Chapter 18
Contact Angle Measurement for Solid Surface

Masahiko Abe

Abstract Contact angle measurement is used for the evaluation of the wettability of liquids to solid surfaces as a combination. Liquids with larger contact angles correspond to less wetting, while smaller means more wetting to solids. For example, the contact angle of water and clean glass surface is close to zero, but in contrast, it reaches up to about 110° for water- and paraffin-treated glass surface. This chapter deals with the measurement of contact angles to evaluate the wettability of water on solid surfaces.

Keywords Contact angle · Spreading wetting · Immersional wetting · Adhesional wetting · Critical surface Tension

18.1 Introduction

When water is dropped on a clean glass surface, it spreads rapidly as the glass gets wet, while when dropped on a paraffin-treated glass, the surface water makes droplets that stay at the point and the treated glass will not get wet (Fig. 18.1). The tangent line at P between the solid surface and the liquid surface gives an angle θ, defined as the contact angle. The contact angle for water and clean glass surface is close to zero but reaches about 110° for water- and paraffin-treated glass surface. As such, the contact angle represents the wettability of liquids and solids as a combination, where larger indicates less wetting and smaller indicates more wetting. There are two contact angles, the advancing contact angle θ_a and the receding contact angle θ_r as shown in Fig. 18.2. In general, θ_a is larger than θ_r, and this discrepancy is called hysteresis, which is caused by surface characteristics such as roughness, friction, and absorption.

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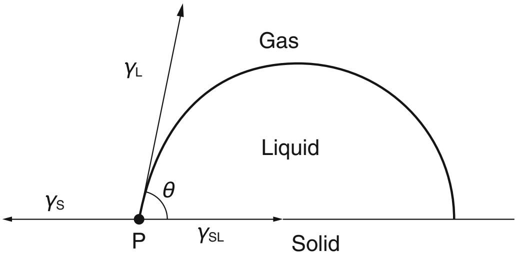

Fig. 18.1 Wettability of a liquid droplet on a flat solid surface. The contact angle (θ) is determined by the balance in horizontal direction of three surface and interfacial tensions of γL, γS, and γSL

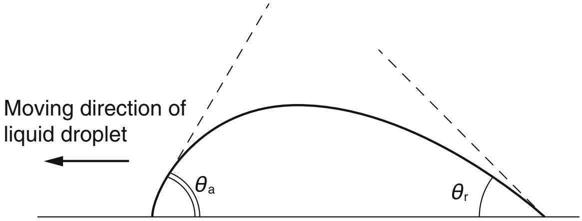

Fig. 18.2 Advancing contact angle and receding contact angle

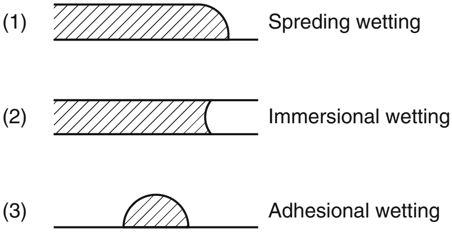

Fig. 18.3 Wetting types

18.2 Wetting and Immersion

When a small amount of liquid is dropped on a surface, it will either spread or stay as a droplet with a certain contact angle. There is an interface between the solid and air which is generally called the surface of solid. In order for the liquid to contact the surface, the liquid has to push air away from the surface to make a new interface between the liquid and solid. Wetting is a phenomenon that creates this liquid/solid interface. There are three types of wetting, namely, spreading wetting, immersional wetting, and adhesional wetting as shown in Fig. 18.3.

18.2.1 Spreading Wetting

Spreading wetting is a type of wetting where water or alcohol spreads over a glass surface, and its work of spreading (W_s) is expressed by Eq. (18.1):

$$W_s = \gamma_s - \gamma_l - \gamma_{\mathrm{sl}} \tag{18.1}$$

where γ_s, γ_l, and γ_{sl} are the surface tension of solid and liquid and interfacial tension between the surface and liquid, respectively. Larger W_s corresponds to higher wettability.

18.2.2 Immersional Wetting

Immersional wetting is a type of wetting where water penetrates into filter paper, and its work of spreading is expressed by Eq. (18.2):

$$\mathrm{Wi} = \gamma_s - \gamma_{\mathrm{sl}} \tag{18.2}$$

18.2.3 Adhesional Wetting

Adhesional wetting is a type of wetting where mercury is dropped on a glass surface, and its work of spreading is expressed by Eq. (18.3):

$$W_s = \gamma_s + \gamma_l - \gamma_{\mathrm{sl}}\theta \tag{18.3}$$

where the contact angle is determined by the balance in the horizontal direction of the three surface and interfacial tensions, γ_s, γ_l, and γ_{sl}, as shown in Fig. 18.1, which is expressed by Young's equation (Eq. 18.4) as follows:

$$\gamma_s = \gamma_{\mathrm{sl}} + \gamma_{\mathrm{l}} \cos\theta \tag{18.4}$$

By applying Young's equation (Eq. 18.4), each work of spreading can be expressed as follows:

$$\mathrm{Ws} = \gamma_l(\cos\theta - 1) \tag{18.5}$$

$$\mathrm{W}_i = \gamma_l \cos\theta \tag{18.6}$$

$$W_a = \gamma_l(\cos\theta + 1) \tag{18.7}$$

The wetting can be determined as:

When:

$\theta = 0°$, $W_s \geqq 0$ spreading wetting occurs.
$\theta \leqq 90°$, $\mathrm{Wi} \geqq 0$ immersional wetting occurs.
$\theta \leqq 180°$, $\mathrm{W}_a = 0$ adhesional wetting occurs.

In summary, solid surfaces can be categorized as hydrophilic surfaces and hydrophobic surfaces. To make a surface non-wettable to both water and oil, the solid surface tension (γ_s) must be smaller than both γ_{water} and γ_{oil}.

18.3 Measurement of the Contact Angle

The most important key for accurately measuring contact angles is to prepare a clean surface by extensive cleansing. There are two typical ways for the measurement.

18.3.1 θ/2 Method

This method is applicable when a liquid is dropped on surfaces and spontaneously shapes as part of a sphere, depending on its surface tension (γ_l) as shown in Fig. 18.4. This picture can be taken using a CCD camera, and the contact angle θ can be determined by the following equation (Eq. 18.8):

$$\tan\theta_1 = \frac{h}{r} \rightarrow \theta = \arctan\frac{h}{r} \tag{18.8}$$

where r is the diameter of the droplet and h is the height of drop. If the drop is small enough in the range of a few μl, the effect of gravity can be ignored, and the droplet shape can be treated as part of a sphere.

18.3.2 Tangent Line Method

As shown in Fig. 18.5, points L_1, L_2, and L_3 on the drop arc are each treated as part of a circle. The center of the circle (M) can be determined, and then the tangent line

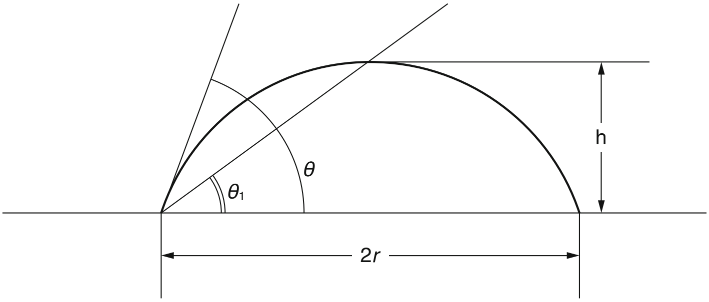

Fig. 18.4 Illustration of *θ*/2 method

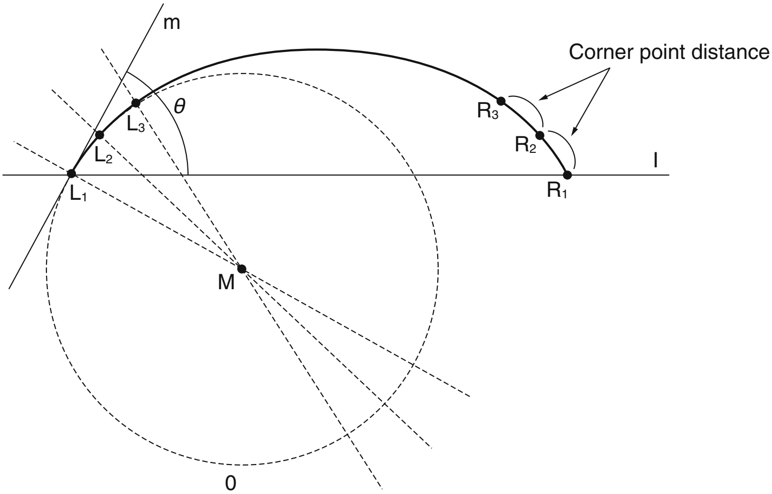

Fig. 18.5 Illustration of tangent line method

(M) at L_1 can be drawn as shown in Fig. 18.5. The contact angle θ at the left side of the droplet can be obtained between the tangent line m and the surface line l. The right-side contact angle can be obtained as well in the same manner from the points R_1, R_2, and R_3.

The contact angle θ by the θ/2method is the average of both sides of the droplet as θ is calculated by width and height of the droplet. As such, the tangent line method would be a better choice when the shape of the droplet is asymmetric such as when on an uneven surface or when the droplet is ascending or receding, as shown in Fig. 18.2.

18.4 Determination of Critical Surface Tension

As mentioned above, wetting phenomena can be determined by the intrinsic surface tension of liquids (γ_l) and solids (γ_s). Although γ_l can be relatively easily measured, experimental determination of γ_s is rather difficult. Utilization of critical surface tension of solids (γ_C) is a method to estimate γ_s from the contact angle of various liquids on the target solid surface. The following are details of the method to determine γ_C.

Table 18.1 shows the surface tension of various liquids [1]. Here, Type A liquids involve liquids whose surface tension (γ_l) derives only from London dispersion force (γd) such as n-alkane (saturated hydrocarbon). Type B liquids include liquids with London dispersion force (γd) and dipol-dipol interaction force (γb) such as n-alkene (un-saturated hydrocarbon). Type C liquids are liquids with (γd), (γb) and hydrogen bonds (γh) such as 1-alnanol (fatty alcohol). Determination of the critical surface tension (γ_C) of solids is summarized as (1) dropping a liquid which γ_l is known, as

Table 18.1 Surface tension of standard liquids at 30 °C

Type	Standard liquids		Surface tension (mN/m)
Type A liquid*1	Dodecane	$C_{12}H_{26}$	25.0
	Tridecane	$C_{13}H_{28}$	25.7
	Tetradecane	$C_{14}H_{30}$	26.5
	Pentadecane	$C_{15}H_{32}$	26.9
	Hexadecane	$C_{16}H_{34}$	27.4
	Heptadecane	$C_{18}H_{36}$	27.9
Type B liquid*2	1-Dodecene	$C_{12}H_{24}$	27.7
	1-Tetradecene	$C_{14}H_{28}$	28.3
	1-Hexadecene	$C_{16}H_{32}$	29.4
	1-Octadecene	$C_{18}H_{36}$	30.1
Type C liquid*3	1-Hexanol	$C_6H_{13}OH$	25.7
	1-Heptanol	$C_7H_{15}OH$	26.6
	1-Octanol	$C_8H_{17}OH$	27.2
	1-Nonanol	$C_9H_{19}OH$	28.0
	1-Decanol	$C_{10}H_{21}OH$	28.4
	1-Dodecanol	$C_{12}H_{25}OH$	29.1

*1: which contains component of London dispersion force (γ^d)
*2: which contains both γ^d and component of polar force (γ^P)
*3: which contains γ^d, γ^P, and component of hydrogen bonding force (γ^d)

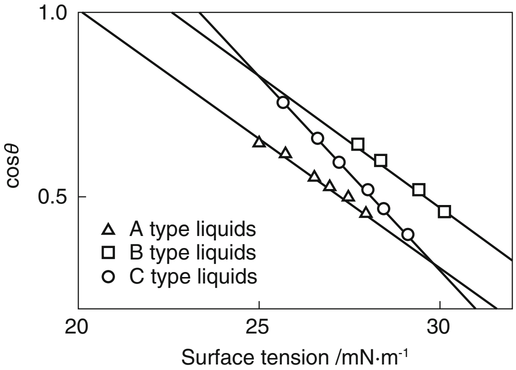

Fig. 18.6 Relationship between cos*θ* and the surface tension of the liquids for PSt-C6F13 (Rf ratio = 16%) film at 30 °C

shown in Table. 18.1, and measuring the contact angle to get cosθ and (2), as shown in Fig. 18.6 [2–3], plotting each cosθ value for the serial liquids (Types A, B, and C) against the surface tension as Zisman plot. The critical surface tension for each type of liquid ($\gamma^A{}_C$, $\gamma^B{}_C$, and $\gamma^h{}_C$) is determined at the intersection between each line and cosθ = 1 as shown in Fig. 18.6. Each contribution of molecular forces for γ_C is calculated as follows [4–6]: (1) The London dispersion force $\gamma^d{}_C$ corresponds to $\gamma^A{}_C$. (2) Polar parts ($\gamma^P{}_C$) can be obtained by subtracting $\gamma^B{}_C$ from $\gamma^A{}_C$ ($\gamma^P{}_C = \gamma^A{}_C - \gamma^B{}_C$). (3) Hydrogen bond contribution can be determined by subtracting $\gamma^B{}_C$ from $\gamma^C{}_C$ ($\gamma^h{}_C = \gamma^C{}_C - \gamma^B{}_C$). The sum of these elements ($\gamma^t{}_C$) gives the contact angle of

Table 18.2 Components of critical surface tension of PSt-CF(CF_3)O{CF_2(CF_3)0}$_m$$C_3F_7$ (mm = 0,1, 2) films at 30 °C

Sample	Rf ratio	γ_c^d (mN/m)	γ_c^p (mN/m)	γ_c^h (mN/m)	γ_c^t (mN/m)
PSt	0%	30.3	4.4	1.0	35.7
m = 0	2%	22.0	4.1	1.1	27.2
	3%	21.6	3.9	1.1	26.6
	5%	19.9	3.6	1.1	24.6
	10%	18.4	3.1	1.2	22.7
m = 1	4%	21.0	2.9	1.5	25.4
	6%	19.2	3.2	1.6	24.0
	13%	12.4	2.9	0.9	16.2
	43%	12.3	2.9	1.0	16.2
m = 2	3%	14.0	3.5	1.1	18.6
	9%	10.1	3.0	1.1	14.2
PSt-C_6F_{13}[a]	16%	20.5	2.3	0.7	23.5

[a]Data from lit [6]

specific solid surfaces as shown in Table 18.2 as $\gamma^t{}_C = \gamma^d{}_C + \gamma^P{}_C + \gamma^h{}_C$. Table 18.2 shows the data for these values of a perfluoroalkanoyl-polystyrene surface [7].

The water and oil repellant property of perfluoroalkanoyl-polystyrene surface is shown in Table 18.2. The degree of fluoro substitution to hydrogen at the alkane moiety remarkably decreases $\gamma^t{}_C$, which reaches 14.2 nm/m and is smaller than Teflon (18 nm/m), and this is why these solids show excellent repellency both for water and oil.

General features of wetting can be found in the recent review article by Tsujii [8].

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