

Washable and Wear-Resistant Superhydrophobic Surfaces with Self-Cleaning Property by Chemical Etching of Fibers and Hydrophobization

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S Supporting Information

ABSTRACT: Superhydrophobic poly(ethylene terephthalate) (PET) textile surfaces with a self-cleaning property were fabricated by treating the microscale fibers with alkali followed by coating with polydimethylsiloxane (PDMS). Scanning electron microscopy analysis showed that alkali treatment etched the PET and resulted in nanoscale pits on the fiber surfaces, making the textiles have hierarchical structures. Coating of PDMS on the etched fibers affected little the roughening structures while lowered the surface energy of the fibers, thus making the textiles show slippery superhydrophobicity with a self-cleaning effect. Wettability tests showed that the superhydrophobic textiles were robust to acid/alkaline etching, UV irradiation, and long-time laundering. Importantly, the textiles maintained superhydrophobicity even when the textiles are ruptured by severe abrasion. Also colorful images could be imparted to the superhydrophobic textiles by a conventional transfer printing without affecting the superhydrophobicity.

KEYWORDS: PDMS coating, washable and wear-resistant, alkali treatment, self-cleaning property



1. INTRODUCTION

Superhydrophobic surfaces, which have contact angles greater than 150° , promise a wide range of uses,^{1–9} thus having been extensively studied during the past decade. Most importantly, much attention has been paid to improving the durability of the superhydrophobicity of surfaces for application-oriented materials.^{4,10–13} As for flexible materials, durable superhydrophobic surfaces on textiles/fibers show great potential in our daily life.^{4,14–18} Utilizing the fibrous microstructured textures, many researchers have coated fibers with nanostructures and hydrophobized the substrate to prepare superhydrophobic textiles.^{14,16,19,20} From the practical point of view, it is still a great challenge to sustain the superhydrophobicity through laundering and abrasion during applications.

To improve the mechanical stability of these surface-coated nanostructures, the formation of covalent bonds between nanostructures and the fibers is considered an important method and has resulted in good improvement.^{19,21–24} The formation of low surface energy polymer nanostructures which were protected from wear on fibers has also been reported as a method to prepare superhydrophobic textiles with good abrasion resistance.^{25,26} Additionally, coating fibers with nanocomposite which contains polymeric materials with excellent durability and inorganic nanoparticles seems more favorable for preparing durable surfaces on textiles,^{27–29} since coating is commonly used for fabric finishing. By this method, Zhou et al.²⁷ used

polydimethylsiloxane, filled with fluorinated alkyl silane (FAS) functionalized silica nanoparticles and FAS, to coat polyester fibers and obtained superhydrophobic textiles which showed remarkable durability against strong acid, strong alkali, repeated machine washing, boiling water, and severe abrasion, while retaining its superhydrophobicity.

In these studies, fibers were mostly roughened with extra-substrate nanostructures, i.e., nanoparticles, which face the issues to strengthen the interfacial interaction between the nanostructures and the substrate for application-oriented superhydrophobic surfaces. Alternatively, surface roughness could also be created directly from the bulk materials at the surface, resulting in hierarchical structures monolithic with the bulk substrate. In such cases, these roughening structures possess strong adherence and mechanical stability.⁴ We have reported that fibers could be roughened through chemical etching at the surface, and superdurable superhydrophobic textiles could be prepared by following diffusion of fluoroalkylsilane into the fibers.¹⁵ However, diffusion of hydrophobic alkylsilanes into fibers shows dependence on specific equipment, and it has been recognized that some fluorochemicals have potential risks to human health and the environment.

Received: March 11, 2014

Accepted: June 19, 2014

Published: June 19, 2014

Here we report a simple method to prepare colorful superhydrophobic PET textile surfaces with self-cleaning property on poly(ethylene terephthalate) (PET) textiles by chemical etching of the fiber surfaces and coating with polydimethylsiloxane (PDMS), as shown in Figure 1. The

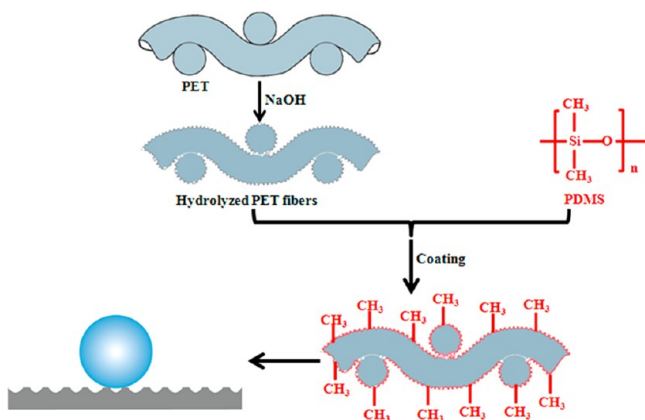


Figure 1. Preparation of superhydrophobic textiles.

obtained superhydrophobic textiles possess remarkable durability against different pH solutions without changing its super-repellent feature and exhibit excellent resistance to washing and abrasion. Importantly, colorful images could be imparted to the superhydrophobic surfaces by a conventional transfer printing on the textiles without affecting the superhydrophobicity.

2. EXPERIMENTAL DETAILS

Chemical Etching of PET Fibers. The original textiles were cleaned with deionized water at 75 °C for 30 min to remove the impurities and dried at 80 °C for 10 min. The cleaned textiles were dipped into 380 g/L sodium hydroxide solution for 10 min. Then the soaked textiles were double-side covered in a polyethylene film and heated at 120 °C for 4 min. Finally, the textiles were rinsed by abundant water until the pH of the textile surfaces reached 7 and dried at 80 °C in an oven. Thus, chemically etched PET textiles were obtained and denoted as E-PET.

PDMS Coating on Textiles. PDMS precursor part-A (Sylgard 186 elastomer base, 0.25 g) was dissolved in THF (30 mL) and ultrasonicated for 20 min to form solution A. PDMS precursor Part-B (sylgard 186 curing agent, 0.025 g) was dissolved in THF (30 mL) to form solution B. Then solution A and B were mixed together at room temperature to form a coating solution. Textile samples (9 g, 28 cm × 14 cm, 392 cm²) were dip-coated with the as-prepared coating solution, dried at 80 °C for 3 min, then cured at 135 °C for 30 min. When the sample used was pristine PET textile, the PDMS coated textile is denoted as PDMS-P-PET. By the same way, PDMS was coated on E-PET to obtain PDMS-E-PET.

To obtain different add-on of PDMS on the textiles, different concentration of PDMS solutions were used to coat the samples. The weight add-on W (wt %) of PDMS on textile was determined as the weight increase of the samples, according to the following equation:

$$W(\text{wt } \%) = \frac{W_1 - W_0}{W_0} \times 100 \quad (1)$$

where W_1 and W_0 are the weights of the samples after and before PDMS coating, respectively.

Textile Coloring or Printing. Dyeing of PET textile was conducted in an infrared rays dyeing machine with disperse dyes in aqueous solution according to the previous report.¹⁵ After the dye and two drops of acetic acid were added into the dyeing containers followed by adding PET textiles, the containers were sealed and heated at 130 °C for 1 h.

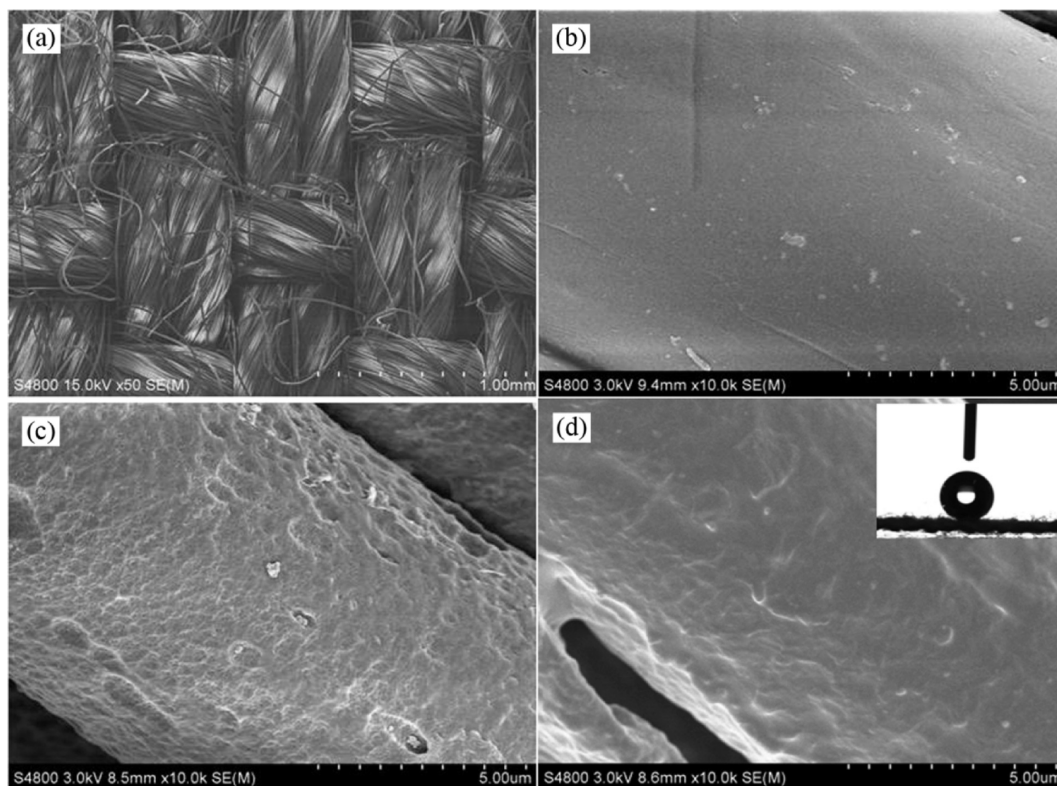


Figure 2. SEM images of (a) pristine PET textile, (b) pristine PET fibers, (c) E-PET fibers, and (d) PDMS-E-PET with a PDMS add-on of 3 wt %. The inset of part d is the image of a static water droplet on the PDMS-E-PET sample.

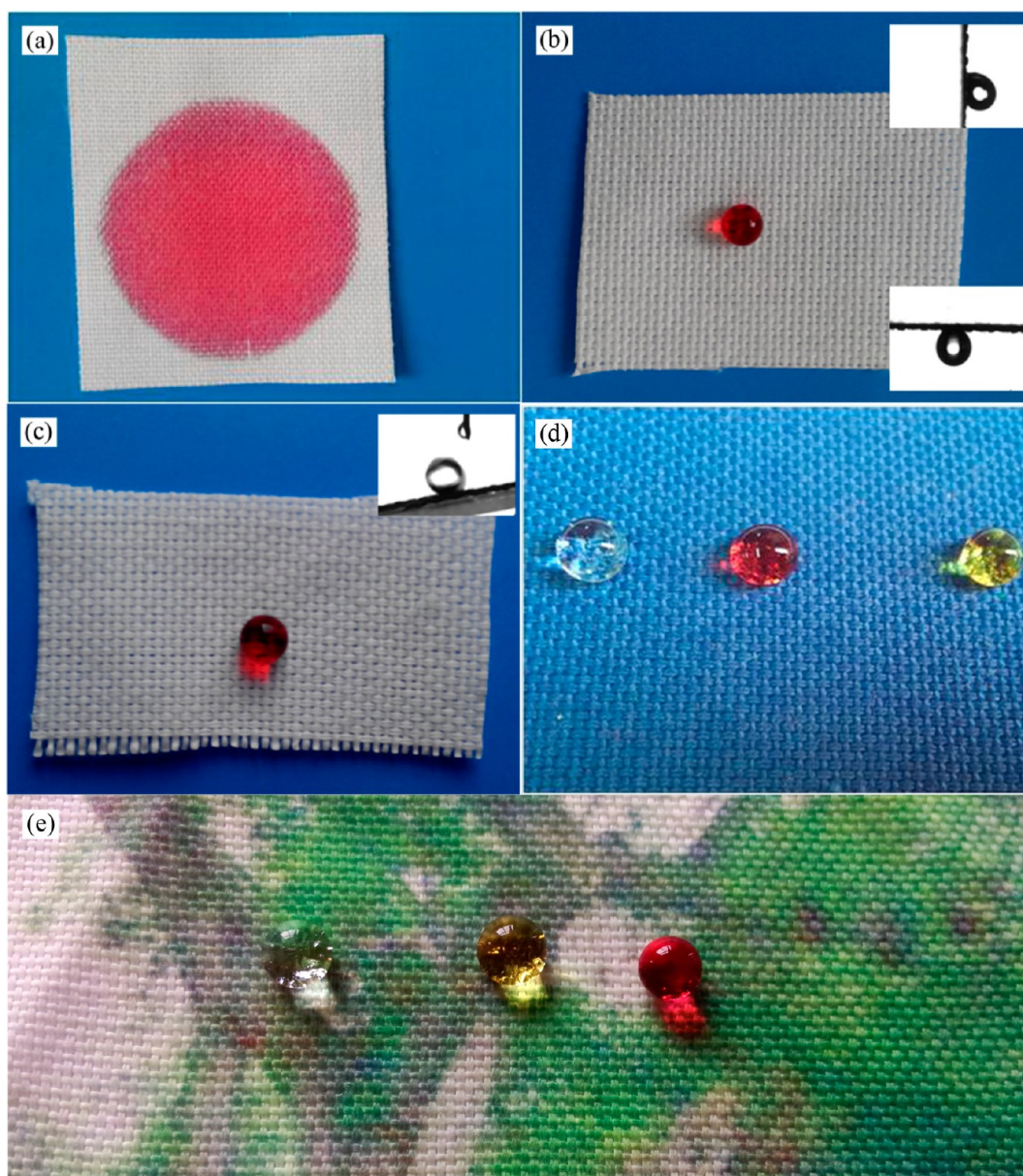


Figure 3. Dyed water droplets on (a) pristine textile, (b) PDMS-P-PET textile, (c) PDMS-E-PET textile, (d) colorful PDMS-E-PET textile, and (e) printed superhydrophobic PDMS-E-PET textile. Insets of part b are shapes of water droplets on the PDMS-P-PET textile with tilt angles of 90° and 180°. Inset of part c is the rolling behavior of the water droplet on the PDMS-E-PET textile.

After the system was cooled to 40 °C, the textiles were taken out, washed, and dried at 80 °C.

For printing of the PET textiles, the mirror image of a given pattern was printed on a piece of dye transfer paper by an inkjet printer using disperse dye inks. Then the paper was spread face down on the PET textile and pressed by two parallel plates heated at 180 °C for 8 s to transfer the pattern from the paper to the textile surface. By this thermal transfer printing method, printed PET textiles were obtained.

Characterization. Scanning electron microscopy (SEM) images were obtained on a Hitachi S-4800 field emission scanning electron microscope. Samples were sputter-coated with gold prior to examination. Water contact angles (CA) of the textiles were measured with a deionized water droplet of 5 μL on a video optical contact angle system (OCA 20, Dataphysics, Germany) at room temperature. All the contact angles and sliding angles (SA) were determined by averaging values measured at six different points on each sample surface. The contact angle hysteresis (CAH) was calculated by taking the difference between the advancing and receding angles. The reflectance of textiles was measured by a color testing instrument (Datacolor Spectropho-

tometer SF600). The textile samples should be folded into over four layers.

Evaluation of Mechanical Robustness. The washing durability of treated polyester textiles were evaluated by a standard procedure according to AATCC Test Method 61-2003 Test No. 1A. Samples were washed using a laundering machine (SW-12 AII, Da Rong, China) at 40 °C in the presence of 10 stainless steel balls with the existence of 0.37 wt % soap powder. One washing cycle (45 min) is approximate to five times of commercial laundering. The washed fabrics were rinsed by abundant water to remove the residual detergent and dried at 35 °C without any tension. The abrasion resistance was tested using a modified procedure based on the AATCCA Test Method 8-2001 according our previous reported method.¹⁵ Using a pure nylon fabric cloth as the abrasion partner, the testing was performed with a loaded pressure of 45 kPa and a moving path of 100 mm. In the test, two moving paths form one cycle.

UV-Durability Tests. It was conducted by irradiation using an artificial light source (UV lamp, Osram Ultra Vitalux 300 W) emitting a Gaussian-shaped spectrum which peaked at 370 nm with a cut off at 290 nm. Textiles were placed under the UV lamp for continuous irradiation.

3. RESULTS AND DISCUSSION

3.1. Morphology of Textiles. SEM was used to determine the morphology of the surfaces on the PET textiles. It was found that the as-received PET textile has a woven structure, as shown in Figure 2a, consisting of twisted yarns with microscale fibers of a diameter about $11.45\ \mu\text{m}$ which are smooth and round, as shown in Figure 2b. In order to incorporate finer structures on the fiber surface for enhancing the roughening effect of textile surfaces, PET textiles were treated with sodium hydroxide. Figure 2c shows that pits were formed on the fiber surface after chemical etching by alkaline hydrolysis and the diameter of the fibers decreased to about $9.68\ \mu\text{m}$. Also importantly, coating of PDMS with an add-on of 3 wt % did not cause great changes in the roughening morphology of the etched fibers, as shown in Figure 2d. Maintaining of the fiber morphology helps to complement the microscale roughness inherent in the textile weave, directing to proper roughness for superhydrophobic surfaces.

3.2. Superhydrophobic Property of Textiles. Surface wettability examination showed that the water can easily spread on the pristine PET textile due to the capillary effects of the fibrous structure, as shown in Figure 3a. However, the textile was rendered superhydrophobic by a simple coating with PDMS, as shown in Figure 3b. Also the CA of the PDMS-P-PET textiles increased (Figure 4) with increasing the add-on of PDMS. This

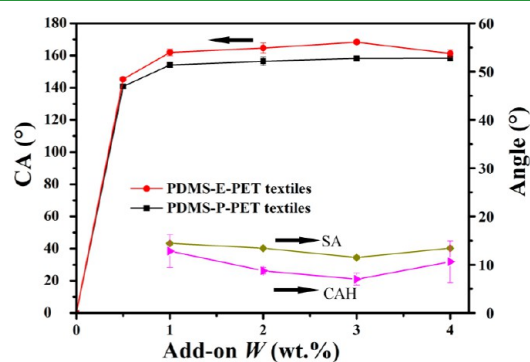


Figure 4. Changes of the CA as well as the SA and CAH of PDMS-E-PET with the add-on of PDMS on the textiles.

indicates that the microscale roughness inherent in the textile weave in combination with the low surface energy of PDMS favors the water repellency, which was also proved by previous studies,^{14,15,30} although water droplets are sticky on the superhydrophobic textiles (inset of Figure 3b). After chemical etching of the fiber surface, it was found that the hydrophobicity of the textile surfaces was greatly enhanced, as judged from the standpoint of CA increase at the same add-on of PDMS on the textiles (Figures 3c and 4). Also water droplets can roll off the textile surfaces when tilting the samples with CA greater than 150° , as shown in the inset of Figures 3c and 4. It should be noted that the CA of the PDMS-E-PET textiles increased with increasing the add-on of PDMS to 3 wt % while decreased close to that of the PDMS-P-PET textiles when the add-on reached 4 wt %. The decrease of CA might be induced by the decrease of roughness of textiles due to the leveling of pits by the overloaded PDMS. Correspondingly, the SA and CAH of the PDMS-E-PET textiles changed slightly with a different add-on of PDMS. The values of CAH were a little lower than the values of SA, which was in accordance with that reported on superhydrophobic fibrous materials.^{31–33} Low CAH with a value

around 8° makes the water droplet roll easily when it comes in contact with the PDMS-E-PET surface.

Figure 3d,e shows that colorfully dyed or printed superhydrophobic PET textiles can be obtained. Also it should be noted that superhydrophobic surfaces were fabricated in this work just by applying PDMS alone to the pristine textiles (the inset of Figure 2d) without using any fluorochemicals, which is different from the previous report.²⁷ This might be due to the difference of the microscale roughness from that reported previously which is caused by the yarn twist and woven structures of the textiles. However, PDMS did not raise the self-cleaning property on the textiles although superhydrophobicity was obtained. When a water droplet is sited on a PDMS-P-PET textile surface, it did not move even when the substrate was tilted vertically or turned upside down (insets of Figure 3b), showing a sticky superhydrophobic property.

In order to further demonstrate the adhering property of the PDMS coated pristine textiles, a PDMS-E-PET textile was used as a bottom with a water droplet on the surface. As shown in Figure 5a, PDMS-P-PET textile was used as a top to contact and

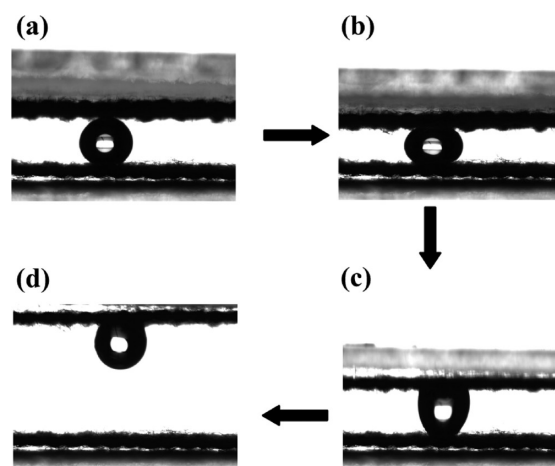


Figure 5. Behavior of a water droplet transferring from PDMS-E-PET (bottom) textile to PDMS-P-PET textile (top). (a) Water droplet on PDMS-E-PET textile, (b) PDMS-P-PET textile was pushed down on the water droplet, (c) PDMS-P-PET textile was lifted up, and (d) the water droplet was adhered on the PDMS-P-PET textile.

pushed down on the water droplet. After the top was lifted up, it was found that the whole droplet adhered on the top away from the bottom, indicating a strong adhesive effect between the water and the PDMS-P-PET textiles. This also shows that water can be easily taken away from the PDMS-E-PET textiles, which is in accordance with the rolling effect of water droplets on their surfaces.

Two distinct models, the Wenzel³⁴ and Cassie–Baxter³⁵ models have been extensively used to explain the roughness effect on the contact angles of liquids on a roughened surface. The Wenzel model describes the wetting regime in which the liquid penetrates into the roughened surface, which results in intimate contact between the liquid and the solid surface, usually leading to high contact angle hysteresis and even to a sticky state as in this case of PDMS-P-PET textiles due to the van der Waals' forces between water and the fiber surface, in which water can penetrate into the space between fibers as shown in Figure 6a.

However, after etching of the solid surfaces of PET fibers, pits were formed which cannot only roughen the textiles decreasing the contact area between the water droplets and the textile

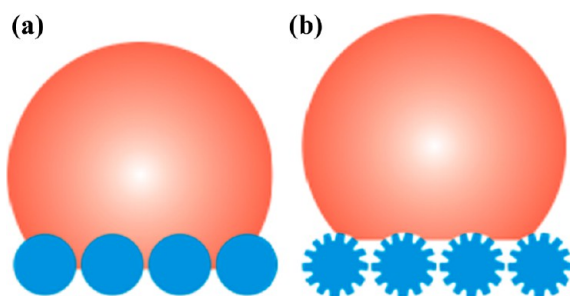


Figure 6. Schematic of water droplets on superhydrophobic textiles of (a) smooth and (b) etched fibers.

surface, lowering the van der Waals' forces between water and fiber surfaces, but also get air trapped improving the hydrophobicity of the fibers, thus making water roll easily on the textiles. This can be illustrated as in Figure 6b, which corresponds to the so-called Cassie wetting regime.³⁵ The enhancement of superhydrophobicity can be demonstrated by contact angle hysteresis. The property difference between the pristine and the etched PET textiles after PDMS coating can also be confirmed by sliding angle measurement as showing in Figure 4. Additionally, previous reports^{36,37} had shown that surfaces with different pitch value (bump density), peak-to-base height of microstructure, and different density of nanostructure showed a distinct difference in superhydrophobicity. In this case of textiles consisting of coarse yarns with microscale fibers, the microstructured surface possesses a large pitch value without any nanostructures; therefore, water can penetrate into the space between yarns and fibers leading to complete wetting between the water droplet and the textile surface. However, etching of the fiber surfaces increased dramatically the density of nanostructure, leading to air pocket formation between the water droplet and the fiber surfaces, which favors the transition from the Wenzel to Cassie–Baxter regime.

In order to show visually the air pocket formation on the textiles of PDMS-E-PET, PDMS coated textiles were immersed into water by force. Figure 7a shows that the PDMS-E-PET textile surface takes on a bright plastron layer, due to the total reflectance of light at the air layer trapped on the surface. This trapped air can effectively prevent a wetting on the textile surface underwater. While under the same conditions, the surface of the PDMS-P-PET textile did not appear on the bright plastron layer. Furthermore, after releasing the force, PDMS-E-PET textile

floated on the surface of the water, while the PDMS-P-PET textile sank to the bottom, as shown in Figure 7b.

The Cassie–Baxter regime with air trapped might be favorable to self-cleaning of surfaces. Water-soluble acid red dye was used as a model stain and sprayed on pristine PET, chemically etched PET, PDMS-P-PET, and PDMS-E-PET textiles. Then a water droplet was put on the dyes. Figure 8 shows that pristine PET

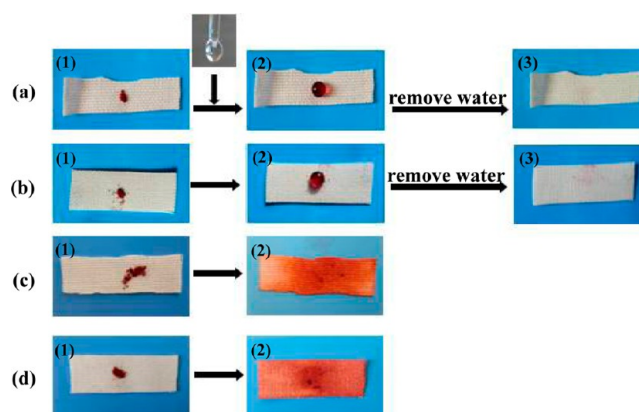


Figure 8. (a) PDMS-E-PET textile, (b) PDMS-P-PET textile, (c) chemically etched PET textile, (d) pristine PET textile. Step 1 is spraying of the acid red dye on samples. Step 2 is dripping of a water droplet on the dye. Step 3 is removal of the water droplet by filter paper.

and chemically etched PET textiles were stained red immediately when the water contacted the substrates due to their hydrophilic property. In contrast, water was dyed red and showed spherical on both PDMS-P-PET and PDMS-E-PET textiles. However, after removing the water by filter paper, some red stains were found on the surface of the PDMS-P-PET textile, while the surface of the PDMS-E-PET textile became as clean as that before the dye spraying, showing an excellent self-cleaning effect.

3.3. Durability of the Superhydrophobic Textiles. The abrasion resistance was evaluated by using a modified procedure according to our previous report¹⁵ based on the AATCCA Test Method 8-2001. It was found that the CA of the PDMS-E-PET textiles remained at 159.1° after the first 2000 cycles of wearing (Figure 9a), showing a slight decrease from 163.1° of the sample before abrasion, while the CA of the PDMS-P-PET textiles decreased to 146.1°. The CA change can be ascribed to the partial loss of the surface roughness and the removal of the

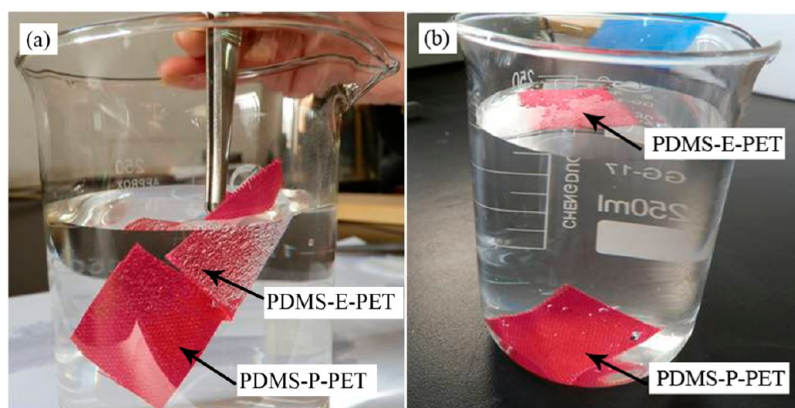


Figure 7. (a) Immersion of PDMS-P-PET and PDMS-E-PET textiles in water by force. (b) Free immersion of PDMS-P-PET and PDMS-E-PET textiles in water.

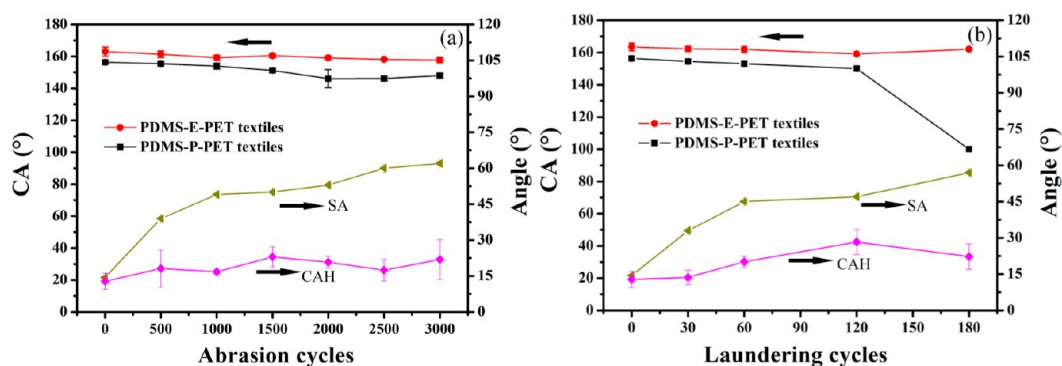


Figure 9. Changes of CA as well as the SA and CAH of PDMS-E-PET with (a) abrasion cycles and (b) washing cycles of textiles with PDMS add-on of 1 wt %.

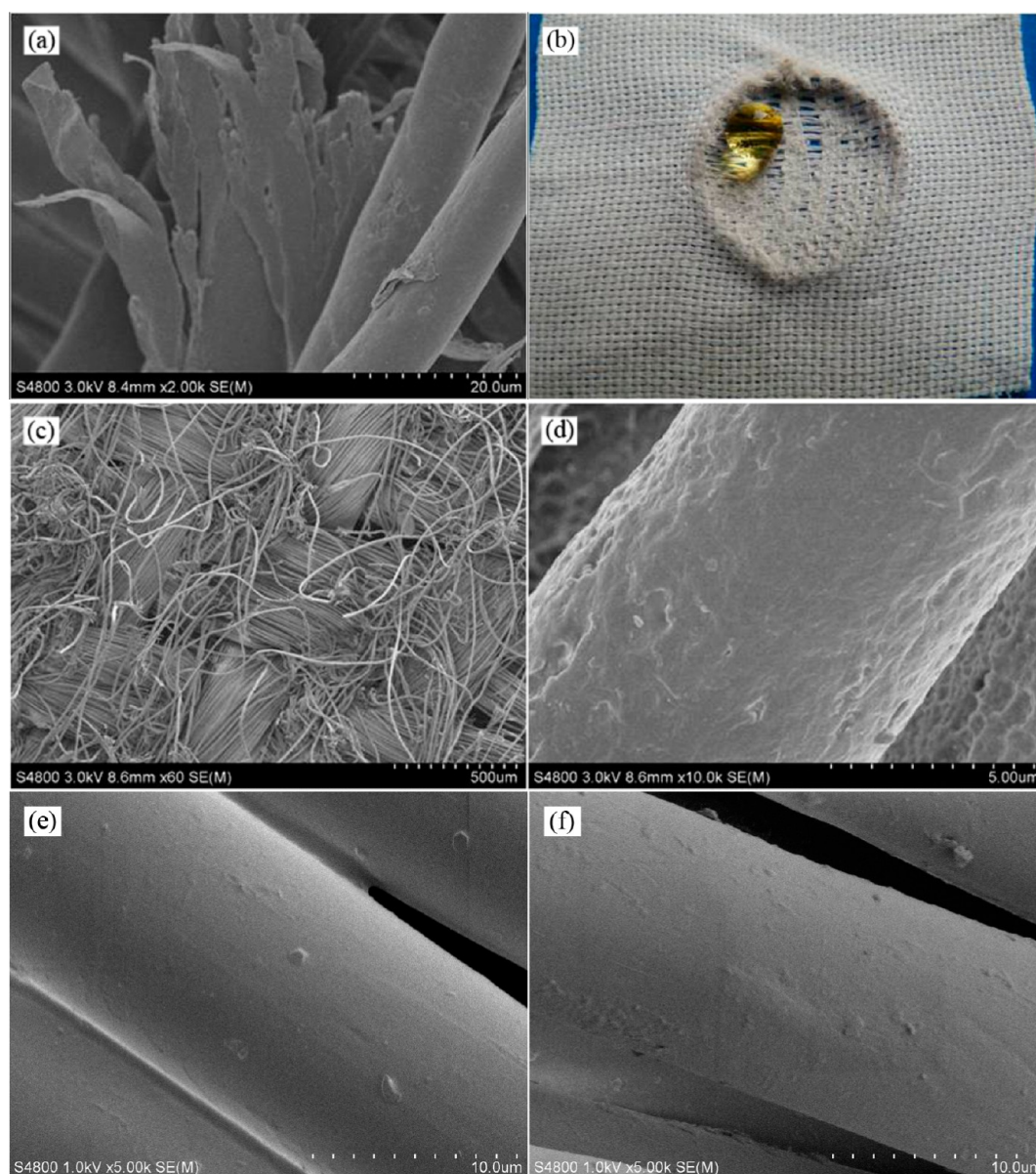


Figure 10. (a) SEM image of PDMS-E-PET fibers after abrasion of 3000 cycles, (b) photograph of a water droplet on the broken area of PDMS-E-PET textiles after abrasion of 3000 cycles, (c) SEM image of PDMS-E-PET textiles, and (d) SEM image of PDMS-E-PET fibers after laundering test of 180 cycles. (e) SEM image of PDMS-P-PET textiles and (f) SEM image of PDMS-P-PET textiles after the laundering test of 120 cycles.

PDMS at the fiber surface. We also evaluated the SA of the fabric. With severe abrasion, some protruding fuzz appeared on the

surface of the sample, causing some force or adhesion to the water on the fabric. Thus, the SA increased with increasing the

abrasion cycles. However, the CAH remained lower than 23° . Further abrasion to 3000 cycles made the sample worn out; however, the PDMS-E-PET textiles still remained superhydrophobic, as shown in Figure 10a,b, indicating excellent durability against abrasion.

The laundering durability were evaluated by a standard procedure according to AATCC Test Method 61-2003 test no. 1A. Figure 9b shows the change in the value of CA and SA with laundering cycles. The CA of PDMS-E-PET still remained at 159.1° after 120 laundering cycles, showing a slight decrease from 168.1° , while the SA increased a little. Here the CAH of the treated fabrics after the laundering test was also examined. The CAH still remained about 13° after 30 cycles of home machine washing, which indicated a durable superhydrophobicity. With increasing laundering cycles to 120 cycles, the CAH increased to 28.3° with an error of $\pm 8.29^\circ$. The CA of PDMS-P-PET decreased to 149.2° and sharply to 100° when the samples were further laundered to 180 cycles. For PDMS-E-PET textiles, the CA showed a little increase due to the roughness enhancement by the fuzz formation on the textiles which can be observed by naked eyes. This might be induced by strong mechanical action during laundering. The protruding fuzz also caused further increase of the SA, however a slight decrease of CAH. The SEM image of the laundered fibers revealed that the surface retained its roughening morphology even after 180 cycles of repeated washing (Figure 10c,d), indicating excellent durability of the superhydrophobicity to washing. As a comparison, SEM images of PDMS-P-PET before and after the laundering test of 120 cycles were also shown in Figure 10. It was found that PDMS-P-PET fibers were very smooth with some coating filled between fibers (Figure 10e). However, after 120 cycles of repeated washing, the filled coating was removed showing very clean spaces between fibers and the morphology of the fiber surfaces changed little. This indicates that the decrease of CA was mostly caused by partial removal of PDMS.

These results showed that the PDMS coated textiles have excellent durability against strong mechanical action during laundry and abrasion tests. This might be because the reformation of the elastomer PDMS coating on fibers can rebound after the load is withdrawn.^{12,27} Additionally, roughening of PET fiber surfaces contributed to the maintaining of PDMS on fibers, which also helped the lasting of superhydrophobicity of PDMS-E-PET textiles.

We also evaluated the durability of superhydrophobicity of the PDMS-E-PET textiles by dipping the sample in solutions with different pH (pH = 1–13) for 24 h. Figure 11 shows that the CA of the superhydrophobicity changed little, indicating strong resistance to different pH solutions.

Figure 12 shows the CAs of PDMS-E-PET textiles as a function of UV irradiation time. It was found that the CA declined a little from 168.3° to 163.2° after the first 12 h UV exposure, however showed no great change for further irradiation. Also it should be noted that the paper under the sample, which was white before UV exposure (Figure 12a), became yellowish (Figure 12b) after 384 h, i.e., 16 days, of UV exposure, while the textile surface still remained superhydrophobic with a CA of 158.9° . This indicates that the superhydrophobicity of the PDMS-E-PET textile possesses excellent resistance to UV light.

Additionally, we investigated the dyeing property of the PDMS coated textiles. Interestingly, although the superhydrophobic textiles could not be dyed evenly by the dip-and-cure dyeing method because of the difficulty of wetting the fibers,

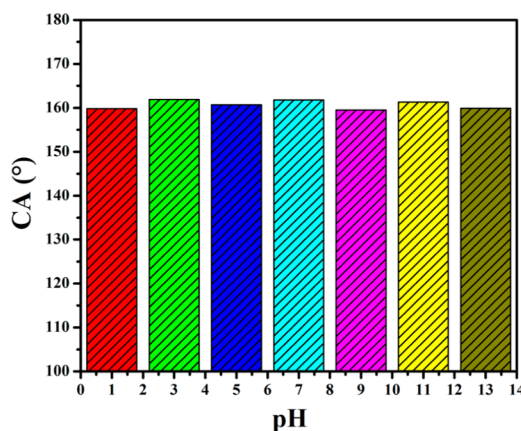


Figure 11. Superhydrophobicity of the fabrics with different pH solutions.

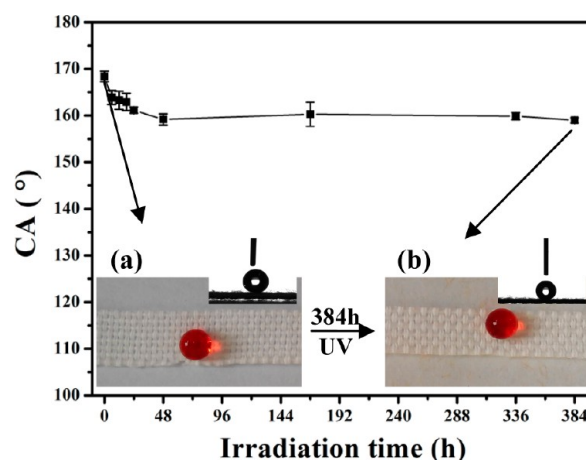


Figure 12. Relationship between the CA of PDMS-E-PET with add-on of 3 wt % and the irradiation time of UV, and photographs of red color water droplets on PDMS-E-PET samples above printing paper (a) before exposure and (b) after UV light exposure. Insets are images for CA measurement.

they could be dyed uniformly by disperse dyes in the sealed container using the infrared rays dyeing machine. Figure 13 shows that the reflectance curves of the superhydrophobic textiles dyed after and before PDMS treatment overlapped and traced very close to that of the commonly dyed textiles without hydrophobization. This indicates that PDMS treatment could be

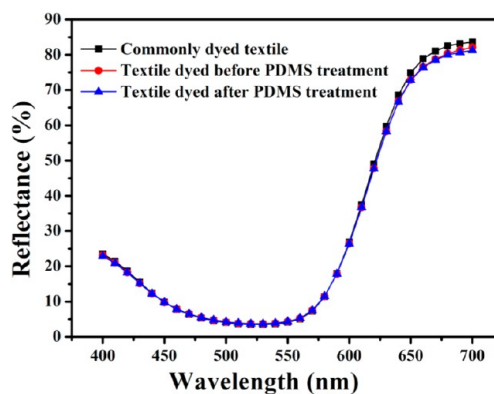


Figure 13. Reflectance of the commonly dyed textiles and the superhydrophobic textiles dyed after and before PDMS treatment.

done after dyeing of textiles because it changed little the color of the dyed textiles, which might be due to the thinness and excellent optical transparency of the PDMS coating.^{38,39} Also the superhydrophobic textiles could be dyed uniformly by disperse dyes in our experiment obtaining the same color as that of commonly dyed textiles. This might be because the sublimed disperse dyes could penetrate into the PET fibers through the PDMS coating in the sealed container using the infrared rays dyeing machine, because of the high gas and solute permeability of PDMS.^{38–40}

4. CONCLUSIONS

We have demonstrated that washable and wear-resistant superhydrophobic colorful surfaces with self-cleaning property were successfully constructed on PET textiles by chemical etching of the fiber surfaces followed by coating with PDMS. Chemical etching favors the transition of the wetting property of the hydrophobized textiles from the Wenzel to Cassie–Baxter regime. It was shown that the as-obtained textiles possess remarkable durability against different pH solutions without changing its super-repellent feature and exhibit excellent resistance to washing, abrasion, even exposure to UV light. Importantly, colorful images could be imparted onto the superhydrophobic surfaces by conventional dyeing or thermal transfer printing on the textiles without affecting the superhydrophobicity. The method is simple and requires no special equipment, which is suitable for large-scale production.

■ ASSOCIATED CONTENT

Supporting Information

SEM images and EDX mapping of the cross section of PDMS-P-PET and PDMS-E-PET fibers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by National Natural Science Foundation of China (Grant 51372146), Program for New Century Excellent Talents in University (Grant NCET-12-1042), Research Fund for the Doctoral Program of Higher Education of China (Grants 20116125110002 and 20136125110003), Major Program of Science Foundation of Shaanxi Province (Grant 2011ZKC05-7), and Key Scientific Research Group of Shaanxi Province (Grant 2013KCT-08).

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