

Effect of Marangoni Convection in a Droplet Containing Surfactant on Thin Film Shape

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Abstract In printed electronics, uniform and solute film formation by the inkjet method is very important. This study aims to clarify the relationship between Marangoni convection generated by adding surfactant and thinning of solute film. First, four types of surfactants were added one by one to the anisole-polystyrene solution with varying concentrations, and then a little amount of fluorescent polymer was added as tracer to each solution. Next, each solution was dropped on a hydrophilic substrate with a droplet diameter of 80 micrometers using an inkjet method, and the flow in the evaporation process and the shape of the solute film after drying were observed. As a result, Marangoni convection occurred when any surfactant was added at a certain concentration or more, and the solute film after drying of the droplets to which two kinds of surfactants were added became thin and approached a uniform shape. In addition, the measurement of surface tension showed that the visualized flow is the Marangoni convection.

1 Introduction

Printed electronics that uses inkjet technology for wiring of electronic devices and manufacturing of organic EL displays are attracting attention. It is hoped that this technology will make it possible to economically deposit expensive materials such as functional materials at predetermined locations on the substrate. However, there is a problem that it is difficult to form a uniform and thin film by the inkjet method.

An important issue has been the “coffee stain” problem, caused by outward flow that concentrates a solute near the edge of a liquid film. (Deegan *et al.*, 1997) In our laboratory, however, we have investigated thinning of liquid film by addition of surfactant. The thinning of solute film was considered to be due to Marangoni convection towards the center of the droplet at the surface (inward convection) based on the difference in surface tension of the liquid film caused by the surfactant (**Figure 1**). (de Gans *et al.*, 2004) However, the detailed mechanism of thinning by the addition of surfactant has not been clarified.

In this study, firstly, the dependency of surface tension on polystyrene and surfactant concentrations were measured. Next, the internal flow of the inkjet droplet added with surfactant was visualized, and influence of the surfactant on the internal flow and the film shape were examined.

2 Experimental

2.1 Materials

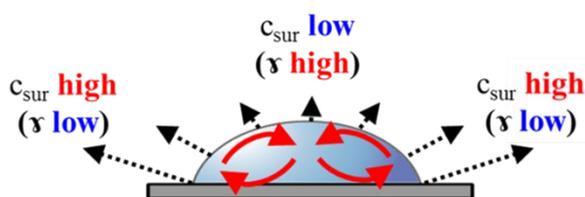


Figure 1. Inward Marangoni convection

A commercial ITO glass plate was prepared as a target surface. The solid surface was cleaned with acetone and UV/ozone before use. Polystyrene (Molecular weight $M_w = 260000$) was chosen as the solute. Anisole (Boiling point $T_b = 154^\circ\text{C}$, $\gamma = 34.6 \text{ mN/m}$, $\eta = 0.984 \text{ mPa}\cdot\text{s}$) was used as solvent. The concentration of Polystyrene was fixed at 3 wt.% for coating experiments. Siloxane type BYK322, BYK348, BYK307 and fluorine type S420 were used as surfactants. Powdery fluorescent polymers were used as a tracer particle for coating experiments.

2.2 Methods

2.2.1 Coating experiments

Samples of the anisole-polystyrene solution including a surfactant and a small amount of fluorescent polymer were prepared by stirring and ultrasonication. Each surfactant was mixed to a concentration of 0, 0.1, 0.5, 1 or 2 wt.%. These solution droplets were applied onto the ITO substrate at about 25°C by the inkjet device, and the evaporation process was photographed with a camera

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from the side and bottom (Figure 2). The shape of the film was measured by a laser microscope.

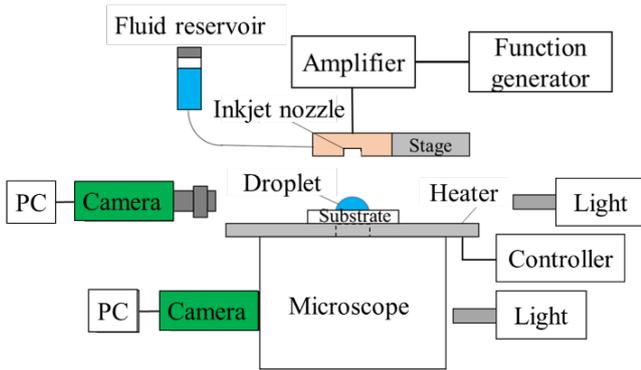


Figure 2. Facilities of coating experiment

2.2.2 Measurements of surface tension

Samples of the anisole-polystyrene solution with a surfactant are prepared. The surface tension of the solution was measured by the maximum bubble pressure method which measures surface tension from the maximum pressure of bubbles generated in the solution. The probe was submerged in the solution in the petri dish, and bubbles were generated in the solution from its tip. The time-dependent change of the surface tension of the solution was measured by changing the time until the bubble reached the maximum pressure.

3 Results and Discussion

3.1 Coating experiments

3.1.1 Film Morphology

Figure 3 shows thickness data of polystyrene solid film formed on ITO substrate from anisole solutions containing 1.0 wt.% surfactant. In the evaporation process, BYK307, spread wet after landing on the substrate and dried out with little shrinkage. On the other hand, the solution droplets with BYK348 and S420 shrank gradually. The film with BYK348 was suppressed in the tendency to ring-like and showed a biased dot-like, and other films showed ring-like.

3.1.2 Contact angle and receding distance

Figure 4 shows the contact angle immediately after a droplet lands on the substrate (initial contact angle) and Figure 5 shows the droplet receding distance made dimensionless by the droplet diameter (dimensionless receding distance). The shape of plots in these graphs show the direction of visualized convection during evaporation. Circle plots show the inward flows towards

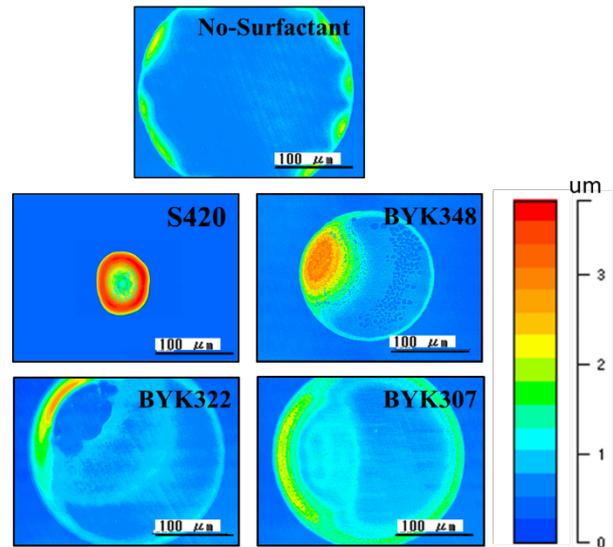


Figure 3. Thickness data of polystyrene layer formed from anisole solution with surfactants on ITO substrate

the contact line of the droplets at the surfaces (outward convection), square plots show the inward convections. Cross plots show that no convection has occurred in the droplets, and triangular plots show that the inward convections occurred in the early stage of the evaporation process and the directions of the convections were reversed in the late stage. And the color of the plot represents the type of surfactant. As shown in Figure 4, the initial contact angle of droplets containing surfactant was larger than that without. Figure 5 reveals that the solutions with BYK348 and S420 shrink significantly during the evaporation process. Figures 4 and 5 suggest that the droplets with a large contact angle and the inward convection are greatly retracted, except for the droplet with 0.1 wt.% BYK348.

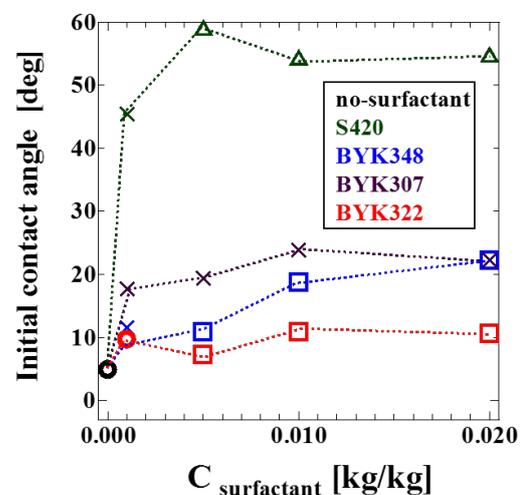


Figure 4. Concentration dependence of surfactant on initial contact angle of droplets

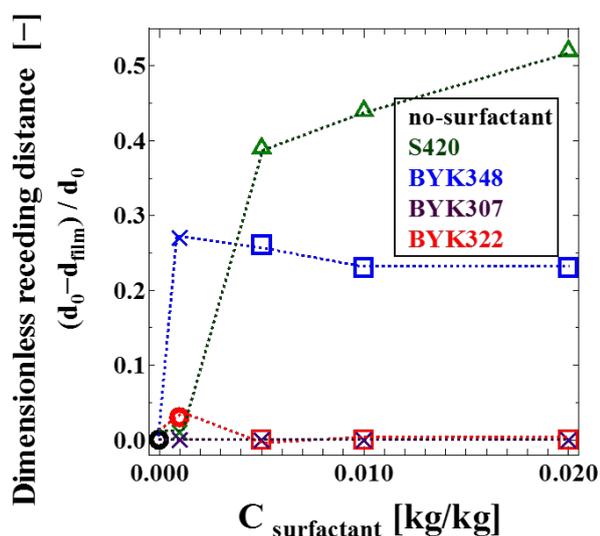


Figure 5. Concentration dependency of surfactant on dimensionless receding distance of droplets

3.2 Measurement of surface tension

Surface tensions for the each solvent are shown in Figure 6. The surface tension of a solution containing polystyrene or a surfactant decreased with time and saturated after $10^1 \sim 10^2$ ms. The surface tension of the solution containing polystyrene was higher than the one without the solute, and the solution containing surfactant was smaller.

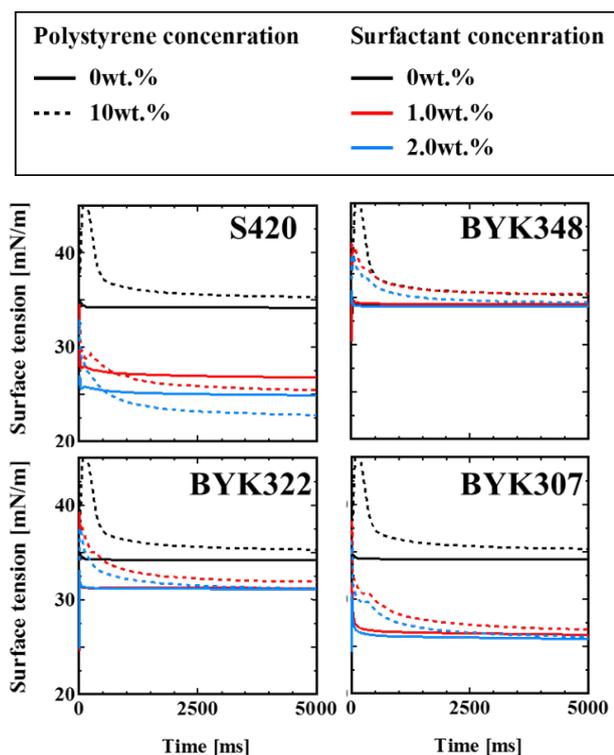


Figure 6. Temporal change of surface tension of solution containing surfactant

3.3 Discussion

Above results indicate that increase in contact angle and inward Marangoni convection cause recession of droplets on substrate. Additionally, the solution added with BYK 348, which showed a large receding distance, suppressed a ring-like trend. However, the solution film with 0.5 wt.% or more of S420 showed ring-like shape despite the large receding and the same convection as that of BYK 348. Figure 5 shows the concentration dependency of surfactant on dimensionless receding distance of droplets. It is considered to be the cause that polystyrene was pushed out near the contact line by this flow that occurred at the end of the evaporation process. Figure 7 shows the state of convection inside the droplet in the evaporation process containing 1 wt.% surfactant (a) and the polystyrene concentration dependency of the surface tension of the solution containing 1 and 2 wt.% surfactants (b). The black arrows in Figure 7 (b) represent the transition of the surface tension of the droplets in the evaporation process. Since the evaporation rate of the droplet is higher at the contact line than at the top of the head, the contact line is faster in increasing and decreasing the surface tension due to the increase in solute concentration. Therefore, by the change in surface tension, the direction of Marangoni convection can be predicted as follows. First, if the surface tension of the droplet decreases, the inward Marangoni convection will occur because the surface tension on the top of the head is greater than the contact line. Next, if the surface tension of the droplet increases, a surface tension gradient opposite to the above occurs, and an outward Marangoni convection occurs. And if the surface tension of the droplet does not change, it can be predicted that Marangoni convection will not occur. In fact, when compared with the direction of convection shown in Figure 7 (a), it can be seen that it agrees with the prediction except for the droplet with 1.0wt.% BYK 348. In addition, the direction of convection predicted from surface tension matched the actual direction also for droplets of other concentrations except for the droplets with BYK348. It indicates that the visualized convection was Marangoni convection. The reason why the trend of convection with BYK 348 does not follow the mechanism above is possible to be because of the accuracy of experimental data for surface tension. There are few data for surface tension with BYK348 at the present.

4 Conclusion

It was revealed that addition of surfactant causes Marangoni convection due to the surface tension difference. In addition, required conditions for thinning of film are increasing of initial contact angle and inward convection.

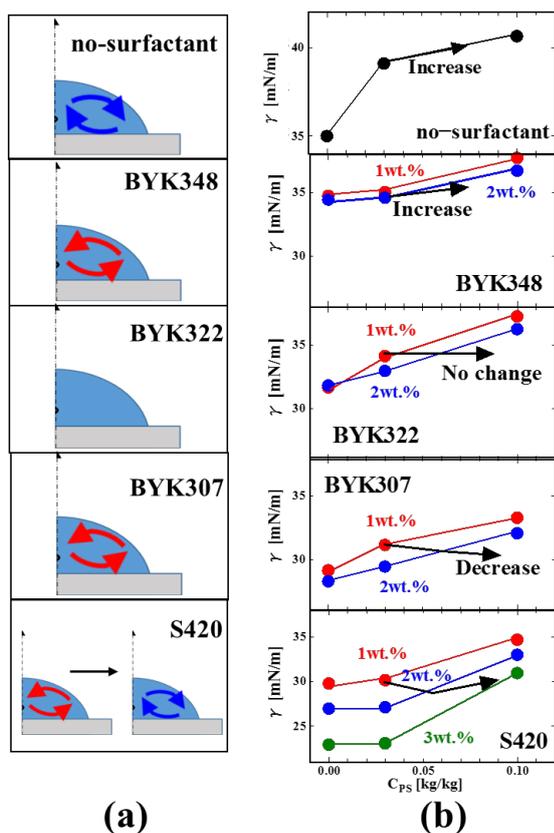


Figure 7 (a) The state of convection inside the droplet in the evaporation process containing 1 wt.% surfactant (b) The polystyrene concentration dependency of the surface tension of the solution containing 1,2 wt.% Surfactant

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