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A modified captive bubble method for determining advancing and receding contact angles

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ABSTRACT

In this work, a modification to the captive bubble method was proposed to test the advancing and receding contact angle. This modification is done by adding a pressure chamber with a pressure control system to the original experimental system equipped with an optical angle mater equipped with a high speed CCD camera, a temperature control system and a computer. A series of samples with highly hydrophilic, hydrophilic, hydrophobic and superhydrophobic surfaces were prepared. The advancing and receding contact angles of these samples with highly hydrophilic, hydrophilic, and hydrophobic surfaces through the new methods was comparable to the result tested by the traditional sessile drop method. It is proved that this method overcomes the limitation of the traditional captive bubble method and the modified captive bubble method allows a smaller error from the test. However, due to the nature of the captive bubble technique, this method is also only suitable for testing the surface with advancing or receding contact angle below 130°.

1. Introduction

Wettability of a solid surface plays a crucial role in many wide-spread applications, such as artificial organs [1], contact lenses [2,3], biomaterials [4], biofilm growth [5], superhydrophobic surfaces [6,7], non-sticky [8] and self-cleaning coatings [9]. The wetting phenomena are usually described by its contact angle θ and contact angle hysteresis. The latter is normally defined as the difference between advancing contact angle θ_A and receding contact angle θ_R [10]. Here, θ_A and θ_R are considered as the maximum and minimum experimental contact angles of a surface and they also represent the contact angles of an imminently three-phase boundary moving in wetting or de-wetting process, respectively.

At present, there are many methods for determining contact angle [10,11]. They are divided into three categories [12]. First, force measurement, based on the force between the specimen and the liquid, such as Du Nouy Ring method [13] and Wilhelmy Plate method [14]. Second, pressure measurement, using Young–Laplace equation to calculate the contact angle based on the pressure difference between both sides of the interface, for example, the capillary rise method [15]. Third, goniometry method, based on the liquid or gas shape on the testing surface captured by a camera at the equilibrium state, including tilting-plate method and sessile drop method [16,17]. The third category is more intuitive and convenient by directly reading the contact angle from the image of a water droplet or air bubble captured by a camera. This approach is widely adopted and used most frequently in the literature [18]. Captive bubble method belongs to the sessile drop method. It is widely used in the contact angle testing of hydrophilic materials, such as contact lenses [2,3] and biomaterials [4], while other methods are rarely applied in this field. However, the captive bubble method has a needle involvement in the measurement for adding and removing gas, the wetting between the liquid and the needle outer wall will impact the results [12].

In this article, we proposed a modification to the captive bubble method in order to eliminate the interference of the needle to the measurement. Therefore, in this modified captive bubble testing device, the core testing components were equipped inside a pressure chamber. After an air bubble was introduced onto the surface of the specimen, the needle was removed and the chamber was pressurized or depressurized in order to continuously change the size of the air bubble for detecting advancing or receding contact angle. In order to evaluate this new method, samples with four representative surface wettabilities were prepared. The advancing and receding contact angle of these samples obtained from this modified captive bubble method were compared with the data determined by the traditional captive bubble method. As a result, the modified method successfully overcame the limitations of the traditional methods by eliminating the needle contact, so that the interference of the needle to the measurement used for introducing air into or removing air from the air bubble in the

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traditional method was removed. Therefore, this method gives a more reliable and highly repeatable data, comparable to the result from the well-established optical contact angle measurement using a water droplet. And it is suitable for determining the advancing or receding contact angle which was smaller than 130°.

2. Materials and methods

2.1. Materials

Aluminum (99.0%) plates with a thickness of 1.5 mm were purchased from Southwest Aluminum (China). Perfluoroalkyltriethoxysilanes with $[CF_3(CF_2)_6CH_2CH_2Si(OC_2H_5)_3$, PFO] and 3-aminopropyltrimethoxysilane (APTS) were obtained from Fluorochem. The other chemicals including ethanol, acetone, toluene, xylene, hydrofluoric acid (HF, 40 wt.%) and hydrochloric acid (HCl, 37 wt.%) were obtained from Nanjing Chemical Reagent Co. Ltd. (China) and used as received without further purification. Deionized water (electrical resistivity was 18.2 MΩ cm and the surface tension was 7.2 × 10–2 N/m at 25 °C)

2.2. Sample preparation

Specimens with four different surface wettabilities including highly hydrophilic (A040), hydrophilic (A060), hydrophobic (A110) and superhydrophobic (A160) were prepared from commercial aluminum plates with size of 25 × 25 mm^2, where the samples were named by A followed by a number (xxx), which represents aluminum plates with a surface contact angle of xxx (see discussion for details). The preparation of these samples was described below:

2.2.1. Hydrophilic specimens (A60)

The hydrophilic specimens (A60) were cleaned aluminum plates. They are prepared by a thorough cleaning of commercial aluminum plates by washing ultrasonically with toluene, acetone and deionized water subsequently and dried at room temperature for 24 h.

2.2.2. Hydrophobic specimens (A110)

The hydrophobic specimens (A110) was prepared from the cleaned aluminum plates by a surface modification using a PFO solution, which was prepared by dissolving PFO (0.5%) in a mixture of ethanol (88 wt.%), deionized water (10 wt.%) and HCl (0.1 M, 1.5 wt.%), The cleaned aluminum plate was dipped into the PFO solution and withdrawing to let the specimen dry. This process was repeated for 4 times and then heated in an oven at 100 °C for 12 h to completely cure the coated PFO layer to produce A110.

2.2.3. Superhydrophobic specimens (A160)

The superhydrophobic surface and highly hydrophilic surfaces were prepared on surface roughened aluminum plates. Therefore the cleaned aluminum plates was etched by a mixed acid solution to roughen the surface following the method reported in our previous work [7]. Briefly, the mixed acid solution was prepared by adding 2.5 mL of HF (40 wt.%) and 40 mL of HCl (37 wt.%) in 12.5 mL of deionized water with stir. The cleaned aluminum plates were then immersed into this mixed acid solution for 40 s, followed by thorough cleaning with deionized water using an ultrasonic bath to remove residual acids and drying in an oven at 100 °C for 2 h. Then the etched aluminum plate surface was modified with the PFO solution by following the same procedure as for the preparation of A110 described above.

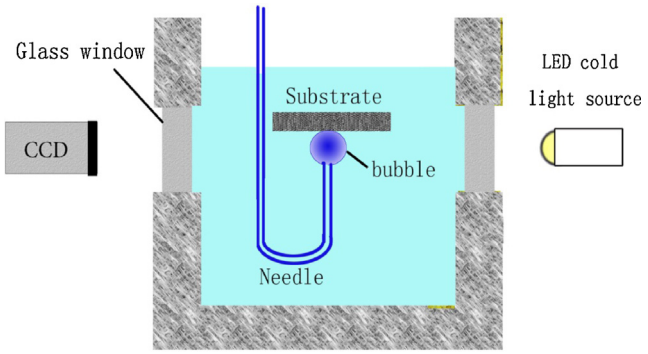

Fig. 1. The schematic illustration of the setup of the traditional captive bubble method.

2.2.4. Highly hydrophilic specimens (A40)

These specimens were prepared by modifying the etched aluminum plates following the same procedure as for the preparation of superhydrophobic surface by APTS solution instead of the PFO solution. The APTS solution was prepared by dissolving APTS (0.5%) in a mixture of ethanol (88 wt.%), deionized water (10 wt.%) and HCl (0.1 M, 1.5 wt.%). The surface modification was done by dipping the etched aluminum plates and withdrawing to let the specimens dry. This process was repeated for 4 times and then heated in an oven at 70 °C for 12 h to let the coated APTS layer to be completely cured to produce A40. All prepared specimens were stored in a desiccator until they were used or tested for avoiding dust contamination.

2.3. Traditional captive bubble method

The setup of a traditional captive bubble method comprises of an optical angle meter (CAM 200, KSV Instrument Ltd., Finland), a thermostatic bath with a glass window and an air injecting system with a J-shaped needle to introduce air bubble as schematically illustrated in Fig. 1. After the specimen was placed in the liquid in the thermostatic bath, an air bubble (5 μL) was extruded from the J-shaped needle below the specimen to contact the sample surface. As soon as the air bubble getting equilibrated with the three-phase contact line stabilized, the bubble profile was recorded by the camera for static contact angle calculation. Then air was introduced into the air bubble again through the J-shaped needle at a rate of 0.1 μL/s until the three phase contact line start to move, with the bubble profile recorded by the CCD camera during this process. The profile right before the three phase contact line start to move was used to calculate the receding contact angles. On the other hand, when the air in the air bubble was pumped out in the same way at a rate of 0.1 μL/s, the profile right before the three phase contact line start to move was used to calculate the advancing contact angles.

2.4. Modified captive bubble method

This test apparatus is a modified version of captive bubble technique with the whole layout illustrated in Fig. 2. The key part is the optical angle meter (CAM 200, KSV Instrument Ltd., Finland) with a high speed CCD camera (256 × 256 pixels at 10 frames per second) attached to a pressure chamber (Fig. 3), in which the temperature is controlled by the control system. The pressure chamber is made from 304 stainless steel, and linked to a vacuum/pressure control system through the pressure port, by which the pressure inside the chamber can be accurately adjusted in a range of −50 to +50 kPa relative to atmosphere pressure. The whole system including the temperature control system, vacuum/pressure control system and