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Preparation of a super-hydrophobic poly(vinyl chloride) surface via solvent–nonsolvent coating

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Abstract

A new simple approach was developed to obtain a super-hydrophobic PVC surface via solvent–nonsolvent coating without addition of low-surface-energy compounds. Also, the PVC film is nearly or still maintains its super-hydrophobicity when contacting with acid, alkali or salt solutions. SEM shows that compared with common smooth PVC surface, a lotus-like structure with micro- and nano-papillae was obviously observed on the hydrophobic PVC surfaces. Such a special surface microstructure may result in the super-hydrophobicity. A brief explanation to the formation of the special microstructure was put forward on the basis of diffusion, tension break and micro- and nano-phase separation.

Keywords: Super-hydrophobic; Poly(vinyl chloride); Solvent–nonsolvent coating

1. Introduction

Wettability is important for solid surface. A surface having water contact angle greater than 150° is commonly called super-hydrophobic [1]. Super-hydrophobic surfaces have attracted much attention from both industrial and fundamental research. Recently, many works focused on super-hydrophobic surfaces have been carried out [1–25], such as super-hydrophobic fluorocarbon coating with ribbon surface structures [9], super-hydrophobic silica aerogels [10], chemical vapor deposition of trimethylmethoxysilane [11], super-hydrophobic surface based on a steric acid self-assembled monolayer over polyethyleneimine thin films [13]. We have succeeded in preparing super-hydrophobicity carbon films in a wide range of pH values [18], super-hydrophobic zinc oxide thin films after modification with fluoroalkyl silane [20], and honeycomb-like aligned carbon nanotube films [21]. Most of these super-hydrophobic surfaces were prepared by first functionalized the precursor materials with low-surface-energy groups such as fluorinate, silicon and fluoroalkyl silane [15–18,20,21] or some expensive ones such as carbon nanotubes [9–11,14,19]. Thus, how to prepare a super-hydrophobic surface from a commonly hydrophobic material without addition of low-surface-energy ingredients is commercially important and scientifically challenging. Although some progresses have been reported [22,24,25], the preparation procedures were rather complicated or carried out at fairly high temperatures. Besides surface functionalization, the roughness and surface microstructure are important factors to surface hydrophobicity [26]. For example, natural lotus leaf with micro- and nano-papillae two-length-scaled hierarchical structure shows super-hydrophobic. Utilizing the difference in solubility of polymer materials in solvent, a super-hydrophobic surface of poly(methyl methacrylate) (PMMA) and fluorine-end-capped polyurethane with lotus-like microstructure [23], and a submicrometer-scale heterogeneous surface of polystyrene (PS)–PMMA [27] were obtained. By controlling the crystallization time and nucleation rate, super-hydrophobic surfaces of a semicrystalline polymer, low-density polyethylene (LDPE), were achieved [28]. In addition, a flow-induced stripe pattern with improved surface roughness occurred in phase-separated polymer fluids by introduction of temperature gradient [29]. In this work, we report a simple and novel method using solvent–nonsolvent coating to prepare super-hydrophobic surfaces with micro- and nano-papillae hierarchical microstructure. More specifically, a commonly used amorphous polymer, poly(vinyl chloride) (PVC), was adopted, and no low-surface-energy material was added.

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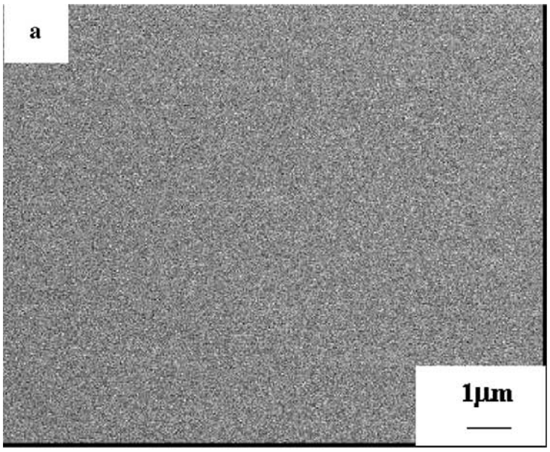
2. Experimental

one gram of PVC resin (obtained from Beijing No. 2 Chemical Corporation, SG5 type) was dissolved in 18 g tetrahydrofuran to form a pre-solution. At room temperature, one volume of nonsolvent was dropped onto a clean glass plate. Then, it was coated with 1–1.5 times the volume of the PVC solution rapidly. Three nonsolvents were adopted, i.e. 2:1 (v/v) ethanol/water, 5:1 (v/v) acetone/water, and ethanol. By control of the ratios of the solvent and the nonsolvent, porous PVC films were obtained. After drying for 2 h in vacuum, the wettability of the porous film was measured on a dataphysics OCA20 contact-angle system at ambient temperature with about 7 μl droplets. The surface morphology of the porous film was collected on a scanning electron microscopy (SEM) of JEOL JSM-6700F (Fig. 1).

3. Results and discussion

In general, PVC is an amorphous material, and coating the PVC solution on a glass plate normally forms a smooth film. The morphology of the PVC smooth film is shown by SEM in Fig. 1. And its water contact angle of the smooth film is about 103±1.8°, indicating it is hydrophobic.



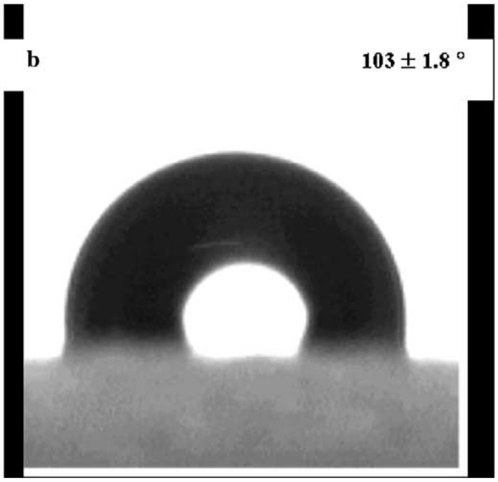


Fig. 1. Surface morphology (a) and water contact angle (b) of smooth PVC film formed by coating directly on a glass plate.

Table 1
The contact angle (θ/°) of PVC film contacting with water, acid, alkali, and salt aqueous solutions

Precipator	Pure water	HCl	Na_2CO_3	KCl
None	103±1.8	79.4±1.6	78.9±1.8	79.9±1.5
2:1 CH_3CH_2OH/H_2O	155.3±1.9	147.6±2.2	148.5±1.8	143.8±2.0
5:1 CH_3COCH_3/H_2O	163.5±2.1	149.5±2.3	150.3±2.5	151.2±1.9
CH_3CH_2OH	163.6±1.8	150.9±1.9	154.7±1.7	150.5±2.1

Table 1 shows the contact angles of the PVC films contacting with water, 2% (w/w) hydrochloric acid, sodium carbonate, and potassium chloride aqueous solutions. For the smooth PVC film, the contact angle with water is 103±1.8° and becomes lower than 90° when contacting with acid, alkali and salt aqueous solutions. This may suggest that the smooth PVC film could be wetted by acid, alkali or salt aqueous solution. By solvent–nonsolvent coating procedure, hydrophobic PVC surfaces could be successfully obtained with their contact angles with water higher than 150°, using any of the three nonsolvents, 2:1 (v/v) ethanol/H_2O, 5:1 (v/v) acetone/H_2O or ethanol, as shown in both Table 1 and Fig. 2. It is also interesting that these super-hydrophobic surfaces maintained high hydrophobicity after being wetted by acid, alkali and salt solutions. Their contact angles are slightly lower than 150° or still higher than 150°.

As is well known, Wenzel [26] first derived the relationship between contact angle of a liquid on a smooth surface (θ) and on a rough surface (θ_r) made of the same material (Eq. (1)), where r is the roughness factor. According to the equation, if the roughness is high enough, a super-hydrophobic surface can

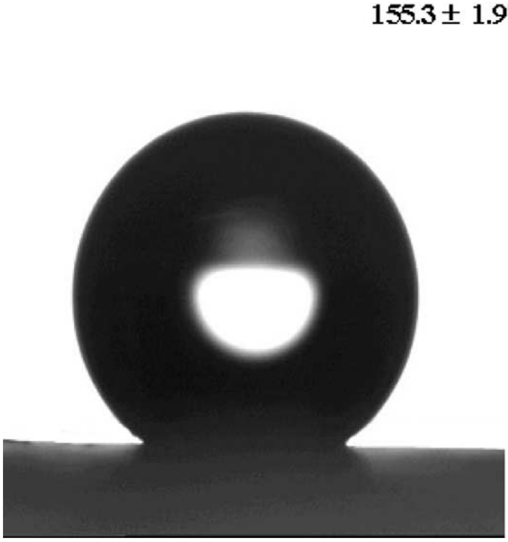


Fig. 2. Water contact angles of super-hydrophobic PVC films prepared by coating on a glass plate with 2:1 CH_3CH_2OH/H_2O.

be fabricated.

$$\cos \theta_r = r \cos \theta \tag{1}$$

Fig. 3 shows the SEM images of the porous super-hydrophobic PVC film using a mixture of 2:1 (v/v) ethanol and H_2O as nonsolvent. Its contact angle for water is 155.3 ± 1.9° (higher than 150°) and a sliding angle is 4.8 ± 0.6° (lower than 5°), characteristic of a super-hydrophobic surface. In Fig. 3(a), the film surface is composed of micro-papillae whose diameter ranges from 300 nm to 2 μm, thus increasing the surface roughness when compared with the commonly smooth PVC film. Enlarge these papillae in Fig. 3(a), many lotus-like structures can be observed obviously in Fig. 3(b). Each micro-papilla in Fig. 2(a) is covered by nano-papillae ranging from 35 to 48 nm in diameter. The special surface structure with micro-papillae and nanoscale lotus-like papillae may be the main reason contributing to the much-increased surface roughness and the super-hydrophobic surfaces. Similar super-hydrophobic surface with lotus-like surface structure can be seen in Ref. [5].

A possible formation process of the lotus-like surface structure may be described in Fig. 4. When PVC solution is coated onto the glass substrate with nonsolvent, an interface between solvent and nonsolvent appeared (Fig. 4(a)). As the solvent and nonsolvent diffused each other and the tensions shrank, the smooth interface was divided into many curved ones (Fig. 4(b)). The tension of the curve interface was broken at last and the solvent met the nonsolvent, which might cause the micro-phase separation [30] of PVC solution (Fig. 4(c)). The curved interface was further separated into less ones, micro-phase separation and solidification took place, and the fine nano-structure on the micro- or nano-papillae was formed (Fig. 3(d)). Therefore, the nonsolvents play an important role in this process, which may cause micro-phase separations and the formation of micro- and nano-structures. In contrast, when

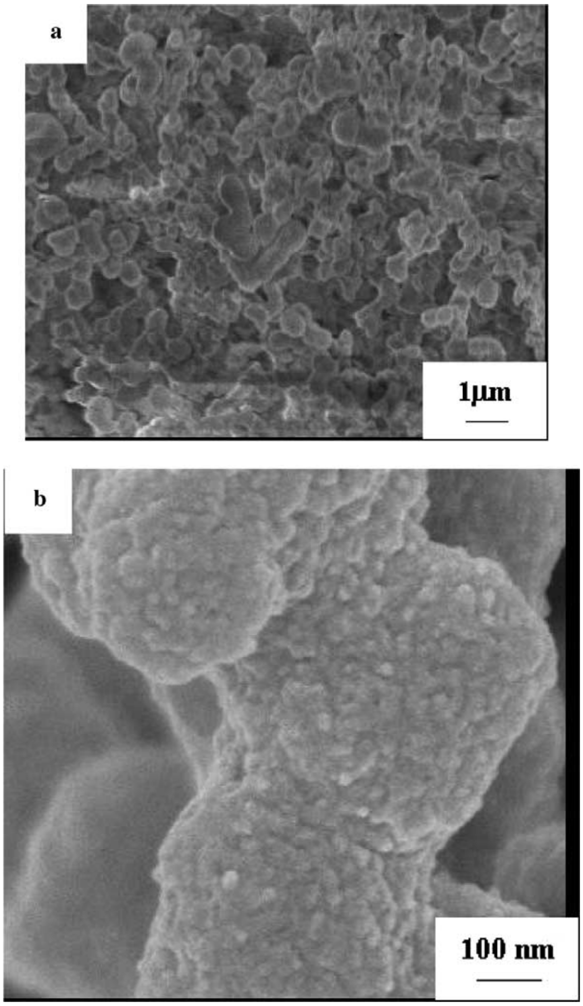


Fig. 3. The SEM images of super-hydrophobic PVC films by coating on a glass plate with a mixture of 2:1 (v/v) ethanol and H_2O as nonsolvent.

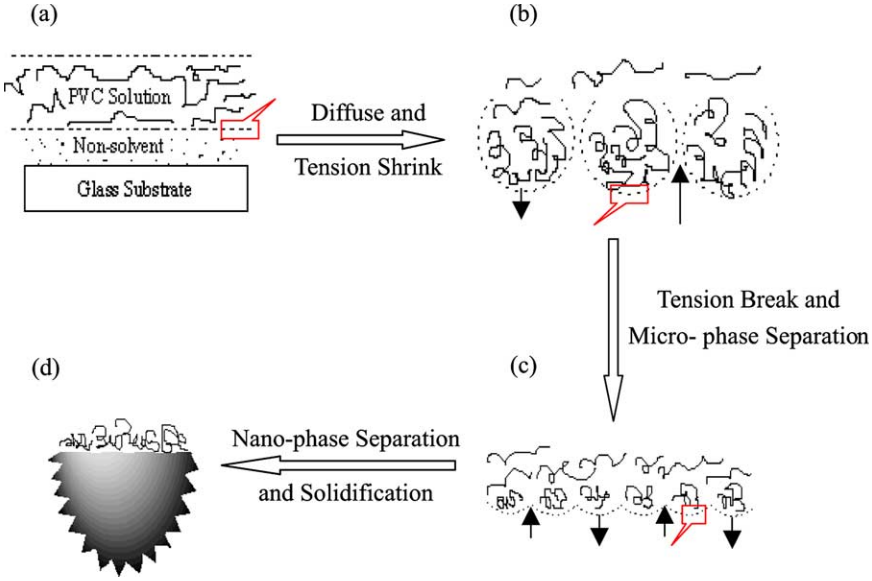


Fig. 4. A possible formation process of the lotus-like surface structure of the porous film of PVC, wherein the curves, the broken lines and the arrowheads represent the chains of PVC in solution, the interface of two phases and the diffuse direction of solvent and precipator, respectively.

PVC solution was directly coated onto the glass substrate, there was no micro-phase separation of PVC solution and the chains would be solidified with order and a smooth surface film was obtained.

In conclusion, we have developed a new simple approach that could directly transform the PVC film into a super-hydrophobic surface without addition of low-surface-energy compounds. Also, the PVC film is nearly super-hydrophobic contacting with acid, alkali or salt solutions, which may widen the applications of the PVC plastics to seawater resistant coating or other areas. Other polymers such as PMMA and PS can also be used to create super-hydrophobic surfaces with micro- and nano-papillae microstructure by solvent–nonsolvent coating method [31].

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