Fabrication of Superhydrophobic Fabric Coating Using Microphase-Separated Dodecafluoroheptyl-Containing Polyacrylate and Nanosilica

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ABSTRACT: Superhydrophobic coating was developed on cotton fabric in this article using a dodecafluoroheptyl-containing polyacrylate (DFPA) and nanosilica. Film morphology of DFPA on cotton fibers/fabrics and chemical compositions of the treated cotton fabric were investigated using scanning electron microscopy (SEM), atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS), respectively. DFPA could form a relatively even film on the cotton fabric/fiber under SEM observation; however, it presented a rough and microphase-separated pattern under AFM observation. There were many mountain-like protuberances. The height of the protuberances and the root mean square roughness (R_{ms}) of the film reached about 20–50 nm and 12.511 nm in $2 \times 2\text{-}\mu m^2$ scanning field (as the scale data was 100 nm). XPS analysis indicated that the perfluoroalkyl groups had the tendency to enrich at the film–air interface. DFPA could make the treated cotton fabric with a water contact angle (WCA) at about 138.5°. Cotton fabric was previously roughened using a 1 wt % silica sol with an average particle size of 20–30 nm and then finished by DFPA; hydrophobicity of the resultant cotton fabric was strongly improved, and WCA could reach 153.6°. The color of this superhydrophobic fabric would not be influenced, but its softness decreased compared to untreated fabric. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

A superhydrophobic surface is defined as having a water contact angle (WCA) larger than 150°.[1] Its remarkable properties, including self-cleaning ability and water repellency, have attracted much academic and industrial interest recently because of the potential use of such surfaces in various applications.[2,3] In superhydrophobic surface fabrication, a high WCA can be obtained by a combination of a low-surface energy composition and a well-designed surface with a nanoscale and microscale roughness.[4–6] Thus the tuning of surface properties, both in terms of surface free energy and roughness, is primordial to obtain superhydrophobic surfaces. To lower the surface free energy, a large variety of polymers have been commonly tested. Among others, fluorinated polymers are widely used due to their extremely low surface energy. In addition, the incorporation of fluorine atoms into the polymer structure results in other peculiar properties such as low refractive index, low friction coefficient, and chemical resistance. Especially, fluorinated acrylic polymers can not only easily form stable films on various matrixes such as textile, leather, paper, glass, metal, and others but endow them with low surface free energy. They were, thus, widely used to fabricate superhydrophobic surfaces.[1,7–12] For instance, Chang et al.[7] fabricated organic superhydrophobic films on glass substrate using TA-N fluoroalkylate (TAN) and methyl methacrylate copolymer as low surface energy substance and inorganic silica powder as surface roughness material. P(St-co-HFMA) bulk polymer was synthesized by Wei et al.[8] and then dissolved in tetrahydrofuran and ethanol-mixed solutions to form the casting film solution; finally, the superhydrophobic copolymer films on glass were prepared subsequently via phase-separation technique using the above low surface energy fluorinated acrylate copolymer solution. Hsieh et al.[9] first used an assembly technique to prepare the well-ordered silica nanosphere arrays, and then an appropriate amount of perfluoroalkyl methacrylic copolymer emulsion was used as low surface energy material to lower the surface energy of silica nanosphere arrays. At last, a superhydrophobic film on glass was obtained. Grignard et al.[10,11] separately exploited chemisorption and electrospinning methods to engender superhydrophobic surfaces on aluminum substrates using fluorinated block copolymer solutions as low surface free energy substance. However, most of them have been fabricated on rigid substrates such as silicon wafers, glass slides, and metal surfaces and seldom on soft material surfaces, for

example, textile and paper. These might limit the practical application as well as the large-scale production of superhydrophobic surfaces.

Recently, Miao et al.[13] and Deng et al.[14] grafted fluorinated acrylate monomers, the perfluoroalkyl phosphate acrylates, and 1H, 1H, 2H, 2H-nonafluorohexyl-1-acrylate onto cotton fabrics via γ-ray irradiation, respectively. Then the treated cotton fabrics displayed the superhyhydrophobic characteristic. However, let us note that a special method and installations, γ-ray irradiation, and relevant devices are necessary to construct the superhydrophobic cotton fabric, which is probably unfavorable to scale-up production. Li et al.[15] had synthesized amphiphilic triblock azide copolymers containing poly(ethylene glycol) and poly(2,2,3,4,4,4-hexafluorobutyl acrylate) blocks via room temperature RAFT polymerization using redox initiation and then used those copolymers to fabricate superhydrophobic cotton fabric. Although they claimed that the superhydrophobic cotton fabric possessed high stability and chemical durability due to the fluorinated polymer chains covalently attached on the cotton surface, it still contained several tedious steps and adopted ATRP preparation technique needing severe conditions. It is therefore imperative to prepare suitable fluorinated acrylic polymers used in fabricating superhydrophobic cotton fabrics.

On the other hand, as the roughness of the cotton is usually on a relatively large scale, two classes of methods are generally needed to generate small-scale structures to increase the hydrophobicity of the cotton fabrics. One is using alkyl trichlorosilanes via gas-phase reaction routes, solvent-solution reaction routes, and low-temperature CVD routes, respectively, to produce nanoscale silicone coating attached to the cotton surface. The other is introducing inorganic nanosize particles such as SiO_2,[16–19] TiO_2,[20] and ZnO[21] onto the cotton surface through sol–gel and LBL methods. Among them, nanosilica is frequently chosen to fabricate the superhydrophobic fabric because of its low cost and easy availability characteristics. It is also known that in the synthesis of fluorinated polyacrylates, the strongly repulsive interaction between fluorinated alkyl groups and the other groups easily engenders the final products show phase-separated structures or form uneven, rugged films on substrates,[22] which could no doubt increase the microroughness of the treated surface and make a contribution to the hydrophobicity in fabricating superhydrophobic surfaces.

In our present work, a dodecafluoroheptyl-containing polyacrylate (DFPA), dodecafluoroheptyl methacrylate (DFMA)-co-butyl acrylate (BA)-co-dimethylaminoethyl methacrylate (DM)-co-2-hydroxypropyl acrylate (HPA), was simply synthesized and used to construct the superhydrophobic fabric in combination with a 1 wt % silica sol through a solution-immersion method. And herein a reactive monomer, HPA, and a tertiary amine-containing monomer, DM being changed to positive after neutralization, which would probably aid for the fluorinated polymer electrostatic interaction on negatively charged cotton fibers, were incorporated into the molecule to solve the fixation of the fluorinated polyacylate and improve the DFPA film-forming ability as well as the curing effect in application. We reported film morphology of DFPA on the cotton fibers/fabrics and chemical compositions of the treated cotton fabric as well as

hydrophobicity of the treated fabrics using scanning electron microscopy (SEM), atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS) analyses. And also the performance properties of the treated cotton fabrics, such as softness, color, and washing durability, were investigated.

EXPERIMENTAL

Materials
DFMA (Harbin Xeogia Co., China) was washed with 2 wt % NaOH aqueous solution and distilled water, respectively, to remove the inhibitor. BA, t-butanol, and ethyl acetate (EA), all analytical reagents, were used as received. DM and HPA were purified by distillation before use. Thirty weight percent silica sol (Qindao Hengsheng Chemical Co., China) with a pH of about 6 and the SiO_2 particle size between 20 and 30 nm were used without further treatment.

Defatted cotton fibers and a cotton fabric with a density of 133 × 72 (the yarn counts of warp × fill, 10 cm × 10 cm) were, respectively, ultrasonicated with distilled water and acetone at 25°C for 20 min in order to remove the slurry or contaminants adhered onto the fibers or the fabric and then dried at 80°C for 5 min.

Synthesis of DFPA
Dodecafluoroheptyl-containing polyacrylate (DFPA) was synthesized in our previous work.[23] In the presence of α,α′-azobis-iso-butirronitrile as an initiator, and the bubbling of N_2, DFMA was copolymerized with BA, DM, and HPA in t-butanol solution. At the end of the reaction, the t-butanol was recovered by distillation. The mixture was respectively washed in distilled water and ethanol and then stripped off by a vacuum. Finally, a viscous copolymer, DFBA-co-DFPA was obtained, and its structure diagram was shown in Figure 1(a). For DFPA, the viscosity and the number–average molecular weight (M_n, measured by Waters gas permeation chromatography) as well as the surface tension (γ) were 5.28 Pa s, 14,300, and 22.31 N/m, respectively.

Preparation of Superhydrophobic Fabric
A piece of cotton fabric was impregnated into a 1 wt % silica solution (diluted from the 30 wt % with water) for 3 min, padded to wet pick-up at about 70%, and then dried at 100°C, so that the silica particles were deposited and fixed onto the cotton surface. It was noted as cotton/SiO_2.

DFPA was dissolved using EA to form a finishing liquor bath containing 0.03 wt % fluorinated polyacrylate, and then a few drops of acetic acid were added to neutralize the tertiary amine side groups in DFPA. The silica-roughed cotton fabric was impregnated in the aforesaid DFPA liquor for several seconds, drawn out, and squeezed to remove the superfluous solution. Then it was dried at 80°C for 5 min and cured at 170°C for 3 min. The sample was kept in a desiccator to balance for 24 h and noted as DFPA/SiO_2 [Figure 1(b)]. Meanwhile, another defatted cotton fabric was treated using the same DFPA liquor to make comparison according to the above procedure and noted as DFPA/cotton [Figure 1(c)].
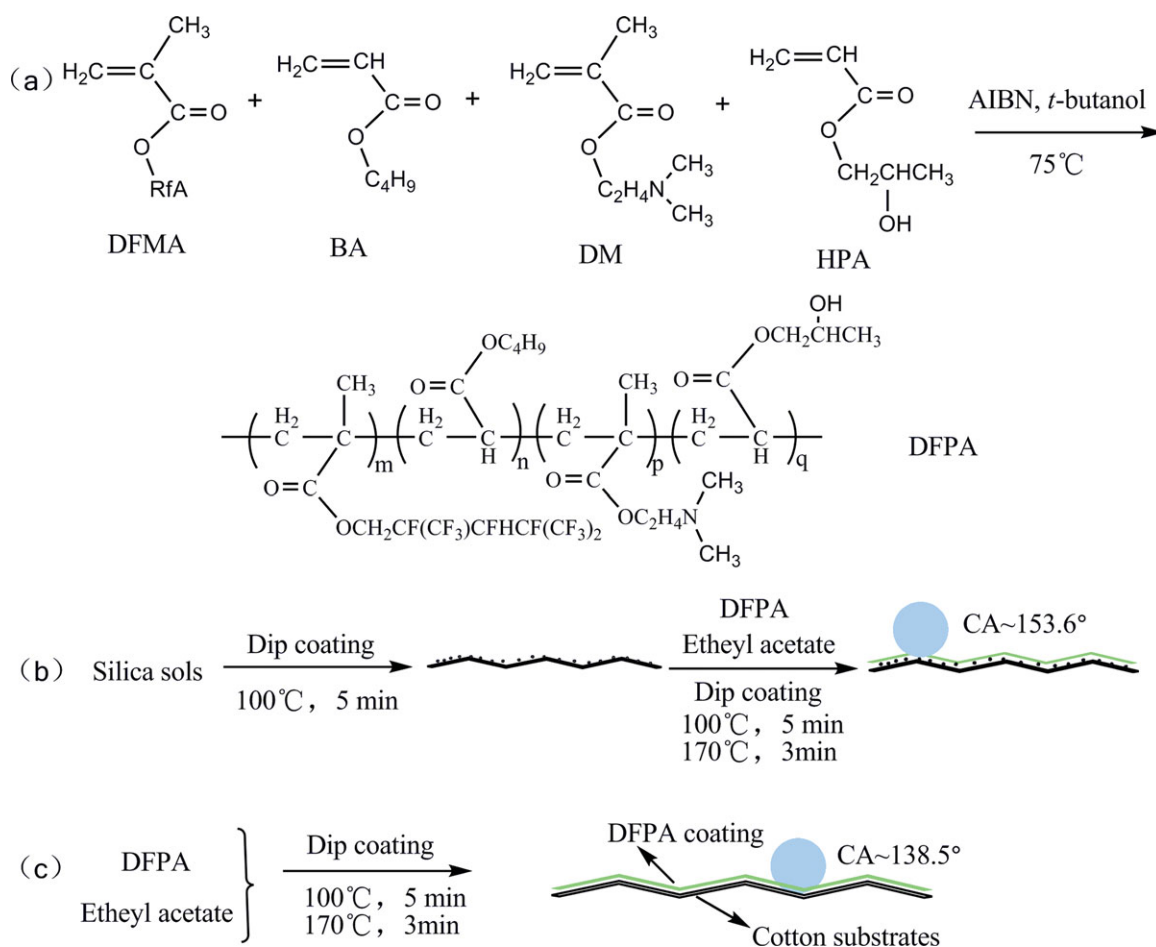
Figure 1. Preparation of the (a) DFPA solution, (b) DFPA/SiO$_2$ coating, and (c) DFPA/cotton coating. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Characterization

AFM images were observed for untreated fabric and DFPA/cotton with a Nanoscope IIIA atomic force scanning microscope (Digital Instruments, USA) at 22°C and in air of relative humidity of 48% in noncontacting mode. SEM photographs were taken by a Hitachi S-570 scanning electron microscope after the fibers/fabrics coated with gold in vacuum. Surface composition of the treated cotton fibers/fabrics was analyzed by XPS, in which XPS spectra were obtained on a Physical Electronics Model 5700 X-ray photoelectron spectrometer (PHI Co.) equipped with an Al monochromatic source (Al Kα energy of 1486.6 eV). The photoelectron take-off angle was 30°, and the vacuum degree of analysis chamber was 6.7×10^{-8} Pa. In the XPS measurement, the deviation of the binding energy was corrected by the C$_{1s}$ signal occurring at 284.8 eV due to hydrocarbon contamination on the sample surface.

Cotton fabric samples were air-conditioned at 25°C ± 2°C and 65% ± 2% relative humidity for 24 h, and the performance properties were measured as follows. WCA was measured by a JC 2000C contact angle tester (Shanghai Zhong Chen Power-each CO., China) at ambient temperature. The water droplet volume was 5 μL, and the average of five readings was used as the final contact angle of each sample. Bending rigidity (BR)

and whiteness of the treated fabrics were measured with a Drick softness measure instrument (DRK119, Jinan, China) and an YQ-Z-48B fluorescent whiteness tester, respectively. The washing durability of the superhydrophobic cotton fabric was examined by washing the treated fabrics in a washing machine according to the method specified in Australian Standard (AS 2001.1.4).

RESULTS AND DISCUSSION

Film Morphology of DFPA on Cotton Substrate

It is well known that properties or application performances of a polymer depend largely on its structure or morphology on substrates. Thus, exploration of its morphology on substrates is of great value. Fluorinated polyacrylates possess low surface tension. This property makes them outspread easily and adsorbed stably onto the surface of hydrophilic matrix (e.g., fabric), forming films of molecular dimensions. As such films sheath the fibers, more or less modified morphology of the treated fibers should be observed in experiments. Hence from observation of the treated fiber surface, we can get some information about morphology of fluorinated polyacrylate on the fiber substrate. Figure 2(a–f) is a series of SEM images of pure cotton fabrics/fibers untreated or treated by DFPA, silica sols, or DFPA/silica sols. At lower magnification (×50), the as-received
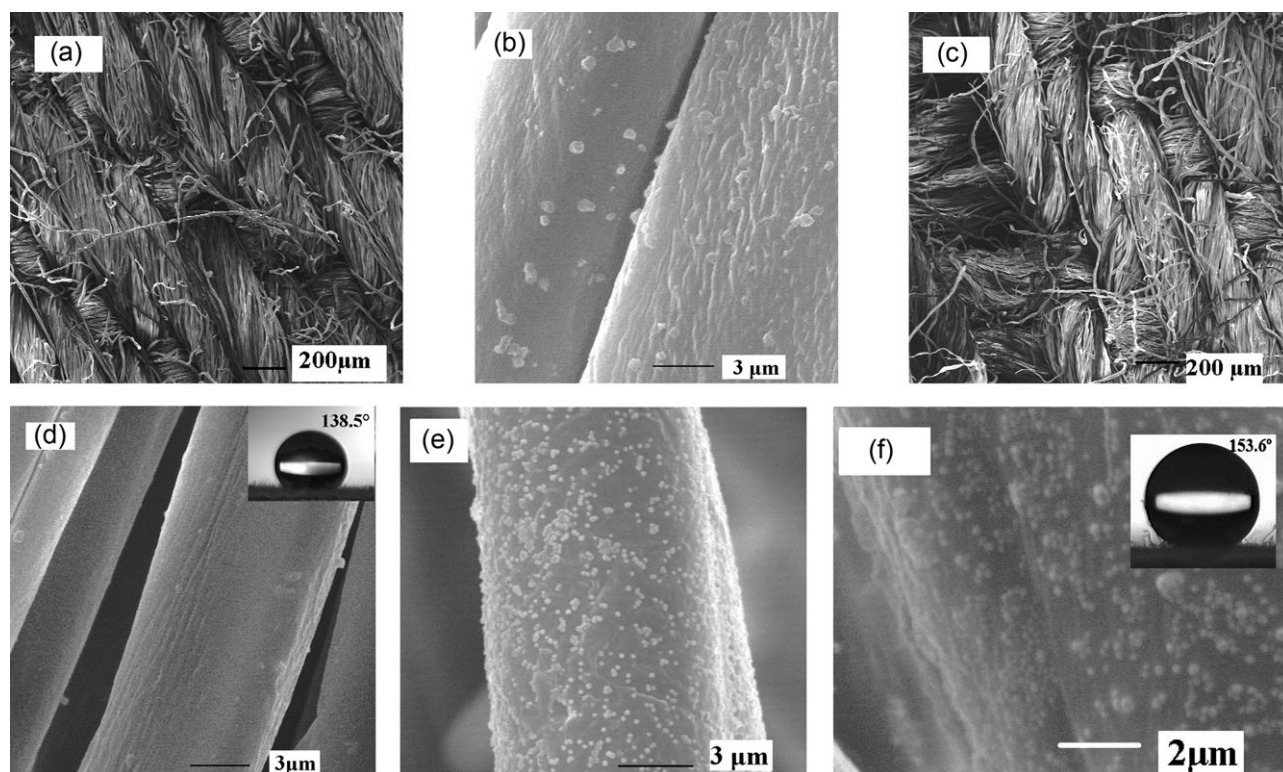
Figure 2. SEM images of blank cotton fabrics [(a) (×50), (b) (×5000)], DFPA/cotton [(c) (×50), (d) (×5000)], and cotton/SiO$_2$ (e) (×5000) as well as DFPA/SiO$_2$ (f) (×8000).

cotton fabric displayed a tightly woven, fibrous structure [Figure 2(a)], but at higher magnification (×5000), the single fiber showed a heterogeneous model, and there were many grooves on its surface [Figure 2(b)]. In contrast, at lower magnification, appearance of the treated cotton fabric showed no change and still possessed this tightly woven, fibrous structure [Figure 2(c)] after treatment. However, at higher magnification, the concaves almost disappeared on smooth surface of single root fabric after the DFPA treatment, and there was distinctly a relatively even film coated on the surface of the treated cotton fabrics [Figure 2(d)]. On the other hand, many nanoscaled nubs or burls emerged on the rugged surface of a single fiber after the silica sols treatment, and the average sizes of those nubs were about 20–90 nm estimated from scale bar in Figure 2(e), which had some difference with actual size of silica sol, and this would probably be resulting from agglomeration of nanosilica on fiber surface. However, those particles were coated evidently beneath a layer of film after the DFPA/SiO$_2$ treatment [Figure 2(f)].

To further ascertain the real morphology of DFPA on fabrics/fibers substrate, AFM was used to investigate the fine morphologies of the DFPA molecules on fabrics/fibers substrate and also the untreated cotton fabrics as control. The results are presented in Figure 3. Let us note that surface morphologies of the treated fabrics show fully different patterns between SEM and AFM observations. Relatively smooth DFPA film coated on the surface of the treated cotton fabrics emerged as more rough pattern instead. As shown in Figure 3(a), the rugged pattern of untreated cotton substrate, which may have a more or less effect on the morphology of DFPA/cotton in AFM observation, was

presented. Even so, it could be clearly seen from Figure 3(b) that DFPA/cotton presented a continuous film with many small mountain-like protuberances on the film surface. By comparing this result with the reported experiments,[24–26] these small mountain-like protuberances on DFPA surface should result from the packed and phased-separated poly(dodecafluoroheptyl methacrylate) segments in DFPA. The height of the protuberances and the root mean square roughness (R_{ms}) of the film reached about 20–50 nm and 12.511 nm in 2 × 2-μm^2 scanning field (as the scale data was 100 nm) via AFM software analyses. Obviously, a nanorough DFPA film on fabrics/fibers substrate was yielded in this experiment.

It is well known that the nanometer-roughed surface is an essential premise for fabricating a superhydrophobic surface. It is, thus, possible for us to use DFPA to create a strong or superhydrophobic surface on cotton fabrics.

Surface Analysis

In this procedure, DFPA/cotton was used as an example, and its XPS spectra were investigated and are shown in Figure 4. Obviously, four signals at 285, 400, 532, and 689 eV, respectively, were clearly observed in the experiment corresponding to C$_{1s}$, N$_{1s}$, O$_{1s}$, and F$_{1s}$. The integrated peak intensities showed atomic mass concentrations (%) of 41.97 : 15.71 : 0.06 : 42.26 for F/O/N/C and was not in good agreement with the theoretical ratio of 45.59 : 11.23 : 0.32 : 39.37. Apparently, the F/N mass ratio (41.97/0.06, 699.5) is much bigger than the theoretical value (45.59/0.32, 142.9), demonstrating that the fluorinated heptyls from DFPA enriched onto the polymer–air interface. Meanwhile,
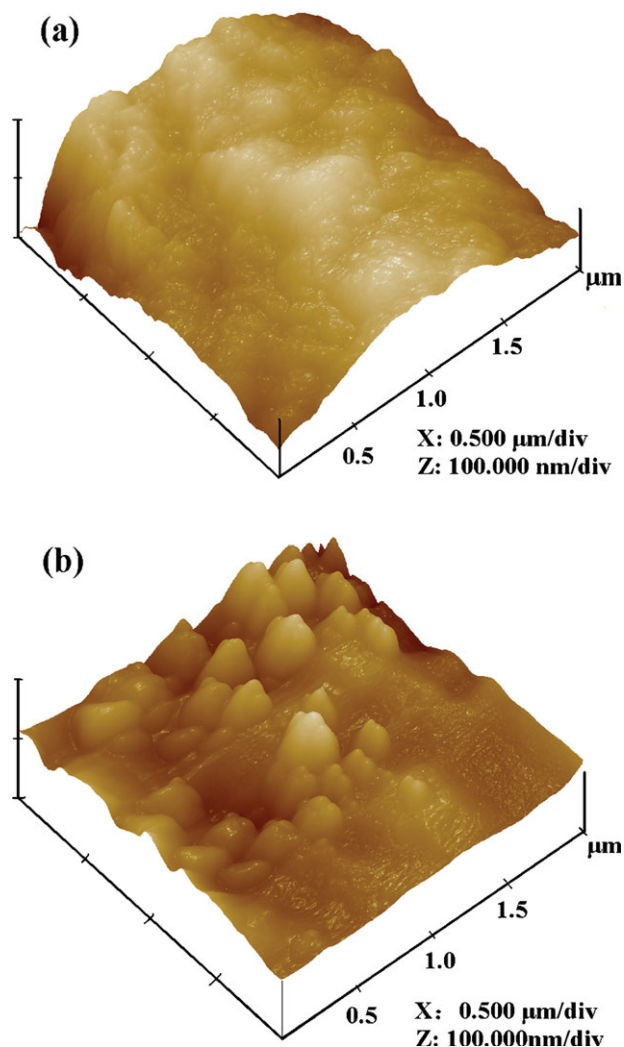
Figure 3. AFM images: (a) cotton; (b) DFPA/cotton. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the N atoms laid below the fluorinated resin film interacting with the cotton substrate in H-bond or electrostatic force. As we all know that migration or enrichment of fluorinated groups onto the treated surface is another important factor for creating a superhydrophobic surface.[27–29]

High-resolution C_{1s} spectrum is also shown in Figure 4(b). Clearly, the C_{1s} in DFPA was split into five different subsidiary signals. The signal at 284.8 eV was attributed to C—H from the C—CH$_2$ and C—CH$_3$ groups, and the signals at 286.3 (C—O, C—N) and 287.9 eV were due to the C—O and C—N as well as the ester C=O groups.[30] Because two types of fluorocarbon groups existed in DFPA molecule, the corresponding absorptions were assigned to —CF and —CF$_3$ groups occurred at 288.9 (—CF) and 293.1 (—CF$_3$) eV, respectively.[26]

Hydrophobic Analysis and Other Performance Properties of Cotton Fabrics

Hydrophobicity (usually expressed by WCA) is dominated by the topography and chemistry of surfaces.[1,27] As shown in Figures 2(a) and 3(a), cotton fabrics are not only porous and ab-

sorbent but also fairly rugged on surface owing to its intrinsic cellulose texture and woven structures. In addition, the natural cotton fiber is not smooth on surface [shown as Figure 2(b)], there were many concaves or strips that no doubt could increase the roughness of the treated substrate in DFPA finishing. Furthermore, cotton textiles are commonly considered to be physically heterogeneous (air pockets at the interface) irrespective of their different roughness scales[31] as a result of their porous character. Thus, the superhydrophobic fabric surfaces are expected to be modeled by Cassie's model,[32] which assumes that a liquid does not completely wet the rough hydrophobic surface and attributes the increased CA to the presence of air pockets (composite surface) at the liquid solid interface: $\cos \theta_r = f_1 \cos\theta - f_2$ (1), where θ_r is the observed water CA on a rough, porous surface, θ is the intrinsic water CA on the corresponding smooth surface, f_1 is the liquid/solid contact area divided by the projected area, and f_2 is the liquid/vapor contact area divided by the projected area. Equation (1) has recently been modified to account for the local surface roughness on the wetted area as follows[33]: $\cos\theta_r = rf\cos\theta + f - 1$ (2), where f is the fraction of the projected area of the solid surface in contact with (thus, we have $f_2 = 1 - f$) and r is the roughness of the portion of the solid that is in contact with water. The curvature of the cotton
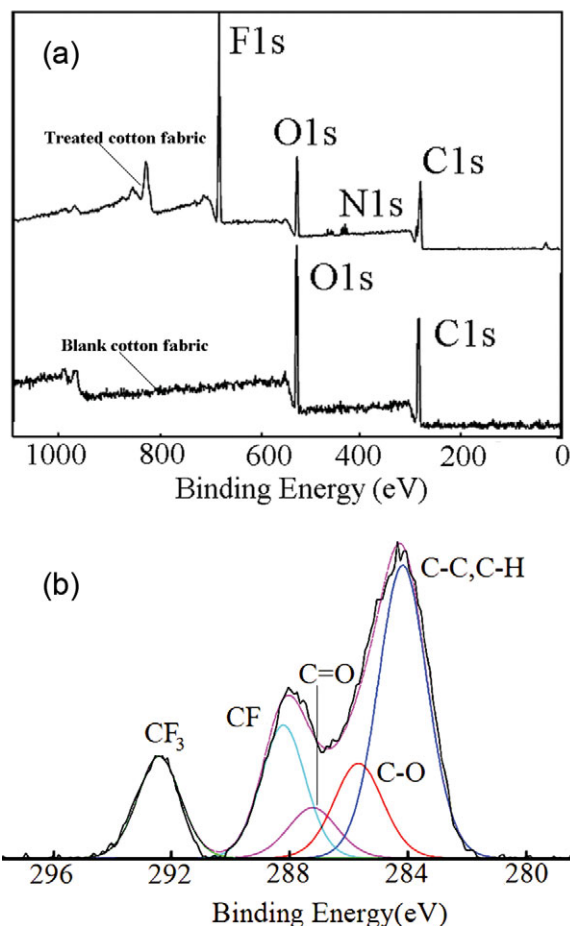
Figure 4. XPS spectra of (a) the treated and blank cotton fabrics (b) high-resolution C_{1s} spectrum of DFPA/cotton. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Performance Properties of the Treated and Untreated Cotton Fabrics

Cotton fabrics	WCA (°)	Whiteness (°)	BR (mN)	
			w	f
Blank cotton fabric	0	85.42	101	189
DFPA/cotton	138.5	84.50	108	197
Cotton/SiO$_2$	0	86.03	131	219
DFPA/SiO$_2$	153.6	85.21	135	223

fiber as the substrate renders $r > 1$, which, in comparison with a smooth wetted area, can enhance surface hydrophobicity.

So, while the low surface free energy DFPA was incorporated onto the cotton fabric, the higher CA value, that is, 138.5° for the modified cotton fabric, was obtained. However, the expected superhydrophobic surface on the DFPA treated cotton fabric could not be created. It is probable that on one hand, the DFPA-treated cotton fabric does not achieve the desirable roughness, namely the nano- and microscale roughness, although there were small mountain-like protuberances with dozens of nanometers on the DFPA-treated surface; on the other hand, those nanoprotuberances might not be arranged so compactly that enough air could not be trapped in air pockets at the interface. Based on Hsieh's analysis of superhydrophobic behavior by the Cassie–Baxter model, a smaller contact area between the curved surface and water droplet, a greater contact angle of water droplet can be achieved.[8] Therefore, a 1 wt % silica sol (with an average particle size of 20–30 nm) roughed cotton fabric [Cotton/SiO$_2$, Figure 2(e)] was used in DFPA finishing, which should roughen the cotton substrate and made r further increase. As a result, the WCA reached as high as 153.6° on such treated cotton fabrics. This indicates a predominant contribution of the low surface energy DFPA coating to the superhydrophobicity of the surface, silica nanoparticles here increased roughness of the treated substrates, which could be in favor of forming more pockets, trapping more air, and minimizing the contact area; thus, the surface hydrophobicity was further enhanced. In addition, the contribution of the woven structures on the hydrophobicity of the surface cannot be ruled out.[33]

Textile finishing is to improve or modify a certain property of the treated fabric. So, it is possible that some performance properties of the treated fabrics are improved, and others are transformed adversely according to the characteristic of the used finishing agents. Commonly, effect of textile finishing on its pristine color is expressed as whiteness of the fabrics before and after being treated, which can be determined by a whiteness tester. In addition, BR is one of the determining factors in assessing the fabric handle. A decrease in the BR leads to improve the fabric drape and produces a desirable fabric handle. On the contrary, an increase in BR would engender stiffer fabric handle. Thus, besides hydrophobicity, whiteness and BR of the treated cotton fabrics were also investigated in this work to illustrate the effect of textile finishing, and results are shown in Table I.

As can be seen from Table I, whiteness of all the treated fabrics almost showed no change and was even slightly more than that

of blank. Those results were probably attributed to transparent DFPA film and white silica nanoparticles. In addition, both the warp and fill bending rigidities of the DFPA treated fabric were slightly higher than those of blank while those of the cotton/ SiO$_2$ and DFPA/SiO$_2$ fabrics greatly increased compared to the blank. This was mainly caused by rigid silica nanoparticles, which would exert an adverse effect on the softness of the treated fabrics.

Washing Durability

Durability is an important criterion for the practical application of superhydrophobic cotton fabric. So, the washing durability of the superhydrophobic fabrics was evaluated based on a standard washing procedure for testing the washing durability of fabrics, and result is given in Figure 5. As seen from Figure 5, WCA on the treated cotton fabrics reached 148.5° after one laundering cycle and could still attain 141.5° after five laundering cycles; however, after 20 laundering cycles, it greatly reduced to 120.5°. In comparison with the published works,[14,15,17,19,34,35] washing durability of the superhydrophobic fabric in the present work seems unfavorable. This result illustrated that on one hand, DFPA could form stable films on cotton fabric, which made the treated fabric retain a higher WCA after fewer laundering cycles; on the other hand, because of no chemical bonds amongst silica nanoparticles and textile fibers as well as the DFPA layer, the micro- and nanoscale structure might be damaged to some extent after intense laundering that should in turn adversely influence hydrophobicity of the treated fabric. Therofore, WCA rapidly decreased to 120.5° after 20 laundering cycles.

CONCLUSIONS

DFPA could form a relatively even film on the the cotton fabric/fiber under SEM observation; however, it presented a rough and microphase-separated pattern under AFM observation in fact. There were many mountain-like protuberances. The height of the protuberances and the root mean square roughness (R_{ms}) of the film reached about 20–50 nm and 12.511 nm in 2×2-μm^2 scanning field (as the scale data was 100 nm). XPS analysis indicated that the perfluoroalkyl groups had the tendency to enrich at the film-air interface. DFPA also made the treated cotton fabric with a WCA about 138.5°. Cotton fabric was
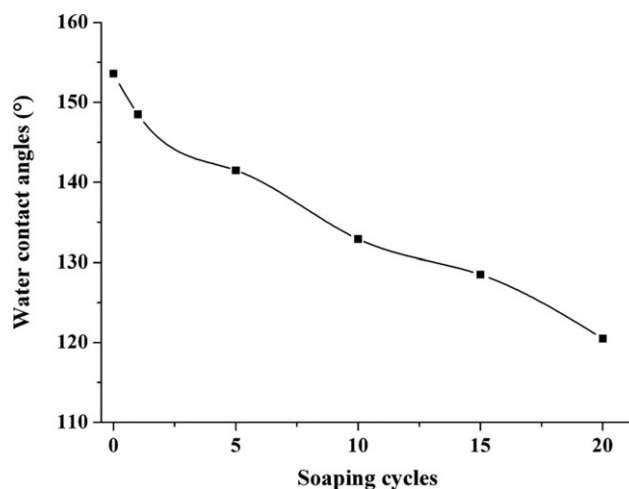
Figure 5. Washing durability of the superhydrophobic fabric.

previously roughened using a 1 wt % silica sol with average particle size of 20–30 nm and then finished by DFPA; hydrophobicity of the resultant cotton fabric was strongly improved and WCA could reach 153.6°. The color of the superhydrophobic fabric would not be influenced, but its softness decreased compared to untreated fabric. However, the superhydrophobic fabric possessed unfavorable washing durability, and WCA rapidly decreased to 120.5° after 20 laundering cycles.

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