Superhydrophobic surface directly created by electrospinning based on hydrophilic material

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We describe a method to form hydrophobic surfaces using PHBV (Poly (hydroxybutyrate-co-hydroxyvalerate))—a kind of intrinsically hydrophilic material. The concentration of polymer solutions was varied to control the surface morphology and resultant wetting property. The as-prepared films were characterized by micro-scale valley-and-hill structure, which was formed by aggregating of electrospun beads. The bead morphology changed from smooth to porous and popcorn-like with decreased concentrations. The shape of water droplet on these surfaces had contact angles ranging from 110.7 to 158.1°, with a maximum standard deviation of 2.5°. It was found that both the micro and nanostructure were important to create a superhydrophobic surface.
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1. Introduction

Electrospinning is a unique technology that produces polymer fibers with diameter in the range of nanometers to a few microns using an electrically driven jet of a polymer solution or melt [1]. Ultrafine fibers produced by electrospinning often exhibit bead-on-string structure, which is caused by two kinds of axisymmetric instabilities of an electrically driven jet and is influenced greatly by several parameters including operating conditions (applied voltage, solution flow rate) and solution properties (conductivity, viscosity, surface tension) [2]. Conventionally, beads on electrospun fibers have been considered as undesirable "by products" or defects [3] as the presence of beads greatly reduces the large surface area per unit mass, which is an important property for superfine or nano-scale fibers. However, here we report employing of popcorn-like beads to obtain superhydrophobic surfaces.

It is well known that the lotus leaves are dry and incontaminable from the mud (Lotus Effect). In 1997, Bathlott [4] revealed the interdependence between surface roughness, reduced particle adhesion and water repellency to be the keystone in self-cleaning mechanism of many biological surfaces. The secret of water repellency of lotus leaves is due to surface roughness caused by branchlike nanostructures on top of the micropapillae and the low surface energy epicuticular wax [5]. Herminghaus reported that it was theoretically possible to construct a water-repellent surface from a material with CA (contact angle) less than 90° and it was achieved by extrusion method [6]. Here we report that elecrospinning also holds the ability to prepare superhydrophobic surfaces from hydrophilic material. As a result, the secret of superhydrophobicity of surfaces was not primarily the chemistry but predominantly in the nanostructure of the surface and resultant roughness. Nowadays many technologies have been developed to form rough surfaces including: extrusion, chemical vapor deposition, sol-gel processing and self-assembling, heat or laser treatment and irradiation of UV-light [5, 7–11].

Recently, Lei Jiang [12] and Kazim Acatay [13] reported the examples of superhydrophobic coatings created from electrospinning. Compared to the literatures, this paper paid more attention to the formation of some interesting morphologies and the resultant wetting property. In addition, we also demonstrated that besides micro-scale roughness, nano-scale roughness also played an important role in achieving superhydrophobic surfaces.

2. Experimental

PHBV ((Poly (hydroxybutyrate-co-valerate))) ($M_w = 460\,000$ g/mol) solutions were prepared by dissolving PHBV in chloroform with gentle stirring in a water bath of 60°C for 30 min. PHBV solution concentration varied from 0.75 to 4 wt%.

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The electrospinning apparatus consisted of a syringe with a flat-end metal needle, a syringe pump for controlled feeding rates, a grounded aluminum board, and a high voltage DC power supply (JG-5001, Shanghai Shenfa Electronic Co., Ltd.). In a typical electrospinning experiment, PHBV solution was transferred into a syringe and delivered to the tip of the syringe needle by the syringe pump (AJ-5803, Angel Electronic Equipment Co., Ltd.) at a constant feeding rate. A high voltage was applied to solutions via the stainless steel syringe needle. The subsequently ejected polymer fibers or beads were collected on the glass slide for further investigation. In this work, all polymer solutions were electrospun at 20 kV potential, 0.7×10^{-9} m^3 s^{-1} feeding rate from the syringe and a 0.12 m distance from the syringe tip to the grounded target.

The morphologies of the electrospun films were examined by scanning electron microscopy (JSM-5600LV, Jeol). Contact angles were measured by OCA40 contact angle system (OCA40, Dataphysics Co.,). The volume of the water for each measurement was kept at 3×10^{-9} m^3. Solution viscosity measurement was carried out by viscometer (NAX-1, Shanghai Experimental Equipment Co., Ltd.).

3. Results and discussions

3.1. Morphology of electrospun films

At first we look at the effect of solution concentration on the morphology of electrospun PHBV films. Figs 1–4 show SEM micrographs of the film surfaces prepared from different concentrations. The concentration varied from 4, 2, 1.5 to 0.75 wt% and the corresponding viscosity was 2, 0.25, 0.14 and 0.07 $N \cdot s \cdot m^{-2}$, respectively. Ultrafine fibers produced by electrospinning often exhibit bead-on-string structure, which is caused by two kinds of axisymmetric instabilities of an electrically driven jet. As shown in Fig. 1, electrospinning of 4 wt% PHBV solution yields products exhibiting such structure, with an average fiber diameter of 0.8 μm and an average bead size of 4.2 μm. The film consists of randomly aligned beaded fibers, which form a characteristic surface of electrospun film. When solution concentration is lowered to 2 wt% while keeping other operation parameters unchanged, the resultant morphology is changed. Several beads, connected by fibers between them, assemble to form hills separated by valleys between them. As a result, the surface of the film is not smooth but very rough.

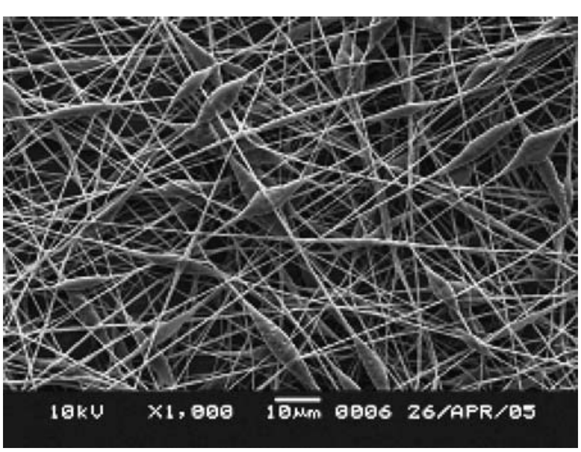


Figure 1. SEM image of beaded PHBV fibers.

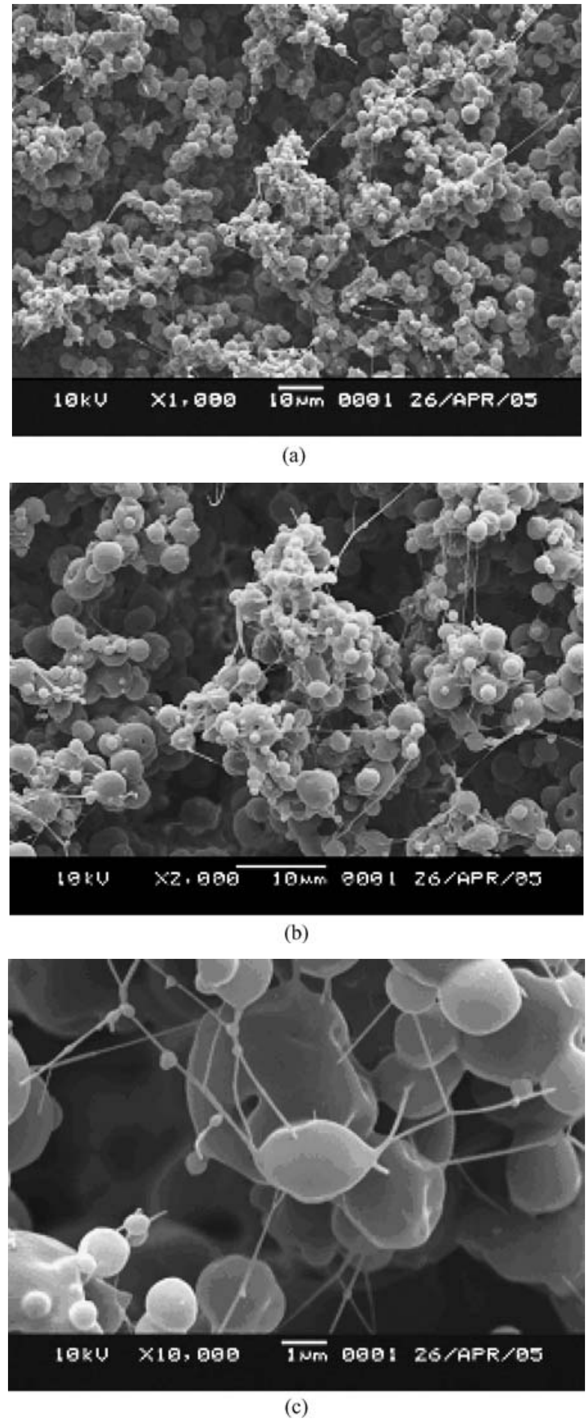
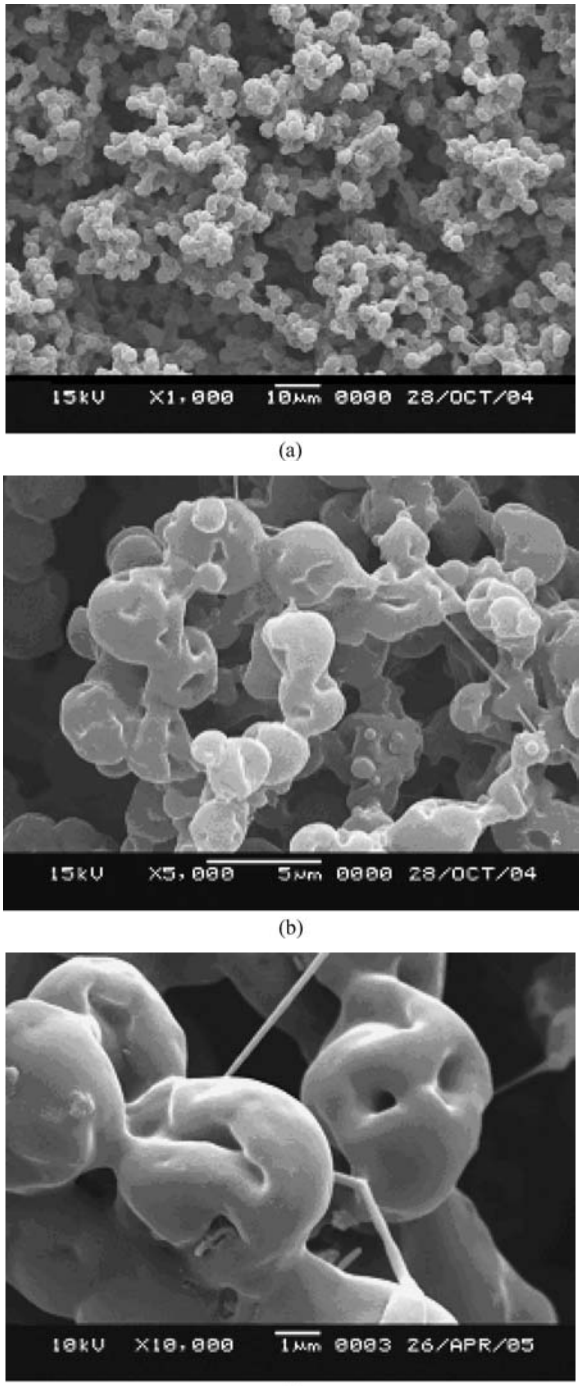
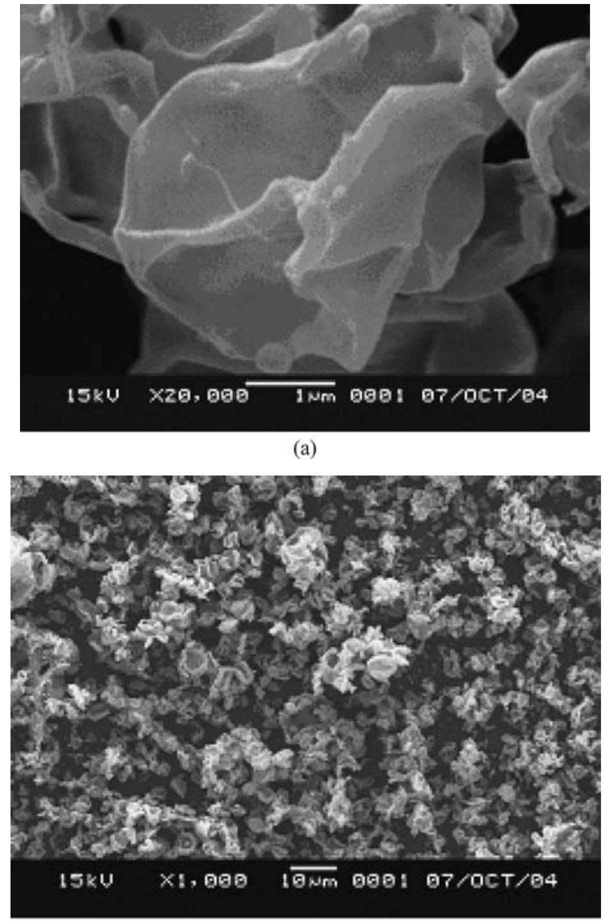


Figure 2 SEM micrographs of electrospun PHBV film at different magnifications: (a) 1,000×; (b) 2,000×; (c) 10,000×. The film was electrospun from a 2 wt% solution of PHBV in chloroform.



(c)

Figure 3 SEM micrographs of electrospun PHBV film at different magnifications: (a) 1,000×; (b) 5,000×; (c)10,000×. The film was electrospun from a 1.5 wt% solution of PHBV in chloroform.



(b)

Figure 4 SEM micrograph of electrospun PHBV film at different magnifications: (a) 20,000×; (b) 1,000×. The film was electrospun from a 0.75 wt% solution of PHBV in chloroform.

Fig. 2b shows the image of one hill and Fig. 2c is a magnified image of the beads, which exhibit relative smooth surfaces. When the solution concentration is 1.5 wt%, morphology on microscale does not change greatly, since hill-and-valley structure can still be seen in Fig. 3a. However, the surface of the bead is not smooth but collapses to form some pores. Fig. 3b and c reveal that the beads exhibit surface pores on the order of 0.5–1.5 μm and a nano-scale roughness is introduced. In addition, in this case there is a decrease in fiber number as revealed by Fig. 3. At a 0.75 wt% solution concentration, the collapse is more pronounced and the resulting bead has an appearance similar to that of popcorn, which seems to be composed of ridges or leaves with an average thickness of 200 nm (Fig. 4a). As a result, roughness on nanoscale is enhanced compared to porous bead and a two-level structure that mimics the surface structure of the lotus leaf is fabricated. Formation of porous or popcorn-like bead is thought to be caused by rapid evaporation of the solvent, which result in formation of a thin, dry polymer layer on the outside, while evaporation is incomplete within the bead. Thus the polymer bead possesses a fixed surface on the outside even before it has completely lost its solvent content. Further loss of the solvent from the inside of the bead by diffusion into the ambience through the outer dry skin causes the bead to shrink to form porous and popcorn-like morphology [14].

3.2. Wetting property of electrospun films

Wetting is an important property of a surface, and is controlled by both the chemical nature and the geometrical

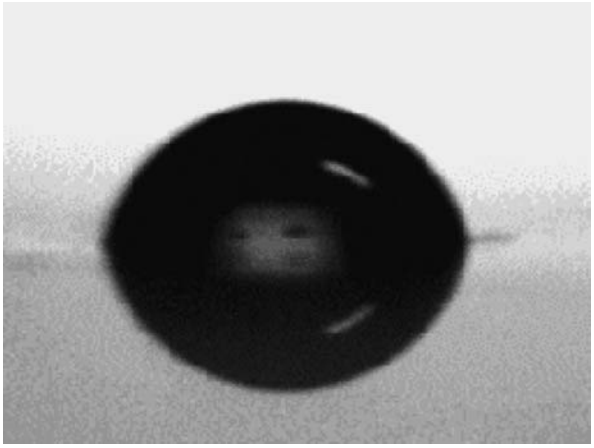


Figure 5 A water droplet on PHBV smooth surface.

structure. Figs 5 and 6 show the wetting property of the discussed film surfaces. Measurement of water contact angle on PHBV smooth surface reads 75.9 ± 1.4° (Fig. 5), indicating that PHBV is an intrinsically hydrophilic material. Fig. 6a shows the shape of a water droplet on the film surface obtained from electrospinning of 4 wt% PHBV solution. The contact angle on this film surface(110.7 ± 2.3°) is higher than 90°, indicating that the surface property has been changed from hydrophilic to hydrophobic. Observation of Fig. 6b and c reveals that films obtained from 2 wt% and 1.5 wt% PHBV solutions have contact angles of 137.5 ± 2.2° and 145.3 ± 1.0°, respectively. The above results reveal that a bead-predominant surface may generate larger contact angles than one mainly consisting of fibers does. This may be due to the fact that bead-rich surface is rougher than fiber-predominant one [13]. Compared to all the above surfaces, surface obtained from electrospinning of 0.75 wt% PHBV solution shows more hydrophobic property. A water droplet placed on this surface remains spherical and rolls quickly even at a small inclination of the surface. Static water contact angle measurement gives a value of 158.1 ± 1.2°, which means a superhydrophobic surface been obtained. All the above observations reveal that it is possible to create surfaces with identical material but with dramatically different wetting characteristics. Introduced porous structure on the bead was thought to be responsible for the increase of contact angle from 137.5 ± 2.2° (from 2 wt% solution) to 145.3 ± 1.0° (from 1.5 wt% solution). Formation of superhydrophobic surface (contact angle of 158.1°) can be explained by the introduction of lotus-leaf-like structure, which further minimizes the contact area between solid and liquid. This is an indication that the surface nanostructure also plays an important role in determining the superhydrophobic behavior of surfaces. The variation of contact angle versus solution concentration is shown in Table I.

The sliding behavior of a water droplet on the various surfaces was also investigated. A water droplet was placed on the textured film surface, which was then inclined at increasing angles until the drop started to roll. The thresh-

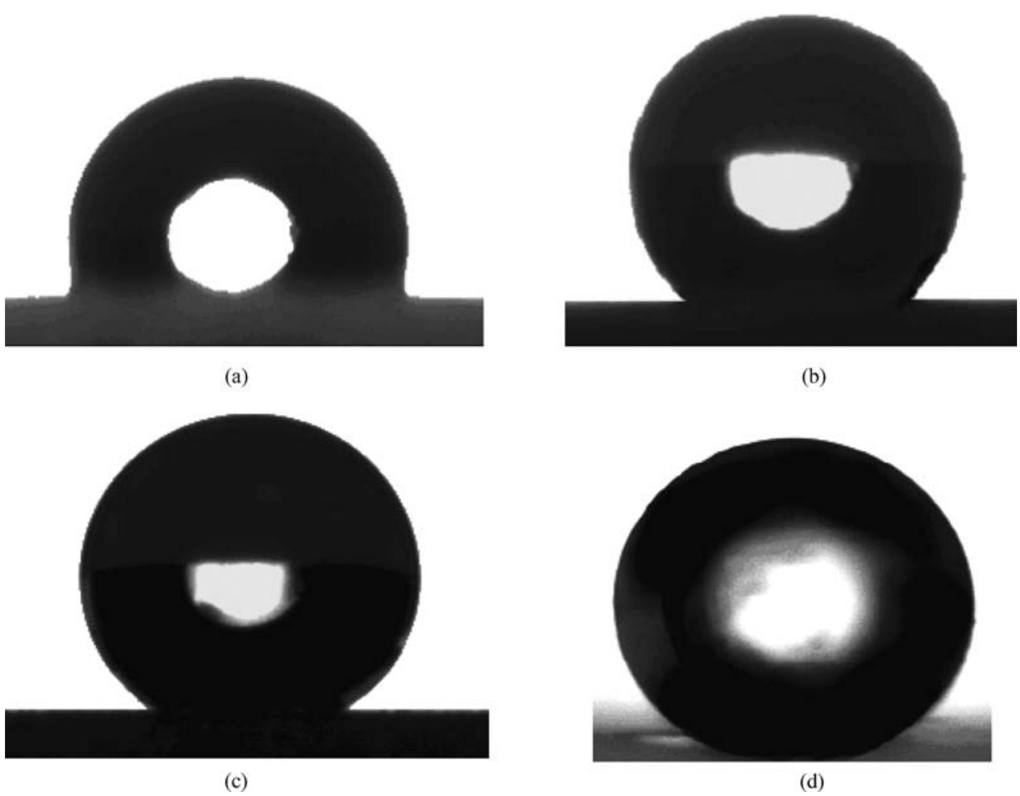


Figure 6 A water droplet on electrospun PHBV film surfaces obtained from different solution concentrations: (a) 4 wt%; (b) 2 wt%; (c) 1.5 wt%; (d) 0.75 wt%.

TABLE I Variation of contact angle and tiltangle versus solution concentration

Concentration (wt.%)	4	2	1.5	0.75
Contact angle (°)	110.7 ± 2.3	137.5 ± 2.2	145.3 ± 1.0	158.1 ± 1.2
Tiltangle (°)	80 ± 5.0	60 ± 5.0	20 ± 3.0	7 ± 2.5

old sliding angle was defined as tiltangle. The variation of tiltangle versus solution concentration is summarized in Table I. For PHBV smooth surface the drop can not run even at an inclination higher than 90°. The smallest tiltangle was obtained on the two-level-structure surface, on which the drop ran so fast that it was difficult to capture the sliding behavior by common camera. A conclusion can be reached that, for various PHBV film surfaces, the higher the contact angle is, the more easily the drop rolls.

The principle connections between surface roughness and water repellency were worked out by Cassies and Baxter [4, 15]. It is possible to develop the following relationship relating apparent contact angle (θ') to the composition of a surface

$$\cos\theta' = f_1 \cos\theta_1 + f_2 \cos\theta_2 \quad (1)$$

where f_1 and f_2 are the fractions of the surface having inherent contact angles θ_1 and θ_2. When the surrounding medium is air, $\theta_2 = 180°$ and the equation can be written in the following form

$$\cos\theta' = f_1 \cos\theta_1 - f_2 \quad (2)$$

Here f_1, f_2 mean the fractions of solid surface and air in contact with liquid respectively [16]. In the case of water-repellent rough surfaces, air is enclosed between the protrusions, forming a composite surface. This enlarges the water/air (f_2) interface while the solid/water (f_1) interface is minimized. As a result, high apparent contact angle is obtained and the surface exhibits superhydrophobicity.

4. Conclusions

PHBV films prepared by electrospinning possessed hydrophobic property that depended on the surface morphology, which was ultimately controlled by varying concentration of polymer solutions. The decreased concentrations leaded to micro-scale rough surface or even two-level structure that conceptually mimicked the lotus leaf surface. The as-prepared films exhibited water contact angles ranging from 110.7 to 158.1°. Air that trapped in the rough surface was believed to be responsible for the increase of anti-wetting property.

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