

A simple model of skin formation in solvent evaporation processes

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高分子溶液の自由表面付近での溶媒蒸発に伴う皮膜形成過程に対する簡単なモデルを提案する。このモデルでは、皮膜をゲル相として捉え、その動的な形成過程を高分子の濃度に依存した協同拡散係数を伴った拡散方程式の移動境界問題として定式化する。理論解析および数値シミュレーションにより、皮膜の形成過程を議論し、皮膜形成に必要な条件に対する理論的な表式を提案する。

A simple model is proposed for the skin formation in the evaporation process of polymer solution at free surface. In this model the skin is regarded as a gel phase formed near the free surface, and the dynamics is described by diffusion equation for polymer concentration with moving boundaries. The equation is solved both analytically and numerically. It is shown that the skin phase appears when the evaporation rate is high or when the initial polymer concentration is high. An analytical expression is given for the criterion for the skin phase to be formed.

1 Model

We consider a layer of polymer solution with initial thickness h_0 placed on a flat substrate whose normal lies in z . When solvent evaporates at the free surface, the volume fraction of polymers ϕ increases and the thickness h decreases in time t , while the total amount of polymers in the system is unchanged (we assume that the polymers do not evaporate). If the evaporation is rapid, ϕ near the free surface increases and forms a polymer rich region. When ϕ reaches a certain value ϕ_g , the polymer solution becomes a gel and a skin phase is formed. As the evaporation proceeds, the whole system finally becomes a gel.

The above process can be described by the following one-dimensional diffusion equation of $\phi = \phi(z, t)$ on $0 < z < h$,

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

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with the diffusion coefficient $A(\phi)$ which is assumed to be

$$A(\phi) = \begin{cases} D & (\phi < \phi_g), \\ D_g & (\phi \geq \phi_g), \end{cases} \quad (2)$$

where D and D_g are constants independent of ϕ , and stands for the cooperative diffusion constants in solutions and in gel phase. Since the osmotic modulus in gel phase is much larger than that in solution due to an extra contribution of the elastic modulus of polymer network in gel phase, we can assume $D \ll D_g$.

Assuming that the amount of solvent evaporation at the surface is written as $J(1 - \phi_h)$ with a constant J and $\phi_h \equiv \phi(h, t)$, and imposing the boundary condition $\partial\phi/\partial z = 0$ at $z = 0$, we obtain the equation for the thickness h as

$$\frac{dh}{dt} = -J(1 - \phi_h) \quad (3)$$

and the boundary condition at the free surface,

$$A(\phi) \frac{\partial\phi}{\partial z} = J\phi(1 - \phi) \quad \text{at } z = h. \quad (4)$$

2 Conclusion

Analyzing the above model in the limit $D_g/D \rightarrow \infty$, we obtain a criterion for the skin phase to be formed:

$$\text{Pe} > \frac{\phi_g - \phi_0}{(1 - \phi_g)\phi_g} - \frac{1 - \phi_0}{\phi_0} \ln \frac{1 - \phi_g}{1 - \phi_0} - \ln \frac{\phi_g}{\phi_0}, \quad (5)$$

where Pe is the Péclet number defined as $\text{Pe} \equiv h_0 J/D$ and ϕ_0 is the initial concentration of polymers which is uniform. This result suggests that the skin formation can be controlled by Pe and ϕ_0 for fixed ϕ_g and that the smaller value of ϕ_0 and the larger value of Pe lead to formation of the well-structured skins.

In practical applications it is important to give a criterion of formation of the well-structured skin layer. The above results provide useful information in explaining the empirical fact that higher evaporation rates lead to more inhomogeneous deposits.

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