

Characterization of Surfaces by Contact Angle Goniometry

—I. Contact Angle Measurement by Laser Beam Projection—

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접촉각측정에 의한 표면의 특성연구

— I. 레이저광선 투영에 의한 접촉각의 측정방법 —

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본 연구에서는 레이저광선의 투영을 이용한 접촉각측정기구가 개발되었다. 이 새로운 방법은 편평한 표면뿐만 아니라 직격이 가는 섬유를 포함한 굴곡진 표면에서는 stationary, advancing 그리고 receding contact angle을 신속하고 정확하게 측정할 수 있게 하여 준다. 가는 레이저광선이 액체와 고체사이 계면의 끝을 통과하여 tangent screen의 각도를 재는 눈금상에 중심으로부터 방사상으로 두개의 선이 나타나게 된다. 이때 눈금상에 투영된 두개의 레이저광선 사이의 각도를 접촉각으로 결정한다. 이 새로운 기구를 사용한 결과, PMMA (Perspex-CQ)에서의 접촉각은 문헌상의 접촉각과 일치함으로써 간편하고 정확한 접촉각 측정법임을 입증할 수 있었다.

ABSTRACT

Contact angle measuring device was developed in this laboratory using laser beam projection. The new method allows for rapid and direct determination of stationary, advancing, and receding contact angles on both planar and nonplanar solid surfaces, including fibers with very small diameters. A narrow laser beam impinges on an edge of an interface of liquid and solid. This makes two projected laser beam lines upon and radiating from the center of a protractor scale on a tangent screen. Contact angle is measured by determining the difference in angle on the protractor scale between the two projected laser beam lines. Contact angles measured on Perspex-CQ using this instrument were in agreement with the literature. It was shown that this instrument provides a novel method for the facile and accurate measurement of contact angles.

I. INTRODUCTION

Among the many instruments available today, the technique of contact angle goniometry is one of the most useful tool to study solid surfaces which have variable composition and properties. The advantage of contact angle measurement is that this method

looks at the surface layer of less than 10 Å, as the forces between molecules and the adsorbing surface exert only at the immediate area of contact. It is known that the major changes in the surface properties of solids or liquids on the adsorption occur within a monomolecular layer. Contact angle measurement can tell surface hydrophilicity, surface structure, variance of surface properties and surface

polarization, etc^{1,2)}.

The measurement of contact angle is rather complicated, since true equilibrium angle is difficult to measure. Usually the angle may be anywhere between two extremes, advancing contact angle and receding contact angle. Advancing contact angle is the maximum angle when the liquid is advancing. Receding contact angle is the minimum angle when the liquid is receding. The difference between the advancing and the receding angle is called the "hysteresis" of the contact angle.

With some limits and difficulties, contact angle measurements are still useful to interpret the wetting properties of solids, which is theoretically and practically very important in all phenomena involving interfacial physics and chemistry. Hence various methods have been employed for measuring the contact angle, for example, the sessile drop method, captive bubble method, capillary rise method, vertical plate, rod method, pendant drop method, drop weight method and others.

All these methods described above give a relatively good and useful information about the contact angle in the solid-liquid-gas, or in the solid-liquid-liquid system. However, they require that the observer determine the point of contact between the liquid and the solid and fit the best tangent at that point. This procedure can be highly subjective in the choice of contact point by the person who decides the contact angle and thus leads to a general lack of precision found in these methods. In addition, these methods are primarily applicable to smooth, planar surfaces and are not generally useful when curved surfaces such as lenses or fibers are encountered. Especially the measurement of the contact angle between very small drops on very small surfaces is not applicable in these conventional methods.

Considering the problems described above, a new method of contact angle measurement has been developed in this laboratory. The advantages of this new technique are: i) contact angle is directly pro-

jected on the screen so that the contact angle does not depend on the human decision. ii) It is directly applicable to the measurement of the contact angle between very small sized droplet on very small surfaces. iii) It is useful not only on the planar surfaces but also on the curved surfaces as well. This new technique allows for rapid and direct determination of stationary, advancing and receding contact angles for systems in the sessile drop, bubble, vertical plate and rod, and tilted plate configurations.

II. EXPERIMENTAL

1. Description of the Instrument

Contact angles were measured using the instrument developed in this laboratory which is schematically shown in Figure. 1. All the optical components that include laser, filter, sample stage, and screen are mounted on an optical bench, which can be placed exactly horizontally by adjusting its screws.

A He-Ne laser (Spectra physics Model 155) is used as the source of a narrow beam of coherent light, which is substantially parallel beam having a divergence of up to 1 milliradian. It has a power of from 0.5 milliwatts to 1 watt and diameter of up to 2 millimeters.

The beam is passed through a filter to absorb heat and through an aperture to narrow the beam diameter. The beam then impinges on the point of contact between the liquid and the solid sample placed on a stage which can be adjusted in three ways, i.e., vertically, laterally, and can be rotated by 360°. Then the beam is reflected from the solid surface and liquid surface at the point of three-phase contact. This makes two projected lines radiating from the center of a protractor scale on a screen normal to the solid surface: one beam originating from the solid surface and the other originating from the liquid surface. The contact angle, which is the angle difference between these two lines, is determined by a protractor scale on a screen.

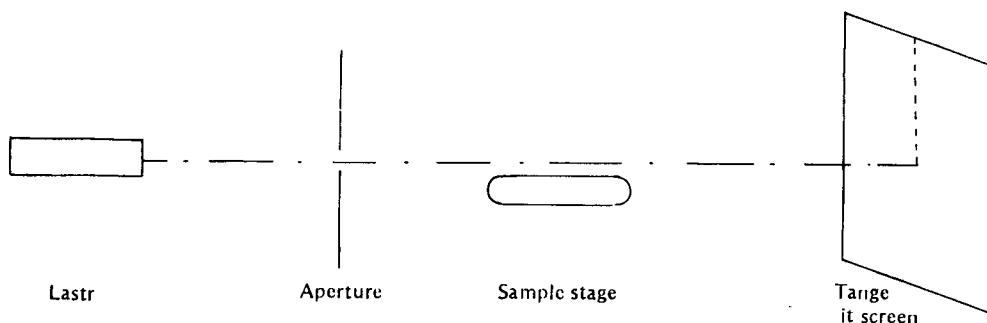


Fig. 1. Schematic view of the instrument.

2. Procedure

PMMA (polymethylmethacrylate: Rerspex-CQ) was purchased in a sheet form. These solid samples were cleaned with detergent solution and thoroughly rinsed with deionized and distilled water, conditioned in distilled water for 48 hours, and then dried in the air. Sessile drop method was employed to measure the contact angle. All the measurements were done at room temperature and contact angles were determined at least three times for one sample and the average value was then determined.

The sample stage is first adjusted horizontally by placing a water level on it, and the solid sample is placed on the sample stage. The laser beam is focused as a dot at the center of the protractor scale on the screen. The stage is adjusted vertically such that the impinging laser beam parallel to the solid surface just grazes the surface of the solid sample, thus resulting in a projected laser beam line originating from the solid surface and projected upon and radiating from the center of the protractor scale. A drop of distilled water is placed on the solid sample. The sample stage is then adjusted horizontally such that the impinging laser beam just grazes the interface edge of the liquid drop with the solid surface. This is evidenced by the appearance of a second projected laser beam line originating from the interface edge and projected upon and radiating from the center of the protractor scale. The contact angle is

measured by determining the difference in angle on the protractor scale between the two projected laser beam lines. By the lateral adjustment of the horizontal position of the sample stage, a stationary contact angle measurement may be obtained from each side of the liquid drop. The laser projection technique is particularly adaptable to contact angle measurements on fibers, since fibers of very narrow diameters can be measured.

In a similar fashion, advancing and receding contact angles may be measured using a sample stage that allows 360° rotation. The liquid drop is placed on the solid sample and the sample stage is rotated manually such that the system is tilted. Measurements are made on the lower (advancing) interface edge and on the upper (receding) interface edge of the liquid drop. The table is then rotated to greater angles of tilt until the maximum advancing and the minimum receding angles are observed. If the system is tilted beyond this point, the liquid drop would flow from the surface of the solid. Alternatively, the advancing and receding angles may be determined by observing the angle while increasing or decreasing the size of the drop.

III. RESULTS & DISCUSSION

This method can be used to determine the stationary, advancing, and receding contact angles for solid-liquid-gas systems in the sessile drop, bubble,

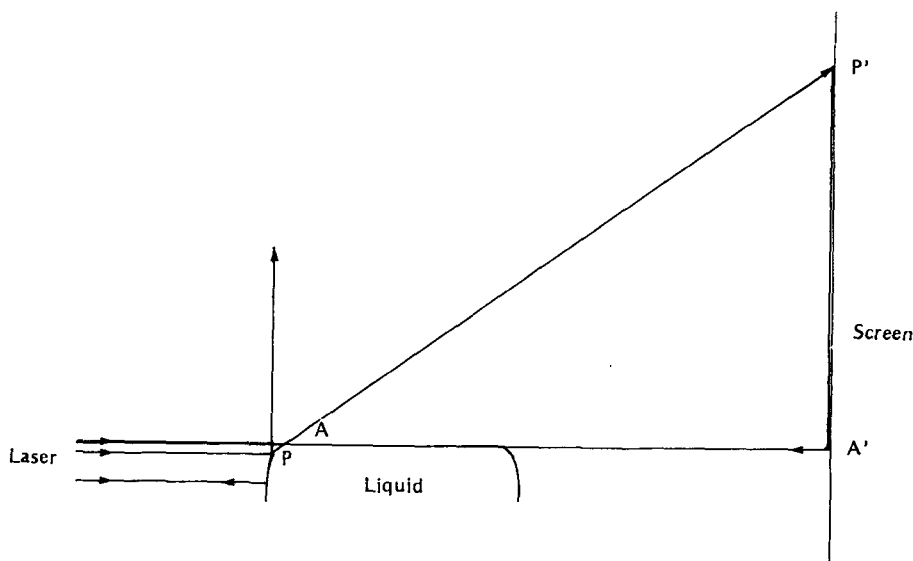


Fig. 2. Reflection of light beams from a horizontal liquid surface.

vertical plate, vertical rod and tilted plate configurations.

Figures 2 and 3 show how the light beams are projected normal to the surface onto the protractor scale in screen. For example, the light beams reflected from the horizontal liquid surface are projected as a vertical line onto the screen as can be seen in Figure 2. Laser can be assumed as a bundle of light beams although its diameter is very small. These bundles of light beams will impinge around the surface edge of the liquid on the plane normal to the liquid surface, resulting in a vertical line on the screen.

Also as shown in Figure 3, the light beams reflected from the vertical rod are projected as a horizontal line on the screen. A bundle of light beams impinge around the circumference of the vertical rod and these series of reflections around the circumference at the same height makes the horizontal line on a screen.

For the case of a liquid drop on a flat solid surface, the light beams reflected from the interface edge of the liquid drop are projected onto the screen, making a line normal to the edge of the liquid surface. This

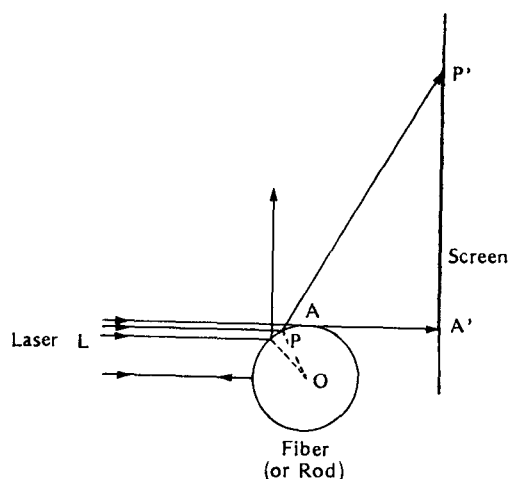


Fig. 3. Reflection of light beams from a vertical rod.

is shown in Figure 4. A bundle of light beams impinge around the circumference of a liquid drop (i.e. a circumference which passes through A and B in Figure 4) and these series of reflections at the interface edge on the circumference make the line $A'P'$ which is normal to the surface that includes the line TT' . The stationary contact angle is measured by reading the difference in angle on the protractor

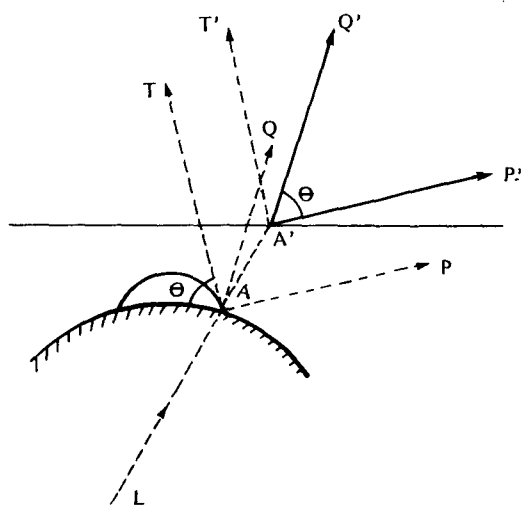


Fig. 4. Reflection of light beams from a liquid drop on a curved solid surface.

scale between the two projected lines $A'P'$ and $A'Q'$.

Figure 5 illustrates how contact angle of a drop is measured on a curved surface. The light beams reflected from the curved surface which is in contact with the edge of the liquid drop are projected as the line $A'Q'$ on the screen. Also the projection of the light beams reflected from the edge of the liquid drop will make the line $A'P'$, and contact angle is determined as the angle between $A'Q'$ and $A'P'$.

Employing the apparatus, a stationary contact angle of 76° was measured on Perspex-CQ with a distilled water drop at room temperature. This value is in agreement with the literature³⁾. An advancing contact angle of 87° and a receding contact angle of 47° were obtained on Perspex-CQ. These values also compare favorably to those cited in the literature⁴⁾.

It is shown that this instrument provides a direct and precise method to measure contact angles which does not depend on the human decision. This also provides a simple, inexpensive, and nondestructive method since only small amount of solid sample is required and its properties are not changed after having been used for this measurement.

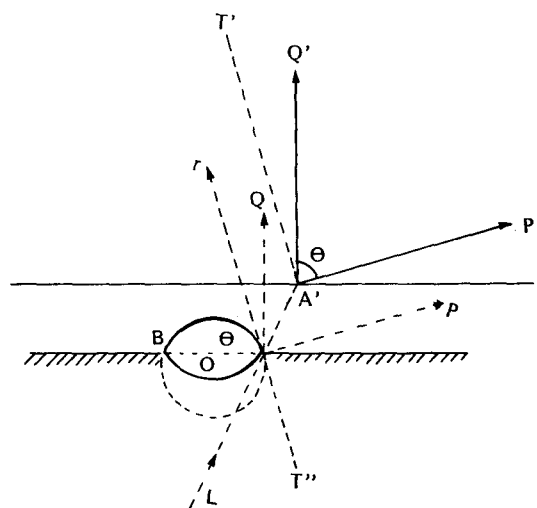


Fig. 5. Reflection of light beams from a liquid drop on a flat solid surface.

IV. CONCLUSION

Employing the new instrument which measures contact angle by laser beam projection, contact angles could be determined directly from the protractor scale on the screen. A stationary contact angle of 76° was measured on Perspex-CQ. An advancing contact angle of 87° and a receding contact angle of 47° were obtained. These values were in agreement with the literature. Therefore, it can be concluded that this new instrument can be a useful method to measure contact angles without depending on the human decision and thus provides a direct, simple, and precise method to study interfacial phenomena.

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