Experimental studies of contact angle hysteresis phenomena on polymer surfaces — Toward the understanding and control of wettability for different applications

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ABSTRACT

Contact angle hysteresis phenomena on polymer surfaces have been studied by contact angle measurements using sessile liquid droplets and captive air bubbles in conjunction with a drop shape method known as Axisymmetric Drop Shape Analysis — Profile (ADSA-P). In addition, commercially available sessile drop goniometer techniques were used. The polymer surfaces were characterized with respect to their surface structure (morphology, roughness, swelling) and surface chemistry (elemental surface composition, acid–base characteristics) by scanning electron microscopy (SEM), scanning force microscopy (SFM), ellipsometry, X-ray photoelectron spectroscopy (XPS) and streaming potential measurements.

Heterogeneous polymer surfaces with controlled roughness and chemical composition were prepared by different routes using plasma etching and subsequent dip coating or grafting of polymer brushes, anodic oxidation of aluminium substrates coated with thin polymer films, deposition techniques to create regular patterned and rough fractal surfaces from core–shell particles, and block copolymers. To reveal the effects of swelling and reorientation at the solid/liquid interface contact angle hysteresis phenomena on polyimide surfaces, cellulose membranes, and thermo-responsive hydrogels have been studied. The effect of different solutes in the liquid (electrolytes, surfactants) and their impact on contact angle hysteresis were characterized for solid polymers without and with ionizable functional surface groups in aqueous electrolyte solutions of different ion concentrations and pH and for photoresist surfaces in cationic aqueous surfactant solutions.

The work is an attempt toward the understanding of contact angle hysteresis phenomena on polymer surfaces aimed at the control of wettability for different applications.

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1. Introduction

Wetting involves the interaction of a liquid with a solid, including the formation of a contact angle at the solid/liquid/fluid interface, the spreading of a liquid over a surface, or the penetration of a liquid into a porous solid medium. Wetting and non-wetting phenomena play important roles in nature and are of considerable technical interest. Numerous industrial applications, such as coating and printing processes, textile finishing, and microfluidics, include the wetting of solids by liquids. A frequently used parameter to quantify wetting phenomena is the contact angle between a liquid and a solid surface. Fig. 1 shows the different wetting situations of a liquid droplet in contact with a solid surface. From the point of view of thermodynamic equilibrium two wetting regimes occur, namely complete or partial wetting. In the case of complete wetting, the equilibrium contact angle between a liquid and a flat solid surface is zero ($\theta_e = 0°$, see Fig. 1c) and the liquid forms a thin film on the solid surface. Partial wetting occurs if the equilibrium contact angle is finite ($\theta_e > 0°$, see Fig. 1a and b). Partial wetting, with contact angles greater than 90° (Fig. 1a), is often called a "non-wetting" situation when the liquid tends to ball-up and run-off the surface easily. Partial wetting situations present three interfaces and three interfacial tensions are involved: γ_{sv}, γ_{sl} and γ_{lv}, respectively, the solid/vapor, solid/liquid and liquid/vapor interfacial tensions. The mechanical equilibrium at the triple-phase contact line determines the value of the contact angle θ_e according to Young's relationship (Eq. (1), Fig. 2):

$$\cos\theta_e = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}. \tag{1}$$

This equation represents the connection of the microscopic contact angle to the interfacial tensions acting at the contact line and arising from the molecular and microscopic structure and chemistry of the interfaces [1]. According to Young's equation, the contact angle θ_e is a unique function of the interfacial tensions γ_{sv}, γ_{sl} and γ_{lv}. A single contact angle is, therefore, predicted for each material system in the case of homogeneous and time invariant surfaces. However, real surfaces can be rough or heterogeneous to some extent, anisotropic, non-inert and deformable in contact with liquids. In most practical situations, a given liquid usually exhibits a range of contact angles on a given solid surface. Each contact angle gives rise to a mechanically stable liquid meniscus. When the liquid is advanced over a previously un-wetted surface (e.g. when the solid/liquid contact area increases) (see Fig. 3)

a maximum contact angle at the three-phase contact line is termed an advancing angle (θ_a). A minimum contact angle is measured at the contact line when the liquid is retracted over a previously wetted surface (e.g. when the contact area shrinks). In this case, it is termed a receding angle (θ_r). Contact angle hysteresis is defined as the difference between the (maximum) advancing and (minimum) receding angle:

$$\Delta\theta_{hyst} = \theta_a - \theta_r. \tag{2}$$

It is of fundamental but also of practical interest to obtain a better understanding of contact angle hysteresis phenomena. Both from theoretical and experimental viewpoints, it is generally accepted that the hysteresis of contact angles can be caused by deviations of the solid surface from ideal behavior as mentioned above [2]. Within this context, chemical heterogeneity and surface roughness are accepted origins of contact angle hysteresis. It is of great interest to define the level of roughness and/or heterogeneity that will influence contact angle hysteresis. Fortunately, progress made in the past with respect to the preparation and characterization of polymer surfaces has facilitated the fabrication of surfaces with well-defined roughness (and heterogeneity). We used polymer surfaces that have been characterized with respect to the surface structure (morphology, roughness, swelling) and surface chemistry (elemental surface composition, acid–base characteristics) by scanning electron microscopy (SEM), scanning force microscopy (SFM), ellipsometry, X-ray photoelectron spectroscopy (XPS), and streaming potential measurements. In the first part of this paper, we will focus on the design of polymer surfaces with controlled hysteresis which we have studied over the past decade in our research group. The following approaches were applied to prepare these polymer surfaces:

— fluoropolymer films on smooth and etched silicon wafers [3–6]
— preparation of rough polymer surfaces by plasma etching and subsequent dip-coating of polymer films or grafting of polymer brushes [3,7]
— preparation of rough, anodically oxidized aluminium substrates coated with thin polymer films [8,9]
— regularly patterned and rough fractal surfaces from core–shell particles prepared by deposition techniques [10–12].

A second route of our studies was inspired by the concept that the surface state of a material adjusts to the conditions of the surrounding
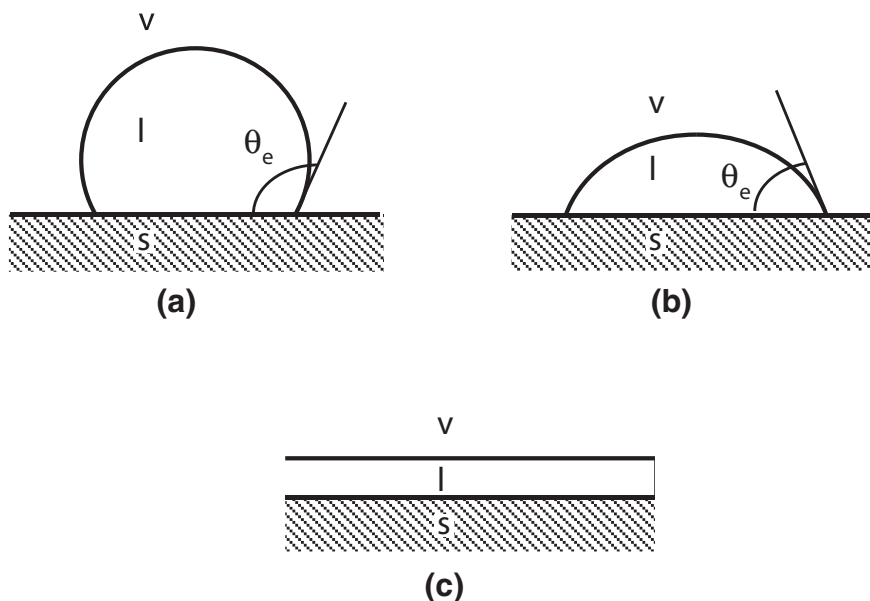

Fig. 1. Different wetting situations of a small droplet in contact with a solid surface: (a) and (b) correspond to partial wetting ($\theta_e > 0$) and (c) corresponds to complete wetting ($\theta_e = 0$).