

A Stable Porous Superhydrophobic High-Density Polyethylene Surface Prepared by Adding Ethanol in Humid Atmosphere

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ABSTRACT: A stable porous superhydrophobic high-density polyethylene (HDPE) surface with water contact angle of $160.0 \pm 1.9^\circ$ and sliding angle of $2.0 \pm 1.6^\circ$ was obtained by adding ethanol in humid atmosphere at 5°C . Soaked in water with temperatures ranging from 5 to 50°C for 15 days, even suffering compressive forces, and the water contact angles were still higher than 150° . After water flowed through the surface continuously for 30 min,

even water droplets with a diameter of 4 mm dropped onto the HDPE surface from 30 cm high for 10 min, the water contact angles were also higher than 150° . A brief explanation to the formation of the porous superhydrophobic HDPE surface was put forward. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 1626–1632, 2009

Key words: phase separation; polyethylene; surfaces

INTRODUCTION

Wettability is an important property governed by both the chemical composition and the geometrical structures of solid surfaces.^{1–3} A surface having water contact angle greater than 150° is commonly called superhydrophobic.⁴ Recently, superhydrophobic surfaces have attracted much attention because of great potential applications in agriculture, industrial, and biomedical fields.^{5,6} To fabricate superhydrophobic surfaces, many methods have been proposed, such as the sol–gel method,^{7–10} the plasma fluorination method,^{11–13} electrochemical deposition on a polyelectrolyte multilayer,^{14–17} chemical vapor deposition,^{18,19} arrays of carbon nanotubes,^{20,21} reformation of polymers,^{22–26} electrostatic self-assembly,²⁷ and other methods.^{28–32} Polyethylene is a common and important plastic, which is used widely in many fields. Thus, superhydrophobic polyethylene has great potential applications. Superhydrophobic low-density polyethylene (LDPE) has been reported.^{33,34} How-

ever, to the best of our knowledge, there are few articles to describe about superhydrophobic high-density polyethylene (HDPE) till now. Although HDPE has the same chemical composition with LDPE, the molecular structure of HDPE is different from that of LDPE, and accordingly many physical properties are also different. For example, the anti-heating property, rigidity, and strength of HDPE are all better than those of LDPE, thus the application fields of HDPE are different with LDPE. Therefore, fabricating and studying the superhydrophobic HDPE surface is necessary. Herein, we report a facile and novel preparation of stable superhydrophobic HDPE surface by adding ethanol in humid atmosphere at 5°C . It should be noted that our preparation process needs neither special apparatus nor complicated chemical treatment. Furthermore, the as-prepared HDPE surface shows both high stability and durability in atmosphere.

EXPERIMENTAL

Materials

A commercial grade high-density polyethylene (obtained from Lanzhou Petroleum Chemical Corporation of China, $d = 0.951 \text{ g cm}^{-3}$, and the average molecular $M_w = 200\,000 \text{ g mol}^{-1}$) was used without further treatment. Xylene (mixture of isomer, obtained from Changsha Huihong Chemical Plant of

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China) was chosen as the solvent. The glass plates ($25 \times 50 \text{ mm}^2$) were cleaned with detergent, then rinsed in deionized water for several times and dried with nitrogen gas.

Preparation of superhydrophobic HDPE surface

A total of 0.3 g of HDPE resin was dissolved slowly in 30 mL xylene to form a uniform solution at 120°C . Then, some of HDPE solutions were dropped onto the cleaned glass plates and the solvents were evaporated in a dry atmosphere in the oven at 120, 70, 20, and 5°C . Other solutions were dropped onto the cleaned glass plates and the solvents were evaporated in humid atmosphere with different relative humidity at 5°C . To obtain a porous superhydrophobic HDPE surface, 3 mL ethanol was added into the HDPE solution at a speed of 2 mL s^{-1} in humid atmosphere at 5°C , and then the solution was dropped onto the cleaned glass plate and the solvent was evaporated in humid atmosphere (the relative humidity is between 60 and 75%) at 5°C .

Characterization

The wettability of the HDPE surfaces was measured on a data-physics OCA 20 contact-angle system at ambient temperature with about $5 \mu\text{L}$ droplets. The equilibrium contact angles of $5 \mu\text{L}$ water droplet were measured by sessile drop method. The advancing contact angle and receding contact angle were measured as follows: a $2 \mu\text{L}$ water droplet was placed on the sample using a syringe, and the advancing contact angle was recorded by increasing water volume to $5 \mu\text{L}$ with a speed of $0.3 \mu\text{L s}^{-1}$, then the receding contact angle was recorded by decreasing the water volume at the same speed of adding water. The sliding angle was measured by tilting the sample stage from 0° to higher angles and then placing 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. The surface morphologies of the HDPE surfaces were observed on a scanning electron microscopy (SEM) of HITACHI S-3000N. To know the durability of the superhydrophobic HDPE surface, the HDPE surfaces were soaked in water from 1 h to 15 days with temperatures ranging from 5 to 50°C , and the water contact angles were measured at each process condition. The static compressive forces were applied on the superhydrophobic HDPE surface to test the effect of static pressure on superhydrophobicity by putting mass. We also made the water flow through the superhydrophobic HDPE surface for 10–30 min, and dropped the water droplets with a diameter of 4 mm onto the surface from 10 to 30 cm high to test the durability.

RESULTS AND DISCUSSION

When HDPE solution was dried at 120°C , a smooth transparent film was formed [shown in Fig. 1(a)], and the resulting surface had a water contact angle of only $103 \pm 2^\circ$ [shown in Fig. 2(a)]. To obtain a superhydrophobic HDPE surface, we should change the preparation condition. The investigation of Erbil et al.³⁵ showed that lower drying temperature for polypropylene solution increased the surface roughness of polypropylene coating, and the corresponding water contact angle was increased. Similar to the investigation of Erbil et al.,³⁵ we also decreased the solvent evaporation temperature of the HDPE solutions to obtain superhydrophobic HDPE surfaces. Figure 1(b–d) is the SEM image of the HDPE surfaces prepared by evaporating solvents of HDPE solutions at 70, 20, and 5°C , respectively, and water contact angles increased accordingly to $126.0 \pm 2.0^\circ$, $142.0 \pm 1.7^\circ$, and $152.0 \pm 1.8^\circ$, respectively. And the sliding angles were $37.0 \pm 3.0^\circ$, $23.0 \pm 2.0^\circ$, and $11.0 \pm 1.9^\circ$, respectively. It may suggest that a superhydrophobic HDPE surface can be obtained by evaporating the solvent of the HDPE solution at 5°C . The changes of water contact angles on the HDPE surfaces with different surface morphologies can be explained by Wenzel model³⁶ shown in eq. (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 the equation, if the roughness is increased, the contact angle of a hydrophobic solid surface will also increase. From Figure 1(a–d), we can find that the HDPE surface obtained at lower solvent evaporation temperature is rougher. Thus, the water contact angle increased. Using the similar method, Lu et al.³³ prepared an LDPE surface with a water contact angle of $151.0 \pm 1.9^\circ$ at a solvent evaporation temperature of 30°C , but water droplet cannot slide off even though the LDPE surface was tilted until vertical, indicating that the sliding angle was too high and the water droplet was pinned on the surface. However, in our investigation, we obtained an HDPE surface with water contact angle of $152.0 \pm 1.8^\circ$ and sliding angle of only $11.0 \pm 1.9^\circ$ at the solvent evaporation temperature of 5°C . To improve the water contact angle and decrease the sliding angle, Lu et al.³³ added some cyclohexanone (the aim of adding cyclohexanone is to increase the crystallization time and nucleation rate, which resulted in the change of microstructures of LDPE film) into the LDPE solution at 80°C , and superhydrophobic LDPE surface was obtained with water contact angle of $173.0 \pm 2.5^\circ$ and sliding angle of 1.9° . However, the evaporation velocity of the

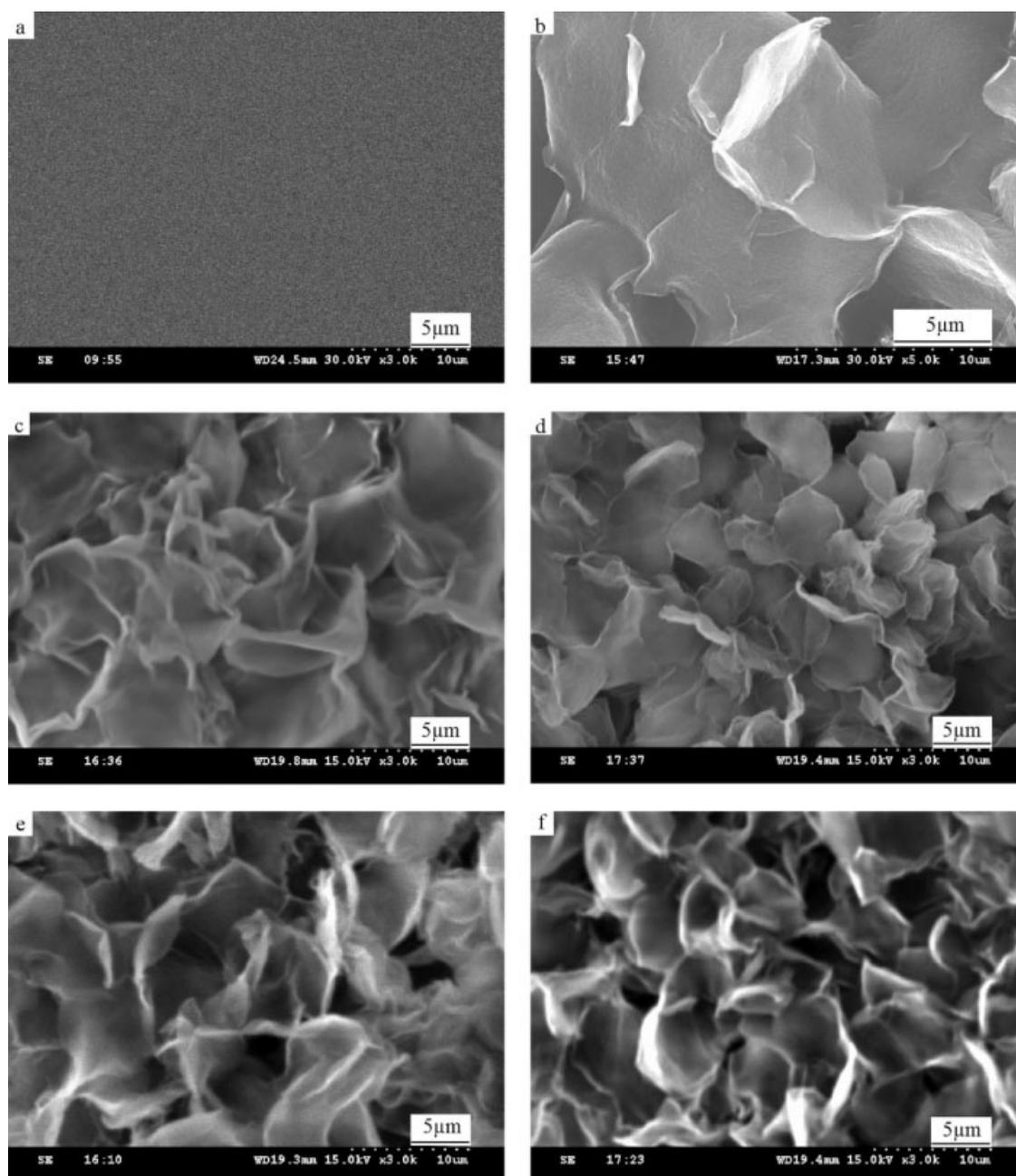


Figure 1 SEM images of HDPE surfaces prepared at different conditions: (a)–(d) are prepared by evaporating the solvent of the HDPE solutions in the oven at 120, 70, 20, and 5°C, respectively, (e) is prepared by evaporating the solvent of the HDPE solution in humid atmosphere at 5°C, and (f) is prepared by adding 3 mL ethanol into the HDPE solution and evaporating the solvents of the mixed solution in humid atmosphere at 5°C. The magnification of (b) is 5.0 K, and the other magnifications of (a), (c), (d), (e), and (f) are all 3.0 K.

cyclohexanone is too slow because of the high boiling point (155.7°C), and the solvent evaporation time to obtain the superhydrophobic surface is long. Zhao et al.²⁸ argued that humid air was important to obtain a superhydrophobic surface, and they obtained a superhydrophobic polycarbonate coating with a water contact angle of $161.8 \pm 2.2^\circ$ and sliding angle of $9.4 \pm 2.6^\circ$ by casting polycarbonate solution at humid atmosphere (relative humidity is 75%). Yabu and Shimomura³¹ fabricated a transpar-

ent superhydrophobic honeycomb-patterned fluorinated polymer film by casting polymer solution in humid condition (the aim of using humid condition is to produce the honeycomb-like microporous structures on the polymer film by the condensed water droplet from humid air). Herein, we also studied the effect of humid air on the formation of the superhydrophobic HDPE surfaces. When relative humidity was less than 60%, the effect of relative humidity on the water contact angles of HDPE surfaces was

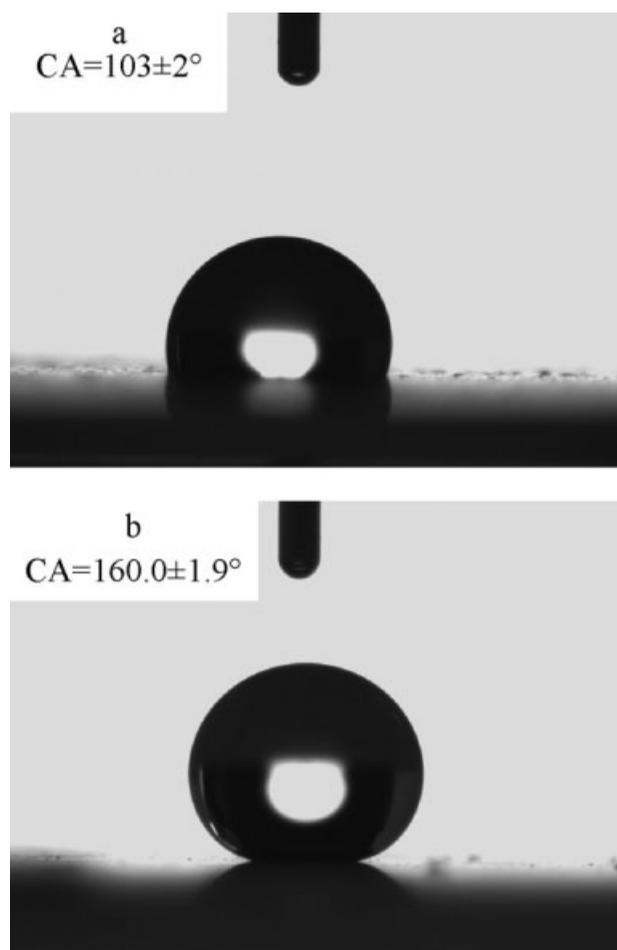


Figure 2 The shapes of water droplets on (a) smooth HDPE surface and (b) porous superhydrophobic HDPE surface prepared by adding ethanol in humid atmosphere.

weak; however, when relative humidity was higher than 75%, large obvious cracks with diameters ranging from 0.1 to 0.5 mm were observed, that is not suitable for practical application. We found that relative humidity ranging from 60 to 75% was the relatively better condition to obtain a superhydrophobic HDPE surface at 5°C [SEM image is shown in Fig. 1(e)], and the corresponding water contact angle and sliding angle were $158.0 \pm 2.1^\circ$ and $5.0 \pm 1.8^\circ$, respectively. As we all know, the contact angle and sliding angle of the lotus leaf are about 160° and 2° , respectively. In practice, sliding angle is an important criterion for a superhydrophobic surface.⁶ In some cases, e.g., self-cleaning, the sliding angle is more important than maximum water contact angle since sliding angle is directly related to driving force of a liquid drop.³⁷ To obtain a superhydrophobic HDPE surface with a lower sliding angle (similar to the wettability characteristic of the lotus leaf), we should adjust the preparation process further. In previous reports,^{33,35} adding some nonsolvents with high boiling point into polymer solutions was believed an effective way to obtain

a superhydrophobic surface. However, the evaporation time of polymer solutions will become longer if the nonsolvent with higher boiling point is added. To reduce the evaporation time, a nonsolvent with low boiling point should be selected. As we all know, ethanol is a nonsolvent of HDPE with low boiling point (about 78°C), and the evaporation velocity is quick. Thus, we added 3 mL ethanol into the HDPE solution at 5°C to modify the preparation process, and after stirring the mixed solution 5 min, we dipped the mixed HDPE solution onto a cleaned glass plate. After the solvent of the HDPE solution was evaporated for 10 h in humid atmosphere (relative humidity is between 60% and 75%) at 5°C , a superhydrophobic HDPE surface [shown in Fig. 1(f)] with water contact angle of $160.0 \pm 1.9^\circ$ [shown in Fig. 2(b)] and sliding angle of $2.0 \pm 1.6^\circ$ was obtained, indicating that a water droplet could roll easily on this superhydrophobic HDPE surface. From Figure 1(f), a lot of pores can be observed on the superhydrophobic HDPE surface. Theoretically, air can be trapped in these pores. Thereby, the porous HDPE surface can be considered as a composite comprised of the air trapped in the pores and the HDPE. Cassie and Baxter³⁸ proposed an equation:

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

To describe the contact angle θ_r of a hydrophobic surface comprising solid and air. Here, f_1 and f_2 are the fractions of solid surface and air in composite surface, respectively (i.e., $f_1 + f_2 = 1$), while θ is the equilibrium contact angle on a flat solid surface. This equation predicts that increasing the fraction of air (f_2) will increase the contact angle of the HDPE surface; otherwise the contact angle of the HDPE surface will decrease if f_1 (the fraction of solid surface) increase. According to the water contact angle data on the smooth HDPE film and the porous HDPE surface, f_2 value calculated by eq. (2) is about 0.923. This means that air occupies about the 92.3% of contact areas when the porous HDPE surface contacts with the water droplet, which is responsible for the superhydrophobic property of the surface. For the low sliding angle of the porous superhydrophobic HDPE surface prepared by adding ethanol in humid atmosphere, we can explain the possible reason according to the viewpoint of Öner et al.^{39,40} and Miwa et al.³⁷ In general, surfaces always have two contact angles defined as the advancing contact angle and the receding contact angle due to the unevenness and the pollution of the surfaces and can be described by the contact angle hysteresis, which is equal to the difference between the advancing contact angle and the receding contact angle.^{37,39,40} The contact angle hysteresis is commonly used as a criterion for the sliding property of water droplet.³⁷ Öner et al.^{39,40} argued that the structure

(shape, length, continuity of contact, amount of contact) of the three-phase (solid–liquid–air) contact line was important for advancing contact angle and receding contact angle: discontinuous, unstable and contorted contact line were necessary to form a superhydrophobic surface with low contact angle hysteresis. Miwa et al.³⁷ believed that the surface structures that could trap air were important for the preparation of low-sliding-angle surfaces. According to the SEM image of the as-prepared HDPE surface [shown in Fig. 1(f)], the three-phase contact line is discontinuous on the surface and the porous surface structure can trap air, suggesting that the as-prepared HDPE surface may have a low contact angle hysteresis and water droplet can slide easily on the surface. In addition, the surface roughness is also an important influence factor for contact angle hysteresis. Johnson and Dettre⁴¹ theoretically simulated the effect of the surface roughness on the contact angles hysteresis, and they suggested that the contact angles hysteresis on hydrophobic surfaces would increase with increasing surface roughness in the low-roughness region but decrease drastically when the roughness became large and the composite surface comprised solid and air trapped in troughs would form, and the water droplet could not penetrate into the troughs. Thus, we tested the surface roughness of the as-prepared superhydrophobic HDPE similar to Burton's method,⁴² and the value of the surface roughness was about 2.63. For the as-prepared superhydrophobic HDPE surface, the surface roughness is high enough, and water cannot penetrate into the pores of the superhydrophobic HDPE surface due to the trapped air. In this case, the contact angle hysteresis will be low. According to the above discussions, we believe that the contact angle hysteresis of the as-prepared superhydrophobic HDPE surface should be low. Herein, we tested the contact angle hysteresis (difference between the advancing contact angle and the receding contact angle), and the value of contact angle hysteresis was only 1.8°, which can explain the reason of the low sliding angle of the obtained superhydrophobic HDPE surface.

According to the SEM images shown in Figure 1 and some phenomena observed in experiments, we can explain the possible formation process of the

porous superhydrophobic HDPE surface as follows. In general, the polymer solution becomes thermodynamically unstable when drying the solution under certain conditions. As a result, phase separation will occur to form a polymer-rich phase and a polymer poor phase. The concentrated phase solidifies after phase separation and forms the matrix, whereas the polymer poor phase forms the pores.²⁸ When HDPE solution was dried at 120°C, the temperature was so high that the solvent evaporated quickly and phase separation was forbidden. Therefore, a smooth transparent film was formed [shown in Fig. 1(a)]. As the temperature decreased, the solvent evaporation rate was lower, and phase separation occurred and rough surfaces were formed [shown in Fig. 1(b–d)]. When the HDPE solutions were dropped on the glass plates in humid atmosphere, water from the moisture penetrated into the solution continuously.²⁸ Water is a nonsolvent for HDPE. If the amount of water in the solution were enough, water would act as a precipitator, and some HDPE aggregates would appear. The precipitated polymer (HDPE) acted as nuclei and the polymer-rich phase preferred to aggregate around the nuclei to decrease surface tension.³⁵ Thus, the phase separation was promoted further. But when the relative humidity was too high (greater than 75%), too much water penetrated into the HDPE solution continuously, and most of the HDPE were precipitated out of the solution. As a result, some large HDPE aggregates were hard to stick together to form uniform porous network structure, resulting in the appearance of large cracks. When relative humidity was less than 60%, the little water from moisture would penetrate into the HDPE solution, and the effect of water was weak. When the relative humidity was between 60% and 75%, the effect of water penetrated into the HDPE solution could not be ignored, and the water would cause the appearance of many HDPE aggregates, leading to the increase in phase separation, and cause the formation of the porous network structure. Ethanol is also a nonsolvent of HDPE, the addition of 3 mL ethanol decreased the solubility of HDPE and caused the formation of more uniform HDPE aggregates, and the more pores were formed by the aggregates in the solidification. When more ethanol

TABLE I
The Contact Angles of the Superhydrophobic HDPE Surface When Soaked in Water with Temperatures Ranging from 5°C to 50°C for 1 H to 15 Days

	5°C	10°C	20°C	30°C	40°C	50°C
1 h	160.0 ± 1.8°	160.0 ± 2.0°	159.0 ± 1.6°	159.0 ± 1.9°	158.0 ± 2.0°	158.0 ± 1.5°
1 d	160.0 ± 2.1°	159.0 ± 2.3°	160.0 ± 1.9°	158.0 ± 1.5°	158.0 ± 1.6°	157.0 ± 1.9°
5 d	159.0 ± 1.6°	159.0 ± 1.9°	159.0 ± 2.2°	158.0 ± 2.0°	158.0 ± 1.9°	156.0 ± 2.1°
10 d	159.0 ± 2.0°	159.0 ± 1.8°	159.0 ± 1.7°	159.0 ± 1.6°	157.0 ± 2.0°	156.0 ± 1.6°
15 d	158.0 ± 1.7°	159.0 ± 1.5°	158.0 ± 1.8°	158.0 ± 2.1°	156.0 ± 1.7°	155.0 ± 1.7°

TABLE II
The Effect of Applied Compressive Forces on the Water Contact Angles of the Superhydrophobic HDPE surface. The Pressure Was Calculated by Dividing the Force by the Apparent Area of the Superhydrophobic HDPE surface

Compressive pressure (MPa)	1	2	3	4
Contact angle (°)	159.0 ± 1.6	157.0 ± 2.1	155.0 ± 1.8	152.0 ± 2.0

was added into the HDPE solution, some large obvious cracks were also observed showing similar result at high relative humidity (relative humidity is higher than 75%). Thus, 3 mL ethanol was suitable in our experiment.

In previous reports, most of articles focused on the preparation of superhydrophobic surfaces, and the contents reporting the durability and stability of the superhydrophobic surfaces were few. Herein, we studied the durability of the as-prepared HDPE surface by several ways in atmosphere. When soaked in water with temperatures ranging from 5 to 50°C for 1 h to 15 days and water contact angles were measured at each condition, the water contact angles remained higher than 150.0° (shown in Table I). To know the wear resistance, we leaned the as-prepared HDPE surface about 5°, and made water flow through the surface continuously, and the water contact angles were measured after 10, 20, and 30 min. Interestingly, the water contact angles were 160.0 ± 1.7°, 159.0 ± 2.1°, and 159.0 ± 1.9°, respectively. In practical application, the ability to bear different forces is important. Thus, we made water droplets with a diameter of 4 mm drop onto the superhydrophobic HDPE surface from 10, 20, and 30 cm high for 10 min. After we stopped dropping the water, the water contact angles were 159.0 ± 1.7°, 158.0 ± 1.8°, and 158.0 ± 1.9°, respectively. Static compressive forces were also applied by putting masses on the surface, water contact angles were measured after application of compressive forces, and the water contact angles were still higher than 150° up to 4 MPa (shown in Table II). The above test results showed that the as-prepared porous superhydrophobic HDPE surface was rather stable and durable to satisfy the request of applications.

CONCLUSIONS

In conclusion, we obtained a stable porous superhydrophobic HDPE surface by adding ethanol in humid atmosphere (relative humidity is between 60 and 75%) at 5°C. The water contact angle and sliding angle of the as-prepared HDPE surface were 160.0 ± 1.9° and 2.0 ± 1.6°, respectively. Soaked in water

with temperatures ranging from 5 to 50°C for 15 days, the water contact angles were all higher than 150°. When water droplets with a diameter of 4 mm from 30 cm high dropped onto the superhydrophobic HDPE surface for 10 min, the water contact angle was also higher than 150°. Moreover, suffering static compressive forces up to 4 MPa, water contact angles were still higher than 150°. Compared with other methods of synthetic superhydrophobic surfaces, the presented method is much simpler and can be readily scaled to create large-area uniform superhydrophobic surface and can be applied in commercial manufacturing.

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