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Applicability of Washburn capillary rise for determining contact angles of powders/porous materials

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ABSTRACT

The Washburn capillary rise (WCR) technique has been widely utilized for determining contact angles of powders or porous materials; however, there are concerns regarding powder size and powder packing, especially for materials that exhibit large contact angle hysteresis. In this paper, some of these concerns were addressed. Due to the large water contact angle hysteresis on flat nylon 6/6 films, these films were ground into powders of different sizes and then used as model packing materials. The powders were packed in glass tubes to result in various packing structures that affected the penetration (i.e. advancing) rate of the test liquids. While all advancing contact angles obtained from WCR were found to be overestimated, more reasonable values were resulted when relatively large powders (e.g. 500–2000 μm) were used to pack the tubes. With larger powders, the packing contained bigger voids and consequently lead to slower penetration rates of the liquids, hence a relatively smaller advancing contact angle. The smaller advancing contact angle obtained from the slower advancing rate was also observed by using the sessile drop method. To verify the applicability of using large powders (500–2000 μm) for contact angle determination by using WCR, the advancing water contact angles of a bacterial cellulose/alginate composite sponge (BCA) with and without UV/ozone treatment were measured. The results showed that by using relatively large powders, WCR could be applied to obtain a reasonable advancing contact angle and assess the wettability change of complex porous materials.

1. Introduction

Surface wettability, one of the most crucial surface properties of materials, is a key parameter for understanding the interactions of materials with their surrounding and for their applications. As a result, proper characterization techniques to obtain the accurate surface wettability of these materials are highly desired.

Surface wettability is generally characterized by contact angle of a liquid on a solid surface. For a flat solid surface, many common techniques, e.g. sessile drop and Wilhelmy plate [1], can be applied for measuring contact angles. For powders/porous materials, capillary rise, i.e. flowing of a liquid up a capillary by attractive forces between the liquid and the solid surface, is normally used to characterize their wettability. In particular, the Washburn capillary rise (WCR) method, which is derived from the rate of capillary rise of liquid penetrating in a packed cylindrical tube, has been widely employed. To deduce the contact angle values, either the rate or the height of the capillary rise is measured. The equation is based on Poiseuille's law as expressed below:

$$dV = \frac{r^4 \pi \Delta P}{8\eta h} dt \tag{1}$$

where V is the volume of the liquid, r is the radius of the cylindrical tube, ΔP is the pressure drop, η is the viscosity of the liquid, h is the height of the liquid risen, and t is the time that the liquid flows to a certain height.

In this case, pressure drop (ΔP) is a pressure difference between the capillary pressure (P_c) and the hydrostatic pressure (P_h), i.e. $\Delta P = P_c - P_h$, which can be further expressed as:

$$\Delta P = \left(\frac{2\gamma \cos\theta}{r}\right) - \rho g h \tag{2}$$

By comparison, the hydrostatic pressure (ρgh) is much smaller than the capillary pressure $\left(\frac{2\gamma\cos\theta}{r}\right)$, therefore, the liquid rising upward through the tube is primary contributed by the capillary pressure. For Eq. (1), the volume of liquid inside the cylindrical tube can be written as $V = \pi r^2 h$, substitute this and Eq. (2) into Eq. (1) and integrate it with an initial condition (at $t = 0$, $h = 0$) and a particular time (i.e. at $t = t$, $h = h$) leads to

$$h^2 = \frac{r\gamma \cos\theta}{2\eta} t \tag{3}$$

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Eq. (3) is Washburn's equation that presents the relation between a squared height of the penetrating liquid and the penetrating time. In the case of powders or porous materials packed in a tube, voids between materials could be described as many bundles of capillary tubes [2]. Therefore, WCR can be applied to obtain contact angles for powders or porous materials and can also be expressed in term of a squared mass of the penetrating liquid ($m = \rho A h \varepsilon$) and the penetrating time as:

$$m^2 = \frac{C\rho^2\gamma\cos\theta}{\eta}t \text{ with } C = \frac{r_{eff}A^2\varepsilon^2}{2} \quad (4)$$

where r_{eff} is the effective radius or the equivalent radius of voids in the packed powders or porous materials, A is the cross-section of the tube, and ε is the porosity of the packing in the tube. To determine contact angles of liquids on powders or porous materials using WCR, four conditions have to be satisfied for the process (i.e. Washburn's equation is derived based on these four assumptions): (1) steady state laminar flow, (2) no external pressure, (3) negligible gravitational force and (4) zero velocity of the liquid at the solid/liquid interface (no slip).

Washburn's equation based on the principle of capillary rise has been widely applied to determine the contact angle or surface free energy of powder materials [3,4]. However, a main concern for contact angles characterized by using WCR is how reasonable the determined values are. This concern is based on several facts regarding to applying WCR. First, the packing of materials is expected to affect liquid penetration, hence contact angle values, although some researchers have reported that packing with particles of different sizes and pore sizes had no effect on contact angles [5–7]. Second, some unsuccessful contact angle characterizations of porous materials by applying WCR have been documented [8]. One limitation of WCR is to find a suitable complete wetting liquid to be used for determining the geometric factor of the packing, i.e. the C value in Eq. (4).

Due to the concerns of applying WCR for contact angle characterization of powders and porous materials, some potential issues of contact angle determination for materials that exhibit large contact angle hysteresis, which is the difference between the advancing contact angle and the receding contact angle, by using WCR are being addressed in this paper. The contact angles characterized by WCR and by the sessile drop method for four common polymers: polystyrene (PS), polymethymethacrate (PMMA), nylon 6 and nylon 6/6, were compared. Based on the results, nylon 6/6, which exhibited the largest water contact angle hysteresis based on sessile drops, was chosen as the model material to grind into powders of different sizes. The effects of powder size and packing on the water and ethanol advancing contact angles of nylon 6/6 powders determined using WCR were examined. It was found that larger powders whose packing contained larger voids slowed down the liquid penetration rate, leading to a smaller and more reasonable advancing contact angles for nylon 6/6. On the other hand, the penetration rate of the packed powders of PS, whose flat films showed a small water contact angle hysteresis, had little effect on the advancing contact angle obtained using WCR. Both cases indicated that larger powders were likely to result in smaller and more reasonable advancing contact angles, and the applicability of such approach was also assessed by using a bacterial cellulose/alginate sponge as a test material.

2. Materials and methods

2.1. Materials and equipment

Polystyrene (PS, *Mw* = 50,000 g/mol, PDI = 1.06) was purchased from Polyscience, Inc. (Warrington, PA), and polymethyl methacrylate (PMMA, *Mw* = 120,000 g/mol, PDI = 1.8), nylon 6 and nylon 6/6 were purchased from Sigma–Aldrich Co. (Saint Louis, MO). Solvents used included ACS grade toluene (99.5%, Fisher Scientific International Inc., Fair Lawn, NJ), acetone (99.5%, Sigma–Aldrich Co.), formic acid (88%, J.T. Baker, Phillipsburg, NJ), octane (99%, Acros Organics, Morris Plains, NJ), decane (99%, Sigma–Aldrich Co.), hexadecane (99%, Acros Organics), ethanol (99.98%, Pharmco-Aaper and commercial alcohols, Brookfield, CT), and de-ionized (DI) water purified in house (with a conductivity of 77.5 μS/cm). Bacterial cellulose was provided by the Institute of Research and Development of Food Products, Kasertsart University, Thailand. Sodium alginate (Na-alginate) was supplied by Carlo Erba, Italy. Other materials included heavy duty aluminum foils (Reynolds, Richmond, VA), sterilize cotton balls (CVS Pharmacy, Inc., Woonsocket, RI), and glass tubes (0.5 cm inside diameter and 9 cm in length, from Friedrich & Dimmock Inc.).

The equipment used include an analytical balance (E1RR80, Ohaus Explorer Pro., Parsippany, NJ, with an accuracy of 0.1 mg), a spin coater (p-6000, Specialty Coating Systems Inc., Indianapolis, IN), an ultrasonic bath (1510 MT, Branson Ultrasonic Corp., Danbury, CT), a grinder (IDS77, MR. COFFEE, Boca Raton, FL), a set of Metric Test Sieves (W.S. Tyler, Mentor, OH), an UV-ozone cleaner (Model 42, Jelight Company Inc., CA), a digital camera (DSC-W100, Sony Corp., Japan), a CCD camera (Sony), Diamond VC500 one-touch video capture software 176 (Diamond Multimedia, Chatsworth, CA) and the ImageJ software (National Institutes of Health, Bethesda, MD).

2.2. Preparation of polymer sheets

A 20% w/w of PS and nylon 6 solutions were prepared in toluene and formic acid, respectively. For PMMA and nylon 6/6, 10% w/w solutions were prepared in acetone and formic acid, respectively. To fabricate the polymer sheets to be ground into powders, these polymer solutions were poured, separately, in home-made cleaned aluminum foil trays (~8 in. × 9 in.) and then were placed in the fume hood until them were dry.

2.3. Preparation of bacterial cellulose/alginate composite sponge

To fabricate BCA, 3% w/w of Na-alginate was prepared by dissolving Na-alginate in DI water, and then the homogenized bacterial cellulose was mixed with the Na-alginate solution by a weight ratio of 6:4. After that, 160 g of the mixer was poured in a plastic tray (~7 in. x 12 in) and then cross-linked with a 0.12 M $CaCl_2$ solution in water for 24 h to form a hydrogel. The hydrogel was rinsed by a copious amount of DI water 3 times and then was immersed in a DI water bath for 24 h to remove the excess Ca^{2+}. The hydrogel was frozen in a freezer at −20 °C. Afterward, the frozen hydrogel was immediately transferred to lyophilize under vacuum pressure (<100 mTorr) at the condenser temperature of −40 °C for 48 h. BCA was then kept in a desiccator prior to its use.

Oxidation of BCA was carried out by using the UV-ozone cleaner. BCA sheets were placed in the UV-ozone chamber at a distance ~2 mm away from the UV light source and were oxidized for 15 min.

2.4. Wettability characterization by using WCR

To characterize the wettability of the polymers using WCR, dried polymer sheets were ground and then sieved into three different size ranges: 0–250, 250–500, and 500–2000 μm. To obtain the fourth size, 0–2000 μm, powders from each sieved size were combined.

The glass tube used to pack the polymeric powders was cleaned sequentially with acetone, ethanol and deionized water by