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Effect of Solute- and Solvent-Derived Marangoni Flows on the Shape of Polymer Films Formed from Drying Droplets

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Significance

The effects of mixed solvents on the shape of films formed on a hydrophilic surface from polymer solute droplets were investigated experimentally. The film shape depended on the two solvents used, and the mixing ratio. It was also found that the flow direction was dominated by solute-derived rather than solvent-derived Marangoni flows. Consequently, the changes in the shape of the film could not be explained only by the Marangoni flow direction.

Keywords: polymer film, inkjet, mixed solvent, Marangoni effect

Introduction

In recent years, much effort has been dedicated to turning inkjet printing into a versatile tool for various manufacturing processes, to produce items such as light emitting devices and polymer electroluminescent devices. The efficacy of inkjet printing for the production of these electronic devices results from its ability to produce uniform films after evaporation.[1,2]

Some pairs of binary solvents have been reported to produce more uniform films.[3–6] The authors believed that the changes in these films resulted from the surface flow generated by solvent-derived Marangoni forces. In their experiments, however, the film shape was related to the receding distance before self-pinning. The same results were obtained even when single solvents were used because of viscous effects.[7,8] Kaneda et al.[9] demonstrated that the solvent-derived Marangoni flow would have terminated in a very short time for the solvent pair investigated by De Gans and Schubert.[3]

With increasing viscosity or contact angle, or decreasing evaporation rate, the film shape typically shifts from ring-like to dot-like, via a flat film. To determine the essential reasons why binary solvents change the film shape, it is necessary to prove that these factors have little effect on changes in the film shape. Unfortunately, past studies did not show such proof. In this study, a droplet was deposited on a circular patterned surface to fix the film diameter. The internal flow patterns in the droplets were observed experimentally to determine how they affected the film shape and to investigate the Marangoni effects.

Experimental Methods

Polystyrene (Acros Organic, average molecular weight 2,50,000 g/mol) was used as a solute. The physical properties of the prepared solvents are shown in Table 1. An homogeneous perfluorohexylethyltrimethoxysilane [$CF_3(CF_2)_5CH_2CH_2Si(OCH_3)_3$] monolayer was first prepared as a silicon surface, using a chemical vapor adsorption method. Patterned organosilane monolayers were fabricated via irradiation with VUV light ($\lambda = 172$ nm) through a photomask with 300 μm-diameter circular holes, to form Si—OH residues on the surface.[10] Using this method, 300 μm-diameter circular hydrophilic Si—OH surfaces were arranged on a hydrophobic surface at 300 μm edge-to-edge intervals. Before the experiments, the substrate was treated with an isopropanol/water solution to remove any contamination and then dried under air flow. A volume of 2.0 ± 0.3 nL of the solution was ejected toward the center of the circular hydrophilic surface, using a dispenser (Nano Master SMP-III, Musashi Engineering), to cover only the hydrophilic surface. Two CCD cameras (30 fps) were used to record the drying droplet, giving side and bottom views. All experiments were carried out at 25 ± 1°C and atmospheric pressure.

Results and Discussions

Film shape

Figure 1 shows the profile of a typical film; the profile was measured using a laser microscope (VK-8500, Keyence). The average film thickness (h_{av}) and the difference between

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Table 1. Physical Properties of Solvents at 298 K and 101.3 kPa

	Symbol	Boiling Point (K)	Surface Tension (mN/m)	Viscosity (mPa·s)	Density (g/cm^3)	Molar Weight (g/mol)
m-xylene	Xy	412.3	28.1	0.581	0.86	106.17
Isopentyl acetate	iPA	415.3	24.2	0.789	0.866	130.18
3-methylpyridine	TMP	417.3	34.5	0.872	0.953	93.13
Anisole	Ani	426.8	34.6	0.984	0.989	108.14
Mesitylene	Mes	437.9	28.3	1.039	0.861	120.9
Acetophenone	AP	475.2	38.8	1.66	1.023	120.15
Tetralin	Tet	480.8	34.5	2.14	0.966	132.20
Cyclohexylbenzene	CHB	512.2	34.1	2.41	0.95	160.26

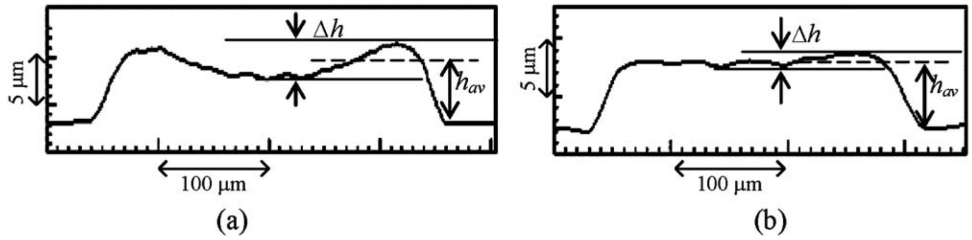

Figure 1. Profile of a typical ring and flat film for AP/Tet at $c_{A0} = 5$ wt %. (a) $\omega_{LB0} = 0$ wt % ($\Delta h/h_{av} = 0.57$) and (b) $\omega_{LB0} = 50$ wt % ($\Delta h/h_{av} = 0.21$).

the minimum and maximum thickness (Δh) were measured from the profile. The film shape became uniform as $\Delta h/h_{av}$ decreased. Table 2 shows the average values and errors for $\Delta h/h_{av}$ calculated from the results of three experiments at an initial solute concentration (c_{A0}) of 5 wt %. ω_{LB0} is the mass fraction of the lower-boiling-point solvent. For all of the solvent pairs, the $\Delta h/h_{av}$ values were smaller with $\omega_{LB0} = 50$ and 80 wt %, especially for Xylene(Xy)/Cyclohexylbenzene(CHB) and Anisole(Ani)/CHB.

As mentioned earlier, the film shape generally depends on the contact angle, viscosity, and evaporation rate. The measured properties of each mixed solvent were roughly linear with ω_{LB} (results not shown here). The film shape was correlated with the viscosity and contact angle under other experimental conditions; it was, therefore, concluded that these properties dominated the film shape in previous study.[8] However, the results shown in Table 2 could not be explained by such linear relationships between these properties and ω_{LB0}. Consequently, it is likely that the changes in the film shape were influenced by Marangoni flows.

For $c_{A0} = 1$–3 wt %, the film shapes were clearly ring-like and independent of ω_{LB0} (results not shown here). In this range, viscous effects were expected to dominate the film shape.

Effects of Marangoni flows

The solvent- and solute-derived Marangoni flows inside the droplet were investigated using a visualization method reported by Kaneda et al.[11] Inward surface flow was found at $c_{A0} = 0$ (Figure 2a), whereas outward surface flow was found at $c_{A0} = 5$ wt % (Figure 2b). The average particle velocity in the dotted area in Figure 2 was measured using the method reported by Kaneda et al.[11] The time variation of the measured velocity u_{center} is plotted in Figure 3 for $\omega_{LB0} = 50$ wt %. Positive and negative values of u_{center} indicated outward surface flow and inward surface flow, respectively. A comparison between these figures revealed that the solute changed flow direction for AP/Tet and Ani/CHB. The concentration of the higher-boiling-point solvent became higher near the contact line than at the apex; it was consequently determined that solvent-derived forces induced an inward surface flow when $\Delta\sigma < 0$ (Table 2) and induced a flow in the opposite direction when $\Delta\sigma > 0$. In light of this, the experimentally observed flow directions were reasonable. In contrast, outward surface flows were found for all of the mixtures at $c_{A0} = 5$ wt %, because the flow was dominated by solute-derived Marangoni flow. In the present system, polystyrene increased the surface tension of the solvents. u_{center} was initially negative for AP/Tet and Ani/CHB at $c_{A0} = 5$wt %, because the

Table 2. Experimental $\Delta h/h_{av}$ at $c_{A0} = 5$ wt % ($\Delta\sigma = \Delta\sigma_{HB} - \Delta\sigma_{LB}$ for no Solute. HB = Higher-boiling-point Solvent, LB = Lower-boiling-point Solvent)

	ω_{LB0} (wt %)					
	0	20	50	80	100	$\Delta\sigma$ (mN/m)
Ani/Mes	0.62 ± 0.02	0.60 ± 0.01	0.14 ± 0.03	0.24 ± 0.02	0.60 ± 0.02	−6.3
AP/Tet	0.60 ± 0.03	0.62 ± 0.02	0.20 ± 0.02	0.22 ± 0.01	0.62 ± 0.02	−4.3
Ani/CHB	0.40 ± 0.02	0.15 ± 0.01	0.05 ± 0.02	0.03 ± 0.02	0.60 ± 0.02	−0.5
Xy/CHB	0.40 ± 0.02	0.20 ± 0.02	0.04 ± 0.02	0.05 ± 0.03	0.61 ± 0.02	6.0
iPA/TMP	0.72 ± 0.02	0.70 ± 0.02	0.68 ± 0.02	0.68 ± 0.02	0.77 ± 0.01	10.3
Mes/AP	0.64 ± 0.03	0.63 ± 0.03	0.59 ± 0.01	0.56 ± 0.04	0.62 ± 0.02	10.5

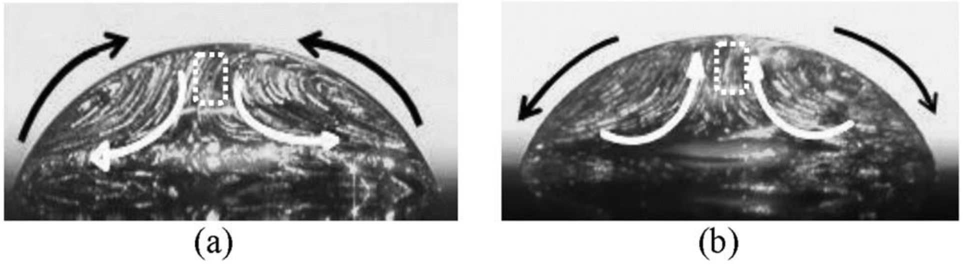

Figure 2. Visualized flow patterns for AP/Tet ($\omega_{AP} = 50$ wt %). (a) $c_{Ao} = 0$ wt % (50–100 s) and (b) $c_{Ao} = 5$ wt % (100–150 s).

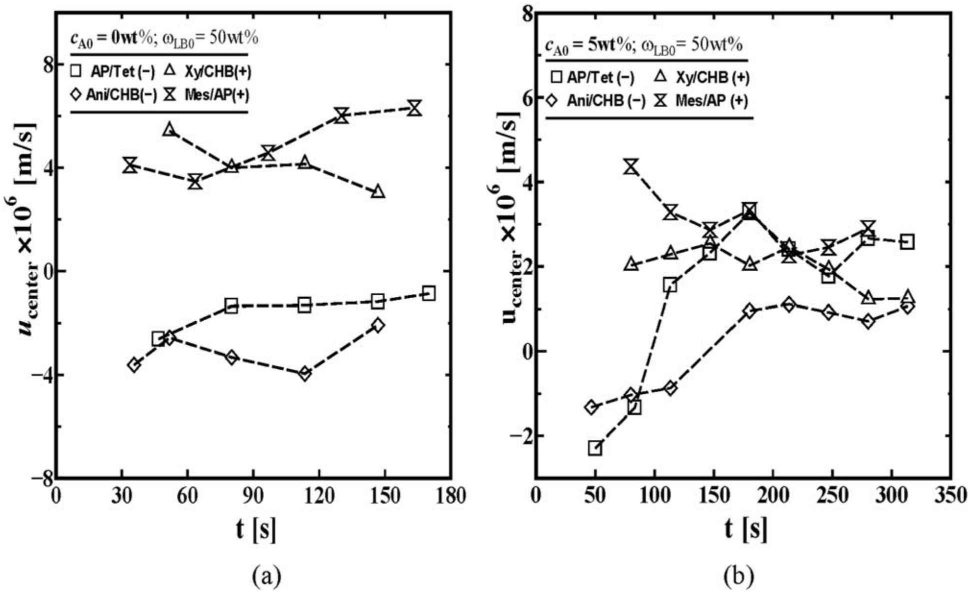

Figure 3. Time variation of the particle velocity in the central region of the droplet. (a) $c_{Ao} = 0$ wt % and $\omega_{LBo} = 50$ wt % and (b) $c_{Ao} = 5$ wt % and $\omega_{LBo} = 50$ wt %.

solute concentration gradient along the free surface was not fully developed. It should be noted that the initial stages (i.e., the first 100–150 s) are short compared with the time taken for the whole drying process ($\approx$ 5000 s).

The visualizations demonstrated that the flow direction resulting from the Marangoni flow was different from that predicted from the $\Delta\sigma$ values of the solvents when $\Delta\sigma < 0$. If only solute-driven Marangoni flows were considered, the surface flows would be expected to be directed outwards for all of the solutions studied here. The results showing that $\Delta h/h_{av}$ (see Table 2) was smaller for the first four solutions (not solvents) than for the last two solutions were not related to the direction of the surface flow. If the initial flow pattern shown in Figure 3b is assumed to be important, the decrease in $\Delta h/h_{av}$ for Xy/CHB cannot be explained by the flow direction. Consequently, it was concluded that the decrease in $\Delta h/h_{av}$ was not related only to the flow directions predicted from the differences between the surface tensions of the solutions (although some past studies have argued for the importance of the flow direction in mixed solvents).

It is noted here that the contact angle observed in the visualizations (66–71°) was necessarily larger than that determined in the experiments (26–32°) investigating the film shape. It is predicted numerically by Yoshitake et al.[12] and Yasumatsu et al.[13] that the internal flow becomes violent and complicated with decreasing contact angle (although it should be noted that their calculations were for single solvents). Because violent flows can significantly affect the transportation of solutes, further discussion of the transport phenomena in droplets is required to clarify the factors essential for changes in the film shape.

The fluid dynamics in evaporating sessile droplets have been studied previously.[14–17] There have also been several numerical studies considering the thermal Marangoni forces.[18–21] However, these past reports targeted single solvents. Numerical approaches for binary solvents are required to discuss the effects of the fluid dynamics on the shape of the formed film in detail.

Acknowledgments

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