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Enhancement of dynamic wetting properties by direct fabrication on robust micro–micro hierarchical polymer surfaces

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ABSTRACT

Understanding evaporation phenomena on hierarchical surfaces is of crucial importance for the design of robust superhydrophobic polymer structures for various applications. This fabrication method enables precise control of the dimensions to elucidate the dynamic wetting behavior affected by geometric parameters. That behavior exhibits three distinct evaporation modes: a constant contact line (CCL), a constant contact angle (CCA), and mixed mode during the droplet evaporation. The droplet evaporation results show that the sticky CCL mode and the Cassie–Wenzel transition can be prevented by engineering hierarchy integration. Moreover, the CCL–CCA transition point time scale exhibits remarkable dependence on surface dimensions such as the area fraction and solid–liquid contact line. Finally, the fabricated hierarchical structures indicate remarkable superhydrophobic properties, static contact angle above 160° and low sliding angle under 10°, with good durability in terms of aging effect and mechanical robustness for 2 months.

Introduction

Superhydrophobic surfaces, which exhibit high water droplet contact angles greater than 150°, have attracted considerable interest in the last decade because of their excellent water-repellent surface properties [1–5]. Such surfaces show great potential for various applications related to self-cleaning, anti-icing repellence, biotechnology, microdevices and nanodevices, and thermal systems [6–16]. An extremely effective method to achieve superior superhydrophobic properties is the development of a hierarchical surface: a nanostructure within a microstructure. Fundamentally, these hierarchies were inspired by a natural structure: a lotus leaf [17,18]. The lotus leaf superhydrophobic behavior is attributed to surface roughness created by randomly dispersed micrometer-sized surfaces covered with nanometer-sized fibers. Water droplets on such a surface rest on the peak of the surface features and cannot penetrate into the bottom of the microstructure or nanostructure because of the low surface tension. The contact angle of a water droplet is believed to be dependent on the ratio of the volume of entrapped air to the volume of the surface structure. Because the decreased area fraction of the two-level structure is much smaller than that of the single-level structure, the superhydrophobic state is best achieved through the adoption of hierarchical structures.

However, the study of the static hydrophobicity alone is insufficient to ascertain the wetting property of a surface. Although the apparent contact angles on the certain superhydrophobic structure are similar, they can show different dynamic phenomena, being either sticky or slippery. They are differentiated by the contact angle hysteresis of the moving water droplet on the surface. On a slippery surface, a water droplet rolls off easily with little contact angle hysteresis, which is known as the "lotus effect". However, on superhydrophobic sticky surfaces, a water droplet does not roll off, even when the surface is turned upside down, because the water droplet is strongly pinned on the solid surface. Such surfaces are also apparent in nature, designated as a "petal effect" [19]. Although the contact angle hysteresis on a superhydrophobic surface has been studied actively in equilibrium conditions [20–22], the contact angle hysteresis during an in-phase transition process such as evaporation has remained virtually unexplored. Most studies of droplet evaporation specifically assess phase transition patterns on the pinning–depinning transition: from a constant contact line (CCL) mode to a constant contact angle (CCA) mode [23–26] or on the Cassie–Wenzel transition occurring at the late stage of evaporation involved with the CCA mode to mixed mode [27,28]. Despite extensive progress, fundamental understanding of how the geometric parameters affect the wetting transition is lacking.

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A myriad of methods has been developed to fabricate micro–nano hierarchical structures on polymer surfaces [29–40]. Although numerous fabrication methods can generate superhydrophobic surfaces, it is particularly difficult to control the nanostructure part dimensions precisely within the hierarchical structures. Therefore, fabrication methods must be developed to control the dimensions precisely and thereby elucidate the dynamic wetting behavior affected by geometric parameters. That knowledge will be invaluable to develop optimized polymer structures. A hierarchy can also be achieved on another scale by combining micro–micro hierarchical structures that can easily control the dimensions and increase the mechanical robustness of structures [41,42]. It is assumed that micro–micro hierarchical structures can also exhibit highly hydrophobic properties because of the hierarchy effect. Furthermore, the mechanical robustness of micro–micro hierarchical structures is expected to be better than that of the micro–nano hierarchical structures [38,43].

Our research group has developed a simple and highly accurate fabrication method for well-ordered microstructures and micro–micro hierarchical structures using direct fabrication with a precision tooling machine. During the fabrication process, these structures can be controlled precisely in all single-level and hierarchy processing.

For this study, four micropillar and hierarchical structures were prepared to assess the enhancement of superhydrophobic properties related to hierarchical integration and the effect of geometric parameters. We demonstrate dynamic wetting properties on the polymer surface during the in-phase transition process governed by wetting hysteresis. To ascertain how the energy transition point is involved in pinning–depinning and how the Cassie–Wenzel transition is affected by the surface morphology, experimentally obtained data related to water droplet evaporation on PMMA surfaces are presented and analyzed.

Experiments

Micropillar and hierarchical structures were fabricated directly on flat polymer surfaces using a precision tooling machine (Robonano α-0iB; Fanuc Ltd.). The flat samples used for direct fabrication were prepared using a micro-injection molding machine (AU3E; Nissei Co. Ltd.) with a commercial transparent polymer, polymethylmethacrylate (PMMA, MFR = 3 at 230 °C/3.8 kg, T_g = 115 °C, PM-7200; Cheil Industries Inc.). The single-level micropillar structures were fabricated by placing a needle-type tool in the tooling machine, by setting the machine program parameters, and by then machining micropitted structures. Each linear axis of the pillar structure is inscribed with a linear motion. The cutting tool can fabricate microscopic grooves on the polymer surface at the rate of five grooves per second. The hierarchical structures are prepared using two-step fabrication: a large-scale micropillar structure is formed, followed by formation of a small-scale micropyramidal structure with a smaller cutting tool. The structured area was 1 cm^2.

Next, fabricated structures were coated with a—CF_2-based amorphous fluoropolymer using dip-coating (dip-coater, M115S; Asumi Giken Ltd.). A primer solution was prepared for pretreatment to enhance the coating properties. A solution of the primer (CT-P10; Asahi Glass Co. Ltd.) was mixed with a solution (isopropyl alcohol and isobutyl acetate in a ratio of 9:5) diluted to 5% concentration. The structured plate was first coated with a pre-treatment solution at room temperature for 5 min. Then it was dried at room temperature for 30 min. The pre-treated plate was then coated with—CF_2-based amorphous fluoropolymer (CTX-109AE, $(C_6F_{10}O)_n$; Asahi Glass Co. Ltd.). The schematic structure of this polymer is presented in Fig. 1. The coated plate was dried at room temperature for 1 h. It was then heated at 80 °C for 1 h.

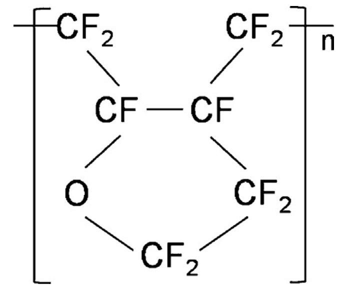

Fig. 1. Schematic structure of the—CF_2-based amorphous fluoropolymer.

Contact angles were measured using the sessile drop method with a contact angle meter (DM 500; Kyowa Interface Science Co. Ltd., Saitama, Japan). Pure DI water (drop volume of about 4 μm) was used for the contact angle and for evaporation measurements. All measurements were performed under atmospheric conditions: 23 ± 1 °C, 40 ± 2% humidity, and atmosphere pressure. The values reported herein are averages of at least five measurements of all samples. During evaporation, the evolution of the contact angle and contact radius was measured from the images observed every 30 s for data analysis.

Images of patterned surfaces were observed using a scanning electron microscope (FE-SEM, SU-8000; Hitachi High-Technologies Corp.). The structure dimensions were evaluated using a laser spectroscope (LEXT OLS 4000; Olympus Corp., Tokyo, Japan).

Results and discussion

Dimensions of fabricated microstructures and hierarchical structures

The dimensions and area fractions of fabricated micropillars and hierarchical structures are shown in Table 1. Herein, M_x and m_y respectively denote the numbers of micropillar structures and micropyramid structures. Hierarchical structures were prepared with four samples, mM_1, mM_2, mM_3, and mM_4, combined individual micropillar structures with fixed micropyramid structures (2.0 μm distance, 1.0 μm height). The micropillar structures were produced to have equal height (40 μm) but with varying pillar width and pillar-to-pillar spacing appearing in a square array for various dimensions in a dewetting Cassie–Baxter state. The dimensions were prepared to have area fractions of the solid–liquid interface: 0.074 in M_1 and M_2 and 0.184 in M_3 and M_4. The width and pillar-to-pillar spacing were then changed in the same area fraction to ascertain the effects of the solid–liquid contact area on hydrophobic properties. The submicro-scale micropyramid structures were applied on the solid–liquid interface parts of micropillars to increase the volume of the three-phase contact line, which can enhance the dewetting properties [1,44]. The micropillar and hierarchical structure dimensions were estimated using laser spectroscopy. The area fraction of the micropillar surface in contact with liquid was calculated according to Eq. (1) below, where X denotes the micropillar width, and D represents the distance between micropillars.

$$\text{area fraction of pillars} = \frac{X^2}{(X+D)^2} \quad (1)$$

Fig. 2 presents SEM images of micropillar and hierarchical structures on a PMMA surface. Well-ordered arrays were observed. Almost all sizes of fabricated structures measured using laser spectroscopy were controlled accurately to less than 10% error.