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Measurement of surface tension by analyzing horizontal oscillation of droplet on substrate

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1. Introduction

Paint's physical properties must be controlled in the coating process to perform its function because unsuitable physical properties cause the poor appearance and other problems. For example, wetting phase right after the paint droplet impacts on the substrate is important process in the spray coating and dominated by paint's surface tension and viscoelasticity. However, the surface tension of the paint cannot be measured accurately by existing methods.

Wilhelmy, du Noüy, and maximum bubble pressure methods are often employed to obtain surface tension. However, the measured values are not satisfactorily accurate for highly viscous samples such as paint. A measurement method of dynamic surface tension by analyzing the oscillation of a flying droplet has also been proposed.[1, 2] The measured value in the method is not affected by its viscosity. However, this method requires continuous and stable ejection, which is difficult for paint because of its high spinnability.

In our previous study, we reported the behavior of the droplet on a vertically oscillating flat substrate.[3] The oscillation can be roughly understood in terms of the theory for the free sphere droplet, however, the droplet on a substrate has the boundary condition that the flow velocity is zero at all the region of the contact plain between the droplet and the substrate, unlike a free sphere droplet. This boundary condition makes the quantitative analysis quite complex. In this study, we propose the measurement of surface tension through the observation of the horizontally oscillating droplet, in which the deformation could be considered simple shear.

2. Theory

The droplet on a flat substrate is considered to be a partial sphere, of which center coordinates are set to the origin. The vector $\boldsymbol{r(\varepsilon)}$ pointing the surface area is modulated by the horizontal shear deformation, which is expressed as:

$$\boldsymbol{r(\varepsilon)} = R\begin{pmatrix}\cos\theta\sin\varphi + \varepsilon(\cos\varphi - \cos\alpha)\\ \sin\theta\sin\varphi\\ \cos\varphi\end{pmatrix}, \quad (1)$$

where R is the radius of the droplet, ε is the coefficient showing the droplet deformation, θ and φ are azimuth and elevation angles, respectively, and α is the contact angle of the droplet. Furthermore, the surface area $S(\varepsilon)$ of the droplet in contact with air is given as:

$$S(\varepsilon) = \int_0^{\alpha}\int_0^{2\pi}\sqrt{EG - F^2}\,d\theta\,d\varphi, \quad (2)$$

where E, F, and G are the inner product of $\boldsymbol{r}_\theta=\partial\boldsymbol{r}/\partial\theta$ and $\boldsymbol{r}_\varphi=\partial\boldsymbol{r}/\partial\varphi$ expressed as $E=\boldsymbol{r}_\theta\cdot\boldsymbol{r}_\theta$, $F=\boldsymbol{r}_\theta\cdot\boldsymbol{r}_\varphi$, and $G=\boldsymbol{r}_\varphi\cdot\boldsymbol{r}_\varphi$. In addition, potential energy $U(\varepsilon)$ is calculated by:

$$U(\varepsilon)= \sigma(S(\varepsilon)-S(0)), \quad (3)$$

where σ is surface tension.

By expanding Eq. (3) to the second order of ε, we obtain the spring constant against the small amplitude shear deformation of the droplet as:

$$U(\varepsilon) = \pi B R^2 \sigma \varepsilon^2/2, \quad (4)$$

where

$$B = -\frac{1}{5}\cos^5\alpha + \frac{2}{3}\cos^3\alpha - \cos\alpha + \frac{8}{15}.$$

Furthermore, the horizontal flow velocity $v(z)$ at height z is expressed as $v(z) = \dot{\varepsilon}(z - R\cos\alpha)$ and the kinetic energy $T(\varepsilon)$ is described by:

$$T(\varepsilon) = \pi A R^5 \rho \dot{\varepsilon}^2/2, \quad (5)$$

where

$$A = \frac{1}{30}\cos^5\alpha - \frac{1}{3}\cos^3\alpha + \frac{2}{3}\cos^2\alpha - \frac{1}{2}\cos\alpha + \frac{2}{15}.$$

Furthermore, resonance frequency f_l is given as:

$$f_l = \sqrt{B\sigma/4\pi^2 A\rho R^3}, \quad (6)$$

which is obtained by solving the Lagrange equation.

3. Experiment

We introduce our experimental system, which is shown **Fig. 1**. We employed a piezo actuator to drive the horizontal vibration of the substrate. The substrate in this study is the glass plate; a circular area of the glass with which the droplet contacted was kept hydrophilic, and the surrounding area was coated with a water-repellent. Therefore, the contact angle could be controlled by changing the volume of the droplet or circular area kept hydrophilic. The substrate is arbitrary because it was just fixed on the attachment. We prepared the droplets in the volume range of 0.5-2μL with micro syringe. In addition, we employed a laser light as a tool to detect droplet

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oscillations with a high time resolution.

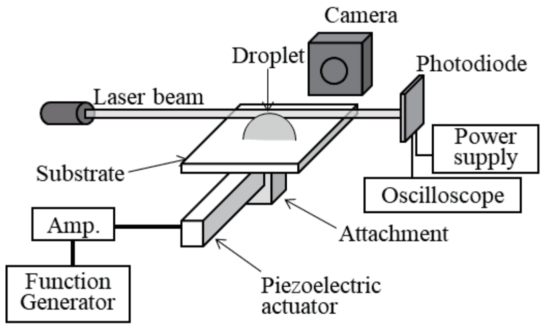

Fig. 1 Schematic of the experimental setup for the measurement of the horizontal oscillation

We determined the resonance frequency from the spectrum peak of the amplitude of the droplet on the sinusoidally oscillating substrate at 10-400Hz, or the frequency of the damped oscillation of the droplet after the impulsive oscillation of the substrate. The sinusoidal oscillation gives not only resonance frequency but also phase delay by the liquid viscosity and the time required to obtain the entire spectrum of the oscillation is less than 1min. The advantage of the measurement of impulse response is that measurement time is shorter and less than a few seconds.

We measured the resonance frequency for the distilled water droplet, of which contact angle α and radius R ranges were 25-115° and 0.35-2.7mm, respectively. **Figure 2** shows the comparison of the measured and theoretical values of their resonance frequency. Measured values and theoretical values calculated in **Eq. 6** are in good agreement.

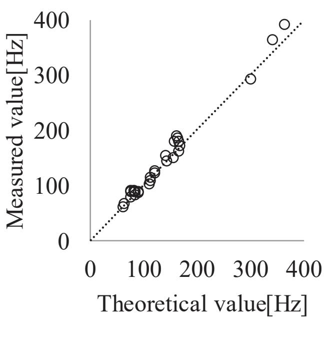

Fig. 2 Comparison of measured and theoretical values of resonance frequency for distilled water droplet. Dotted line shows the linear function with slope of 1 and intercept of 0.

Finally, we will show the measurement results of the time variation of the surface tension. We measured the change of the surface tension of the aqueous solution of ethanol through the evaporation. We set the ethanol aqueous solution droplet with a contact angle of 108° and volume of 1.8μL. Then, we monitored the shape and the oscillation behavior of the droplet from the impulse response. **Figure 3** shows the time evolution of the measured volume and the surface tension obtained through Eq. 6, and the ethanol concentration obtained from the surface tension. As shown, the decrease of the ethanol concentration could be detected using the newly developed system.

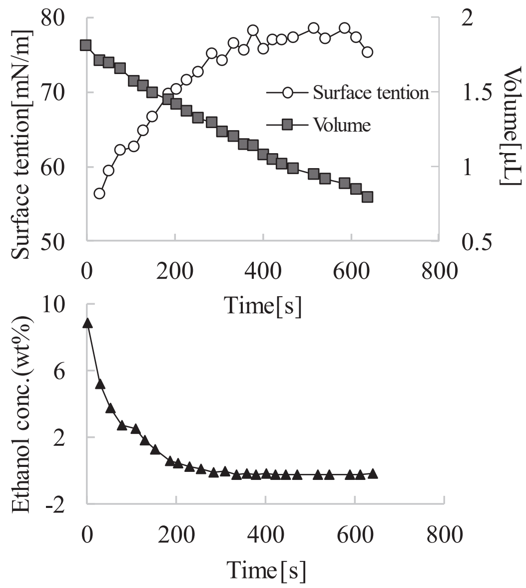

Fig. 3 Time evolution of the surface tension, the volume, and the ethanol concentration of the ethanol aqueous solution droplet set on a substrate.

4. Conclusion

We could measure the resonance frequency of the droplet on the horizontally oscillating flat substrate in brief time. In addition, the measured values agreed with the theoretical values, which we calculated as the function of the surface tension, the contact angle, the density, and the radius, regarding the droplet behavior as shear deformation.

Furthermore, we could detect the time evolution of the surface tension of the droplet on a substrate.

We believe these results lead to the new measurement method of physical properties of the paint droplet immediately after being emitted.

References

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