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Durable superhydrophobic PTFE films through the introduction of micro- and nanostructured pores

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ABSTRACT

A superhydrophobic surface, highly water repellant and self-cleaning, is typically made by introducing micro- and nanoscale roughness onto the surface of a low surface energy material. Herein, we offer a new process of superhydrophobic film formation, accomplishing the same thing through the production of micro- and nanoscale surface porosities. Such a material is prepared by introducing zinc acetate ($ZnAc_2$) and sodium chloride (NaCl) into a commercially available PTFE (polytetrafluoroethylene) emulsion. On drying, baking and washing with acetic acid, the PTFE film produced from the emulsion had both micro- and nanoscale surface porosities, and demonstrated superhydrophobic properties, with a static contact angle >150° and a slide angle <10°. From SEM observation, NaCl contributes microscale porosity, while $ZnAc_2$ decomposes to ZnO, contributing nanoscale porosity. Using either $ZnAc_2$ or NaCl alone produces a surface with a static contact angle >150°, but with a slide angle >10°. Based on XPS and SEM data, we explore herein the affect of chemistry and porosity on the mechanism of superhydrophobic surface formation, and the durability of that surface under abrasion.

1. Introduction

The “lotus effect”, found in nature, refers to superhydrophobic leaf surfaces that are self-cleaning, due to their high water contact angles (CAs), and low water slide angles (SAs). This phenomenon has aroused extensive interest, provoking research into its cause [1]. Recently, artificial superhydrophobic surfaces, with water CAs >150° and SAs <10°, have been the subjects of both fundamental research and practical applications [2–4].

When water is dropped onto a superhydrophobic surface, dirt is removed during the droplet rolling process [5]. Thus, superhydrophobic films have prospects of broad application in pollution avoidance [6], anti-corrosion [7], antioxidation [8], and other fields. Experiments have shown that superhydrophobic surfaces require two necessary features, the first being micro- and nano-scale surface roughness, and the second, that this structure must exist on a low energy surface. In general, superhydrophobic films may be prepared by layer-by-layer self-assembly [9], phase separation [10], electrochemical deposition [11], chemical vapor deposition [12] and sol–gel processing [13,14]. However, these methods generally involve complex routes, high costs and extensive energy consumption, and the methods, themselves, are prone to introduce new problems.

Polytetrafluoroethylene (PTFE) is one of the lowest surface energy materials known, with excellent resistance to chemical reagents, and has a high temperature stability, a low dielectric constant, and a low friction coefficient [15]. The surface of a PTFE plate has a static water CA of ∼108°, and a SA >90°, indicating water adhesion to the PTFE surface [16,17]. Much study has been devoted to the use of the PTFE surface to achieve superhydrophobicity [17–35], including plasma modification [18–20], thin film deposition [21,22], cold pressing and sintering [23], sandpapering [24], filter paper templating [25], hot embossing [26], PTFE-polymer phase separation [27–30], the formation of a PTFE-carbon nanotube composite plate [31], electrospray formation [32], axially stretching porous films [33], RF sputter deposition onto porous Al surfaces

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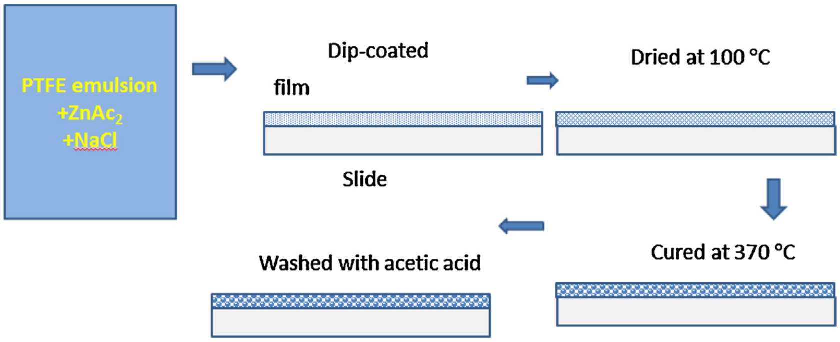

Fig. 1. A schematic of superhydrophobic PTFE film preparation.

[34], and a two-step process with plasma etching and a nanoparticle assembly template to create controllable surface roughness[35]. Based on these studies, the key preparation requirement appears to be the development of a micro- and nanostructured surface. At the same time, due to weaker interactions with the polymer matrix, conventional methods, using micro- or nanoscale particles, rods, wires, etc., have a durability weakness, which is the most serious problem limiting the application of superhydrophobic surfaces.

In the present study, zinc acetate ($ZnAc_2$) and sodium chloride (NaCl) were blended into a commercial PTFE emulsion. During the preparation, the $ZnAc_2$ was decomposed to zinc oxide (ZnO) [36,37] by high temperature calcination, then washed with acetic acid. When ZnO and NaCl were dissolved in the acetic acid solution (other inorganic and organic acids, such as HCl, H_2SO_4, oxalic acid, etc., may also be used), micro- and nanoscale pores were produced on the film surface, introducing superhydrophobicity.

2. Experimental

2.1. Materials

The PTFE water emulsion (JF-4DCA, PTFE content 60 ± 2%; pH, 8–10) was purchased from Zhejiang Juhua Co., Ltd., China. NaCl was obtained from Wuxi Jingke Chemistry Co., Ltd., China, and $ZnAc_2 \cdot 2H_2O$, from Shanghai Zhenxin Reagent Co., Ltd., China.

2.2. Preparation of superhydrophobic thin films

A schematic of the film preparation process is found in Fig. 1. Solid $ZnAc_2$ and NaCl were dissolved into deionized water (>18 MΩ) and then mixing with the PTFE emulsion, with constant stirring, for 1 h at ambient temperature. Films were fabricated by dip-coating the emulsion onto glass slides, which were then dried in an oven at 100 °C for 20 min, to remove water. They were then cured at 370 °C for 30 min. Following this, the films were immersed in 1 M aqueous acetic acid for 30 min, to remove NaCl and ZnO, after which, they were dried in an oven at 100 °C for 10 min; these films are 10 ± 2 μm thick, estimated by profilometer measurement (Ambios Technology). In order to better understand the role of the aqueous acid, films before and after soaking were prepared for comparison.

2.3. Characterization

2.3.1. Water contact angle (CA) and sliding angle (SA) measurements

Contact angles were measured using a SL200B Static and Dynamic Optical Contact Angle Goniometer (Shanghai SOLON Information Technology Co., Ltd.), with an accuracy of ±1°. The sessile drop method was used to determine the static contact angles, employing ~5 μL water drops. Droplet shape photo analysis software was used to measure the contact angles by the circle fitting method. Average CA and SA values were determined by measuring three or more locations, on at least two samples.

2.3.2. Scanning electron microscopy (SEM)

Scanning election photomicrographs of several typical superhydrophobic PTFE films were obtained on a Hitachi S4800 scanning electron microscope. All samples were pre-coated with a thin layer of gold, to prevent charging.

Table 1
CA and SA values of different PTFE concentrations ($ZnAc_2$ = 5 g, NaCl = 5 g).

PTFE:H_2O	Average CA (°)	Average SA (°)
25:10	153	7
25:15	149	>20
25:20	152	>20
20:10	151	>20
20:15	151	>20
20:20	151	>20
15:10	149	>20
15:15	149	10
15:20	149	>20
5:10	150	>20
5:15	156	4
5:20	151	16

Table 2
CA and SA values for different $ZnAc_2$ and NaCl contents.

$ZnAc_2$:NaCl	Average CA (°)	Average SA (°)
5:0	145	>20
8:0	154	>20
11:0	153	>20
5:3	148	>20
5:7	151	11
0:5	152	>20
3:5	146	>20
7:5	152	12
9:5	155	7
0:0	125	>90

Table 3
List of samples prepared under different conditions.

Sample number	PTFE:H_2O:$ZnAc_2$:NaCl	Treatment condition
1	5:15:0:0	Untreated, pure PTFE
2	5:15:5:5	Immersed in acetic acid
3	5:15:5:5	Immersed in water
4	5:15:5:5	Untreated
5	5:15:0:5	Immersed in acetic acid
6	5:15:5:0	Immersed in acetic acid