Finite Element Simulation of the Drying and Deformation Process of Polymer Solution Droplet on Substrates Using ALE Method

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In the drying process of polymer solution droplets on substrates, some coupling effects of several phenomena such as contact line receding, surface skin formation by viscosity change, gelation of contact line (self-pinning) and outward flow in a droplet, are important. For a droplet having large contact angle, the lubrication approximation for thin films cannot be applied. Here, we have made the finite element simulation for a drying polymer solution droplet having 90 degree contact angle on a substrate using ALE (Arbitrary-Lagrangian-Eulerian) moving boundary method with experimentally measured rheological and transformation properties of polystyrene/anisole polymer solution and solved the contact line receding, outward flow by surface tension, solute distribution, and the buckling of a surface skin, which reproduces the experimentally observed results.

1. Introduction

How to control the shape of the solute deposit in the drying process of a polymer solution droplet on a substrate is an important problem in the ink-jet printing.

In the case of dilute solution, commonly observed phenomenon is the "coffee stain"[1]: the evaporation of solvent induces an outward flow and creates a ring-like deposit after drying.

De Gans and Schubert showed that when a polymer solution is dried on a glass slide coated with hydrophobic materials, it leaves a small dot after the evaporation by the receding motion of contact line related to delaying of self-pinning.[2]

In the previous paper, we have experimentally shown that the drying process generally takes place in three stages.[3] In the first stage, the droplet radius remains constant, i.e., the contact line is pinned. This first pinning is considered to be the same as the usual pinning of fluid droplet on substrate caused by the irregularities or defects on the substrate. In the first stage, while the droplet radius remains constant, the contact angle keeps decreasing. In the second stage, when the contact angle reaches to a receding contact angle, the droplet starts to shrink with a receding contact angle. In the third stage, the contact line becomes pinned again. This second pinning is considered to be the self-pinning: the polymer concentration near the edge becomes so high that

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the solution at the edge loses the mobility.

The shape of the final polymer deposit, changes from concave dot for dilute cases, to flat dot for 5wt% initial density case, and then to concave dot again in dense cases with the increase of the initial polymer concentration for a polystyrene/anisole polymer solution droplet.[3] We have made a conclusion that this shape change is caused by the gradual transition from the solute piling mechanism by an outward flow proposed by Deegan et al. to the crust buckling mechanism by a skin formation proposed by de Gennes and Pauchard.[4-6]

In these evaporation process, understanding of the solute distribution is important. During the contact line receding in the second step, the solute becomes rich on surface and diffuse in the inner direction of a droplet, which decides the solute distribution in self-pinning time and the pinning radius itself. After the self-pinning, the outward flow from the center to the edge in a droplet becomes important. The solute distribution in the self-pinning time and the outward flow with the viscosity change make the solute distribution and skin formation on the surface in the third stage, which decide the final stain shape.

In order to clarify the solute distribution and the mechanism of stain formation, numerical studies are effective. Numerical studies of the distribution of the film thickness in the drying process of polymer solution have been made using the lubrication approximation for thin films. In these studies, the vertical solute distribution are assumed to be uniform according to the sense of the lubrication approximation and only horizontal flow and horizontal distribution of thickness are analyzed.[7, 8] Simulation studies of the drying polymer solution droplet have been also made using the lubrication approximation, which is applicable for thin droplets having small contact angle on hydrophilic substrates, where the outward flow and the shape of ‘coffee stain’ are calculated.[9-11]

In the analysis of a droplet having large contact angle, both the outward flow by surface tension which makes ‘coffee stain’ and the vertical solute distribution which decides the skin formation becomes important. In such cases, we need to make full simulation both of flow field and solute distribution. Full finite element analysis for leveling of a drying polymer/solvent film with the viscosity change depending on solute distribution has been done.[12] Hu and Larson have made both a detailed numerical study using the finite element method and a analytical solution by the lubrication approximation for the outward flow of a drying spherical droplet of pure solvent. They assume a spherical shape and don’t solve the surface tension in detail, which shows a fast algorithm to solve the outward flow of a spherical droplet.[13] However, the drying process of a polymer solution droplet on substrate having large contact angle has not been solved.

In this paper, in order to clarify the mechanism of these stain formation, we construct a full finite element simulation to solve the surface tension flow, the flow and diffusion of solute, the ther-
nal flow and diffusion, and the surface deformation by the ALE (Arbitrary-Lagrangian-Eulerian) method. Using this simulation, three steps in the evaporation process of a polymer solution droplet on substrate having large contact angle are solved using actual rheological and transformation properties of a polystyrene/anisole solution: the solute distribution in the contact line receding process before the self-pinning, the outward flow by surface tension with the viscosity change and the solute distribution after the self-pinning, and the elastic buckling process and the shape of a dot after skin formation on droplet surface.

II. BASIC EQUATIONS AND SIMULATION METHOD

A droplet on a substrate is described by a two-dimensional triangular lattice.

A droplet surface deforms by the flow due to the solvent evaporation and the surface tension. The moving velocity \( \mathbf{V}(\mathbf{x}) \) at a position \( \mathbf{x} \) on an evaporating surface is described as follows, which means the conservation law of solvent.

\[
\mathbf{V}(\mathbf{x}) \cdot \mathbf{n}(\mathbf{x}) = \mathbf{v}(\mathbf{x}) \cdot \mathbf{n}(\mathbf{x}) - j(\phi(\mathbf{x})) \tag{1}
\]

where \( \mathbf{n}(\mathbf{x}) \) denotes the normal unit vector of the surface, \( \mathbf{v}(\mathbf{x}) \) the flow velocity and \( j(\phi) \) the evaporation rate of solvent depending on the volume fraction of polymer \( \phi \) at a position \( \mathbf{x} \) on a surface of droplet.

Grid points on a droplet surface are moved according to the normal velocity \( \mathbf{V} \cdot \mathbf{n} \), and ones in a droplet are moved by ALE (Arbitrary-Lagrangian-Eulerian) method which deforms the triangular lattice of a droplet as an elastic media having the neo-Hookean constitutive equation. The deformed shape of triangular lattice is solved by the elastic force balance equation under the Dirichlet's boundary condition of the moving surface eq.(1), as follows.

\[
\frac{\delta}{\delta \mathbf{x}} \mathbf{W} = 2 \frac{\partial X_i}{\partial x_j} \frac{\delta}{\delta x_j} \left( \frac{\partial X_i}{\partial x_j} \right) = 0 \tag{2}
\]

where \( \mathbf{W} \) is the Finger strain tensor defined as \( W_{ij} = \partial X_i / \partial x_k \cdot \partial X_j / \partial x_k \), where \( \mathbf{X} \) denotes the reference position defined by the initial shape and \( \mathbf{x} \) denotes the deformed position depending on time \( t \).

The ALE method describes all partial differential equations by the reference coordinates \( \mathbf{X} \) defined by the initial shape and solves fields on the reference coordinates \( \mathbf{X} \). A differential operator \( \partial f(\mathbf{x}) / \partial x_i \) is solved as \( \partial X_j / \partial x_i \cdot \partial f(\mathbf{X}) / \partial X_j \) using the deformation gradient tensor \( \partial X_i / \partial x_j \) of grid points (Jacobi's matrix), which is stable even for large deformed shape. Here, basic equations are explained using the deformed coordinate \( \mathbf{x} \) as follows. Flow field is solved by the Navier-Stokes
equation for a Newtonian fluid without the inertial term under the incompressibility condition,

$$\rho \frac{\partial \mathbf{v}}{\partial t} = \nabla \cdot \left\{ -p \mathbf{I} + \eta(\phi) \left( \nabla \mathbf{v} + (\nabla \mathbf{v})^T \right) \right\}$$  \hspace{1cm} (3)

$$\nabla \cdot \mathbf{v} = 0$$  \hspace{1cm} (4)

where $p$ denotes the pressure and $\eta(\phi)$ the viscosity depending on the volume fraction of polymer $\phi$. The Navier-Stokes equation is solved by the finite element method using Galerkin method on the linear interpolation triangle elements, and the predictor-corrector method is used for the explicit time evolution. Solving the predictor velocity, the surface tension force $\mathbf{f} = \gamma \partial \mathbf{t} / \partial s$ is applied to fluid on surface edge elements of a droplet, where $\gamma$ denotes the surface tension, $\mathbf{t}$ a tangent unit vector of the surface and $s$ a length of droplet surface.

The distribution of solute is solved by the flow and diffusion equation,

$$\frac{\partial \phi}{\partial t} = -\nabla \cdot \left( \phi \left( \mathbf{v} - \frac{d\mathbf{x}}{dt} \right) \right) + \nabla \cdot (D(\phi) \nabla \phi)$$  \hspace{1cm} (5)

where $D(\phi)$ denotes the collective diffusion coefficient of solute depending on the volume fraction of polymer $\phi$ and $d\mathbf{x}/dt$ the deformation velocity of a grid point. The Neumann’s boundary condition of the volume fraction of polymer on an evaporating surface is described as follows, which means the conservation law of solute.

$$D(\phi)(\nabla \phi) \cdot \mathbf{n} = \phi \left( \mathbf{v} - \mathbf{V} \right) \cdot \mathbf{n} = \phi j(\phi)$$  \hspace{1cm} (6)

On the substrate, there is no solute flux : $D(\phi)(\nabla \phi) \cdot \mathbf{n} = 0$. The flow and diffusion equation is also solved using the explicit time evolution by the finite element method using Galerkin method on the linear interpolation triangle elements.

According to a simple one-dimensional model, the evaporation rate $j(\phi)$ is described by

$$j(\phi) = \frac{D_g}{l} \left( c(\phi) - c_a \right).$$  \hspace{1cm} (7)

where $D_g$ is the gas diffusion coefficient of solvent, $l$ the thickness of diffusion layer of solvent gas in the gas region, $c(\phi)$ the partial concentration of solvent gas on evaporation surface and $c_a$ the atmosphere concentration of solvent gas. On the evaporation surface, the chemical potential of the polymer solution and the solvent gas is balanced by the local equilibrium condition of liquid-gas interface, which is described using the Flory-Huggins model for the polymer solution as follows,

$$\ln \frac{c(\phi)}{c_0} = \ln(1 - \phi) + \phi + \chi \phi^2$$  \hspace{1cm} (8)

which leads

$$c(\phi) = c_0(1 - \phi) \exp(\phi + \chi \phi^2)$$  \hspace{1cm} (9)
where $c_0$ is the saturated concentration of pure solvent gas and $\chi$ is the polymer-solvent interaction parameter. In the dilute limit of the polymer volume fraction, the Henry's law $c(\phi) = c_0(1 - \phi)$ is given. In this paper, the temperature dependence of the evaporation rate is ignored, the atmosphere concentration of solvent gas is assumed to be zero: $c_g = 0$ and only the $\phi$-dependence of it is considered in the dilute limit. Therefore, the following evaporation model is used in the simulation,

$$j(\phi) = j_0(1 - \phi)$$

(10)

where $j_0$ is the evaporation rate of pure solvent.

In the simulation, the Muffin simulator on the OCTA system (Open Computational Tools for Advanced Material Technology), which is freely distributed from http://octa.jp, is used by adding the functions of the boundary conditions and the ALE finite element method.

A droplet on a substrate having 90 degree contact angle (a half circle) is covered by 300 linear triangle elements, and the two dimensional simulation is done using the linear approximation of triangle elements. A linear matrix is solved by CG method.

III. SOLUTION PROPERTIES AND INPUT PARAMETERS

Three cases of a polymer solution droplet, which have the uniform polymer distribution initially with the initial polymer volume fraction $\phi_0 = 0.01, 0.05, 0.1$, are simulated with the mass density of polymer solution $\rho = 10^3$[kg/m$^3$], the initial radius of droplet $R_0 = 0.5 \times 10^{-4}$[m], the surface tension $\gamma = 3 \times 10^{-2}$[N/m], the specific heat $C_p = 2000$[J/kg K], the thermal diffusion coefficient $k_B = 0.1$[J/sec m K], and the latent heat $L = 5 \times 10^8$[J/kg]. The equilibrium and receding contact angle before the self-pinning is assumed to be 90 degree. Actual transformation and rheological properties are measured for a polystyrene (Sigma-Aldrich, $M_w = 280,000$) / anisole (Sigma-Aldrich, the boiling point $T_{bp} \sim 425$ K) polymer solution.[14] The evaporation rate of pure solvent is experimentally measured as $j_0 = 1.0 \times 10^{-6}$[m/sec]. The viscosity change depending on the polymer volume fraction measured using a rheometer (MARS,HAAKE) is described as follows about between 0.1vol% and 30vol%.

$$\eta(\phi) = 6.6 \times 10^{-3} + 57.0\phi^{1.04}[\text{Pa sec}]$$

(11)

The intrinsic viscosity [$\eta$] is about 100, which means the critical volume fraction of polymer $\phi^*$ is about 0.01. The polymer volume fraction in the gelation point $\phi_g$ is about 0.3. The constant diffusion coefficient $D$ measured by the dynamic light scattering is $1.1 \times 10^{-11}$[m$^2$/sec] for between 1vol% and 5vol%.
Here, the non-dimensional parameters in the system are discussed. The Reynolds number \( \text{Re} \equiv \rho v R / \eta \) is about \( 10^{-2} \), in which we can ignore the inertial term of the Navier-Stokes equation and use the Stokes approximation. The capillary number \( \text{Ca} \equiv \eta v / \gamma \) is about \( 10^{-6} \) for dilute solutions and changes according to the viscosity change as shown in Fig.1. When the polymer volume fraction increases more than about 30vol\%, \( \text{Ca} \) becomes more than \( 10^{-4} \) and the leveling relaxation time becomes large, which makes the surface uneven. The Bond number \( \text{Bo} \equiv \rho g R^2 / \gamma \) is about \( 10^{-2} \),

![Graph showing the capillary number Ca dependence on the polymer volume fraction. Ca increases as the viscosity increases.]

in which we can assume the spherical shape of a droplet surface without gravity. The Peclet number \( \text{Pe} \equiv R j / D \) is about 10, which means the evaporation time and the solute diffusion time is competitive and the vertical solute distribution becomes important to describe the drying process.

**IV. SIMULATION RESULTS**

**A. Step 1: Receding process of contact line**

As the first step in the evaporation process of a polymer solution droplet having large contact angle. The receding process of contact line before the self-pinning is solved for the three kind of the initial polymer volume fraction \( \phi_0 = 0.01, 0.05, 0.1 \). The receding contact angle keeps 90 degree in the simulation.

Fig.2 shows the same initial shapes, whose radius is 50\( \mu \text{m} \), and the shapes at the self-pinning, in which the polymer volume fraction on the contact line is assumed to be 0.3. The droplet radius and the time at the self-pinning are 25\( \mu \text{m} \) and 26sec for \( \phi_0 = 0.01 \) (Fig.2(a)), 40\( \mu \text{m} \) and 11sec for \( \phi_0 = 0.05 \) (Fig.2(b)) and 45\( \mu \text{m} \) and 5sec for \( \phi_0 = 0.1 \) (Fig.2(c)). As the initial polymer density
becomes dilute, the self-pinning radius becomes small and the self-pinning time delays, which nicely reproduce the experimental results reported in ref.[3].

![Diagram of shape change](image)

**FIG. 2**: The shape change in the contact line receding step. The initial shapes ($R_0 = 50\mu m$) and the shapes and polymer distribution at the self-pinning where the polymer volume fraction on the contact line becomes 0.3 are shown. The droplet radius and the time at the self-pinning are 25\mu m and 26sec for $\phi_0 = 0.01$ (a), 40\mu m and 11sec for $\phi_0 = 0.05$ (b) and 45\mu m and 5sec for $\phi_0 = 0.1$ (c).

Fig.3 shows the time evolution of the density profile of polymer for $\phi_0 = 0.01$ (Fig.3(a)), $\phi_0 = 0.05$ (Fig.3(b)) and $\phi_0 = 0.1$ (Fig.3(c)). In the evaporation process, the polymer becomes rich on the evaporating surfaces and diffuse to the inner region of a droplet. The polymer density in inner region of a droplet is still dilute, when the initial polymer volume fraction is dilute ($\phi_0 = 0.01$), however the size of a droplet becomes smallest in the case at the self-pinning time.

![Graphs of density profile](image)

**FIG. 3**: The time evolution of the density profile of polymer in the contact line receding step for $\phi_0 = 0.01$ (a), $\phi_0 = 0.05$ (b) and $\phi_0 = 0.1$ (c).
FIG. 4: The shape change in the solute gathering step after the self-pinning by the outward flow. The droplet shape, the outward flow (arrow) and the polymer distribution (contour) of the dilute polymer solution droplet $\phi_0 = 0.01$, at just after the self-pinning (upper figure) and those at 5sec later than the self-pinning (lower figure) are shown.

FIG. 5: The shape change in the solute gathering step after the self-pinning by the outward flow. The droplet shape, the outward flow (arrow) and the polymer distribution (contour) of the middle density polymer solution droplet $\phi_0 = 0.05$, at just after the self-pinning (upper figure) and those at 5sec later than the self-pinning (lower figure) are shown.

B. Step 2: Outward flow after self-pinning

Fig. 4 shows the droplet shape, the outward flow (arrow) and the polymer distribution (contour) of the dilute polymer solution droplet $\phi_0 = 0.01$, at just after the self-pinning (upper figure) and those at 5sec later than the self-pinning (lower figure). The viscosity change depending on the
polymer volume fraction is considered in these calculation.

The outward flow is large due to low viscosity, and the polymer becomes very rich near the contact line, while the dense polymer layer is very thin and poor on the top of the droplet. These results show that there is no skin formation on the top of droplet surface and the ring-like stain (coffee stain) is created on the contact line for the dilute solution droplet, which nicely agree with the experimental results shown in ref.[3].

Fig.5 shows the results of the middle density polymer solution droplet $\phi_0 = 0.05$. The outward flow is fast at the beginning, but decreases in the evaporation process as the viscosity increases and the evaporation rate decreases by the increasing surface polymer density. While the viscosity increases, the shape of the droplet surface keeps a spherical shape. The polymer rich layer near the contact line becomes thinner than that of the dilute case, but on the top of the droplet surface, the polymer layer becomes thicker than that of the dilute case. These results show that the polymer distribution becomes uniform and the shape of stain change from the ring-like shape to the flat shape by the increasing viscosity as the initial polymer volume fraction increases.

Fig.6 shows the results of the dense polymer solution droplet $\phi_0 = 0.1$. The outward flow is very small by the very high viscosity and the low evaporation rate due to the rich polymer layer on the droplet surface. High viscosity makes the capillary number large and the leveling relaxation time becomes long, which made the surface uneven from the spherical shape shown in the lower figure of
Fig. 6. The dense polymer layer is created on all of the droplet surface. The thickness of the dense polymer layer is large near the contact line, but it is still large on the top of droplet surface.

These results of the initial polymer density and the viscosity change dependency of the outward flow and the polymer distribution on the droplet surface, which decides the shapes of stain after evaporation, qualitatively reproduce the experimental results of changing of stain shapes reported in ref.[3].

C. Step 3 : Elastic buckling after skin formation

![Diagram showing elastic buckling process](image)

FIG. 7: The elastic buckling process of the drying dense polymer solution droplet \( \phi_0 = 0.1 \) having elastic skin. The thickness of the surface skin is 5% of the radius on the top of the droplet and 10% of it on the contact line. We assume the Poisson ratio to be 0.495. The droplet shape and the strain energy on surface membrane (contour) are shown for the negative pressure in a droplet : \( 0.001 \times G \) (\( G \) denotes the shear modulus of the membrane) (a), \( 0.05 \times G \) (b), \( 0.1 \times G \) (c), \( 0.15 \times G \) (d), \( 0.175 \times G \) (e) and \( 0.2 \times G \) (f).

In the dense polymer solution droplet \( \phi_0 = 0.1 \), we can observe the dense polymer layer on all of the droplet surface shown in the lower figure of Fig. 6. Actually, in such a high polymer density, the dense polymer layer becomes a gel membrane and has elasticity.

Here, we make an elastic membrane on the droplet surface according to the thickness distribution of skin layer given by the density profile of polymer solved in the step 2, and continue to simulate
the evaporation process of a droplet having an elastic membrane on the surface using the linear elasticity model with the geometrical non-linearity. [15, 16]

The thickness of the surface skin is 5% of the radius on the top of the droplet and 10% of it on the contact line. We assume the Poisson ratio to be 0.495. Fig.7 shows the buckling process of the drying droplet having elastic skin. Each figure of Fig.7 show the droplet shape and the strain energy on surface membrane (contour), in which the negative pressure in a droplet becomes $0.001 \times G (G$ denotes the shear modulus of the membrane) (a), $0.05 \times G$ (b), $0.1 \times G$ (c), $0.15 \times G$ (d), $0.175 \times G$ (e) and $0.2 \times G$ (f).

In this case, both the top and side of the droplet buckle and this buckling mode agree with the experimental results of the high density polystyrene / anisole droplet shown in ref.[3].

V. CONCLUSION

The finite element simulation using ALE moving boundary method has been done for the drying process of the polymer solution droplet having large contact angle and three kind of the initial polymer density for the three separated steps: the contact line receding step, the solute gathering step by the outward flow after the self-pinning, and the elastic buckling step for high density solution: using the actual solution properties of polystyrene / anisole polymer solution droplets.

In the simulation, the flow field with surface tension, flow and diffusion of polymer, the temperature distribution, the contact line slip and the surface deformation are calculated under the evaporating boundary condition.

Results reproduce the polymer density dependency of the self-pinning radius and the self-pinning time in the contact line receding step and the polymer distribution both on the contact line and the top of a droplet, which depend on both the changing viscosity (polymer density) and the outward flow, in the the solute gathering step. The dilute solution shows the ring-like polymer distribution, and the middle dense solution shows the uniform polymer distribution which makes the stain flat.

In the high density solution, the elastic membrane is assumed on the droplet surface and the elastic buckling mode is solved. Results agree the experimental and theoretical results of the buckling mode.

We wish the work of the drying process simulation using the actual solution properties becomes a primitive step forward to the computer aided engineering design (CAE) of the micro liquid process, such as the ink-jet printing process, for controlling the drying process to make required stain shapes of polymer solution droplets.
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