Apparent Dynamic Surface Tension of Polymer Solutions

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Dynamic surface tensions of aqueous solutions of polymers were measured using a measuring device based on the maximum bubble pressure method. The measurements implied that extra increase in the measured surface tension was induced by the elasticity of the polymer solutions at high frequencies of bubble life cycle. Furthermore, at high polymer concentrations, the surface tension exceeded that of the solvent. These results mean that the measurements for polymer solutions having strong elasticity with the maximum bubble pressure method correspond to apparent dynamic surface tension including the effect of elasticity.

Key Words: Dynamic surface tension / Maximum bubble pressure method / Polymer solutions

1. INTRODUCTION

Dynamic surface tension affects various engineering processes such as spraying, printing, coating, foam molding, and gas-assisted injection molding, in which area of the interface between liquid and gas quickly changes with time. When additives such as surfactants and polymers are dissolved into a solvent, the dynamic surface tension of the solution differs from its static surface tension and depends on the expansion rate of the interface.

In the present study, we measured the dynamic surface tension of aqueous solutions of polymers using a measuring device based on the maximum pressure method1). The results indicate the existence of effects of the elasticity of polymeric liquids on the surface tension. It means that the measurements correspond to apparent dynamic surface tension including the effect of elasticity that works as resistance to the growth of interfaces.

2. EXPERIMENTAL METHOD

We measured the dynamic surface tension of test fluids using a surface tension meter (SITA t60, SITA Messtechnik GmbH), which is a measuring device based on the maximum bubble pressure method. Figure 1 schematically illustrates the measuring principle of the maximum bubble pressure method. In this method, air is pumped into a capillary immersed in a test fluid. The air passes through a filter to be cleaned and dehumidified before the pumping. The resulting bubble at the end of the capillary tip expands as air is pumped and finally detaches from there. During this life cycle of a bubble, the pressure difference Δp between the inside and the outside of the bubble becomes the maximum when the bubble radius becomes the maximum when the bubble radius is identical to that of the capillary (r). In the present system, the capillary diameter (2r) is 0.8 mm and the depth of the capillary tip end from the surface of test fluid is around 25 mm. The surface tension σ can be estimated by the force balance at that time using the Young-Laplace equation,

\[ \sigma = \frac{\Delta p_{\text{max}} \times r}{2} \]

where \( \Delta p_{\text{max}} \) is the maximum pressure difference. The period from the emergence of a bubble at the end of the capillary to its detachment is called the lifetime of the bubble. We plotted the surface tension as a function of the bubble-life-cycle frequency f, which is defined by the inverse of the lifetime.

We used aqueous solutions of polyacrylamide (PAA, SANFLOC AH70P) supplied by Sanyo Chemical Industries.
as test fluids. In the present measurements, PAA was dissolved in distilled water supplied by Wako Pure Chemical Industries at the concentrations of 0.02, 0.03, and 0.05 wt%. The density of each solution is almost the same as that of the distilled water. Aqueous solutions of PAA are known as viscoelastic fluids and have been utilized in numerous studies of viscoelastic flows. Before each measurement, the measuring system was calibrated using the measurement of the distilled water at low frequencies, at which the dynamic surface tension corresponds to the static surface tension. The measurements were carried out at room temperatures, 16-18 °C and the surface tension was evaluated by the average of five measurements under each condition.

3. RESULTS

Figure 2 shows the dynamic surface tension of the distilled water. The surface tension does not depend on the frequency because the distilled water does not contain any additives and hence the expansion rate of a bubble does not affect the surface tension. In general, when additives such as surfactants and polymers are added into a solvent, the dynamic surface tension of the solution is similar to the static surface tension at low frequencies and approaches to the surface tension of the solvent liquid with increasing the frequency. This phenomenon is relevant to the following mechanism: Dissolved molecules adsorb onto the surface of a bubble and it decreases the interfacial energy and induces the decrease in the surface tension. Consequently, if the bubble expansion rate is higher than the adsorption rate, the decrease in the surface tension is reduced.

Next, we show the results for polymer solutions. The measurements were carried out by changing the frequency from high to low values. In this case, bubbles remaining on the fluid surface may affect the measurements because adsorption of polymers on the bubbles can cause the distribution of polymer concentration in the test fluid. In the present measurements, however, we did not capture this effect although we changed the range of frequencies in one set of measurement. This effect can appear in measurements for much dilute solutions. Figure 3 shows the dynamic surface tension σ of the aqueous solutions of PAA. The average surface tension of the distilled water σw is also indicated by a break line in the figure. For the 0.02 wt% solution, the surface tension is low as compared with the distilled water at low frequencies and approaches to the value of the distilled water as the frequency increases. For both the 0.03 wt% and the 0.05 wt% solutions, the surface tensions show anomalous behavior: The surface tension is lower than σw at low frequencies, while it exceeds σw at moderate to high frequencies. That is, the surface tension of the solution exceeds the counterpart of the solvent. Especially for the 0.05 wt% solution, the surface tension is much higher than σw.

We consider that this phenomenon is caused by the elasticity of PAA solutions. The PAA solution near a bubble is elongated along its surface and hence the elastic stress, which works as resistance to the bubble growth, increases in this region. Therefore, the tension on the bubble surface apparently increases and this phenomenon appears more significantly for higher concentration polymer solutions, which have
It is difficult to separate the effect of the elasticity from data obtained by the measurements using the maximum bubble pressure method. Consequently, for visco-elastic fluids such as polymer solutions, we can only measure apparent dynamic surface tension including the elastic effect using this method. In addition, elongational deformation of PAA solution around a bubble can delay the bubble detachment at high polymer concentrations and it may affect the measurements, while such a behavior was not observed under the present experimental conditions.

4. CONCLUSION

The dynamic surface tensions for aqueous solutions of PAA were measured using the maximum bubble pressure method. The results imply that extra increase in the measured surface tension is induced by the elasticity of the polymer solutions with increasing the frequency of bubble life cycle. At high polymer concentrations, the surface tension exceeded that of the solvent. Therefore, the measurements with this method for viscoelastic fluids such as polymeric liquids correspond to apparent dynamic surface tension including the effect of elasticity. If we can evaluate the deformation rate of fluid around a bubble based on images captured with a high-speed video camera recorder, we can discuss the relationship between the apparent dynamic surface tension and rheological properties such as elongational viscosity and elasticity; this is an interesting issue in future studies.

REFERENCES