

Modeling of Drying Processes of Polymer Solutions

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高分子溶液またはゲルに対する二流体モデルを用いて、固体基板上的高分子溶液の乾燥過程に関するモデルを構築する。このモデルでは、溶媒の蒸発に伴って気液界面付近で形成されるゲル状の膜（スキン）のダイナミクスを考慮し、スキンの形成が乾燥過程に及ぼす影響について考察する。スキンの形成に伴って、高分子の協同拡散係数が大きくなることと、溶媒の蒸発速度が小さくなることのどちらも、スキン（ゲル相）における弾性効果の結果として示される。

Based on the two-fluid model for polymer solutions or gels, we construct a simplified model of drying processes of polymer solutions on a solid substrate. In this model, effects of gelation near the free surface due to the solvent evaporation are taken into consideration. We show that the elastic stress in the gel phase affects both the evaporation rate of solvent and the collective diffusion coefficient.

Here we consider an isothermal system of a polymer solution extended on a solid substrate whose normal lies in z -axis. If the system is homogeneous in x and y directions, we can express the system with a one-dimensional model. In a drying process, we assume that only the solvent evaporates at the free surfaces $z = h(t)$ and the volume fraction ϕ of polymers near the free surface increases in time t . When ϕ at $z = h$ reaches a certain value, ϕ_g , a thin gellike layer, called a skin, is formed near the free surface.

The above dynamical processes can be described by the two-fluid model [1] for polymer solutions or gels with appropriate boundary conditions discussed later. One of the key concepts in the two-fluid model is the stress–diffusion coupling which is expressed, in our simplified model, as,

$$\frac{\partial \phi}{\partial t} = \frac{\partial}{\partial z} \left[A(\phi) \frac{\partial \phi}{\partial z} \right], \quad (1)$$

with

$$A(\phi) \equiv \frac{\phi^2(1-\phi)^2}{\zeta} \left[f''(\phi) + \frac{K(\phi)}{\phi^2} \right], \quad (2)$$

where ζ is the friction coefficient between polymers and solvent, $f(\phi)$ the mixing free energy of the Flory–Huggins type, $K(\phi)$ is the bulk osmotic modulus. The last term in Eq.(2) expresses

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the dynamical coupling between stress and diffusion. Since $K(\phi)$ reflects the elastic effect of polymer network, it can be modeled as

$$K(\phi) = \begin{cases} 0 & (\phi < \phi_g) \\ K_g & (\phi \geq \phi_g) \end{cases} \quad (3)$$

where K_g is a large positive constant [2]. Hence the collective diffusion coefficient $A(\phi)$ increases, when ϕ exceeds ϕ_g [3].

In the gas phase, we introduce a diffusion layer $h < z < h + l$ with a fixed thickness l [4]. In this diffusion layer the solvent number density ψ is assumed to obey a simple diffusion equation,

$$\frac{\partial \psi}{\partial t} = D_a \frac{\partial^2 \psi}{\partial z^2}, \quad (4)$$

with a diffusion constant D_a . Provided that the local equilibrium condition at the interface $z = h$ is always valid, the chemical potential of the solvent must be continuous at $z = h$, which leads to the relation between ψ just above the interface and ϕ just below the interface,

$$\psi/\psi^* = (1 - \phi) \exp[\phi + \chi\phi^2 - \hat{K}(\phi) \ln(\phi/\phi_g)] \quad \text{at } z = h, \quad (5)$$

where ψ^* is the number density of saturated vapor of pure solvent, $\hat{K}(\phi) \equiv (v_l/k_B T)K(\phi)$ with the volume v_l per a monomer. In Eq.(5) we have used the expression $f(\phi) = (k_B T/v_l)[(1 - \phi) \ln(1 - \phi) + \chi\phi(1 - \phi)]$ with the parameter χ .

From the mass conservation of polymers and solvent we obtain

$$\dot{h} = -\frac{A\partial_z \phi}{\phi} = \frac{v_l D_a \partial_z \psi}{1 - v_l \psi} \quad \text{at } z = h, \quad (6)$$

where $\dot{h} \equiv dh/dt$. The above equations together with Eq.(5) give the boundary conditions for Eqs.(1) and (4) and the time evolution of h . When a constant value ψ_∞ of ψ out side of the diffusion layer ($z > h + l$) is given and a steady state holds, \dot{h} is written as

$$\dot{h} \simeq \frac{v_l D_a}{l} \{ \psi_\infty - \psi^* (1 - \phi) \exp[\phi + \chi\phi^2 - \hat{K}(\phi) \ln(\phi/\phi_g)] \} \quad \text{at } z = h. \quad (7)$$

Therefore, the evaporation rate $|\dot{h}|$ decreases, when ϕ exceeds ϕ_g , whereas the $A(\phi)$ increases as mentioned before. These two properties come from the same origin that the elastic effect is relevant in the skin layer.

References

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