

WETTING BEHAVIOR ON MICROSCALE WRINKLED SURFACES*

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Introduction

We present a systematic study of the wetting behavior on the anisotropic microstructure having a simple sinusoidal profile. The micro-patterned surface was generated by using the buckling-based technique^{1,2}, and its wetting properties were examined by contact angle measurements perpendicular and parallel to the direction of the grooves. The results obtained show that the apparent contact angles in two orthogonal directions appear to be quite different; the one in the perpendicular view was larger than the other. Interestingly although the surface is inherently hydrophilic, the angle in the perpendicular view on the patterned surface increases with increasing surface roughness. The observed behavior is in marked contrast to the common belief that roughness promotes wetting for a hydrophilic surface^{3,4}. We demonstrate that this phenomenon is attributable solely to anisotropic surface morphology and the change of contact angles on a real rough surface is significantly affected by the nature of the three-phase contact line structure⁵.

Experimental⁶

We fabricated the micro-wrinkled surfaces by mechanical compression of an ultraviolet/ozone (UVO) treated poly(dimethylsiloxane) (PDMS) network, using a previously described procedure² (see Fig. 1a). A PDMS network was prepared by mixing Sylgard 184 (Dow Chemical) with a 10:1 resin to curing agent and curing at 75 °C for 2 h. A 1-mm-thick flat sheet of the cross-linked PDMS was initially mounted on a custom-designed strain stage¹ and subsequently stretched uniaxially by ΔL . The PDMS sheet was then exposed to UVO radiation for extended periods of time, which oxidizes the outer surface of PDMS to convert into a silicate layer. Upon releasing the strain ($\varepsilon = \Delta L/L$) from the pre-stretched UVO-PDMS substrate, a sinusoidally wrinkled pattern perpendicular to the direction of the strain was obtained. The wavelength of the wrinkled surface can be controlled by adjusting exposure dose (which affects both the thickness and Young's modulus of the silicate layer), and the amplitude is controlled by the degree of compression. In addition, the thin film of UVO-PDMS shows an excellent elastic recovery at least within the range of strains used in the

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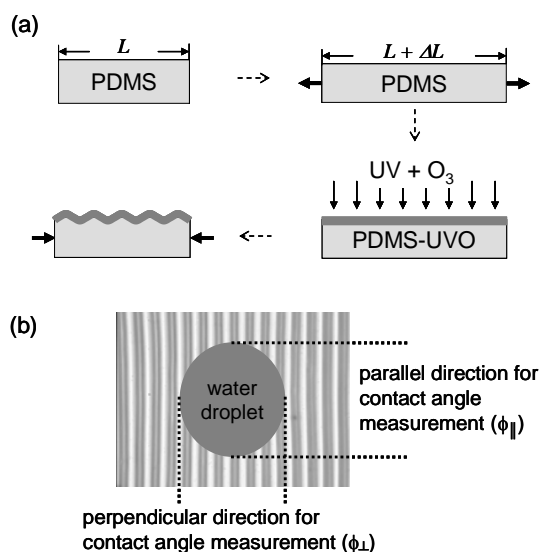


Figure 1. (a) Schematic illustration of steps for generating a sinusoidally micro-wrinkled pattern on the PDMS substrate. (b) Configurations for contact angle measurements perpendicular (ϕ_{\perp}) and parallel (ϕ_{\parallel}) to the direction of the grooves.

present study ($\varepsilon \approx 50\%$). As a result, a precise and reversible control of patterned surface structure with a well-defined roughness aspect ratio (amplitude versus wavelength of the sinusoidal wrinkles) becomes possible.

Results and Discussion

We characterize the wetting properties by measuring the apparent water contact angles in two orthogonal directions (see Fig. 1b). Figure 2 shows the static water contact angles measured perpendicular (ϕ_{\perp} , left axis) and parallel (ϕ_{\parallel} , right axis) to the direction of the grooves as a function of compressive strain ($\varepsilon = \Delta L/L$). Here, the UVO-PDMS substrates were prepared by exposing the surface (stretched previously by 50%) to UVO for 1 h. The resulting UVO-PDMS surface showed a hydrophilic nature at the initial stage with $\phi_{\perp} = \phi_{\parallel} = 64.3^{\circ} \pm 0.8^{\circ}$. At a compressive strain raised stepwise from 0% (pre-stretched state) to 50%, the three distinct regimes were observed to be representative of the wettability of the wrinkled UVO-PDMS surface. At low strains, the contact angles in both views (ϕ_{\perp} and ϕ_{\parallel}) do not change until $\varepsilon \approx 16\%$, where

buckling instability occurs. As further increase in ε above around 16 %, ϕ_{\perp} starts to increase almost linearly with increasing ε until $\varepsilon \approx 40$ % (black circles). Conversely, ϕ_{\parallel} begins to decrease with increasing ε until $\varepsilon \approx 40$ %, and then increases slightly for $\varepsilon > 40$ % (gray triangles). Specifically, UVO-PDMS substrates compressed at relatively large strain (> 40 % in this case) contain a form of cracking along the strain direction (perpendicular to the wrinkled patterns). We believe that the origin of surface cracking is most likely due to the lateral deformation caused by the Poisson effect, which causes fracture of the silicate layer when the compressive strain reaches its failure strain.

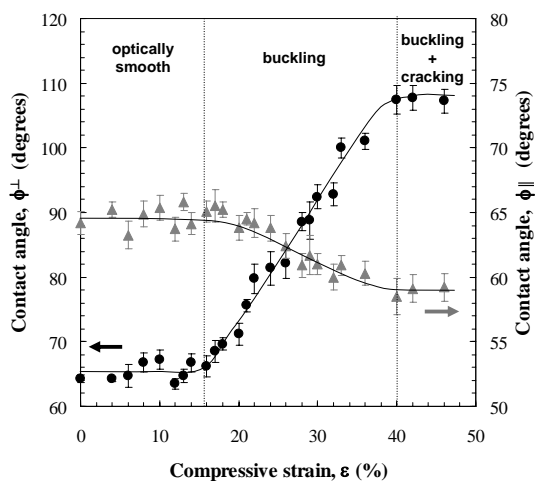


Figure 2. The water contact angles measured in two orthogonal directions (ϕ_{\perp} and ϕ_{\parallel}) as a function of the degree of compression of the PDMS substrate (ε). The lines are drawn to guide the eye. The error bars represent one standard deviation of the data, which is taken as the experimental uncertainty of the measurement.

The main result in Figure 2 indicates that a structural anisotropy leads to a directional variation of surface wettability. Thus, the shape of the three-phase contact line structure can be greatly affected. Microscopic observations of the contact-line movement revealed that the contact line in the perpendicular view exhibits periodic stick-slip behavior, whereas the contact line in the parallel view undergoes continuous motion⁵. These observations imply that the uniaxial structural constraint presents a high pinning barrier for droplet movement against the grooves as well as easy spreading of the droplet along the grooves. Increase in pinning barriers due to increase in the height of the sinusoidal grooves is believed to be responsible for the experimental observation that a hydrophilic surface can be changed into a hydrophobic one.

Conclusions

Surface roughness and the nature of the three-phase contact line structure both play an important role in the surface wettability⁷. An understanding of the contributions of each is necessary to accurately interpret the wetting behavior on a real rough surface. More detailed aspects will be discussed on the basis of the comparison of the experimental values with the theoretical ones obtained from both the Wenzel model³ and Johnson and Dettre model⁸.

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