Dot formation kinetics induced by Marangoni flow in the drying process of polymer solution drop

Dept. of Applied Physics, The Univ. of Tokyo Tatsuya Yamaue[1], Jung Youngki and Masao Doi

高分子液滴の乾燥過程と乾燥後のドット形状の制御はインクジェット印刷の重要な課題である。ここでは、蒸発速度の非常に異なるアニソール/エチルアセテートの混合溶媒とポリスチレン溶質の高分子液滴の乾燥過程と乾燥後のドット形状を計測し、ドット形状の中央の凹みが最小となる混合比が存在することを観測した。外交流と温度マランゴニ流の競合モデルを用いたマランゴニ効果を含む液滴の乾燥過程での溶質濃度分布とドット形状の解析結果と合わせて実験結果を考察する。

How to control the shape of the solute deposit in the drying process of a polymer solution drop on a substrate is an important problem in the ink-jet printing. In the case of dilute solution, a commonly observed phenomena is the "co ee stain" : the evaporation of solvent induces an outward ow and creates a ring-like deposit after drying. [1] The outward ow is a result of the combined action of the increased evaporation rate at the droplet edge, and contact line pinning caused by solute deposition near the edge.(self-pinning) [2] De Gans et.al. showed that when a polymer solution is dried on a glass slide coated with hydrophobic materials, it leaves a small dot after the evaporation. [3] They observed that the dots have small dimple in the center, the size of which can be changed by solvent. They, however, did not conduct any quantitative study for the phenomena.

In previous works, we have studied the shape change and contact line motion in drying process of polystyrene-anosile polymer solution drops about $100\mu m$ radius placed on a hydrophobic substrate, and shown that the shape of the nal polymer deposit changes from concave dot for dilute cases, to at dot for $5wt\%$ initial density case, and then to concave dot again in dense cases by the gradual transition from the solute piling mechanism proposed by Deegan et.al. to the crust buckling mechanism proposed by de Gennes and Pauchard. [5]

Here, we studied the shape change, ow and contact line motion in drying process of polystyrene polymer solution drops having anisole(low volatile)/etylacetate(high volatile) mixed solvents, whose evaporation rates are quite di erent. The drying process takes place in three stages. First, the droplet evaporates keeping the contact line xed. Second the droplet shrinks

[1]E-mail: yamaue@rheo.t.u-tokyo.ac.jp

with receding contact line. Finally the contact line pinned again by self-pinning, and the droplet starts to be deformed. As the mixed ratio of etylacetate increases from pure anisole in the initial density $0.5wt\%$ case, the dimple of the final polymer deposit decreases, and the shape becomes flat, when anisole/etylacetate mixting ratio is about 60/40. This change is considered to be caused by the temperature Marangoni flow induced by high volatile solvent conponent. In the other hand, the mixed ratio of etylacetate increases between 60% and 80%, the dimple of the final polymer deposit increases again. This change is considered to be caused by increasing of the outward flow induced by high volatile solvent. When the mixed ratio of etylacetate is about 90%, both a ring-like deposit and a dot-like deposit in it can be observed together.

We analyze and simulate the flow of polymer solute in the evaporation process of polymer solution drops using the competetion model of the Marangoni flow and the outward flow, each model is based on Hu-Larson model [6].

Acknowledgment

The authors acknowledge the support from the Japan Science and Technology Agency (CREST-JST).

References

[1] R. D. Deegan, et. al. : Nature **389**, 827 (1997) : Phys. Rev. **E62**, 756 (2000) : Phys. Rev. **E61**, 475 (2000).

[2] M. D. Haw, M. Gillie and W. C. Poon, Langmuir **18**, 1620 (2002).

[3] B. J. de Gans and U. S. Schubert : Langmuir **20**, 7789 (2004).

[4] L. Pauchard, et. al. : Europhys. Lett **62**, 897 (2003) : Phys. Rev. **E68**, 052801 (2003) : Langmuir **20**, 5138 (2004).

[5] T. Kajiya, E. Nishitani,T. Yamaue,M. Doi : Phys. Rev. **E73**, 11601 (2006).

[6] H. Hu and R. G. Larson : Langmuir **21**, 3963 (2005) : Langmuir **21**, 3972 (2005).