Chapter III

固体材料の表面張力の制御とその評価

－Zisman プロットと表面処理手法－

Contact Angle Goniometry for Surface Tension Measurements of Solid Surfaces

—Zisman Plot and Surface Treatment Techniques—

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1. Introduction

Contact angle goniometry, a shape of drops on solid surfaces, allows insight into the most fundamental properties of both liquids and solids, including their cohesive forces, adhesive behavior, wetting properties, and morphological properties. Their properties are an integral part of our daily lives, as seen in painting, sticking adhesive, a Teflon®-coated frying pan, water-repellent and hydrophilic coatings for a car body and a car windshield, etc. Also, wettability is determined by the outermost chemical groups of the solid surface, and is an important parameter in evaluating the surface properties. The purpose of this experiment is to learn the concept of "wettability of solid surfaces" from measurements of contact angles and Zisman plots, and attempt to control the surface wettability by using various types of "surface treatments".

2. Background and basic knowledge

2-1. Contact angle

Contact angle goniometry is one of the most basic and important techniques for evaluating the wetting of solid surfaces. Measuring of contact angles has a long history. It started in early 19th century with Laplace and Young evaluating wettability with differential calculation, a new calculation method at the time. The contact angle is the most basic physicochemical phenomenon related to both solids and liquids, and closely associated with the understanding of physical properties, such as cohesive forces between liquid-solid, adhesiveness and tackiness, wettability, and morphology.

By observing the contact angle formed by a liquid droplet in contact with a solid surface, information about the surface tension and surface energy of the material can be obtained. Figure 1 shows a schematic diagram where a contact angle is formed with a droplet in contact with a solid surface. When the droplet on the solid is stationary (in a state of equilibrium), the relationship between each free energies (γ_S, γ_L, γ_{SL}) and Young's contact angle (θ) are given by:

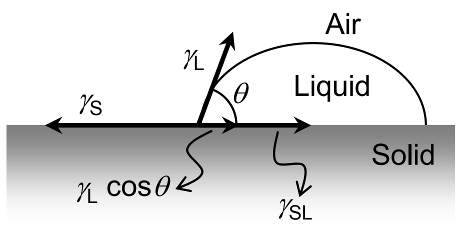

Figure 1. Graphical vector display of sessile drop parameters.

$$\gamma_S = \gamma_L \cos\theta + \gamma_{SL} \quad \text{(Young's Equation)}$$

(θ; Young's contact angle, γ_S; solid-vapor interfacial free energy, γ_L; liquid-vapor interfacial free energy, γ_{SL}; solid-liquid interfacial free energy)

It is a simple relationship; but since contact angles are sensitive to properties of the outermost surface, many researchers use the qualitative and quantitative measurements of contact angles as a simple method for evaluating surfaces. (There is also the measurement of advancing/receding contact angles, where **surface roughness, shape, uniformity**, and molecular motility can be evaluated in detail. However, since the discussion will be too complex, it will not be covered in this experiment.)

2-2. Zisman plot

Zisman's technique obtains the surface tension of a material experimentally. This technique uses the following principle: "when liquid is completely spread over a solid surface (i.e. $\theta = 0°$), the surface tension of this liquid is the same or lower than the surface tension of the solid surface". Zisman called the surface tension where "surface tension of liquid" and "surface tension of solid surface" are equal as critical surface tension (critical surface tension; γ_c). To obtain γ_c of a solid surface, several liquids with varying surface tensions are prepared as probing solutions. We then measure contact angles of the solid surface for each probing solutions **from the liquid of high surface tension to low surface tension**. Specifically, surface tension of the liquid is plotted on the X-axis, and cos θ relative to contact angle θ is plotted on the Y-axis (Zisman plot). The surface tension at $\theta = 0°$ ($\cos\theta = 1.0°$) is extrapolated from the plots (Figure 2). This extrapolated surface tension value is γ_c, and can be estimated as the surface tension of the analyzed solid (the intersection of dotted line and X-axis on the figure). (Generally, this process is conducted for various liquids. Values of γ_c for a liquid material in the same family as a specific solid surface are measured, at times quantitatively, and at times its correlation is estimated.)

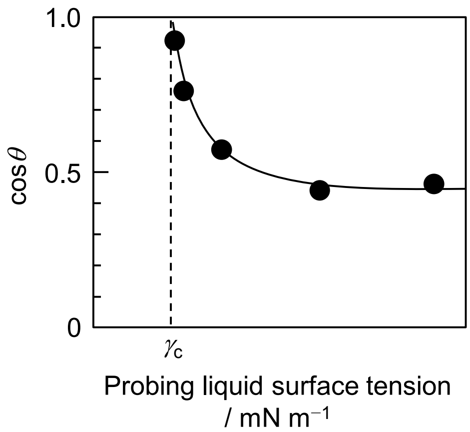

Figure 2. A typical Zisman plot.

2-3. Surface treatment

The surface treatment is to modify solid surfaced of materials such as metals, resins, and ceramics by chemical treatment. It gives properties such as aesthetics, reflective properties, corrosion resistance, electrical and heat conductivity, lubrication and wear-resistance properties, and wettability to the solid surface. Typical examples include rust-resistance and plating. In this experiment, we will focus on controlling the surface wettability.

Wettability of a material surface is sensitive to the outermost surface. For example, by covering the outermost surface with a monomolecular membrane, wettability can be changed drastically. Also, wettability, in this case, is strongly influenced by shapes, chemical structure and conformation of the surface in the order of magnitude in micron to nanometer. In this experiment, by application of each surface treatment starting with treatment, we would like you to predict the change in the molecular structure and shape of the outermost surface, and experience how contact angle and surface tension of water change.

3. Experimental section

Conduct the following 4 experiments. Using 7 probe solutions marked in Table 1, measure the contact angles several times for each solution.

Attention 1: use from probe solutions with low methanol concentrations.

Attention 2: the number of measurements should be determined in consideration of data variations.

Attention 3: There are only 3 contact angle meters. Once your group has enough data for drawing a Zisman plot on one sample, please give the equipment to the waiting group. Work efficiently by performing plots, discussions, literature surveys, sample preparation for the next measurement, etc. during the waiting time.

3−1. Teflon® substrate

Measure the contact angle of the Teflon substrate and estimate the critical surface tension from the Zisman plot. Moreover, measure the contact angle of a Teflon substrate polished with a file and estimate the critical surface tension. Use two of more files. Consider the effect of surface roughness on wettability.

3−2. Silicon substrate

Measure the contact angle of silicon substrate and estimate the critical surface tension from the Zisman plot.

3−3. Ultrathin film coating

You can obtain silicon substrate modified with 1,1,1,3,3,3-hexamethyldisilazane (HMDS). The HMDS coating layer is an ultrathin film (single nanometers thick). Measure the contact angle of the HMDS ultrathin film and estimate the critical surface tension from the Zisman plot. Consider the relationship between the chemical structure and wettability.

3−4. UV-O_3 treatment of silicon substrate

TA perfoems UV-O_3 treatment on the silicon substrate used in 3-2. Measure the UV-O_3 treated silicon substrate and estimate the critical surface tension. Consider what changes have occurred on the surface after UV-O_3 treatment and how these changes have affected wetness. (Note: Since the substrate after UV-O_3 treatment is easily contaminated, measure the contact angle immediately after treatment. Also, do NOT touch the treated surface as much as possible.)

Table 1. Surface tension in mN m^{-1} for the specified mass % [1]

Compound	t / °C	**0%**	**10%**	**20%**	30%	**40%**	50%	**60%**	70%	**80%**	90%	**100%**
Acetic acid	30	71.2	51.4	43.3	41.2	38.2	37.4	36.1	33.5	31.5	30.2	26.3
Acetone	25	72.0	44.9	40.5	36.7	33.0	30.1	29.4	29.4	27.6	24.5	23.1
Acetonitrile	20	72.8	48.5	40.2	34.1	31.6	30.6	30.0	29.6	29.1	28.7	28.4
1,2-Butanediol	25	72.0	66.1	60.4	55.1	50.1	45.6	43.3	41.9	40.8	39.2	35.8
1,3-Butanediol	30	71.2	58.1	51.6	48.7	45.8	43.9	42.4	41.2	40.0	39.0	37.0
1,4-Butanediol	30	71.2	61.2	56.9	54.2	52.0	50.7	49.5	47.9	46.6	45.2	43.8
Butanoic acid	30	71.2	42.4	37.5	35.5	34.8	32.2	30.8	29.2	27.4	26.3	25.5
2-Butanone	20	72.8	41.6	32.2				25.2				24.6
γ-Butyrolactone	30	71.2	64	58	53	50	48	46	45	44	42.8	42.7
Chloroacetic acid	25	72.0	59.8	53.6	51.3	49.7	48.3	47.5	46.1			
Diethanolamine	25	72.0	66.8	63.2	60.7	58.8	57.2	55.7	54.3	52.7	50.6	47.2
N,N-Dimethylacetamide	25	72.0	72.0	72.0	72.4	73.5	74.9	75.4	73.0	65.7	54.7	36.4
N,N-Dimethylformamide	25	72.0	65.4	59.2	53.8	49.6	47.3	46.9	44.9	42.3	38.4	35.2
1,4-Dioxane	25	72.0					41.2	39.6	37.9	36.2	34.5	33.7
Ethanol	25	72.0	47.5	38.0	33.0	30.2	28.0	26.2	25.0	23.8	22.7	21.8
Ethylene glycol	20	72.8	68.5	64.9	61.9		57.0					48.2
Formic acid	20	72.8	66	60	55.7	52.2	50.3	48.8	47.1	44.7	40.9	38.0
Glycerol	25	72.0	70.5	69.5	68.5	67.9	67.4	66.9	66.5	65.7	64.5	62.5
Methanol	25	**72.0**	**56.2**	**47.2**	41.1	**36.5**	32.9	**29.8**	27.5	**25.5**	23.9	**22.5**
Morpholine	20	72.8	65.1	60.7	58.9	56.7	53.0	49.6	47.0	43.7	41.8	38.7
Nitric acid	20	72.8	71.9	70.7	68.9	66.6	63.8	60.6	56.8	52.6	47.9	42.6
Propanoic acid	30	71.2	46.6	42.2	37.7	35.6	33.1	31.7	30.2	28.2	27.4	25.8
1-Propanol	25	72.0	34.3	27.8	26.0	25.3	24.8	24.5	24.1	23.9	23.6	23.3
2-Propanol	25	72.0	40.4	30.6	26.8	25.3	24.3	23.5	22.7	22.1	21.7	21.2
1,2-Propylene gycol	30	71.2	60.5	54.9	50.7	47.2	44.5	41.5	38.6	37.6	36.3	35.5
1,3-Propylene gycol	30	71.2	62.6	58.8	55.7	53.8	52.8	51.7	50.8	49.6	48.2	47.0
Pyridine	25	72.0	52.8	51.2	48.0	46.8	46.6	45.8	45.0	43.6	40.9	37.0
Sulfolane	20	72.8					62.5	61.6	59.6	57.1	54.9	50.9
Sulfuric acid	50	67.9	73.5	75.1	73.6	71.2	68.0	64.1	60.0	56.4	53.6	51.7
Trichloroacetaldehyde	25	72.0	56.7	51.0	46.7	44.1	43.0	42.5	41.5	38.9	34.7	29.4
Trichloroacetic acid	25	72.0	55.8	46.5	42.8	41.6	40.6	39.4	38.3	37.4	36.5	

4. Assignment

List the techniques for surface treatment (as many as you can), then list which technique is used for what effect.

5. References

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