EFFECTS OF RELAXATIONAL DIFFUSION IN FILM BOILING OF A POLYMER SOLUTION


Effects of relaxational diffusion during rapid evaporation of a solvent from a polymer solution taking place as a result of a thermal shock from the side of the free surface of the liquid are investigated. It is shown that, as a result of diffusional resistance to evaporation, a polymer-enriched layer is formed in the vicinity of the phase interface that can stabilize substantially the shape of the phase interface.

Diffusional transfer in polymer systems depends substantially on the temperature and concentration conditions, the quality of the solvent, and the hereditary factor. The contribution of the latter can be characterized by the Deborah number $D_e = \lambda / t_D$, where $t_D$ is the characteristic diffusion time. When $D_e >> 1$, the system has no possibility of rearranging in the process of diffusional transport, and the solvent diffuses practically through the macromolecular matrix. If $D_e << 1$, processes of macromolecular relaxation in the solution occur on a much shorter time scale than diffusional transport, and calculation of the concentration field can be carried out on the basis of the classical diffusion equation. In the case where $D_e \sim 1$ rearrangement of polymer chains takes place on a time scale comparable to the characteristic time of concentration equilibration in the solution. The instantaneous macromolecular conformation is not equilibrium, and therefore one should expect the diffusional transfer to have a relaxational character. According to [1], the diffusional flux $n$ is defined in this case as

\[ n = -\rho_2 \int_0^t \mu(t - t') \nabla k(t', x) \, dt' + \mu(t) = D_i \delta(t) + \frac{D_0 - D_i}{\lambda} \exp \left(-\frac{t}{\lambda}\right). \] (1)

where $\mu$ is the memory kernel for a single relaxation time.

Conditions favorable for manifestation of relaxational processes are difficult to create in traditional diffusion experiments due to high values of the time scale $t_D$. The reverse situation is observed during rapid evaporation of a solvent from a polymer solution under the action of a thermal shock from the side of the evaporation surface. In this case, diffusional resistance to the evaporation process can turn out to be attributable to the value of not only the equilibrium transfer coefficient $D_0$, but also the nonclassical parameters $\lambda$ and $D_i$.

The objective of the present work was modeling of the processes under consideration during nonstationary evaporation of the solvent from the surface of the solution with rapid heat supply.

1. Let us consider a horizontal layer of a polymeric liquid heated uniformly to the temperature $T_{20} = T_s(p_0, k_0)$. The initial layer thickness is $L$. The space over the layer is occupied by the saturated vapor at the same temperature. At the initial instant, a constant heat flux $q$ is applied to the surface. It is assumed that the process takes place at a constant vapor pressure $p_0$ and transfer of the evaporating component to the phase transition interface in the liquid is effected by means of a diffusional mechanism. Let us direct the $0x$ axis from the bottom $(x = 0)$ to the free surface $(x = h(t))$.

The heat flux fed to the evaporation surface goes into evaporation of the solvent and heating of the liquid $q = jl + k_2 dT/dx$. We derive the equation of motion for the boundary based on the assumption that the densitie:
of the substances comprising the solution are additive and vary negligibly during evaporation and diffusion. For \( h(t) \) we obtain

\[
lp_2 \frac{dh}{dt} = q - k_2 \frac{dT}{dx}, \quad x = h(t) .
\]

The temperature and concentration fields are obtained from the equations

\[
\frac{dT}{dt} = a_2 \frac{d^2 T}{dx^2}, \quad a_2 = \frac{k_2}{\rho_2 c_p},
\]

\[
\frac{dk}{dt} = D_i \frac{d^2 k}{dx^2} + \frac{D_0 - D_i}{\lambda} \int_0^t \exp \left(-\frac{t - \tau}{\lambda}\right) \frac{d^2 k}{dx^2} d\tau .
\]

The initial and boundary conditions are as follows:

\[
h(0) = L; \quad T(0, x) = T_0; \quad k(0, x) = k_0; \quad \frac{dk}{dx} \bigg|_{x=0} = 0 ;
\]

at \( x = h(t) \): \( T(t, 0) = T_0 \); \( n = -\left(1 - k_h\right) \frac{dM}{dt} \); \( i \frac{dM}{dt} = q - k_2 \frac{dT}{dx} \);

\[
n = -\rho_2 D_i \frac{dk}{dx} - \rho_2 D_0 - \frac{D_i}{\lambda} \int_0^t \exp \left(-\frac{t - \tau}{\lambda}\right) \frac{d^2 k}{dx^2} d\tau ;
\]

\[

\Phi_1 = k_h \left[k_h + (1 - k_h) \Psi\right]^{-1} ; \quad \psi = \frac{\nu_p}{\nu_{sol}} ; \quad \Phi_1 = A \exp \left(-\frac{B}{T_h}\right).
\]

Equation (8) characterizes the phase equilibrium \( P_s = P_s(T_h, k_h) \), for which the Flory–Huggins relationship [2] was used.

Let us consider the initial stage of evaporation, when the relationship \( h = L \) is fulfilled. For simplicity, we consider phase transitions as taking place according to an equilibrium scheme, and we make Eqs. (2)-(8) dimensionless. We choose \( k_0, T_{20}, L, \) and \( \rho_2 \) as scaling factors. Assuming that \( k_h^* = 1 + K, M^* = 1 + m, \) and \( T^* = 1 + \Theta \), where \( K, m, \) and \( \Theta \) are small perturbations of the equilibrium quantities, we obtain upon linearization a system of equations whose solution is sought using the Laplace transform. After passing to the image space, we find an asymptotic expression for the dimensionless mass perturbation at \( s \to \infty \):

\[
\hat{m} = k_0 \sqrt{\alpha_D} K (1 - k_0)^{-1} s^{-1/2}; \quad \alpha_D = D_i / D_0
\]

(here and in what follows we drop the asterisk in dimensionless quantities).

As is shown in [3], in a system with the small parameter \( D_i \), manifestation of diffusional slowing down of the evaporation process can be expected at higher values of \( k_0 \) than would follow from results obtained without taking into account relaxation effects. Let us consider the limiting situation \( D_i \to 0 \) (\( D_i \to 0 \)) at finite \( \lambda \). Upon coming back to the inverse transform space we find

\[
m = 4t^{3/2} q L k_0 a_2^{1/2} (1 - k_0)^{-1} (\pi \lambda)^{-1/2} (3k_2 T_0 T_{sk})^{-1}.
\]