

One-Step Fabrication of Fluoropolymer Transparent Films with Superhydrophobicity by Dry Method

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ABSTRACT: Fluoropolymer transparent thin films were deposited on different substrates by one-step vacuum evaporation method, which exhibit superhydrophobic property with water contact angle (CA) greater than 150° . Polytetrafluoroethylene (PTFE) film with network structure shows high oleophobicity with oil CA of 138° , whereas polytetrafluoroethylene-perfluoropropylvinylethers (PFA) film with

particle structure is superoleophilicity with oil CA near 0° . It is believed that different conformation of $-\text{CF}_2-$ groups at the surface lead to this different surface activity. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 524–529, 2011

Key words: vacuum evaporation; superhydrophobic; superoleophilic; fluoropolymer

INTRODUCTION

The wetting phenomena of solid surfaces depending on surface free energy and the geometry of surface structures have been widely studied.^{1–4} The contact angle (CA) is one of the most important properties associated with a solid surface. The superhydrophobicity, characterized by both high water contact angle ($>150^\circ$) and low water sliding angle ($<5^\circ$), typical as lotus leaf surfaces, whereas the superhydrophilicity, presents low water contact angle ($<10^\circ$), has many important applications, for instance, self-cleaning coating, textiles, and microfluidic systems. Similarly, the superoleophobicity and superoleophilicity takes on high oil contact angle ($>150^\circ$) and low oil contact angle ($<10^\circ$), respectively. Till now, many methods have been used to fabricate surfaces with especial wettability (e.g., superhydrophobic surfaces), including heterogeneous nucleation process,^{1,2} lithography,^{5,6} template methods,^{7,8} plasma etching,^{3,9} pyrolysis method, sol-gel methods,^{10–12} chemical deposition,^{13–16} physical vapor deposition,¹⁷ self assembly of a monolayer,^{16,18,19} electrochemical method,^{20,21} and photocatalysis.²² However, these methods are difficult to commercialize because of high cost, complexity, long fabrication time, and limited scale.

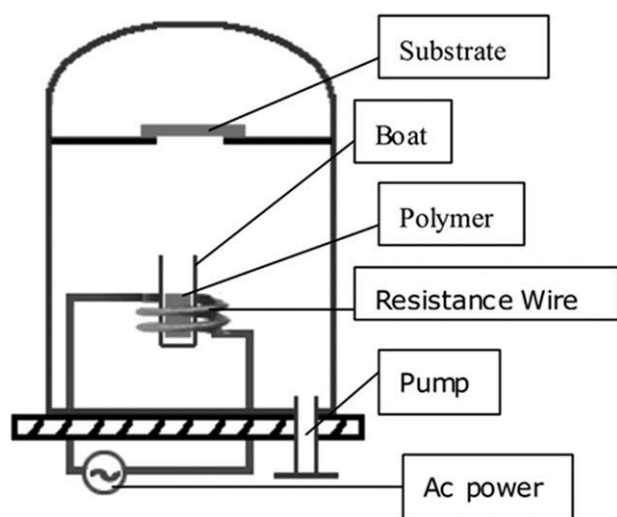
Fluoropolymer, such as polytetrafluoroethylene (PTFE), and polytetrafluoroethylene-perfluoropropylvinylethers (PFA), as a kind of new type functional material, possesses characteristics of high strength, high flame retardancy, high chemical resistance, and high aging resistance. It also owns impact resistance, shear resistance, fatigue resistance, and good dielectric properties. For the polymer's low polarity property and low surface energy property, it is widely used for the preparation of hydrophobic surfaces for antisticking, antifouling and reduction drag, and flow noise. As a typical low surface-free energy material, fluoropolymer has been widely used for preparation of superhydrophobic surfaces, e.g., Lau et al.¹³ reported the preparation of superhydrophobic nanotubes coated by PTFE high-porosity materials, Song et al.²³ also proposed a simple and an inexpensive method for forming a surface coated by PEEK-PTFE composite. However, these results contain complicated deposition techniques, multistep processes, and low surface coverage, which limit the practical applications of superhydrophobic surfaces. Furthermore, it cannot provide an effective method for the preparation of superhydrophobic surface on reactive substrates that cannot be prepared by wet process.

Here, we prepared superhydrophobic thin films, with water CAs higher than 150° , by one-step dry method of vacuum evaporation using two different fluoropolymer as the precursor. The PTFE film has highly oleophobic property with a CA of $\sim 126^\circ$, whereas the PFA film has superoleophilic property with a CA of 0° . In addition, a water droplet can easily roll off the PFA film surface, with a sliding angle of 7° . It is believed that different conformation of $-\text{CF}_2-$ groups at the surface lead to the different

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Scheme 1 Sketch map of the Experimental Unit.

surface activity. More importantly, the superhydrophobic films are transparent when deposit on glass substrates. This study provides an efficient way to fabricate transparent superhydrophobic films, which can be widely used in microelectronics, architecture, and biotechnology.

EXPERIMENTAL

Materials

The PTFE and PFA were obtained from DuPont Co.

Experimental

The sketch map of the experimental unit was shown in Scheme 1. The substrates were washed in an ultrasonic bath of detergent solution for 15 min and an equal volume of acetone (HPLC grade) and ethanol (HPLC grade) mixture for 15 min, followed by deionized water rinsing for 15 min twice at room temperature. The washed substrates were dried under an infrared light for 3 h in nitrogen atmosphere. The PTFE and PFA thin films were deposited through sublimation using the molybdenum boat evaporation method. The substrates were placed above the evaporator source, with a distance between the substrate and the boat crucible of 0.5 m. Before the evaporation process, the deposition chamber was pumped out to a base pressure of $<8 \times 10^{-2}$ Pa. The deposition rate of PTFE and PFA is 0.01 nm/s and 0.1 nm/s, respectively. The deposition rate was controlled by a quartz monitor as a real-time thickness gauge. The substrates used were made of fused silica substrates. The thickness of both PTFE and PFA films was 100 nm.

Characterization

The morphological characterization of the samples was observed using scanning electronic microscope

(SEM, JEOL 6700F) at 3 kV. A dataphysics OCA20 contact angle system was used to measure the surface wetting properties. A deionized water droplet (2 μ L) was dropped carefully onto the sample surface at ambient temperature, and a photograph of the water droplet was taken with the camera. The average contact angle was obtained by measuring at five different positions of the same sample or five times at the same position of the same sample. X-ray photoelectron spectroscopy data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300W AlK α radiation. The base pressure was $\sim 3 \times 10^{-9}$ mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. FTIR (Fourier transform infrared spectra) spectra were recorded using a Perkin-Elmer FT-IR GX spectrometer. For evaluation, 32 scans were taken with 4 cm^{-1} resolution. FTIR spectra were recorded within the range of 4000-400 cm^{-1} . The atomic force microscopy (AFM) was characterized by the dynamic force mode (DFM) with SPA400 (Seiko, Japan), and the morphology images were recorded in the height mode.

RESULTS AND DISCUSSION

Surface morphology and surface wettability of fluoropolymer films

Figure 1(a) is the typical SEM image of the PTFE film on a flat silicon substrate, showing a random network structure with the pore diameter from 23 to 64 nm and the fiber diameter from 18 to 43 nm. As reported, PTFE is a typical polymer used for

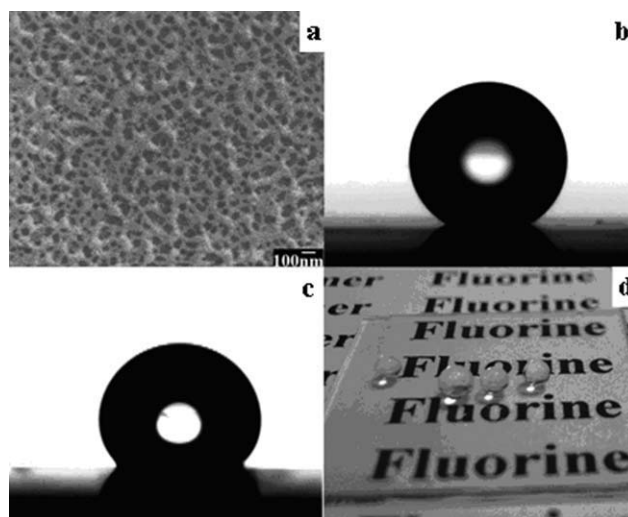


Figure 1 (a) SEM images of the PTFE film on flat silica substrate. (b) Water droplets (2 μ L) on the PTFE surface of flat silicon substrate (CA = 151°). (c) Oil droplets (2 μ L) on the PTFE surface of flat silicon substrates (CA = 138°). (d) Optical images of water droplets (3 μ L) on the PTFE surface of flat glass substrate.

preparing hydrophobic surface because of its low surface energy, with an intrinsic CA of 109° – 120° .^{24,25} For this low surface energy of PTFE, the hydrophobicity can be enhanced by being textured with different scale structures. As a result, the network PTFE film with dual nanostructures composed of pores and fibers exhibits a superhydrophobic property with a CA of 151° (Fig. 1b). This PTFE film performs a highly oleophobic property a salad oil CA of 138° (Fig. 1c). Similar effects can be observed when using glass, ITO-glass as the substrates. Moreover, the high transparency is shown by the optical image of PTFE film on flat glass substrates (Figure 1d). Such transparent superhydrophobic film can be widely used for self-cleaning coatings.

Another fluoropolymer, PFA, also has low surface energy, with an intrinsic CA of 115° ,²⁴ showing a hydrophobic property. Figure 2a is the typical SEM image of the PFA film on a flat silicon substrate, which clearly revealed that these particles with a diameter from 9 to 25 nm are densely packing. However, the CA for water on such PFA films is only 125° (Fig. 2b), which cannot reach superhydrophobicity. Compared with the superhydrophobic PTFE film prepared at the same conditions, this may be because of the single nanostructure and the surface composition of PTA film. To increase the hydrophobicity, we change the substrate to etched silicon with micro and nanostructures (Fig. 2c and d). The size of the silicon pillars made by etching technique of Inductive Couple Plasmas with the length, width, height, and interval of 3, 3, 30, and 6 μm , respectively. The magnified SEM image in Figure 2d indicates the densely packing particle structure of PFA film similar to that on the flat silicon substrate. For the low surface energy of PFA, enhanced by micro- and nano structures, the PFA film exhibits a superhydrophobic property with a CA of 156° (Fig. 2e). Moreover, a water droplet can hardly stick to the surface, as indicated by a sliding angle of around 7° (Fig. 2g), allowing droplets to roll off quite easily. We interpret this performance as due to that three-phase contact lines are contorted and discontinuous on the surface and extremely unstable, owing to the multiscale structure of the surface, which produce sufficient air traps to reduce the sliding resistance drastically.^{3,26} Different to the highly oleophobic PTFE film, the CA of oil for PFA films on etched silicon substrates approaches 0° (Fig. 2f), indicating that the PFA film has superoleophilic property. The PFA films have high transparency, which is shown by the optical image of PFA films on flat glass substrates (Fig. 2h). The high water CA and low-sliding angle of the PFA film on etched silicon surface indicate that the water droplets on these dual-scaled modified surfaces cannot penetrate into the surface but rather suspended on the microscale pillars. This behavior is very similar to the self-cleaning of lotus

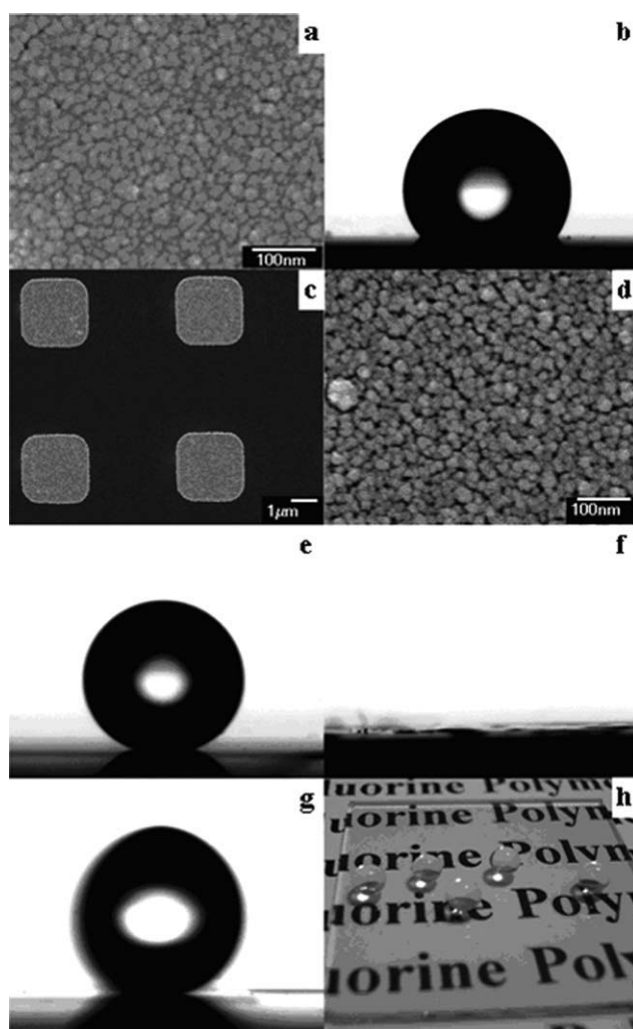


Figure 2 (a) SEM images of the PFA film on flat silica substrate. (b) Water droplets (2 μL) on the PFA surface of flat silicon substrate (CA = 125°). (c) SEM images of the PFA film on etched silica substrate. (d) SEM images of the PFA film on etched silica substrate. (e). Water droplets (2 μL) on the PFA surface of etched silicon substrate (CA = 156°). (f) Oil droplets (2 μL) on the PFA surface of etched silicon substrate (CA = 0°). (g) A sliding water droplet (2 μL) on a PFA surface of etched silicon substrates tilted at 7° . (h) Optical images of water droplets (3 μL) on the PFA surface of flat glass substrate.

leaves, which can be effectively used in industry and architecture.

Mechanism of the formation of superhydrophobic fluoropolymer surfaces

Theoretically, on a flat smooth and chemically homogeneous solid surface, the CA of a liquid droplet is defined by the Young's equation:²⁷

$$\cos \theta = \frac{\sigma_{sv} - \sigma_{sl}}{\sigma_{lv}} \quad (1)$$

where σ_{sv} , σ_{sl} , and σ_{lv} are the interfacial-free energy per unit area of the solid-vapor, solid-liquid, and

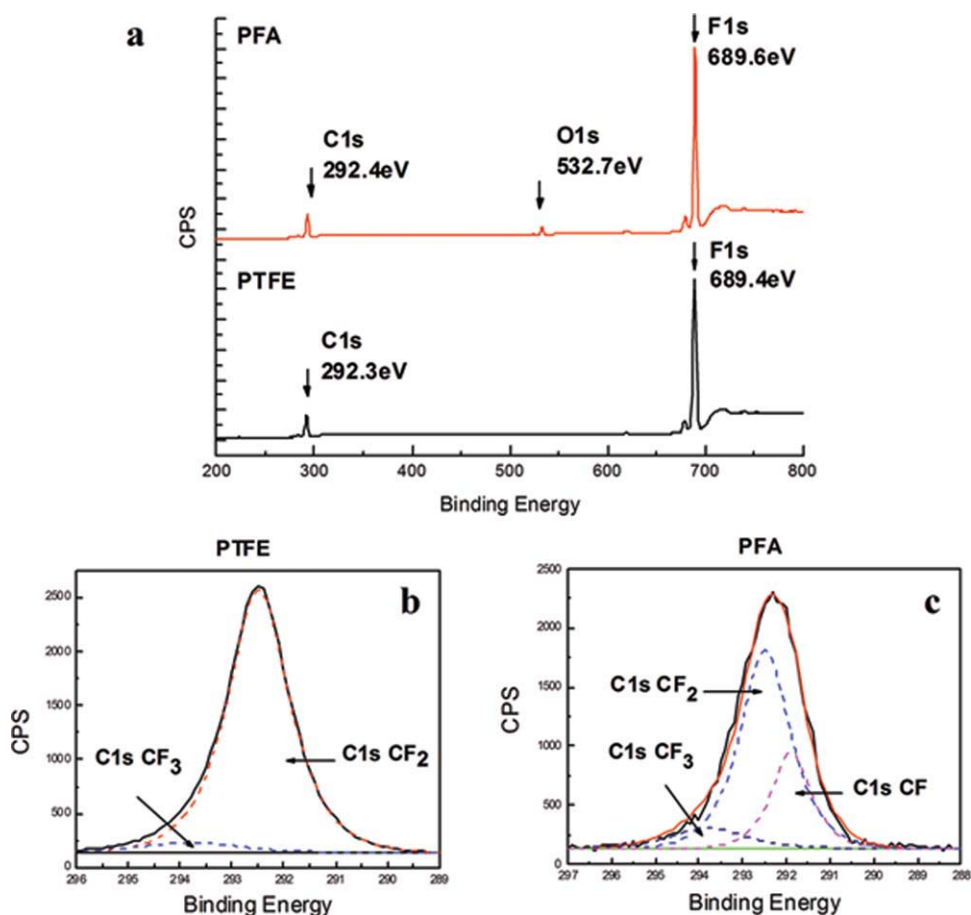


Figure 3 The XPS analysis of the PTFE films and PFA films, showing the different surface components. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

liquid-vapor interfaces, respectively. It is expected that the random network structures of the PTFE and the particle structures of the PFA increase the surface roughness so that air can be trapped in the aperture of the fibers and particles. As a result, a liquid droplet is laid on a patchwork of polymer and air, leading to part of surface under the drop covered with liquid. As reported, this performance can be suggested by Cassie-Baxter equation. The apparent contact angle θ_r observed on a rough surface and the equilibrium contact angle θ obtained on a smooth surface of the same chemical composition have a relationship as follows²⁸:

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

where f_1 and f_2 are the fractions of solid surface and air in contact with water, respectively, ($f_1 + f_2 = 1$). The equation provides a strong deduction for supporting that the surface roughness enhances superhydrophobic behavior. In our work, surface roughness is affected by increasing solid ratio to create a rough surface, such as the random network structure and particles piled up randomly. The treated surface is textured with microscale and

nanoscale hydrophobic fluorocarbon polymers with low surface-free energy, preventing penetration of water into valleys, which leads to a superhydrophobic surface.

It's very interesting that PTFE film provides an oleophobic surface, whereas PFA film provides an oleophilic surface. The XPS analysis (Fig. 3) showed that the obtained films consisted mainly of $-\text{CF}_2-$

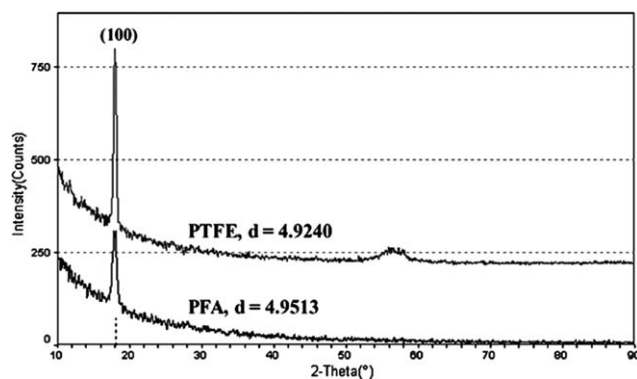


Figure 4 Grazing-incidence X-ray diffraction profiles measured at surface region for the polymer thin films synthesized by vacuum evaporation.

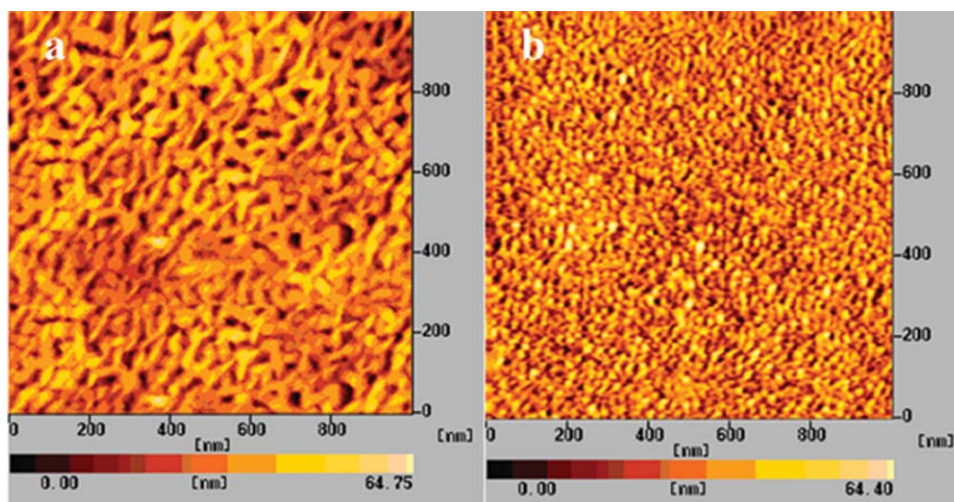


Figure 5 (a) The AFM image of PTFE thin films, showing a fiber-like structure, with the RMS of 9.86 nm; (b) The AFM image of PFA thin films, showing a particle-like structure, with the RMS of 11.69 nm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(292.4eV) bonds. The PTFE film's C1s spectra consist of two components. The first component is centered at 292.48 eV (referred to as C^{+2}), which represents $-CF_2-$ groups. The second component is centered at 293.8 eV (referred to as C^{+3}) attributed to $-CF_3-$ groups. These mean PTFE film consisted of polymer molecular with long straight chain structure. The PFA film's carbon region consists of three main components: (a) a C^{+1} component at 291.89 eV due to the CF group; (b) a C^{+2} component at 292.48 eV due to $-CF_2-$ group; and (c) a component at 293.8 eV (referred to as C^{+3}) is due to the $-CF_3-$ groups. These mean PFA film consisted of a short polymer molecular with branched chain structure. The results of FT-IR Reflection-Absorption Spectroscopy analyzes (details see supporting information) showed that the strongest absorption peak of C-F appeared at 1239 and 1156 cm^{-1} . It appears from the above results that two kinds of thin films synthesized by vacuum evaporation had the different surface component, which can induce different surface wettability.

The grazing-incidence X-ray diffraction (GIXD) profiles measured at surface region for the thin films (Fig. 4) show that PTFE films have the smaller interplanar distance than PFA films. It means the distance of PTFE molecules is smaller than PFA molecules. The polymer molecules of PTFE films exhibit a more compact structure than PFA films. The peak height shows the PTFE molecules is longer than PFA molecules. This result is consistent with XPS analyzes and the evaporating rate; the high melt viscosity of PTFE reduces the rate of chain initiation, producing few free radicals, thus the evaporating rate is low and a long chain polymer was obtained, while the PFA film is opposite. The AFM image of PTFE and PFA thin films showed the former a fiber-like structure and the latter a particle-like structure

(Fig. 5), which is consistent with the SEM results. The reason to form different structure using the same method is that the molecular structures of PTFE and PFA are different. Because the diameter of fluorine is larger than carbon, PTFE will form a fiber-like helix structure. However, the existence of tiny perfluoroalkoxyl groups in PFA will destroy the helix structure, forming a folded structure and particle-like morphology. According to all these results, the possible conformation of the two kinds of polymers at the air/solid interface can be proposed in Figure 6. On the surface of PTFE film, carbon atoms are formed in the interior, whereas fluorine atoms are present at the surface for the helical structure (Fig. 6a). As a result, PTFE film exhibits an oleophobic property because of

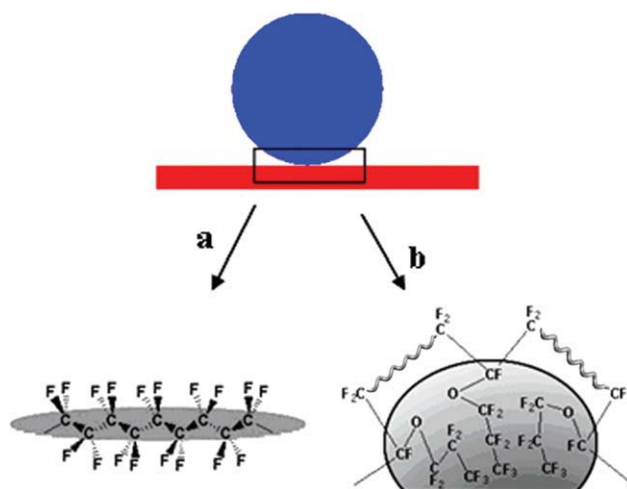


Figure 6 Possible conformation modes of the PTFE and PFA molecules at the air/solid interface. (a) The helical structure of the network structure on PTFE film. (b) The folding structures of the particle surface on PFA film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the rich of $-\text{CF}_2-$ group on the surface. On the surface of PFA film, oxygen atoms have a much stronger binding force with substrates than fluorine atoms lead to a planar structure of PFA molecules at air/solid interface. The polymer molecules chain less density and the branched chain structure lead to an appearing of more carbon atoms at the surface, supplying the PFA film surface with more oleophilicity (Fig. 6b). Therefore, oil can wet the surface, spreading on it. Accordingly, conformation of molecules at the surface does the most contribution to the surface activity.^{24,29}

CONCLUSIONS

We developed a simple method for fabrication thin fluoropolymer films with superhydrophobic property through one-step dry process. Polytetrafluoroethylene (PTFE) film with network structure shows high oleophobicity with oil CA of 138° , whereas polytetrafluoroethylene-perfluoropropylvinylethers (PFA) film with particle structure is superoleophilic with oil CA near 0° . It is believed that different conformation of $-\text{CF}_2-$ groups at the surface lead to this different surface activity. This coating technology can be expanded to the preparation of some reactive surfaces, which can not be prepared by wet process or template methods. This study of transparent superhydrophobic thin films will open new avenues for potentially applications in various fields such as microelectronics, architecture, new material, and biotechnology.

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