SURFACE ENGINEERING, 2018
VOL. 34, NO. 2, 121–127
https://doi.org/10.1080/02670844.2016.1209623

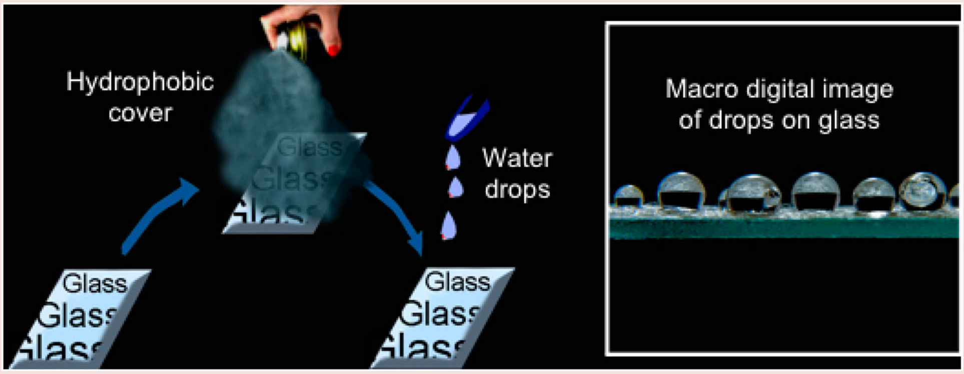
Preparation of transparent hydrophobic polymeric films spray-deposited on substrates

F. N. Viechineski[a], E. T. Kubaski[b], S. Schmidt[c], T. Sequinel[d], J. A. Varela[c†] and S. M. Tebcherani[a]

[a]Federal University of Technology – Paraná, Ponta Grossa, PR, Brazil; [b]State University of Ponta Grossa, Ponta Grossa, PR, Brazil; [c]UNESP – Institute of Chemistry, Araraquara, SP, Brazil; [d]Federal University of Grande Dourados, Dourados, MS, Brazil

ABSTRACT

This paper describes the production of transparent hydrophobic polymeric films made of poly(vinyl chloride) and paraffin wax. A liquid polymeric solution was prepared and spray-deposited on silica glass and nonwoven fabric surfaces. The contact angle between water droplets and glass substrate was 102° while that between droplets and nonwoven fabric was 120°. The films exhibited hydrophobic behaviour regardless of the droplet size. Field emission gun scanning electron microscopy revealed complete adhesion of the film on the substrate and a film thickness of 0.16 µm. The atomic force microscopy micrographs showed a nanoscale rough film surface, which was responsible for air entrapment, preventing water from penetrating the film. This fact explains the high contact angle obtained. The raw materials also contributed to the film's hydrophobicity because of their non-polarity, which prevents miscibility between water droplets and film.



ARTICLE HISTORY
Received 7 April 2016
Accepted 1 July 2016

KEYWORDS
Hydrophobicity; polymeric film; contact angle; lotus effect; non-polar film; water repellency; glass substrate; transparent film

Introduction

The so-called lotus effect refers to the self-cleaning properties of highly water-repellent surfaces, such as the leaves of the lotus flower, which renders them hydrophobic. The angle between liquid and surface is greater than 90°, and surfaces with this characteristic are called hydrophobic. These surfaces are of scientific and technological interest because of their anti-sticking, anti-contamination and self-cleaning properties [1].

Studies of hydrophobicity must necessarily consider the property of wettability, i.e. the tendency of water to spread over the solid surface of a given material [2]. The contact angle (θ) between a liquid droplet and a solid surface is a quantitative measure of the wettability of this surface by a liquid. Therefore, the contact angle is a direct measurement of the interaction between liquid, solid and gas phases, including the surface tension between these phases that occurs when a liquid droplet comes into contact with a solid surface. Contact angles lower than 10° indicate a hydrophilic regime, i.e. the solid surface has a tendency to be wetted by water spreading over its surface. The higher the contact angle the lower the interaction of water with the surface. A surface is considered hydrophobic when contact angles are higher than 90°, and it is considered superhydrophobic when the contact angels are higher than 150°, which means that a water droplet remains virtually spherical on it [3–5].

Several researches have focused on reproducing hydrophobic surfaces found in nature, such as lotus leaves, in order to develop functional properties; this study is called biomimetic. Microscopic analysis of

---

CONTACT T. Sequinel sequinel.t@gmail.com
[†]Deceased.

hydrophobic plants has revealed structures of different morphologies, which nevertheless share a common property, i.e. their surfaces are covered with microcavities that entrap air and thus prevent water droplets from infiltrating the surface [6].

According to the Cassie–Baxter model [7], a surface with microcavities is not completely wetted by a liquid because of the presence of air within the cavities [7–10]. This model can be used to explain the hydrophobic behaviour of surfaces. As a matter of fact, the liquid interface separates into two phases, a liquid/solid interface, and a liquid/vapour interface, and each phase contributes with a different contact angle. When a droplet evidence the behaviour of the Cassie–Baxter state, the low contact area between the droplet and the solid surface allows the droplet to roll-off easily [7,10,11].

Several studies on hydrophobic surfaces have been conducted and published in the last decade; see, for example [12–27]. The results of these studies revealed contact angles between the liquid droplet and solid surface ranging from 107° to 168° and indicated variations in the roll-off angle of the droplet according to the substrate upon which the hydrophobic film was deposited. However, despite the numerous applications of hydrophobic surfaces, their preparation methods are still complex, requiring the use of special equipment and long preparation and drying times [16,20–23,26,28]. Therefore, more research is needed in this field.

The various research papers in this field describe several applications for hydrophobic surfaces: surface protection against weather conditions such as precipitation and condensation of water [18,20]; water or oil-proof surfaces for devices and utensils [15,28–31]; and impermeable or self-cleaning surfaces of fabrics that can prevent the growth of fungi and bacteria [12,16,17,25]. Hydrophobic films protect metallic surfaces by preventing them from coming into contact with water, thus decreasing corrosion and also improving the lubrication of systems, reducing the wear of metallic components [14,19,21,23,26,32].

Hydrophobic films applied on glass surfaces are also reported in the literature. For example, Hozumi *et al* [28]. described a hydrophobic film based on fluoroalkylsilane and prepared by radio-frequency plasma-enhanced chemical vapour deposition. This film was deposited on glass, polished silicon wafers and polycarbonate substrates, and the authors obtained contact angles of about 107°. Jindasuwan *et al.*, [18] who coated glass substrates by means of layer-by-layer deposition of a polyelectrolyte, followed by the deposition of silica and a semifluorinated silane, reported contact angles ranging from 132° to 154°.

Several different materials have been used as hydrophobic systems, including compounds containing fluorine [28], polytetrafluoroethylene [12], silanes [14–17,20,26,33], poly(ethylene terephthalate) [17], polypropylene/methyl-silicone [13], silver [20,21], hydrofluoric acid [22], and nanoparticle silica [25]. However, the methods for applying hydrophobic systems are non-standardised, laborious, and in most cases require complex equipment.

This paper proposes the development of a transparent hydrophobic polymeric film using poly(vinyl chloride) (PVC) and paraffin, which is inexpensive, easy to apply and dries rapidly. The hydrophobic film in liquid form is spray-deposited uniformly on the substrate, whereupon it solidifies on the surface by a physical process of solvent evaporation. The substrates used in this study for film deposition were silica glasses and nonwoven fabric. The proposed method of application requires no complex equipment and is easy to perform. PVC was chosen because of its chemical resistance, including resistance to attack by fatty substances, its mechanical strength and abrasion resistance, water repellency, film-forming ability and transparency, which hardly change the appearance of the surface on which it is applied. Moreover, PVC is nontoxic, inert, easily formed and of low density, thus promoting no significant weight changes [34]. Paraffin is a highly nonpolar compound commonly used in applications that require water repellency. Paraffin also possesses high brightness, low odour, low reactivity, and has emulsifying, lubricating and adhesive properties. Given these characteristics, paraffin is suitable for hydrophobic compositions [35].

Material and methods

Production of the hydrophobic film

The following raw materials were used: PVC (69.4% purity) supplied by Vulcan; granulated paraffin wax (98% purity) supplied by AMC do Brasil; and nitrobenzene (99.5% purity) supplied by Synth. Reactants were used in the as-received state.

The hydrophobic film was produced by dissolving 1.50 g of PVC in 66 mL of nitrobenzene at a temperature of 170°C under stirring at 500 rpm. After the PVC was completely solubilised, 21 g of paraffin were added to this solution, which was stirred continuously until the paraffin dissolved. The composition used here showed higher contact angle among several other compositions prepared at preliminary tests. The resulting liquid product was sprayed uniformly on the glass and nonwoven fabric surfaces, using a fine mist spray with a standoff distance between substrate and spray nozzle of 15 cm. The solvent evaporated after 3 min at heating plate (IKA C-MAG HS 7), resulting in a solidified hydrophobic film.

Measurement of the contact angle

Images of the water droplets on the surfaces of silica glass and nonwoven fabric were recorded using a digital camera. The contact angles were measured using Cooling Tech software, which adjusts the droplet profile and measures the contact angle between the droplet and solid surface.

Morphological characterisation of the hydrophobic film

The morphology and thickness of the hydrophobic films on glass surfaces were characterised by means of field emission gun scanning electron microscopy (FEG-SEM, JEOL 7500). The topography of the film surface was measured by atomic force microscopy (AFM – Bruker NanoScope V). Three-dimension roughness profile of film surface was measured in contact mode. The size of the three-dimension scan was 10 µm × 10 µm, and the root means square (RMS) parameter was used.

Cross-cut tape test

Cross-cut tape tests based on ASTM Standard D3359-09 [36] were conducted to assess the adhesion of the hydrophobic film to the glass substrate. The hydrophobic film was applied on glass substrates and, after the proper solidification of the hydrophobic, it was coated with a thin layer of white paint to allow inspecting the grid area of the test.

Results

Contact angle

The glass surface without the hydrophobic film showed no water repellency. In contrast, in Figure 1, note that the water droplet is spread over the surface, resulting in a very low contact angle between the solid and liquid. In addition, when the coated glass surface is tilted, the droplet is trapped and does not roll-off.

After the hydrophobic film was deposited on the glass surface, the water droplets did not spread over it (Figure 2(a)). The measured contact angle between droplet and glass surface was 102° (Figure 2(b)).

When the hydrophobic film was applied on nonwoven fabric, its water-repellent effect was even greater (Figure 3). The measured contact angle between water droplets and the fabric was about 120° (Figure 3).

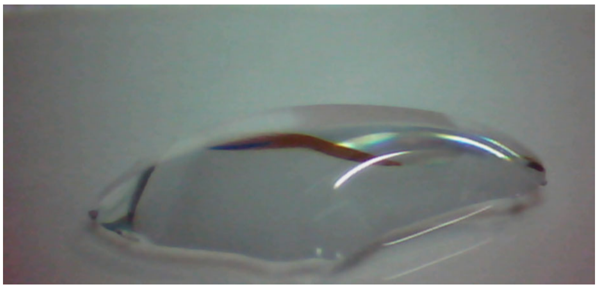


Figure 1. Water droplet on glass surface without hydrophobic film.

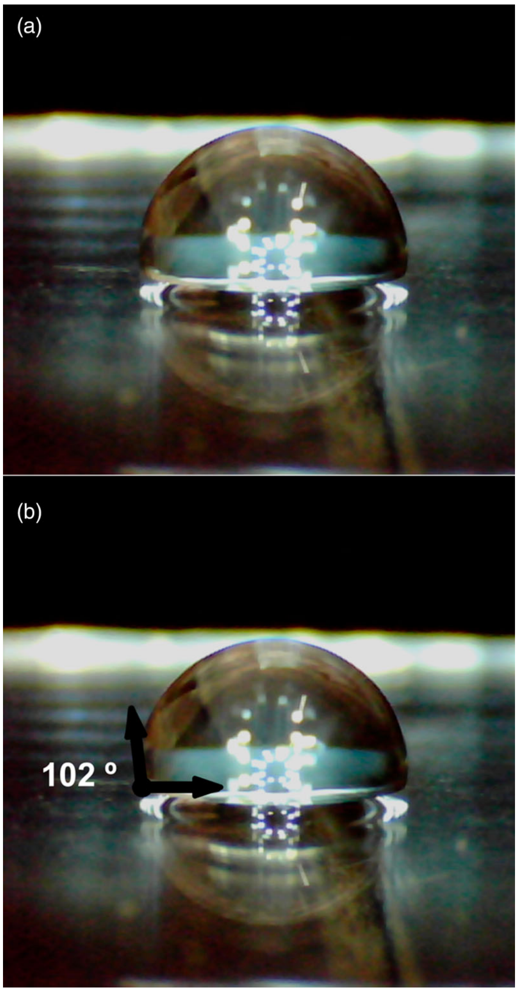


Figure 2. Water droplet on glass surface with hydrophobic film; (a) water droplet on glass surface with hydrophobic film; and (b) contact angle between water droplet and hydrophobic film.

The droplet angle in glass surfaces and nonwoven substrates were about 102° and 120°, respectively, which characterises the film produced here as hydrophobic and, in comparison to other hydrophobic films applied on glass surfaces [18,20,25,28]. Also, these hydrophobic films were transparent in both glass and nonwoven surfaces, without changing their appearance. In addition, the method for preparing and applying the film, which involves only heating, stirring and spraying, makes its use very easy and practical. These are the advantages that differentiate the hydrophobic film presented here.

The contact angle on the nonwoven fabric was higher than on glass because this fabric is made of non-oriented fibres that are bonded together, facilitating the formation of a hydrophobic film with a rough surface. This leads to a higher contact angle between the liquid and a solid surface.

Regardless of the size of the droplet, the hydrophobic film was efficient in maintaining a high contact

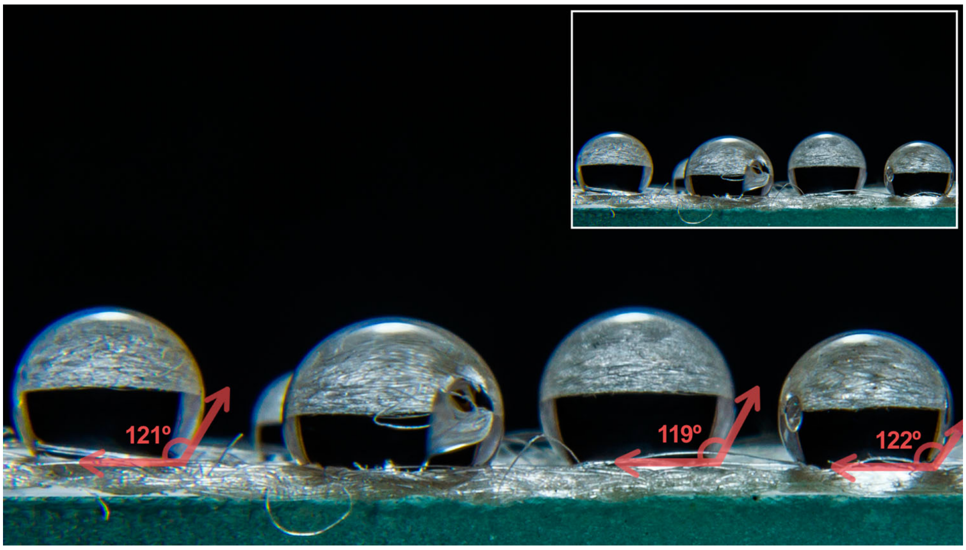


Figure 3. Water droplet on nonwoven fabric surface coated with hydrophobic film, and contact angle between water droplets and fabric surface coated with hydrophobic film. Inset: original photo without contact angle marks.

angle (Figure 4), i.e. the surface continued showing a hydrophobic behaviour.

Water droplets sprinkled on nonwoven fabric not coated with the film were completely absorbed by the fabric, so no pictures of droplets could be taken. In addition to rendering the fabric water-repellent, the film also renders it dirt-repellent.

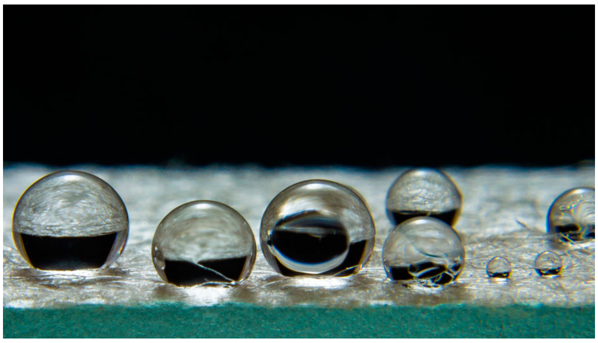


Figure 4. Water droplets of different sizes on glass surface coated with hydrophobic film.

Morphological characterisation of the hydrophobic film

Figure 5 illustrates the surface morphology and the cross-section of the hydrophobic film applied on a glass substrate. Figure 5(a) depicts a continuous film that ensures the hydrophobic properties are distributed uniformly on the substrate. Figure 5 also shows some cracks in the film; however, they do not seem to interfere in the roll-off of droplets from the film surface. It may be possible to reduce or eliminate these flaws by controlling the amount of solvent used in the PVC solution. Figure 5(b) shows the film's thickness and its interaction with the glass surface. As can be seen, this thin film (around 0.16 µm) is distributed evenly over the entire surface of the glass. This image suggests that the good adhesion of the film on the substrate prolongs its hydrophobic properties and its protection of the substrate.

Figure 6(a) shows the smooth surface of the glass substrate with an RMS roughness of about 2.8 nm. In contrast, the AFM shows a rougher surface for the

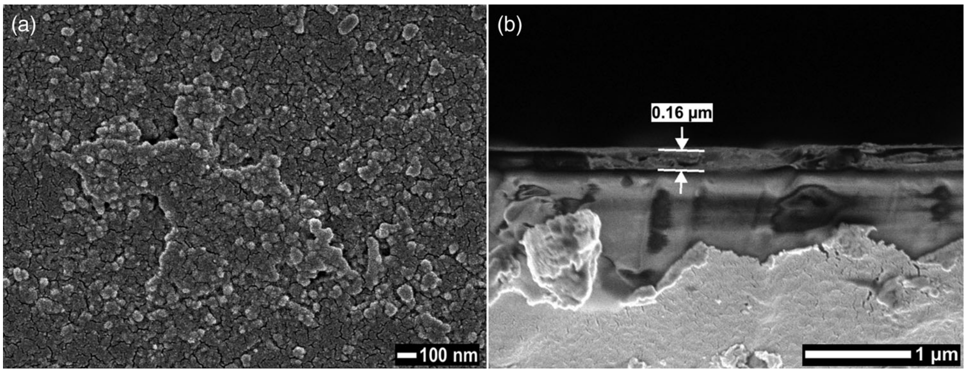


Figure 5. FEG-SEM micrographs of hydrophobic film deposited on a glass surface; (a) film surface morphology; and (b) film thickness obtained by the cross-section of the film on glass surface.

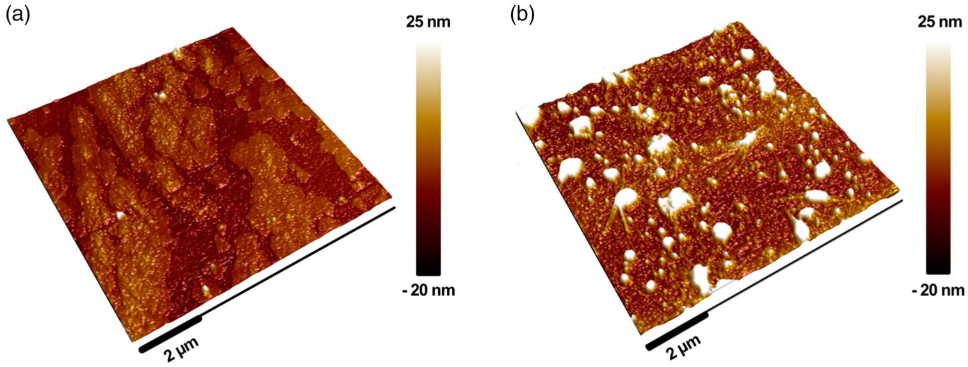


Figure 6. Surface and roughness images obtained by AFM; (a) surface roughness of the glass substrate without hydrophobic film; and (b) roughness of the glass surface with hydrophobic film.

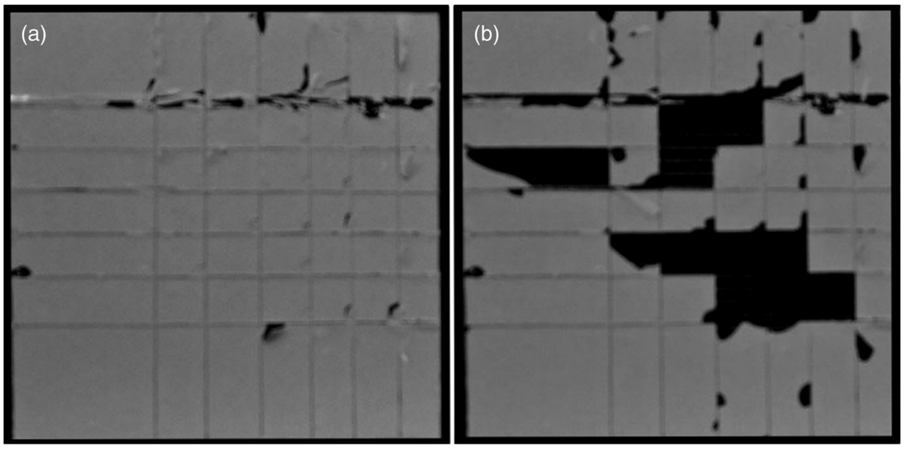


Figure 7. Adhesion test result for the hydrophobic film applied on glass substrate.

hydrophobic film (Figure 6(b)), with an RMS roughness of about 11.6 nm.

The presence of the hydrophobic film results in a surface structure four times rougher than that of the original glass surface. This fact, in addition to the non-polarity of the film, explains the great hydrophobic behaviour of the transparent film produced in this research. The film's water-repellent behaviour could be explained due to two factors, the nonpolar substances used in its preparation and the roughness of the film surface. In this paper, the film deposited on the glass surface is nonpolar, resulting in no interaction with the polar molecules of water droplets, leading to the hydrophobicity of the film. In addition, the surface roughness entraps air preventing the penetration of water droplets [37]. Thus, the area of contact between the droplet and the solid surface is reduced, enabling water droplets to roll-off easily from the surface [10,11].

Cross-cut tape test

The adhesion test results, obtained from cross-cut tape tests, indicated a classification 0B, which means flaking and detachment worse than Grade 1 with a percent area removed greater than 65% (Figure 7) [36]. Although this classification indicates a low adhesion of the hydrophobic film to glass substrates, this adhesion is adequate to the film purpose.

Conclusions

A transparent hydrophobic polymeric film based on PVC was produced. This film presented water repellency on both silica glass and nonwoven fabric substrates. The measured contact angles between water droplets and the glass and nonwoven fabric surfaces were 102° and 120°, respectively. In addition, the film is easy to apply and produce using inexpensive raw materials.

The morphological analysis by FEG-SEM and AFM of the films deposited on glass indicated the presence of nanoscale rough areas on the film surface, which were responsible for its hydrophobicity. This roughness entraps air and prevents water from penetrating the film's structure. In addition, the nonpolar nature of the film renders it immiscible with polar solvents (e.g. water). The FEG-SEM micrograph of the cross-section of the hydrophobic film showed a thickness of about 0.16 µm and good adhesion of film on the entire surface of the substrate.

Acknowledgements

The authors acknowledge the National Council of Technological and Scientific Development (CNPq), grants 310201/2012-8 and 305970/2015-1, and Coordination for the Improvement of Higher Education Personnel (CAPES).

ORCiD

E. T. Kubaski http://orcid.org/0000-0002-5238-8305
T. Sequinel http://orcid.org/0000-0003-3912-3457

References

[1] Nosonovsky M, Bhushan B. Superhydrophobic surfaces and emerging applications: non-adhesion, energy, Green engineering. Curr Opin Colloid Interface Sci. 2009;14(4):270–280.

[2] Liu K, Tian Y, Jiang L. Bio-inspired superoleophobic and smart materials: design, fabrication, and application. Prog Mater Sci. 2013;58(4):503–564.

[3] Bayer IS, Fragouli D, Martorana PJ, et al. Solvent resistant superhydrophobic films from self-emulsifying carnauba wax–alcohol emulsions. Soft Matter. 2011;7(18):7939–7943.

[4] Bayer IS, Fragouli D, Attanasio A, et al. Water-repellent cellulose fiber networks with multifunctional properties. ACS Appl Mater Interfaces. 2011;3(10):4024–4031.

[5] Mates JE, Bayer IS, Palumbo JM, et al. Extremely stretchable and conductive water-repellent coatings for low-cost ultra-flexible electronics. Nat Commun. 2015;6:8874.

[6] Neinhuis C, Barthlott W. Characterization and distribution of water-repellent, self-cleaning plant surfaces. Ann Bot. 1997;79(6):667–677.

[7] Cassie ABD, Baxter S. Wettability of porous surfaces. Trans Faraday Soc. 1944;40(0):546–551.

[8] Lafuma A, Quere D. Superhydrophobic states. Nat Mater. 2003;2(7):457–460.

[9] Martines E, Seunarine K, Morgan H, et al. Superhydrophobicity and superhydrophilicity of regular nanopatterns. Nano Lett. 2005;5(10):2097–2103.

[10] Sheng Y-J, Jiang S, Tsao H-K. Effects of geometrical characteristics of surface roughness on droplet wetting. J Chem Phys. 2007;127(23):234704.

[11] Eral HB, 't Mannetje DJCM, Oh JM. Contact angle hysteresis: a review of fundamentals and applications. Colloid Polym Sci. 2013;291(2):247–260.

[12] Huang F, Wei Q, Liu Y, et al. Surface functionalization of silk fabric by pTFE sputter coating. J Mater Sci. 2007;42(19):8025–8028.

[13] Hou W, Mu B, Wang Q. Studies on wettability of polypropylene/methyl-silicone composite film and polypropylene monolithic material. J Colloid Interface Sci. 2008;327(1):120–124.

[14] Kong L, Chen X, Yang G, et al. Preparation and characterization of slice-like $Cu_2(OH)_3NO_3$ superhydrophobic structure on copper foil. Appl Surf Sci. 2008;254(22):7255–7258.

[15] Li S, Zhang S, Wang X. Fabrication of superhydrophobic cellulose-based materials through a solution-immersion process. Langmuir. 2008;24(10):5585–5590.

[16] Xu B, Cai Z. Fabrication of a superhydrophobic ZnO nanorod array film on cotton fabrics via a wet chemical route and hydrophobic modification. Appl Surf Sci. 2008;254(18):5899–5904.

[17] Zimmermann J, Reifler FA, Fortunato G, et al. A simple, one-step approach to durable and robust superhydrophobic textiles. Adv Funct Mater. 2008;18(22):3662–3669.

[18] Jindasuwan S, Nimittrakoolchai O, Sujaridworakun P, et al. Surface characteristics of water-repellent polyelectrolyte multilayer films containing various silica contents. Thin Solid Films. 2009;517(17):5001–5005.

[19] Liu H, Szunerits S, Xu W, et al. Preparation of superhydrophobic coatings on zinc as effective corrosion barriers. ACS Appl Mater Interfaces. 2009;1(6):1150–1153.

[20] Qi D, Lu N, Xu H, et al. Simple approach to wafer-scale self-cleaning antireflective silicon surfaces. Langmuir. 2009;25(14):7769–7772.

[21] Gu C, Zhang J, Tu J. A strategy of fast reversible wettability changes of WO_3 surfaces between superhydrophilicity and superhydrophobicity. J Colloid Interface Sci. 2010;352(2):573–579.

[22] He S, Zheng M, Yao L, et al. Preparation and properties of ZnO nanostructures by electrochemical anodization method. Appl Surf Sci. 2010;256(8):2557–2562.

[23] Pan L, Dong H, Bi P. Facile preparation of superhydrophobic copper surface by HNO_3 etching technique with the assistance of cTAB and ultrasonication. Appl Surf Sci. 2010;257(5):1707–1711.

[24] Wu J, Xia J, Lei W, et al. Fabrication of superhydrophobic surfaces with double-scale roughness. Mater Lett. 2010;64(11):1251–1253.

[25] Zhao Y, Tang Y, Wang X, et al. Superhydrophobic cotton fabric fabricated by electrostatic assembly of silica nanoparticles and its remarkable buoyancy. Appl Surf Sci. 2010;256(22):6736–6742.

[26] Hozumi A, Cheng DF, Yagihashi M. Hydrophobic/superhydrophobic oxidized metal surfaces showing negligible contact angle hysteresis. J Colloid Interface Sci. 2011;353(2):582–587.

[27] Gao J, Zhao J, Liu L, et al. Dimensional effects of polymer pillar arrays on hydrophobicity. Surf Eng. 2016;32(2):125–131.

[28] Hozumi A, Sekoguchi H, Kakinoki N, et al. Preparation of transparent water-repellent films by radio-frequency plasma-enhanced chemical vapour deposition. J Mater Sci. 1997;32(16):4253–4259.

[29] Guo YB, Yang L, Wang DG. Preparation and hydrophobic behaviours of polystyrene composite coating. Surf Eng. 2016;32(2):95–101.

[30] Cai S, Xue Q, Xia B, et al. Hydrophobic–oleophobic antireflective film with excellent optical property prepared by a imple sol–gel route. Mater Lett. 2015;156:14–16.

[31] Qing Y, Cai Z, Wu Y, et al. Facile preparation of optically transparent and hydrophobic cellulose nanofibril composite films. Ind Crops Prod. 2015;77:13–20.

[32] Wang RG, Kaneko J. Hydrophobicity and corrosion resistance of steels coated with PFDS film. Surf Eng. 2013;29(4):255–263.

[33] Ren X, Kanezashi M, Nagasawa H, et al. Plasma treatment of hydrophobic sub-layers to prepare uniform multi-layered films and high-performance gas separation membranes. Appl Surf Sci. 2015;349:415–419.

[34] Yang F, Hlavacek V. Improvement of PVC wearability by addition of additives. Powder Technol. 1999;103(2):182–188.

[35] Żbik M, Horn RG, Shaw N. AFM study of paraffin wax surfaces. Colloids Surf A Physicochem Eng Asp. 2006;287(1–3):139–146.

[36] ASTM D3359-09e2. Standard test methods for measuring adhesion by tape test. 2009; West Conshohocken, PA, ASTM International. http://dx.doi.org/10.1520/d3359-09e02.

[37] Snoeijer JH, Andreotti B. A microscopic view on contact angle selection. Phys Fluids. 2008;20(5):057101.