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Impact of pillar configuration on the amphiphobicity of micro-patterned polymer surface

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ABSTRACT

Hydrophobic surfaces are easily contaminated by oil owing to its lower surface tension, which significantly limits their potential applications. In this study, micro-patterned surfaces with cylindrical or square pillar arrays were fabricated on a polycarbonate substrate by the thermal imprinting process. The geometry and size of the pillars were varied to obtain different samples, whereas the height of the pillars was kept constant. The surface of each micro-patterned sample was fluorinated with perfluorooctanoic acid. With the aim of characterizing the wetting behavior of the samples, droplets of water and oily liquids with different surface tensions were employed to measure the contact angles. In addition, the applicability of the Wenzel and Cassie equations for explaining the wetting mechanisms of droplets on the surfaces of the micro-patterned samples was systematically investigated. The prediction obtained using the Wenzel equation was found to differ considerably from the experimental results, whereas the Cassie equation was found to be acceptable for satisfactorily explaining the wetting behaviors of liquids on the micro-patterned samples. The main factor influencing the surface wettability of the micro-patterned sample was not the pillar geometry, but rather the pillar configuration, e.g., the solid area fraction, groove fraction, and spacing between pillars.

1. Introduction

Wettability is one of the most important properties of solid surfaces [1]. Control of wettability makes it possible to reduce and even prevent the adhesion of liquid droplets to solid surfaces. Recently, the potential applications of hydrophobic surfaces in self-cleaning [2], tunable water adhesion [3], drag reduction [4], oil-water separation [5], prevention of corrosion [6,7], and hydrophobic electrodes for batteries and fuel cells [8] have attracted intensive interest of researchers studying the fabrication and modification of these surfaces.

Hydrophobic surfaces can be easily contaminated by oil-containing liquids with lower surface tensions; this limits oil-based applications of these surfaces, for example, in microfluidic devices and oil transportation. Therefore, an amphiphobic surface, which is repellent to both water and oily liquids, has attracted increasing research attention. However, the fabrication of amphiphobic surfaces is considerably more difficult than that of hydrophobic surfaces, because oily liquids are prone to wetting a solid surface.

A low surface energy and an appropriate surface microstructure are the two main factors determining the wettability of a solid surface [9]. The surface energy can be simply modified by chemical treatment, e.g., fluorination. However, surface microstructure is a vast research area because a variety of morphologies and structures can be obtained by different techniques and processes. A flat substrate cannot provide amphiphobicity even if it is modified with a material having the lowest surface energy [10]. However, it is possible to make a well-defined patterned surface amphiphobic even without fluorination [11]. Given the importance of the surface microstructure in imparting liquid repellency, the surface microstructure will be the main focus of interest in this research field.

Two distinct theories, those of Cassie and Wenzel, have been utilized to describe the interactions at the liquid/solid contact area with the aim of explaining the effects of chemical heterogeneity and surface roughness on the wettability of a solid surface. According to these theories, a liquid droplet is considered to be suspended over an air pocket trapped in cavities by capillary forces (Cassie state) or to completely wet the grooves on a patterned surface (Wenzel state) [12,13]. Many research groups have compared their experimentally measured results with the predictions obtained using these two theories [1,11,14–17]. He et al. investigated the effect of the geometric parameter of a square pillar on hydrophobicity by changing the spacing on a silicon wafer via micromachining techniques [1]. Liu et al. formed

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pillar, reentrant, and doubly reentrant structures on silicon wafers by complicated processes and analyzed their influences on the omniphobicity of the surface [11]. Yoshimitsu et al. studied the effects of pillar-like structures on the hydrophobicity and water-shedding properties of silicon wafers [15]. Cengiz et al. fabricated cylindrical pillars with various diameters on a silicon wafer by deep reactive ion etching and investigated the effects of diameter on the oleophobicity and superhydrophobicity of the wafer surface [16].

Although many studies have been conducted on the effect of the surface microstructure on the wettability of silicon wafers, the study of micro-patterned surfaces of flexible polymer materials has received less attention despite the essential and ubiquitous roles of these materials in everyday life, such as in biomedical applications, drug delivery systems, biosensor devices, and tissue engineering [18–20]. In addition, the applications of polymers are still increasing rapidly because of their low cost and ease of manufacture. On the other hand, the liquid droplet used in most previous studies merely focuses on water but ignores the oily liquids. Therefore, the effect of the pillar configuration on the amphiphobicity of a micro-patterned polymer substrate needs to be investigated more extensively.

In this study, micro-patterned surfaces with different pillar configurations were fabricated on polycarbonate (PC) substrates by the thermal imprinting process and the chemistry of the micro-patterned surfaces was subsequently modified via treatment with perfluorooctanoic acid (PFOA). Contact angles were measured using droplets of water and oily liquids in order to investigate the effect of the pillar configuration on the amphiphobicity of the micro-patterned surfaces. The applicability of the Wenzel and Cassie equations to the micro-patterned surfaces with pillar arrays was systematically studied by examining the deviation between the experimental measurements and the theoretical predictions. The effects of pillar configuration, e.g., the solid area fraction, groove fraction, and pillar spacing, on the amphiphobicity of the micro-patterned surface were investigated.

2. Theoretical background

Young's equation expresses the contact angle of a liquid droplet on a flat solid surface [15] as

$$\cos\theta = (\gamma_{SV} - \gamma_{SL})/\gamma_{LV} \tag{1}$$

where γ denotes the interfacial tension and the subscripts S, V, and L represent solid, vapor, and liquid, respectively.

For micro-patterned surfaces, two theories (Fig. 1(a) and (b)) were developed, where the wettability could be affected by changing surface roughness and liquid/solid contact area. One theory is that developed by Wenzel, who assumed that a liquid droplet completely fills the grooves between the protrusions on a micro-patterned surface owing to the strong interaction between the liquid and the solid [13]. The Wenzel equation is given as

$$\cos\theta_w = r\cos\theta \tag{2}$$

where θ_w is the apparent contact angle on the wetted surface and r is the roughness factor, which is equal to the ratio of the actual area of the patterned surface to its projected area; the roughness factor is always larger than 1.

The other theory is that developed by Cassie, who assumed the formation of a composite surface, wherein a liquid droplet is lifted up by the air pockets trapped in the groove [12]. The Cassie equation is expressed as

$$\cos\theta_c = f(1 + \cos\theta - 1) \tag{3}$$

where θ_c denotes the apparent contact angle on the composite surface and f is the solid area fraction, which is always smaller than 1.

2.1. Theoretical calculation

Fig. S1 shows the planforms of micro-patterned surfaces with cylindrical and square pillars (hereafter referred to as cylindrical and square pillar surfaces, respectively). The parameters of roughness factor r and solid area fraction f of the Wenzel and Cassie equations, respectively, are used in the investigations in this study. The roughness factor r_c for the cylindrical pillar surface (Fig. S1(a)) can be expressed as

$$r_c = (p^2 + \pi dh)/p^2 \tag{4}$$

where d is the diameter of the cylindrical pillar, p is the pitch between two adjacent pillars, and h is the height of the pillar.

The roughness factor r_s for the square pillar surface (Fig. S1(b)) can be calculated as follows:

$$r_s = (p^2 + 4bh)/p^2 \tag{5}$$

where b is the side length of the square pillar.

The solid area fraction f_c for the cylindrical pillar surface can be calculated as follows:

$$f_c = \pi d^2/4p^2 \tag{6}$$

The solid area fraction f_s for the square pillar surface can be expressed as follows:

$$f_s = b^2/p^2 \tag{7}$$

2.2. Deviation from Wenzel and Cassie theories

Two kinds of calculations can be performed for the parameters r and f in the Wenzel and Cassie equations, respectively [21]. One is a calculation of theoretical parameters r_c, r_s, f_c, and f_s from the geometry of the pillar structure by using equations (4)–(7). The other is a calculation of experimental parameters r^e and f^e by using experimentally measured contact angles on flat (θ) and micro-patterned (θ^e) surfaces:

$$r^e = \cos\theta^e/\cos\theta \tag{8}$$

$$f^e = (\cos\theta^e + 1)/(\cos\theta + 1) \tag{9}$$

Generally, the experimentally measured contact angle (θ^e) is unequal to the theoretical contact angles (θ_w and θ_c) calculated from equations (2) and (3); therefore, the theoretical parameters r_c, r_s, f_c, and f_s (geometry-dependent) are different from the experimental parameters r^e and f^e (angle-dependent). Accordingly, the differences between the geometry-dependent and angle-dependent parameters, Δr and Δf, give the deviations between experimental results and theoretical predictions:

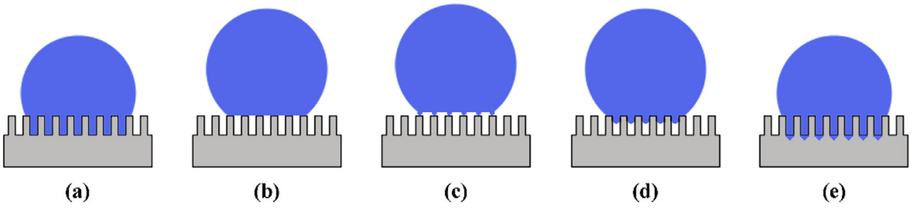

Fig. 1. Sketch of liquid droplet on micro-patterned surface: (a) Wenzel state, wherein the liquid droplet completely penetrates into the grooves; (b) Cassie state, wherein air pockets are trapped beneath the liquid droplet and the liquid droplet comes into complete contact with the entire top surface of the pillar; (c) excessive Cassie state, wherein the liquid droplet is not in complete contact with the entire top surface of the pillar; (d) intermediate state, wherein the liquid droplet partially penetrates into the grooves; and (e) excessive Wenzel state, wherein the liquid droplet sinks beneath the grooves.