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Diffusion Process during Drying to Cause the Skin Formation in Polymer Solutions

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We discuss the diffusion process of polymers in polymer solution undergoing evaporation of the solvent at the free surface, and obtain a diffusion-type equation with a moving boundary condition in one dimension. Taking into account the effect of gelation (or solidification) of the solution, we carry out numerical simulations of the one-dimensional model. Based on the numerical results, we present a detailed description of the condition related to the “skin” formation due to the surface gelation. Furthermore, we also show that the drying dynamics of polymer solutions is strongly related to a gelation, which causes a great increase of diffusion coefficient of polymers. [DOI: 10.1143/JJAP.45.8817]

KEYWORDS: polymer solution, skin formation, evaporation, gelation, ink-jet

1. Introduction

The drying of polymer solutions is an important process which is considered to be the key technologies in painting, coating^{1,2)} and production of electronic-devices.^{3,4)} It is a desired technology to make the electronic devices using ink-jet printing, for example. An important though difficult problem is how to control the drying processes. It is often observed that there are inhomogeneities such as wrinkles and cracks in polymer films which are created as deposits of polymers in the drying processes. These inhomogeneities are seldom desired in many applications. Figure 1 shows the observation of deposits on a substrate for different drying conditions. This implies that the drying condition affects the roughness of the films. Since the buckling of “skin” layer which is a gel phase formed at the free surface of polymer solution due to the evaporation of solvent causes the inhomogeneities, it is important to understand the skin formation in polymer solutions under the solvent evaporation.^{5–8)}

Numerical investigations of drying have been performed by Yamamoto⁹⁾ using a dissipative particle dynamics model. He performed simulation taking into account, explicitly, the interactions between particles of solvent, solute and vapor. Tsige and Grest¹⁰⁾ have carried out molecular dynamics simulations and they reported skin formation in the evaporation process of polymer films. However, they have not discussed the restriction for the skin formation related to practical experiments.

De Gennes has discussed theoretically formation and rupture of the crust which is similar to the skin.¹¹⁾ Although his qualitative argument gives some important features of the crust, we cannot obtain detailed information about the whole process of the crust formation.

In the previous paper,¹²⁾ we have discussed the dynamics of film formation from a droplet on a substrate within the framework of the lubrication theory. In that model the concentration of polymers is passively transported by the hydrodynamical flow and the diffusion of the concentration is ignored. In this paper we concentrate our efforts on studying the diffusion process in the skin formation. We carry out a numerical simulation using a simple model based

on the two-fluid model and discuss the relevant parameters to the skin formation.

2. Model

2.1 Basic equations

The coupling between the stress field and the diffusion was first noticed and studied by Brochard and de Gennes for polymer solutions.¹³⁾ Doi and Onuki have derived general diffusion equations including the dynamic coupling between stress and composition, using the two fluid model.¹⁴⁾ The viscoelastic effect on diffusion has mainly been argued in these studies. Here we apply the two fluid model to the drying phenomenon of the polymer solution without the effect of the stress.

We consider the drying of a solution placed on a flat solid surface. It is assumed that evaporation occurs uniformly on the free surface which is perpendicular to z -axis. Then the system can be regarded as one dimensional. Figure 2(a) shows the schematic representation of our system at $t = 0$ and Fig. 2(b) at some time t . A initial distribution of ϕ sets uniform at a constant ϕ_i as shown in Fig. 2(a). When skin layer forms, the profile of the volume fraction is assumed to be like Fig. 2(b).

In the two fluid model the dynamics of polymer solutions is described by the velocity of polymers v_p , that of solvent v_s , and the volume fraction of polymers ϕ . In the present situation these variables are functions of the coordinate z and time t .

The mass conservation law gives time-evolution equation of ϕ as

$$\frac{\partial \phi}{\partial t} = - \frac{\partial(\phi v_p)}{\partial z}, \quad (1)$$

under the incompressibility condition,

$$\frac{\partial v}{\partial z} = 0, \quad (2)$$

of the average velocity

$$v(z, t) = \phi v_p(z, t) + (1 - \phi)v_s(z, t). \quad (3)$$

Here we choose $v(z, t) = 0$ as a solution of eq. (2) which is consistent with the boundary condition $v = 0$ at $z = 0$. The difference between the velocities v_p and v_s yields the frictional force which is balanced with the osmotic force.

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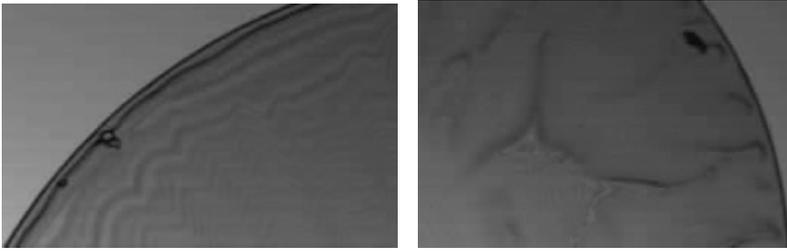


Fig. 1. Microscope images of the deposits from polystyrene solutions. The evaporation rate in the left figure is slower than that in the right figure. We can see many wrinkles on the free surface after drying in the right figure.

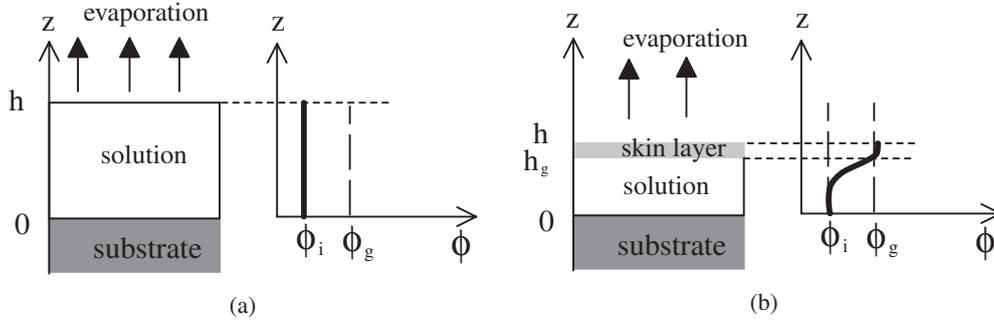


Fig. 2. Schematic representations of our system (left) and a profile of ϕ (right) for an initial situation (a) and a situation after skin formation (b).

This is expressed as

$$\zeta(\phi)(v_p - v_s) = -(1 - \phi) \frac{\partial \pi}{\partial \phi} \frac{\partial \phi}{\partial z}, \quad (4)$$

where $\pi(\phi)$ is the osmotic pressure and $\zeta(\phi)$ is the friction coefficient which depends on ϕ .

Then systems (1)–(4) can be reduced to the general diffusion equation as

$$\frac{\partial \phi}{\partial t} = \frac{\partial}{\partial z} \left[A(\phi) \frac{\partial \phi}{\partial z} \right], \quad (5)$$

where $A(\phi)$ denotes the diffusion coefficient given by

$$A(\phi) = \frac{(1 - \phi)^2 \phi}{\zeta(\phi)} \frac{\partial \pi}{\partial \phi}. \quad (6)$$

Equations (5)–(12) should be subject to the boundary conditions which are determined as follows. In the evaporation process the film thickness $h(t)$ is a decreasing function of the time. If we assume that the evaporation rate is proportional to the volume function of solvent at $z = h(t)$, mass conservation of solvent implies

$$\frac{d}{dt} \int_0^{h(t)} dz (1 - \phi) = -J_{ev}(1 - \phi_h), \quad (7)$$

where J_{ev} is a positive constant and $\phi_h \equiv \phi(h, t)$. On the other hand, the mass conservation of polymers is expressed as

$$\frac{d}{dt} \int_0^{h(t)} dz \phi = 0. \quad (8)$$

Since the flux is zero at $z = 0$,

$$\left. \frac{\partial \phi}{\partial z} \right|_{z=0} = 0. \quad (9)$$

Equations (5), (7), and (8) give a time evolution equation of h and the boundary condition of ϕ at $z = h(t)$ as

$$\frac{dh}{dt} = -J_{ev}(1 - \phi_h), \quad (10)$$

$$A(\phi) \left. \frac{\partial \phi}{\partial z} \right|_{z=h} = J_{ev} \phi_h (1 - \phi_h). \quad (11)$$

Until now, $A(\phi)$ has not been given in its explicit form. We must obtain it as a function of ϕ . Here we assume the following phenomenological expression,

$$A(\phi) = \begin{cases} D_0(1 - \phi)\phi^p & \text{if } \phi < \phi_g \\ D_0[(1 - \phi)\phi^p + d(1 - \phi)\phi^p(\phi - \phi_g)^b] & \text{otherwise} \end{cases} \quad (12)$$

where p and b are positive parameters, and hereafter we take $p = b = 3$. The parameter d in eq. (12) is the most important one which we call diffusion parameter. D_0 means the solvent diffusion coefficient. Figure 3 shows the diffusion coefficient $A(\phi)$ as a function of ϕ for various values of d . For $\phi > \phi_g$, $A(\phi)$ increases typically by a factor of d . The reason why we adopt eq. (12) is as follows:

In a dilute solution, the cooperative diffusion coefficient D_{coop} is expressed as¹⁵⁾

$$D_{coop} \propto \phi^\alpha \quad (13)$$

where α is a positive constant. In the case of $\phi < \phi_g$, $A(\phi)$ is assumed to be in accordance with this general expression. Equation (12) indicates that ϕ exceeds the gelation concentration ϕ_g , the diffusion constant $A(\phi)$ increases sharply.

The sharp increase of $A(\phi)$ might look strange, but it is a necessary condition for the skin phase to appear. The increase is due to the increase of the elastic energy of the gel: when gelation takes place, the elastic energy of polymer network gives extra contribution to the osmotic modulus of the gel, and increases the diffusion constant.

In colloid science, it is known that the diffusion constant (or the osmotic modulus) increases when the system forms a gel. This is observed in the phenomena of sedimentation.¹⁶⁾ When a dispersion settles in a closed container, the particle

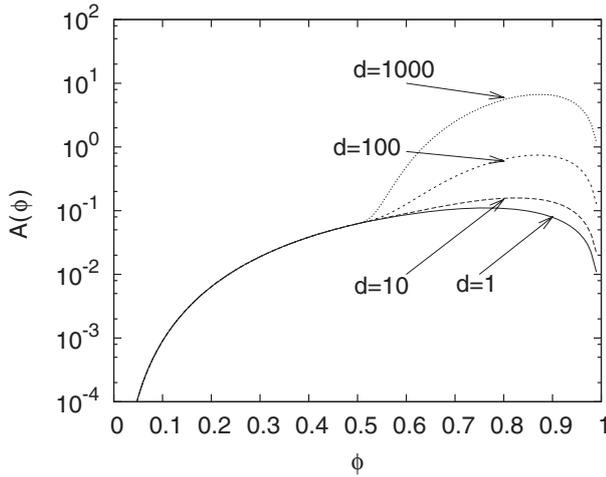


Fig. 3. Functional forms of $A(\phi)$ for various values of the diffusion parameter d .

concentration near the bottom wall increases, and forms a sediment phase (which is a gel phase of colloidal particles). Russel *et al.*¹⁶⁾ discussed that the osmotic modulus K diverges as $K \sim (\phi_m - \phi)^{-1}$, where ϕ_m is the sediment volume fraction.

The physics of skin formation by the drying process is similar to the physics of the sediment formation in the settling process. In the drying process, the diffusion of polymer is driven by the evaporation at the surface. In the settling process, the diffusion is driven by gravity. In both processes, concentration gradient is created at the interface, and a gel phase is formed. Equation (12) stands for this physics.

2.2 Numerical solution

If we choose the initial film thickness $h_0 \equiv h(0)$ and the characteristic time $\tau \equiv h_0^2/D_0$ as units of length and time, respectively, we have the dimensionless form of eqs. (5), (9), (14), and (11) as

$$\frac{\partial \phi}{\partial \hat{t}} = \frac{\partial}{\partial \hat{z}} \hat{A}(\phi) \frac{\partial \phi}{\partial \hat{z}}, \quad (14)$$

$$\frac{d\hat{h}}{d\hat{t}} = -Pe(1 - \phi_{\hat{h}}), \quad (15)$$

$$\hat{A}(\phi) \frac{\partial \phi}{\partial \hat{z}} = Pe\phi_{\hat{h}}(1 - \phi_{\hat{h}}) \quad (16)$$

$$\left. \frac{\partial \phi}{\partial \hat{z}} \right|_{\hat{z}=0} = 0, \quad (17)$$

where $\hat{A}(\phi) \equiv A(\phi)/D_0$, $\hat{h} \equiv h/h_0$, $\hat{z} \equiv z/h_0$, and $\hat{t} \equiv t/\tau$. Here we have introduced the dimensionless parameter

$$Pe \stackrel{\text{def}}{=} \frac{h_0 J_{ev}}{D_0}. \quad (18)$$

which is similar to ‘‘Peclet number’’ introduced by Russel in a sedimentation problem of colloids.¹⁶⁾

It should be emphasized that these set of equations (14)–(17) have dimensionless parameters Pe , d and ϕ_g which can control this system.

For numerical calculations of the moving boundary problem eqs. (14)–(17), it is convenient to rescale the

coordinate \hat{z} by introducing a new coordinate y as

$$\frac{\hat{z}}{\hat{h}} \equiv y. \quad (19)$$

In this coordinate, eq. (14) has the form

$$\frac{\partial \phi}{\partial \hat{t}} = \frac{\dot{h}y}{h} \frac{\partial \phi}{\partial y} + \frac{1}{h^2} \frac{\partial}{\partial y} A \frac{\partial \phi}{\partial y}. \quad (20)$$

where $\dot{h} \equiv dh/dt$, and we henceforth omit the hat ‘‘^’’ attached to the dimensionless variables. The boundary conditions (15)–(17) can be written in this coordinate as

$$\frac{dh}{dt} = -Pe(1 - \phi_h), \quad (21)$$

$$\left. \frac{A(\phi)}{h} \frac{\partial \phi}{\partial y} \right|_{y=1} = Pe\phi_h(1 - \phi_h), \quad (22)$$

and

$$\left. \frac{\partial \phi}{\partial y} \right|_{y=0} = 0, \quad (23)$$

with the initial condition $h(0) = 1$. If the initial distribution $\phi_0(y) \equiv \phi(y, 0)$ is given, we can obtain $\phi(y, t)$ and $h(t)$ from eqs. (20)–(23).

3. Results and Discussion

3.1 Skin formation and growth

We solve eq. (20) under the boundary conditions (21)–(23), numerically, using an explicit finite difference method on a one-dimensional lattice with 100 lattice points and a fixed time increment $\Delta t = 10^{-7}$. We set an initial distribution of ϕ to be uniform, that is, $\phi_0(y) \equiv \phi_i$ with a constant ϕ_i . Although this initial condition is not compatible with the boundary condition (22), the obtained data of ϕ satisfies the condition (22) within the numerical error except for the data in the first several time steps and the results shown below are not affected by this incompatibility. In the following, we study the behavior of ϕ and the skin thickness h_g defined below for various values of the parameters Pe and ϕ_i .

First, we show the typical behavior of h_g and ϕ . Figure 4 shows the time variation of the profile of ϕ in z coordinate for $(Pe, \phi_i) = (0.4, 0.3)$. We can see that there are three time regimes in the evolution of ϕ . In the initial regime, ϕ is uniform except for the region near the free surface where ϕ steeply increases with z near the free surface. In the middle regime, the profile of ϕ is sigmoidal and the skin layer grows. We can define the value h_g such that $\phi(h_g, t) = \phi_g$. In the final regime, the skin thickness reaches the system size and the profile is almost flat in the whole system.

In Fig. 5 we show the time-evolution of $\phi(z, t)$ for $d = 1$ (a), $d = 10$ (b), $d = 100$ (c), $d = 1000$ (d). One can see that the time variation of the profile depends on d and the profile appears to be sigmoidal for $d > 100$. We could interpret the appearance of the sigmoidal profile as a signature of the skin formation. This is reason the why the skin appears on the free surface and fluid solutions exist under the skin.

In the following we examine dependence of the skin formation on the parameter Pe and ϕ_i taking $d = 1000$ and $\phi_g = 0.5$.

We carry out numerical calculations for various values of Pe and ϕ_i . Figures 6–8 show the time evolution of h and h_g and the behavior of ϕ for various parameter set (Pe, ϕ_i) .

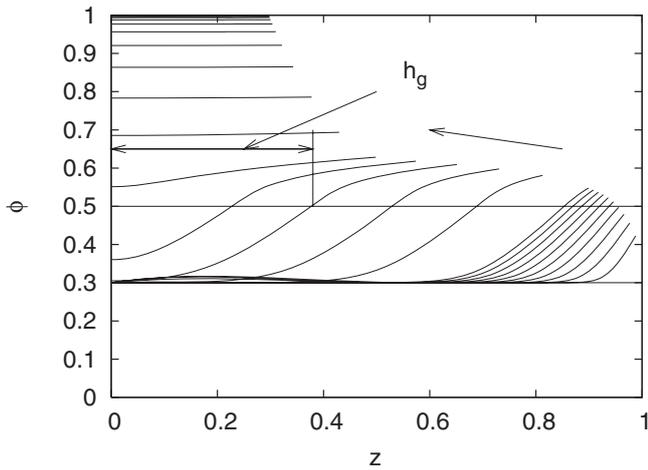


Fig. 4. Typical time variation of the profile of ϕ during drying. The sequential data of $\phi(z, t)$ with a constant time interval except for the initial time regime (smaller time interval) are plotted. The arrow in the figure denotes the definition of h_g . The film thickness $h(t)$ decreases and $\phi_h = \phi(h, t)$ increases in time as shown with the right arrow.

Figure 6 shows the time variation of h , h_g and profile ϕ for $(Pe, \phi_i) = (0.4, 0.4)$ and Fig. 7 for $(Pe, \phi_i) = (0.4, 0.1)$. The profile for $\phi_i = 0.1$ is slightly different from that for $\phi_i = 0.4$. When ϕ_i is much smaller than ϕ_g , it takes much time to be a gel phase near the free surface. When the skin layer is formed on the free surface, the whole film already reaches ϕ_g . Therefore the skin layer cannot grow, although the profile for $\phi_i = 0.1$ is similar to sigmoidal.

Figure 8 shows the time variation of h , h_g and profile ϕ for $(Pe, \phi_i) = (0.1, 0.4)$. For $Pe = 0.1$, there is a region where ϕ gradually increases with z near the free surface in the all time regime. The profile of ϕ is not sigmoidal. Since Pe is small, that is, diffusion is faster compared with evaporation rate, the profile of ϕ is broad. Therefore the skin layer can not form.

When the skin is formed, the thickness h_g decreases almost linearly except for the time region just before the time when h_g vanishes as shown in Fig. 6. However, when the skin does not form, h_g decreases in nonlinear manner [Fig. 8(a)]. The linear trend of h_g indicates that the system is in a steady state. We discuss the steady state solution later.

In order to know the parameter dependence of the profile ϕ , we carry out the simulations for other various values of Pe and ϕ_i . In Fig. 9 we summarize the result. In Fig. 9 open circles or closed squares indicate the parameters (Pe, ϕ_i) for which the skin is formed or not, respectively. When ϕ_i is near ϕ_g and Pe is larger, the skin layer is easy to appear during drying. On the other hand, when ϕ_i is much smaller than ϕ_g and Pe is smaller, the skin is not observed. From Fig. 9, we can know the limitation of the skin formation.

This result agrees with observation in practical situations. For example, in the case of a droplet ejected using a ink-jet head on a substrate, it is hard to see the skin layer in a atmosphere, because the radius and the initial thickness of a droplet is very small. This corresponds to a small Pe region in Fig. 9. However, If evaporation rates is high (that is Pe is large), using a vacuum chamber, the skin layer can be seen (Fig. 1).

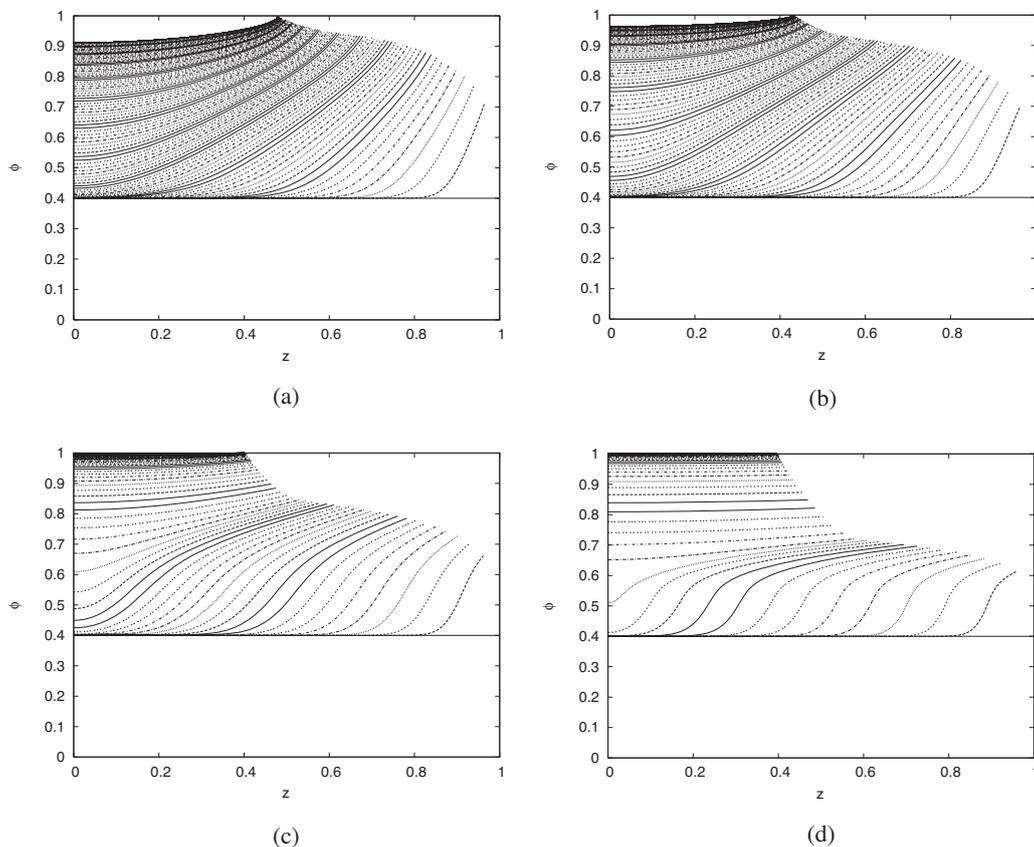


Fig. 5. Time evolution of the profile of $\phi(z, t)$ for $d = 1$ (a), $d = 10$ (b), $d = 100$ (c), $d = 1000$ (d).

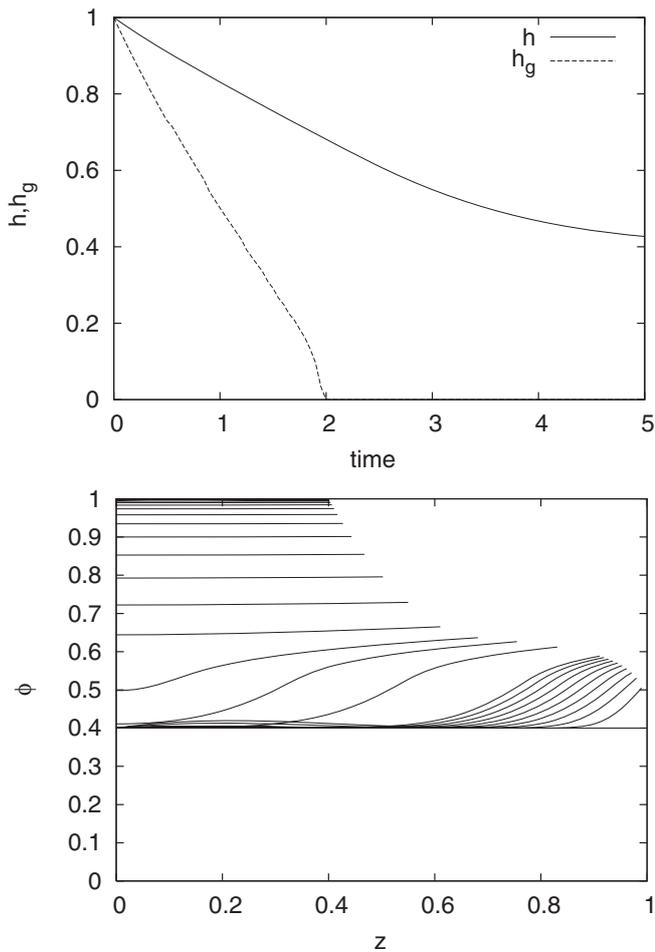


Fig. 6. Time evolution of the total thickness h and the fluid phase thickness h_g (a) and the time evolution of ϕ (b) for the parameter $(Pe, \phi_i) = (0.4, 0.4)$.

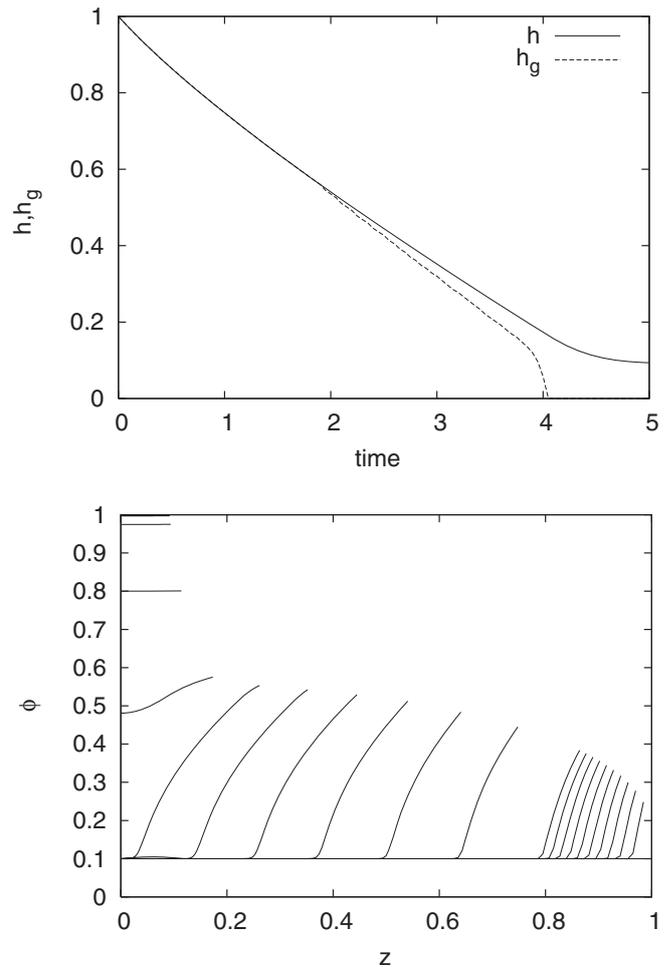


Fig. 7. Time evolution of the total thickness h and the fluid phase thickness h_g (a) and the time evolution of ϕ (b) for the parameter $(Pe, \phi_i) = (0.4, 0.1)$.

It is especially important in applications whether the skin layer is formed or not. The film with the skin layer has a residue stress, or a tension, and these cause a crack or a change of morphology.

3.2 Discussion

Here we show that a steady solution of ϕ exists in this system at least in the middle regime discussed in the previous section. It can be seen that the time evolution of ϕ seems to be constant in Fig. 4. In this regime, we expect the existence of the steady solution in the form. Introducing new coordinate using $\xi \equiv z + ct$,

$$\phi(z, t) = \phi(z + ct) \equiv \phi(\xi), \quad (24)$$

where c is a positive constant. In this coordinate system, eq. (5) becomes

$$\frac{\partial}{\partial \xi} \left[A(\phi) \frac{\partial \phi}{\partial \xi} - c\phi \right] = 0. \quad (25)$$

Integrating eq. (25) with respect to ξ , we have

$$\int \frac{A(\phi)}{\phi - \phi_0} d\phi = \int c d\xi. \quad (26)$$

We perform the integration in eq. (26) numerically to obtain the steady state solution. Figure 10 shows the steady

solution, which c is estimated by the numerical data of the profile. We can see the steady state solution well fit the numerical data obtained in our simulation. The result demonstrates that the constant velocity c exists.

Although our model is rather simple, we believe that our model captures certain aspect of film formation due to the gelation in drying process.

4. Conclusions

In this paper, we have proposed the drying model which describes evaporation and diffusion process of polymer solution. Moreover, we have indicated restrictions on the skin formation.

We have carried out the simulation on one-dimensional drying system. The actual skin layer has properties as elastic membranes. However, on one dimensional model, we could not express the properties. When we have to discuss the skin formation quantitatively, we need to construct two or three dimensional model including the effect of a residue stress and a viscoelastic properties due to a gel.

A crucial point is that we can perform the drying dynamics of polymer solution including the effect of a gelation during drying. And we have progressed understanding the practically important coating process of the film formation.

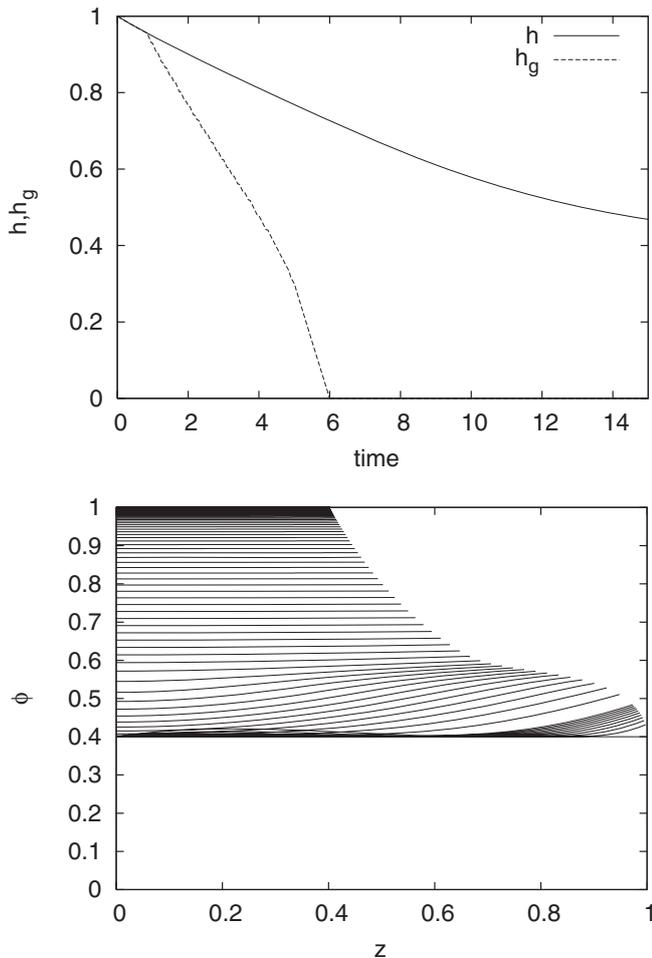


Fig. 8. Time evolution of the total thickness h and the fluid phase thickness h_g (a) and the time evolution of ϕ (b) for the parameter $(Pe, \phi_i) = (0.1, 0.4)$.

In our discussion, there may be insufficient at some points, however our main result is that Fig. 9 may be useful in applications of the coating.

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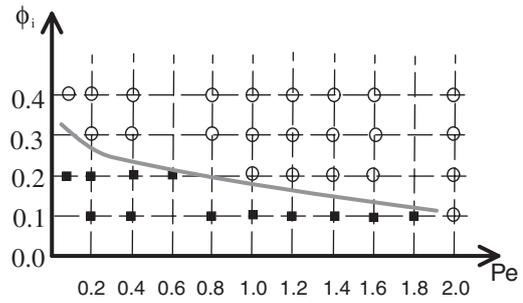


Fig. 9. “Phase diagram” of skin formation obtained in numerical simulations of our model. Open circles and closed squares show the parameter values for which skin layers are formed or not, respectively.

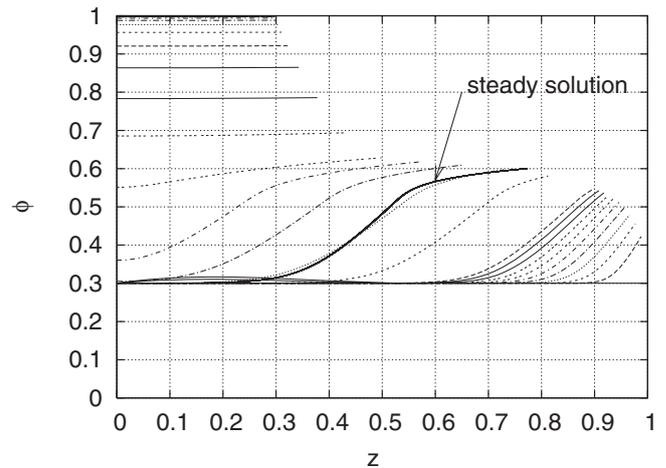


Fig. 10. Comparison of the steady profile of ϕ calculated based on eq. (26) with the profile obtained in our simulation for $(Pe, \phi_i) = (0.4, 0.3)$.

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