Self-Cleaning Surfaces Prepared By Microstructuring System

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Abstract

The wettability of materials is a very important aspect of surface science governed by the chemical composition of the surface and its morphology. In this context, materials replicating nature’s superhydrophobic surfaces, such as lotus leaves, rose petals and butterfly wings, have widely attracted attention of physicists and material engineers [1–3]. Despite of considerable efforts during the last decade, superhydrophobic surfaces are still expensive and usually involved microfabrication processes, such as photolithography technique. In this study, we propose an original and simple method to create superhydrophobic surfaces by controlling elastic instabilities [4–8]. Indeed, we demonstrate that the self-organization of wrinkles on top of non-wettable polymer surfaces leads to superhydrophobic surfaces.

Keywords: Wetting; superhydrophobic surfaces; microstructures; wrinkles and elastomers.

Human skin is essentially composed of two primary layers: the epidermis, which provides waterproofing and serves as a barrier to infection; and the dermis, which cushions the body from stress and strain. The dermis, whose thickness is about a millimeter, consists of a set of proteins, like collagen fibers, which provide flexibility and elasticity to the skin (Young modulus $E$ is around 0.2–3 MPa). The epidermis is essentially composed of keratinocytes and is much thinner than the dermis with a larger elastic modulus due to its lamellar composition.

Systems used to modelize the human skin are Sylgard 184 and Sylgard 186 from Dow Corning Inc. They are essentially composed of a high viscosity base and a curing agent. Artificial skins are prepared by mixing a ratio 10:1 (base: curing agent), defoaming for 30 min and cross-linking at 75°C temperature for two hours. The Young moduli, measured with a Mettler Toledo DMA 861e, are estimated around 3 MPa and 1 MPa respectively for Sylgard 184 and 186. After cross-linking, the PDMS was stretched and oxidized using UV/ozone irradiation for an extended period of time (30–300 min) to increase the number of reticulation points (Fig. 1a). The UV/ozone treatment converts the surface of PDMS into a stiff hydrophilic skin, similar to a silicate (SiO$_x$) layer. After the UV/ozone treatment, the stretching is finally relaxed in order to compress the top layer modelling the epidermis. The compression ratio is defined by $\delta = (L_0 - L)/L_0$. Above some threshold for the compression ratio ($\delta > \delta_c$), we observe...
the formation of sinusoidal wrinkles on the top of the PDMS characterized by a cylindrical symmetry and perpendicular to the direction of the strain.

FIG. 1: (a) Schematics illustrating the steps for fabricating micro-wrinkling pattern on the PDMS substrate. (b), (c) SEM images of wrinkling pattern on a thin stiff PDMS film resting on a thick soft PDMS foundation and obtained with mechanical compression of 28% and 38% respectively.

In order to explain this formation of wrinkles, many theories and experiments have been made since ten years [5–10]. The observed wavelength is explained by the balance between the bending energy $U_b \propto E h^3 (A^2/\lambda^3)$ of the stiff upper membrane and the stretching energy $U_s \propto E_s A^2$ of the “semi-infinite” foundation. We thus obtain $\lambda \propto h (E/E_s)^{1/3}$, where $E$ and $E_s$ are respectively the Young modulus of the upper membrane and of the foundation.

FIG. 2: (A) Optical microscopy images of thin stiff PDMS film resting on a thick soft PDMS foundation, the PDMS foundation is cured with UV/ozone which modifies the elastic properties of its surface. (B) The system composed by the stiff film and the soft foundation is compressed...
uniaxially along the horizontal $x$-axis. The wavelength and amplitudes of the wrinkles are measured for successive values of the relative compression $\delta$. (C) Amplitudes, $A_1$ and $A_2$, and wavelength, $\lambda$, as a function of the compression ratio $\delta$.

The amplitude of the wrinkles is obtained from the inextensibility constraint imposed to the stiff upper membrane: the length of the membrane stay constant during the compression process. This geometric constraint leads to the relation $A \propto \sqrt{\delta}$.

For the small deformation ($\delta < 0.3\%$), we observed that there is a continuous increase of the amplitude $A$ of the wrinkles and a continuous decrease of the wavelength $\lambda$ ($\lambda \propto \lambda_0(1-\delta)$) (Fig. 2c).

For the large deformation ($\delta > 0.3$), the situation is different. The profile of the thin elastic membrane is no longer described by a simple sinusoidal. A more complex pattern emerges and characterized by two amplitudes $A_1$ and $A_2$ (see Fig. 2c). The evolution of the amplitudes of the pattern presents a bifurcation above some critical threshold: some wrinkles grow in amplitude while others decrease. The new pattern emerging is now characterized by a wavelength which is the double of the initial one. The amplitude of the $2\lambda$ mode increases with the compression ratio $\delta$, while the amplitude of $\lambda$ mode vanishes progressively.

Superhydrophobic surfaces are determined by both chemical composition and a dual roughness at both micrometer and nanometer scales, such superhydrophobic surfaces leads to two states: first state is Wenzel state [11,12] describing a liquid in contact with the whole structured solid surface and therefore displaying low contact angle and high hysteresis. This state assumed that the liquid completely wets the grooves of the rough surface. The Wenzel state describes homogenous wetting by the relation:

$$\cos \theta_w = r \cos \theta_e$$

where $\theta_w$ and $\theta_e$ are the Wenzel contact angle and the Young contact angle respectively, $r$ is the roughness factor defined as the ratio of the true area of the solid-liquid to its projected area.

Second state is Cassie-Baxter state describing a liquid which is resting partly on the features of a solid material and bridging air between these features [13, 14]. The relation between the apparent contact angle $\theta_c$ and the equilibrium angle $\theta_e$ described as:

$$\cos \theta_c = -1 + \Phi_s(1 + \cos \theta_e)$$

where $\Phi_s$ is the area fraction of the projected wet area.

FIG. 3: Lateral view images of water droplet on the various surfaces. (a) Smooth PDMS ($\theta_e = 110^\circ$), (b) sinusoidal wrinkled PDMS ($\delta = 33\%$) ($\theta_w = 135^\circ$) and (c) structured PDMS ($\delta = 64\%$) ($\theta_c \sim 180^\circ$).

Despite of considerable efforts done during the last decade, superhydrophobic surfaces are still expensive and usually involved micro-fabrication processes like the photolithography technique. We used the wrinkled topography of the surfaces, as shown before, to study the wettability of surfaces where the wavelength and the amplitude of wrinkles can be conveniently regulated by varying the time of treatment with UV/ozone, the module of elasticity and the applied strain level. By adjusting these parameters, it is possible to get surfaces with very large roughness.

After UV/ozone treatment, the PDMS surface becomes hydrophilic due to the presence of silicate like layer. For small compression, the wrinkles are sinusoidal and characterized by a wavelength $\lambda$. For larger compression ratio,
periodic folds directed downward in the direction of the elastomer and characterized by a wavelength $2\lambda$ emerge. To obtain superhydrophobic surface, those folds should be oriented upward. Consequently, the superhydrophobic surfaces are obtained by replica molding the surface with sylgard 184. The large roughness of the surface leads to a superhydrophobic surface. We tested the hydrophobicity of our surfaces by depositing a millimetric droplet of water on surfaces characterized by three different roughness. First, on the smooth, non-structured surface of PDMS the equilibrium contact angle ($\theta_e = 110^\circ$) (Fig. 3a). For small compression ($\delta = 33\%$), we obtain a wrinkled surface and the apparent contact angle increase to $135^\circ$ and the liquid penetrates into the surface roughness (Fig. 3b) corresponding with Wenzel state. Increasing the compression ratio ($\delta = 64\%$), the apparent contact angle strongly increases and reach values close to $180^\circ$, corresponding to the Cassie state (Fig. 3c).

**FIG. 4:** The contact angle versus the roughness coefficient. The points (■) are experimental results from the simulations, while the red line is the theoretical Wenzel line and the blue line is the theoretical Cassie line.

Figure 4 shows the evolution of $\cos(\theta)$ as a function of the roughness coefficient ($\delta+1$). The observed points (■) for low/high roughness correspond to both Wenzel and Cassie models. For low compression ($\delta < 0.4$), the profile of the surface is sinusoidal. We observe an evolution of $\cos(\theta)$ with a slope equal to 0.4 (advancing contact angle); these results are in agreement with the Wenzel model (red line) (Fig. 4). The theoretical line is obtained from equation (1), where the roughness factor $r = \delta + 1$ and the equilibrium contact angle $\theta_e = 110^\circ$. When the compression ratio increases ($0.4 > \delta > 0.6$), the profile of wrinkles evolves progressively from sinusoidal morphology to more complex pattern characterized by a doubled wavelength. The evolution of the apparent angle as a function of the roughness coefficient shows that we reach an intermediate state in between the Wenzel and the Cassie states. This correspond to a transition regime between these two extreme states. For higher compression ratio ($\delta > 0.6$), the structure of the surface is characterize by a succession of identical “pillars” with a wavelength $2\lambda$ and a larger amplitude (Fig. 4). The ratio between the amplitude and the wavelength becomes larger than $1/3$. In this case, the droplet of water stays above the surface of wrinkles and pockets of air are easily trapped below it. We thus obtain large contact angles close to $180^\circ$. These results correspond to the theoretical line (blue line) of the Cassie model (Fig 4). This theoretical curve is computed from Eq. 2, by assuming that the area fraction, $\Phi_S = \sigma/\lambda$. Where $\sigma$ is the width of the pillars and $\lambda$ is the length between two consecutive pillars.

To conclude, this study showed that the interfacial properties of a material depend not only on its chemical nature but also the morphology of its surface. It is known that the wettability of a surface can be easily modified by adjusting the roughness. The molecules of PDMS have a low surface energy; the value of the contact angle is $\theta_e \sim 110^\circ$. By micro-structuring of PDMS surface, we obtain contact angles significantly large then $110^\circ$. We can control the surface morphology by changing the exposure time to UV/Ozone radiation, the modulus of the PDMS and the
compression ratio. By increasing the compression ratio, we observe a transition from the Wenzel to the Cassie-Baxter regime. These micro-structures characterizing the PDMS surface are similar to those observed on lotus leaves. The superhydrophobic surfaces presented above should also be characterized a self-cleaning property.

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