin surface after the modification of stearic acid, (e) The shape of water droplet on the smooth epoxy resin surface modified by stearic acid.

92°(shown in Fig. 2e), suggesting that only stearic acid is hard to obtain superhydrophobicity. The cooperative effect of stearic acid and microflower-like surface microstructure is the essential reason for the achievement of superhydrophobic property. For understanding the role of stearic acid and microflower-like surface microstructure in theory, we can also discuss it use the Cassie and Baxter [47] model shown in equation (2),

$$\cos \theta_r = f_1 \cos \theta - f_2 \qquad (2)$$

where θ_r and θ represent the contact angles on rough and smooth surfaces, respectively. Here, f_1 and f_2 are the fractions of the solid surface and air in the composite surface, respectively (i.e., $f_1 + f_2 = 1$). The Cassie and Baxter equation indicates that the apparent contact angle θ_r increases with a larger contact angle of its flat surface (θ) and/or with an increasing fraction of air (f_2), According to the Cassie and Baxter equation, f_1 and f_2 are calculated to be about 0.09 and 0.91, respectively. This means that air occupies about the 91% of contact areas when the microflower-like epoxy resin surface contacts with the water droplet. The large fraction of air trapped in the pores of microstructures would greatly increase the air/liquid interfaces, then effectively prevent the penetration of the liquid into the pores, which plays an important role in gaining superhydrophobic property.

Except for contact angle, the sliding angle of water droplet is another important criterion for a superhydrophobic surface because most properties, such as self-cleaning, anti-corrosion, anti-

Table 1
The effect of ZnO amount added into the epoxy resin on the water contact angle and sliding angle of the epoxy resin surface.

Addition amount of ZnO (g)	5	10	20	25	30	35	40
Contact angle (°)	143 ± 1.7	152 ± 1.9	157 ± 1.5	156 ± 1.9	151 ± 2	150 ± 1.8	148 ± 1.6
Sliding angle (°)	63	10	3	4	6	9	8

icing and antibiofouling, are mainly determined by sliding angle [1]. Thus, we tested the sliding angle of the microflower-like superhydrophobic epoxy resin surface. Interestingly, the value of the sliding angle is only 3°, indicating that water droplets can slide easily on the as-prepared microflower-like superhydrophobic epoxy resin surface.

For the possible formation mechanism of the microflower-like surface microstructure, we can explain it as follows: In epoxy resin, the small ZnO particles aggregated to form many large loose spheric agglomerations, and liquid epoxy resin filled the lacune of the loose agglomerations. After solidification, the ZnO agglomerations were trapped in the epoxy resin matrix. After treatment with acetic acid solution, the ZnO particles of the agglomerations were removed due to the corrosion action of acetic acid solution, but the epoxy resin filled in the agglomerations remained because the acetic acid solution was hard to corrupt the epoxy resin, which resulted in the formation of microflower-like rough surface structure. From the above discussion, we know that the ZnO agglomerations acted as template during the formation of the "microflowers".

To know the effect of the amount of ZnO powders, 5 g, 10 g, 20 g, 25 g, 30 g, 35 g, and 40 g ZnO powders were respectively added into the epoxy resins to prepare seven different samples. After treatment with acetic acid and stearic acid, the water contact angle and sliding angle of the seven samples were tested. Table 1 shows the values of the water contact angle and sliding angle of the seven samples. From Table 1, we know that the addition amount of ZnO powders have great effect on the wettability of the epoxy resin. For 20 g epoxy resin, the appropriate addition amount of ZnO is 10–25 g. The possible reason is that the different addition amount of ZnO powders lead to the different surface microstructures of the samples. For example, the 5 g and 30 g addition of ZnO powders resulted in the different surface microstructures (shown in Fig. 3a and b).

The effect of stearic acid immersion time was also investigated. Table 2 shows the water contact angle and sliding angle of the samples immersed in 1 wt.% stearic acid solution for different times. When the immersion time is lower than 30 min, the water contact angle increased with the increase of immersion time. However, the water contact angle decreased with the increase of immersion time when the immersion time is larger than 30 min. The possible reason can be explained as follow: When the immersion time was very short, the stearic acid molecular adsorbed on the microflower-like surface was less. With the increase of immersion time, more and more stearic acid moleculars were adsorbed on the microflower-like surface. When the immersion time reached to 30 min, a continuous stearic acid molecular layer covered on the microflower-like surface but did not change the surface microstructure and roughness because the adsorbed stearic acid molecular layer was enough thin. However, the thin stearic acid molecular layer decreased the surface energy of the microstructure due to the fact that stearic acid was intrinsic hydrophobic, which resulted in the increase of water contact angle. With the further increase of immersion time, the stearic acid molecular layer covered on the microflower-like surface microstructure became thicker, which decreased the surface roughness. When the stearic acid molecular layer was enough thick, the stearic acid filled fully the pores of the microstructure and largely decreased the surface roughness. Thus, the water contact angle decreased with the increase of immersion time.

In previous literatures, some microflower-like superhydrophobic surfaces such as flower-like superhydrophobic polyaniline [48] and silver [49] have been reported. In addition, some superhydrophobic epoxy resin surfaces have also been reported [44]. However, compared with literatures, using ZnO powders agglomerations as template to obtain microflower-like superhydrophobic epoxy resin surface has not been reported. Although some researchers added nano particles into polymer to increase surface roughness to obtain superhydrophobic surface [43]. But they did not remove the nano particles embedded in polymers. That is, they did not use the nano particles as template to obtain superhydrophobic surface. Thus, our method is novel. Furthermore, our method is simpler and easier to control.

Similar to the previous report [9], we also studied the superhydrophobic property of the microflower-like superhydrophobic epoxy resin surface when contacting with liquids with different pH value. Fig. 4 shows the relationship between the pH values and the contact angles on the as-prepared microflower-like superhydrophobic epoxy resin surface. From Fig. 4, we know that the as-

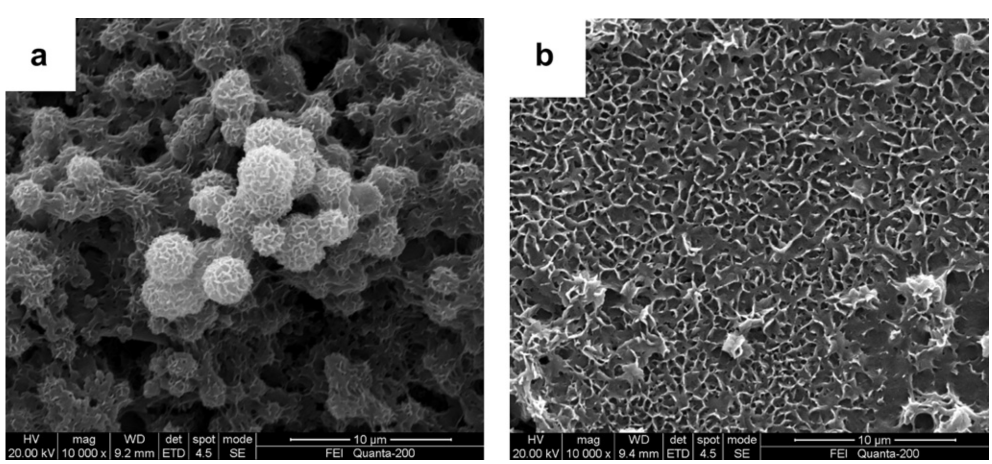

Fig. 3. SEM images of epoxy resin surfaces obtained by adding different ZnO amount into 20 g epoxy resin: (a) 5 g, (b) 30 g.

Table 2
The effect of stearic acid immersion time on the water contact angle and sliding angle of the epoxy resin surface.

Immersion time (min)	1	10	20	30	40	50
Contact angle (°)	82 ± 1.9	136 ± 2	149 ± 1.8	158 ± 1.7	153 ± 1.9	143 ± 1.9
Sliding angle (°)	70	31	13	3	5	15

prepared microflower-like superhydrophobic epoxy resin surface shows superhydrophobic property in the pH range of 3–14. It indicates that pH values of the aqueous corrosive liquids have little or no effect on the water contact angle of the as-prepared microflower-like superhydrophobic epoxy resin surface. These results are very important for the use of the as-prepared superhydrophobic surface in corrosive liquids with a wide pH range.

In practical applications, epoxy resins are often used at different temperatures. Thus, it is necessary to study the superhydrophobicity of the microflower-like epoxy resin at different temperatures. Fig. 5 shows the contact angle values of the microflower-like superhydrophobic epoxy resin surface after thermal treatment at different temperatures. When the thermal treatment temperature was lower than 80 °C, the water contact angles of the microflower-like superhydrophobic epoxy resin surface were still higher than 150° even the samples were treated for 25 h. However, when the treatment temperature was higher than 80 °C, the water contact angles of the samples decreased. The possible reason was the higher treatment temperature closed to the glass transition temperature of the epoxy resin, which made the superhydrophobic surface lose its stability. These test results indicate that the microflower-like superhydrophobic epoxy resin surface is stable and can be used in a wide temperature range of 10–80 °C.

In addition, we also studied the durability of the microflower-like superhydrophobic epoxy resin surface. When stored in ambient environment for one month, its water contact angle and sliding angle remained essential constant, and the surface microstructures did not change within the storage time. Furthermore, we made water wash the superhydrophobic epoxy resin surface for 120 min at a tilt angle of 5° each day. Interestingly, after repeating the washing step for 10 d, the water contact angle of the sample did not change, indicating that the adhesion between stearic acid and microflower-like epoxy resin was strong. The above experiments suggest that the superhydrophobic property of the as-prepared microflower-like superhydrophobic epoxy resin surface has long-term stability and durability.

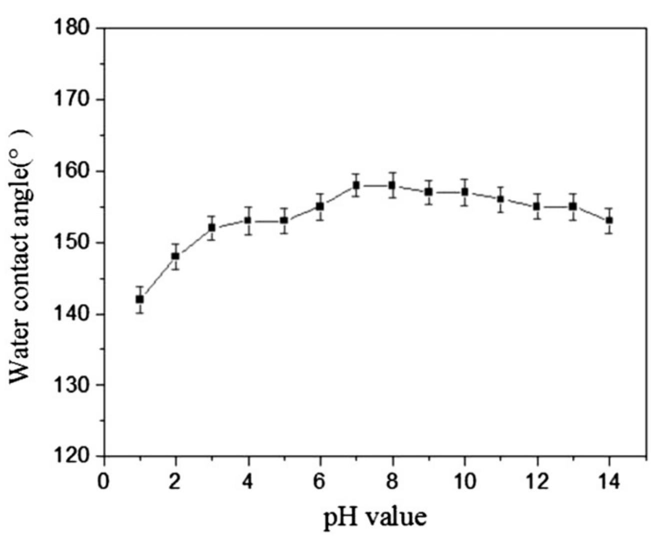

Fig. 4. Relationship between pH value and the contact angles on the as-prepared superhydrophobic microflower-like epoxy resin surface.

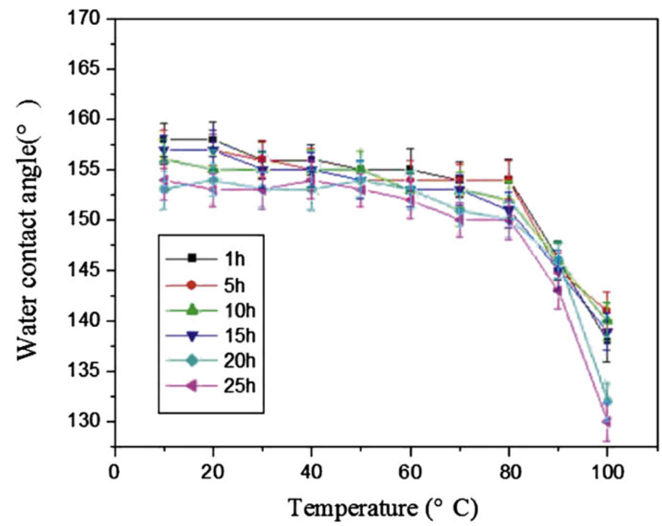

Fig. 5. The contact angles of the as-prepared superhydrophobic microflower-like epoxy resin surface after thermal treatment for different times at the temperatures ranging from 10 to 100 °C.

4. Conclusions

In conclusion, we have prepared a microflower-like superhydrophobic epoxy resin surface by a novel method. The presented method is very facile and can be applied to the generation of other polymer-based superhydrophobic surfaces. The microflower-like superhydrophobic epoxy resin surface also showed superhydrophobic property in the pH range from 3 to 14. When the microflower-like superhydrophobic epoxy resin surface was stored in ambient environment for one month, its water contact angle and sliding angle remained constant. The as-prepared microflower-like superhydrophobic epoxy resin surface has wide applications in many fields such as anti-crossion, anti-icing, self-cleaning, etc.

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