Applied Surface Science 355 (2015) 127–132

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Facile manipulation of receding contact angles of a substrate by roughening and fluorination

Yueh-Feng Li[a], Cyuan-Jhang Wu[a], Yu-Jane Sheng[b,**], Heng-Kwong Tsao[a,c,*]

[a] Department of Chemical and Materials Engineering, National Central University, Jhongli 320, Taiwan, ROC
[b] Department of Chemical Engineering, National Taiwan University, Taipei 106, Taiwan, ROC
[c] Department of Physics, National Central University, Jhongli 320, Taiwan, ROC

ARTICLE INFO

Article history:
Received 30 May 2015
Received in revised form 7 July 2015
Accepted 13 July 2015
Available online 17 July 2015

Keywords:
Contact angle hysteresis
Surface roughness
Wettability
Air pocket stability

ABSTRACT

Contact angle hysteresis plays a paramount role in anti-smudge surfaces. In this study, surface roughness is systematically altered on some polymeric substrates such as polystyrene and poly(methyl methacrylate) by roughening and its effect on contact angle hysteresis is investigated via measuring advancing and receding contact angles of water. The wettability on these substrates is also modified by vapor-phase deposition of perfluorooctyltrichlorosilane, while the surface morphology is kept the same. As surface roughness is increased, the advancing contact angle grows but three types of the receding contact angle (θ_r) behavior have been identified: (i) monotonic reduction of θ_r, (ii) monotonic enhancement of θ_r, and (iii) presence of a minimum of θ_r. A plausible mechanism based on the stability of air pockets is proposed to explain our experimental findings. The manipulation of receding contact angles can be achieved based on our findings.

1. Introduction

The wetting behavior of a solid surface by liquid drops is ubiquitous in our daily lives as well as in industrial processes [1,2]. The wettability can be described by the static contact angle (CA) between the gas–liquid and solid–liquid interfaces. The CA on an ideal flat solid surface is related to the interfacial tensions of solid–gas (γ_{sg}), solid–liquid (γ_{sl}), and liquid–gas (γ_{lg}) by the Young's equation [3], $\cos\theta^* = \left(\gamma_{sg} - \gamma_{sl}\right)/\gamma_{lg}$. In general, the wetting behavior is determined by the two factors: the chemical composition and geometrical microstructures of the solid surfaces. The influences of the latter in terms of surface roughness have been explained by Wenzel [4] and later by Cassie and Baxter [5]. The Wenzel model considers a homogeneous surface and assumes that the liquid filled up the grooves on the rough surface. The apparent CA then follows $\cos\theta = r\cos\theta^*$, where r is defined as the ratio of the actual area of a rough surface to the projected area on the horizontal plane. Therefore, surface roughness can enhance hydrophilicity for CA below 90° and hydrophobicity for CA beyond 90°. When a chemically heterogeneous surface is dealt, the Wenzel model is not sufficient. The Cassie–Baxter model considers a surface comprising two types of homogeneous patches that have different solid–fluid interfacial tensions. The apparent CA is then given by $\cos\theta = f_1\cos\theta_1^* + f_2\cos\theta_2^*$, where f_i and θ_i^* represent the surface area fraction and CA associated with the patch i, respectively.

On a non-ideal solid surface, the CA is not a single unique value, but can be in the range of angles, $\theta_a \geq \theta \geq \theta_r$. Here θ_a and θ_r represent the advancing and receding CAs, respectively. Recently, the receding CA is found to play a paramount role in anti-fingerprint or anti-smudge surfaces and the liquid transfer mechanism between two surfaces [6]. In the process of inflation and deflation of a sessile drop on a real surface, a hysteresis loop can be evidently observed in the plot of CA versus drop volume. This phenomenon is so-called contact angle hysteresis (CAH), which is described by the difference between the advancing and receding CA ($\Delta\theta = \theta_a - \theta_r$) [7–9]. CAH generally appears through the pinning–depinning behavior of the contact line. The transition from pinning to depinning is corresponding to the receding CA. As a result, θ_r can be acquired by approaches involving contact line withdrawal. In the Wilhelmy method, the receding CA is determined, when a thin plate is submerged into a liquid bath and further pulled up. In the tilted plate method, θ_r can be estimated just before the drop starts to slide down along an inclined plate. In the dynamic sessile drop method, θ_r can be obtained by removing volume of the sessile drop until its solid–liquid interfacial area is reduced. The evaporation method is

---

** Corresponding author.
* Corresponding author at: Department of Chemical and Materials Engineering, National Central University, Jhongli 320, Taiwan, ROC.
E-mail addresses: yjsheng@ntu.edu.tw (Y.-J. Sheng), hktsao@cc.ncu.edu.tw (H.-K. Tsao).

http://dx.doi.org/10.1016/j.apsusc.2015.07.078
0169-4332/

a simple modification of the above method and θ_r is acquired as the evaporating drop begins to shrink [10–17]. In general, CAH on a real surface is attributed to two mechanisms: (i) adhesion hysteresis associated with molecular rearrangement on solid surfaces by wetting [7,18,19], (ii) localized defects associated with hydrophilic blemishes or surface roughness [20–23]. In the first mechanism, the restructuring of the solid surface in contact with liquid results in the reduction of solid–liquid interfacial tension, which is corresponding to the receding CA. In the second mechanism, CAH can originate from intrinsic defects which are more wettable than other parts of the surface. As a result, the strength of CAH depends on the area density, wettability, size, and shape of defects [21]. CAH can also be demonstrated by the variation of the apparent CA with the drop volume on a surface with periodical surface roughness, owing to the contact line pinning at sharp-edged grooves.

Although the effect of surface roughness on the apparent CA has been described by the Wenzel and Cassie–Baxter theories, our understanding of the influence of surface roughness on the CAH is still limited [24]. Since the CAH can originate from the aforementioned two mechanisms simultaneously, the effect of surface roughness on CAH is better investigated by keeping the influences of adhesion hysteresis and hydrophilic blemishes the same. In this work, surface roughness is systematically altered on a chosen substrate by roughening and its effect on the wetting property, including advancing and receding CAs of water, is explored. Several polymeric substrates are studied. In addition to the intrinsic wetting behavior, the wettability on these substrates is also modified by vapor-phase deposition of perfluorooctyltrichlorosilane. Three types of CAH behavior are identified and possible mechanisms are proposed.

2. Materials and experimental methods

2.1. Materials and surface roughening

Polymers with different wetting properties are used as substrate in this work, including polystyrene (PS), polycarbonate (PC), polymethylmethacrylate (PMMA), and polytetrafluoroethylene (PTFE). These smooth polymeric substrates are purchased from Kwo-Yi Corporation (Taiwan). The wetting properties of these substrates can be altered by changing their surface roughness. The surface roughness (R_a) on these substrates is generated via roughening the surface by sandpaper with various grit sizes (P100–P4000 in ISO/FEPA designation). This handsanding in carried out in a random direction. After sandpapering, the surface profile is measured by using contact stylus profilometry (Dektak 150 Surface Profiler) in which a stylus is simultaneously moved in contact with a sample vertically and across the sample surface laterally. The surface roughness is represented by the average value of R_a and typically, R_a is in the range from 10 nm to 2.5 μm. The wetting property of a roughened substrate can be further modified by vapor-phase deposition of organosilane. Note that all substrates are pre-cleaned by deionized water and ethanol before measuring their wetting properties.

2.2. Vapor-phase deposition of perfluorooctyltrichlorosilane

Generally, the hydrophobicity on a surface with hydroxyl groups can be elevated via hydrolysis and condensation of organosilane to form a self-assembly monolayer. In this work, the vapor deposition of perfluorooctyltrichlorosilane (PFOTS) is employed to change the wetting properties of roughened polymeric substrates. PFOTS is purchased from Alfa Aesar (USA). First, 90 μl PFOTS is dissolved in 20 ml hexane and the solution is heated to 60°C. Then polymeric substrates are exposed to PFOTS vapor in an inverted Petri dish (0.25 L) until the solution evaporates completely. The wetting property on the surface modified under the same preparation condition can be reproduced. Typically, this process is conducted once. However, to increase the deposition density, this process can be repeated for three times. Nonetheless, a saturation of PFOTS deposition will be achieved as the supply of PFOTS liquid is sufficient. On the contrary, to decrease the deposition density, 45 μl PFOTS dissolved in 10 ml hexane is used for evaporation. After vapor-phase deposition, the substrates are rinsed by hexane to eliminate the residue of PFOTS and then heated at 80°C for 1 day to remove the solvent. According to FTIR spectrum, PFOTS molecules are successfully deposited on the surface.

2.3. Wetting property measurement

Contact angles (CAs) of those polymeric substrates under ambient conditions are measured by a Krüss goniometer (droplet shape analysis system DSA10-MK2) at room temperature. The values of CAs associated with the sessile drops are decided by the tangent method provided by the droplet shape analysis system software. The CAs on both the left and right sides of the droplet are observed and the average value of CA is reported. The advancing CA (θ_a) associated with the outward movement of the contact line is measured after water is added to the sessile droplet by the needle syringe. On the contrary, the receding CA (θ_r) associated with the retreat of the contact line is determined after water is removed from the droplet. Note that the process of inflation or deflation is kept as slow as possible to avoid the disturbance of the contact line by fluid flow [7–9,25]. Typically, two dynamic cycles are performed in the inflation/deflation process. The CAH of the substrate is realized by the difference between the advancing and receding CAs.

3. Results and discussion

In this work, various polymeric substrates are considered, including PS, PC, PMMA, and PTFE. Moreover, to modify the wetting properties of some substrates, PFOTS deposition is also employed. The influence of surface roughness on the wetting behavior of these substrates can be manifested by the advancing and receding CAs (θ_a and θ_r) through the inflation/deflation methods. Three types of the wettability behavior can be identified: (i) reduction of the receding CA by increasing surface roughness, (ii) enhancement of the receding CA by increasing surface roughness, and (iii) presence of a minimum of the receding CA.

3.1. Reduction of the receding CA by increasing surface roughness

The surface roughness of a substrate can be increased via roughening the surface by sandpaper with various grit sizes. It can be quantified by average surface roughness (R_a). For hydrophobic surfaces, the advancing CA grows generally with increasing surface roughness. On the basis of the Cassie–Baxter model, it is attributed to the increment of the area fraction of air pockets. That is, the increase of surface roughness provides more grooves where water is unable to wet. This scenario is also observed for surfaces with the advancing CA as low as about 70° [26,27]. Consider three kinds of polymeric substrates and their advancing CAs on smooth surfaces (before roughening) are $\theta_a \approx 71^\circ$, $\theta_a \approx 72^\circ$, and $\theta_a \approx 84^\circ$ for PS, PMMA, and PC, respectively. As shown in Fig. 1, the advancing CAs are increased more than 30° when R_a is changed from 13 nm to 1.1 μm. Note that the superhydrophobic surface cannot be acquired by sandpaper roughening.

On the other hand, the reduction of receding CAs can be clearly seen as surface roughness is increased. Since all the surfaces are quite smooth before roughening, their receding CAs can be regarded as intrinsic ones and are $\theta_r \approx 61^\circ$, $\theta_r \approx 58^\circ$, and $\theta_r \approx 74^\circ$