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Contact angle hysteresis analysis on superhydrophobic surface based on the design of channel and pillar models

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ABSTRACT

Contact Angle Hysteresis (CAH) is critical to the hydrophobicity of a surface, which describes the dynamic characteristic of droplets. In this paper, two different micro-structured surfaces respectively with micro-channel and micro-pillar structures (20 samples for each structure, with a range of channel and pillar widths between 25 and 250 μm) were fabricated by mechanical micro-milling process to investigate the effect of structural parameters on hydrophobicity of surfaces. It was found that the solid fraction plays a decisive role for a surface in the transition from being hydrophilic to hydrophobic. Quantitative interpretation was conducted and a dynamic methodology was established based on the physical nature of the controllable motion of a droplet. The five key states of a droplet including the initial, pre-forward, forward, pre-backward and backward were the main focus of this research. The prediction results based on the established model showed good consistency with experiments. The proposed model can estimate the advancing and receding angles very well. The outcome of this research will lead to new methodologies for preparing hydrophobic surfaces with micro-machining technology and play an important theoretical guiding role in fabrication of superhydrophobic surfaces.

1. Introduction

For rough or chemically heterogeneous surfaces, metastable phenomenon for the wetting system may occur. The variations of the contact angle are within a range which corresponds to a series of dynamic contact angles [1–2].The maximum value of contact angle before the drop advances is called advancing angle, and the minimum value of the contact angle before the drop retracts is called receding angle [3–4]. Contact angle hysteresis (CAH) is considered to be the difference between the advancing angle and the receding angle. The CAH reveals the contact angle spectrum, within which drops are inhibited of motions. The advancing angle reflects the property of hydrophobicity, while the receding angle indicates the property of hydrophilicity [5].

The use of superhydrophobic surfaces is essentially self-cleaning in nature [6]. Most reported studies have applied superhydrophobic surfaces to increase the extent of hysteresis on neighboring hydrophobic or hydrophilic regions [7]. In recent years, with the rapid development of science and technology, ultra-precision machining technology is promising for potential applications in the hydrophobic surface field [8]. Compared with other methods, high speed micro-milling process receives more attention due to its high machining accuracy, processing efficiency, simple preparation, relatively low cost and fewer limitations on processing materials [9].

In order to understand the nature of the hydrophobicity, the formation mechanism and the wetting phenomena, quantitative research has been carried out [10–11]. The Wenzel model [12] and the Cassie-Baxter model [13] have been used to interpret the phenomenon that the rough surface can increase the contact angle. However, the CAH in these two situations is far different with each other. Johnson and Dettre [14] found that when the surface roughness is relatively small, the droplet resting on the surface is in the Wenzel state. The CAH increases significantly with the increase of surface roughness. However, the CAH decreases rapidly when the surface roughness exceeds a certain value. The rapid decrease of the CAH is due to the fact that the droplet has changed into the Cassie-Baxter state. Compared with the Wenzel state, the trapped air in a rough surface can reduce the adhesion between the liquid droplet and solid surface for the Cassie-Baxter state. Suzuki et al. [15] evaluated the dynamic CAH of water droplets on a silicon surface that had been treated with fluoroalkyl silane. Results implied that the sliding acceleration of the water droplets on hydrophobic surfaces is controllable by changing the pattern structure of the surface and its chemical composition. Eral et al. [16] proposed a brief introduction of

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the CAH starting from a description of the physical phenomena. The model for implementing the CAH into relevant physical phenomena was then introduced. The influences of the CAH on several physical phenomena relevant for industrial applications such as sliding drops, coffee stain phenomenon, curtain and wire coating techniques were explained. Mundo and Palumbo [17] pointed out that the measurements of the CAH included static mode and dynamic mode. The static mode can be realized by simply placing a liquid drop on the surface. The dynamic mode was consistent in forcing the probe liquid to advance and retract, and then recording the angles of the liquid front corresponding to these variations.

Several researchers studied various theoretical bases for analytical models to investigate the effects of structure on surface hydrophobic properties. Miwa et al. [18] investigated the relationships between the sliding angle, the contact angle and the surface structure. A mathematical description of the relationships among them has been established. Results showed that the sliding angles of water droplets decrease with increasing contact angles. The surface structures, which can trap air, are important for the preparation of low sliding angle surfaces. Lv et al. [19] established an explicit analytical model to predict the sliding angles based on the observed mechanisms. With the proposed model, the sliding angle was determined by the fraction of water-solid interface area and Young's contact angle. A number of pillar and channel structured surfaces with different area ratios and different sizes have been investigated. Wang et al. [20] and Cai et al. [21] investigated the dynamic wetting behavior and water drops on micro-grooved surfaces. It was found that the dynamic advancing angle increases with the increase of the drop velocity and the receding angle decreases with it [20]. For droplets with different sizes, on the same substrate, the advancing angle and the receding angle slightly changed, but the CAH basically remained unchanged. Zhang et al. [22] proposed a three dimensional model based on the scanning electron microscopy of cicada wings to determine and explain the CAH in quantity. However, the established model was limited to explain some special circumstances which contain a number of empirical parameters.

This paper aims to investigate the effect of different micro-structures on hydrophobicity of surfaces based on the analysis of a number of hydrophobic surfaces fabricated under micro-milling process. The qualitative analysis based on experiments was conduct to reveal the impact mechanism of the structural parameters on hydrophobic performance. A comprehensive hydrophobic theory was established to explain the quantitative relationship between micro-structures and wetting performance of the rough surface. The established dynamic methodology model can clarify the importance of geometric scales on preparing a superhydrophobic surface. The established theoretical model can also be used to explain the wettability of rough surface and provide guidance on the preparation of superhydrophobic surfaces. Fig. 1 shows the general framework of this research.

2. Experiments

2.1. Micro-structure selection

The advancing angle is the contact state when the droplet resting on a rough surface is about to move with the volume of droplet increasing as shown in Fig. 2. The receding angle is the contact state when the droplet resting on a rough surface is about to move with the volume of droplet decreasing. The advancing angle is always larger than the receding angle. CAH is the difference between the two angles. The magnitude of the CAH represents the degree of difficulty for a droplet to separate from the surface. As the CAH increases, it becomes more difficult for the droplet to separate from the surface. When the CAH is small to a certain level, it is easy for the droplet to separate from the surface, and in this case the surface has the properties of self-cleaning [23–24].

In this paper, two different micro-bump structures including micro-channel and micro-pillar structures are fabricated and analyzed. This paper proposes a 3-dimensional channel and a 3-dimensional pillar structure illustrated in Fig. 3(a) and (b), respectively. These structures can be simplified into a 2-dimensional system by analyzing the system along specific planes, e.g. at $y = 0$, as illustrated in Fig. 3(c).

2.2. Experiments procedure

The material removal process strongly influences the functionality of the machined surfaces. Micro-milling process is the physical treatment for the surface. The material removal can be realized based on the nature of phenomena of mechanical forces. Micro-milling process is believed to be able to get desirable shapes, geometrical accuracy and surface integrity to the maximum extent. Additionally, by using micro-milling process, there are lower environmental impacts than the surface modification approaches including materials treatments.

In this paper, experimental work has been carried out to investigate the effect of different micro-structures on advancing and receding angles through micro-milling process. PMMA was selected as workpiece to reduce the manufacturing error and defects for its characteristics of good transparency and easy to process. The workpiece was machined on a KERN 2522 micro-milling center as shown in Fig. 4 [25]. The cutting tool selected was a double-edged solid cemented carbide micro-milling cutter with diameter of 0.1 mm. The experiments were carried out with a constant feed rate (600 mm/min) and a constant spindle rotation speed (30,000 r/min).

The micro-channel structure and micro-pillar structure were machined as shown in Fig. 5. The micro-channel structure was completed through one pass in vertical direction and the micro-pillar structure was completed through two passes in vertical and horizontal directions.

When the machining process is completed, the finished surface has to be deburred to eliminate the effect of burrs on contact angle. At first, the machined surface was lightly brushed to remove most burrs with a 0.05 mm ultrafine brush. Then the machined surface was treated with alcohol ultrasonic cleaning for 30 min. Fig. 6 shows the comparison graph of the surfaces before and after burr removal. Finally, the machined surface was washed by de-ionized water in ultrasonic cleaning tank to remove impurities on the surface.

The static and dynamic contact angles were obtained through an optical contact angle measuring instrument. In the process of measurement, the workpiece was fixed on the measuring platform. The test liquid is deionized water with density $\rho = 996\ \mathrm{kg/m^3}$, surface tension $\sigma = 0.07275\ \mathrm{N/m}$, viscosity $\mu = 0.001\ \mathrm{kg/ms}$, and the initial droplet volume is 2 μL [25]. Before the cutting experiments, the un-machined original sample was tested, and the average contact angle was about 80°.

Fig. 7 plots the measured advancing contact angle and receding contact angle as a function of a droplet volume on a micro-pillar structure with $c = 150\ \mu\mathrm{m}$, and $e = h = 100\ \mu\mathrm{m}$. The advancing and receding angle were measured through Pendant Drop method by the way of increasing or reducing the volume of the droplet. For the advancing angle, the droplet was gently deposited on the substrate and increased in steps through an automatic dispensing syringe. When a small drop is deposited on the surface, a static contact angle was formed between the advancing and receding values for the rough substrate. The advancing angle was measured after each 0.5 micro-liter volume increment. The drop volume was increased up to about 5 μL. As the drop volume increased, the apparent angle increases until it reaches the maximum static angle which is defined as advancing angle. Once the advancing angle is reached, further increase in volume does not significantly change the apparent angle of the droplet. Fig. 7 gives an advancing angle 137° for a droplet on the rough substrate. Receding contact angle measurements were then conducted by removing water from the droplet in steps. The apparent contact angle was measured after each volume reduced. For the receding angle, the volume reduction began from the last drop obtained in the advancing angle. The