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Notes

Phenomenological Continuum Equations To Describe Case II Diffusion in Polymeric Materials

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Recently a simple phenomenological model of case II diffusion in polymeric materials was proposed by Rossi et al.[1] According to this description, case II diffusion is associated with plasticization, *i.e.*, with the transition from the glassy to the rubbery or plasticized state that occurs when the local solvent volume fraction $\phi(x,t)$ within the polymer exceeds some (temperature dependent) threshold value $\tilde{\phi}$. At the basis of the model is the observation that, in a glassy polymer exposed to a plasticizing solvent, two different physical processes take place. The first, solvent transport, is controlled by Fick's law, which states that the flux is proportional to the concentration gradient. The proportionality factor, *i.e.*, the diffusion coefficient, depends in general on the solvent volume fraction: the simplest situation considered in ref 1 is one where $D(\phi)$ is equal to a constant D_0 in the glassy region of the material ($\phi < \tilde{\phi}$) and to a different constant D_1 ($\gg D_0$) in the plasticized region ($\phi \geq \tilde{\phi}$). The second process is the transition from the glassy to the rubbery state: the kinetics of this transition sets an upper limit on the rate at which material can be plasticized, *i.e.*, an upper limit on the velocity of the surface (plasticization front) separating the glassy and plasticized regions of the material or equivalently an upper limit on the solvent flux across the glassy−plasticized interface. Under the simplest assumption on how the velocity of the front depends on the preexisting level of solvent in the glassy region, the flux of solvent across the interface cannot exceed $\nu_0\tilde{\phi}$, where ν_0 is the front velocity for an initially dry polymeric glass.

The ideas summarized above can be translated into a simple finite difference algorithm[1] that, when implemented on a computer, reproduces the main experimental features observed in systems exhibiting case II diffusion.[2] Notably, an induction time $\tau_0 \sim D_0/\nu_0^2$ precedes the establishment of the plasticization front, and there is a crossover at time $\tau_1 \sim D_1/\nu_0^2$ from the case II regime, where the front velocity is constant, to a Fickian regime where the distance covered by the front increases as $\sqrt{t}$. When coupled to a proper consideration of the macroscopic elastic stresses generated as solvent penetrates the specimen, these results provide a simple framework to understand and classify many of the observed features of solvent diffusion in glassy polymers.[3] In the present paper a continuum formulation of the finite difference algorithm introduced in ref 1 is presented. This formulation has the advantage of making the physical assumptions of the model more transparent and provides confirmation for the computational results obtained in ref 1.

We start by considering a semi-infinite ($x > 0$) initially dry glassy material, so that at $t = 0$ there is no plasticized region and the solvent flux at $x = 0$ is $\nu_0\phi$. Therefore, taking $D(\phi < \tilde{\phi}) = D_0$ and $D(\phi \geq \tilde{\phi}) = D_1$, one simply has

$$\phi_t(x,t) = D_0\phi_{xx}(x,t) \quad \text{for} \quad x > 0 \tag{1}$$

subject to the boundary conditions $\phi(x{>}0,t{=}0) = 0$ and $-D_0\phi_x(x{=}0,t) = \nu_0\tilde{\phi}$; as usual, the apposed subscript t (or x) denotes a partial derivative with respect to t (or x). This is the equation implied by the discrete algorithm of ref 1 in the time interval $0 < t < \tau_0$, where τ_0 is the time, defined by $\phi(x{=}0,t{=}\tau_0) = \tilde{\phi}$, at which the solvent volume fraction at $x = 0$ reaches $\tilde{\phi}$; in other words, τ_0 corresponds to the experimental induction time.[2] Equation 1 expresses the assumption that solvent transport in the glassy region is the only process taking place within the polymer prior to the establishment of the plasticization front. On the other hand, the constant flux boundary condition at the solvent polymer interface $x = 0$ accounts for the kinetics of the plasticization process occurring at the polymer surface. The above problem can be solved exactly;[4] in particular, it can be shown that $\tau_0 = \pi D_0/4\nu_0^2$ and that $\phi(x,\tau_0)$ is given by

$$H(x) \equiv \phi(x,\tau_0) = \frac{\nu_0\tilde{\phi}}{D_0}\int_x^\infty \operatorname{erfc}\left(\frac{\eta\nu_0}{D_0\sqrt{\pi}}\right) \mathrm{d}\eta \tag{2}$$

where erfc(z) is the usual error function complement.[5]

For $t > \tau_0$, a plasticization front is present at $x = \tilde{x}(t)$ and divides the semi-infinite domain $x > 0$ into a plasticized $[0 < x < \tilde{x}(t)]$ and a glassy $[x \geq \tilde{x}(t)]$ region. Thus we have a moving boundary problem (*e.g.*, one similar to the Stefan problem for the advancement of a solidification or melting front[6]) where both the equation $x = \tilde{x}(t)$ for the moving front and the solvent volume fraction $\phi(x,t)$ on either side of the front need to be determined. For $t > \tau_0$, the solvent volume fraction at the boundary ($x = 0$) between the solvent and the (plasticized) polymer is taken to be equal to the final (equilibrium) volume fraction Φ ($>\tilde{\phi}$).[7] This implies that at times immediately following τ_0, the flux of solvent $-D_1\phi_x(\tilde{x}^-(t),t{\rightarrow}\tau_0^+)$ reaching the glassy−plasticized interface from the plasticized side will exceed the prescribed upper limit $\nu_0\tilde{\phi}$ for the flux of solvent into the glassy region across the interface. As a result, solvent accumulates in the plasticized region at the left of the front and $\phi(x,t)$ is discontinuous at the front, with the limiting value $\phi^-(t) = \phi(\tilde{x}^-(t),t)$ on the plasticized side larger than the limiting value $\phi(\tilde{x}^+(t),t) = \tilde{\phi}$ on the glassy side.

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As the front advances, a portion $\dot{\tilde{x}}(t)(\phi^-(t) - \tilde{\phi})$ of the flux $-D_1\phi_x(\tilde{x}^-(t),t)$ of solvent reaching the interface from the plasticized side is spent raising the solvent volume fraction from $\tilde{\phi}$ to $\phi^-(t)$ over the region covered by the front; the rest is the flux $-D_0\phi_x(\tilde{x}^+(t),t)$ through the front into the glassy region. This translates into the following boundary condition at $x = \tilde{x}(t)$:

$$-D_1\phi_x(\tilde{x}^-(t),t) + D_0\phi_x(\tilde{x}^+(t),t) = \dot{\tilde{x}}(t)(\phi^-(t) - \tilde{\phi}) \qquad (3)$$

At times immediately following τ_0, the flux into the glassy region must equal the upper limit $\nu_0\tilde{\phi}$. Both $\phi(x,t)$ in the glassy region and the movement of the front (*e.g.*, $\tilde{x}(t)$) are then determined by

$$\phi_t(x,t) = D_0\phi_{xx}(x,t) \quad \text{for} \quad x > \tilde{x}(t) \qquad (4)$$

subject to the boundary conditions $-D_0\phi_x(\tilde{x}^+(t),t) = \nu_0\tilde{\phi}$ and $\phi(\tilde{x}^+(t),t) = \tilde{\phi}$. In the plasticized region, $\phi(x,t)$ is found from

$$\phi_t(x,t) = D_1\phi_{xx}(x,t) \quad \text{for} \quad 0 < x < \tilde{x}(t) \qquad (5)$$

the boundary conditions being given by eq 3 and by $\phi(x=0,t) = \Phi$.

As time proceeds $\phi^-(t)$ decreases, until at a time τ_1, defined by $\phi(\tilde{x}^-(\tau_1),\tau_1) = \tilde{\phi}$, it becomes equal to $\tilde{\phi}$; correspondingly (see eq 3), the flux $-D_1\phi_x(\tilde{x}^-(\tau_1),\tau_1)$ becomes equal to $\nu_0\tilde{\phi}$, in agreement with the results of the numerical calculations reported in ref 1. For $t > \tau_1$, the flux $-D_1\phi_x(\tilde{x}^-(t),t)$ no longer exceeds $\nu_0\tilde{\phi}$ and the model of ref 1 reverts to the diffusion equation with a discontinuous diffusion coefficient, *e.g.*, to eqs 4 and 5 subject to the boundary conditions $\phi(\tilde{x}^+(t),t) = \phi(\tilde{x}^-(t),t) = \tilde{\phi}$ and

$$D_1\phi_x(\tilde{x}^-(t),t) = D_0\phi_x(\tilde{x}^+(t),t) \qquad (6)$$

at $x = \tilde{x}(t)$. This latter situation corresponds to the transport-limited or Fickian regime of ref 1: in this situation, transport of solvent, rather than the kinetics of the glassy to rubbery transition, is the rate-limiting step controlling the movement of the plasticization front.[8]

Clearly the continuum formulation discussed above can be extended to cover more general forms of the dependence of the diffusion coefficient $D(\phi)$ on ϕ as well as situations where the initial volume fraction of solvent in the glassy material is nonzero. The present continuum formulation underscores the analogies as well as the differences between the problem introduced in ref 1 to account for the solvent-induced glassy to rubbery transition and the conventional Stefan problem[6] that describes first-order phase transitions such as freezing and melting. For these first-order transitions the liberation or absorption of latent heat together with the heat transport characteristics of the material control the movement of the front. By contrast here, the "microscopic" kinetics of the plasticization process plays the crucial role; the model of ref 1 accounts for this process by setting an upper limit for the front velocity that translates into an upper limit for the solvent flux through the interface. In turn, this requirement leads to the three regimes, induction time at $t < \tau_0$, plasticization limited at $\tau_0 < t < \tau_1$, and transport limited for $t > \tau_1$, discussed above.

References and Notes

(1) Rossi, G.; Pincus, P. A.; de Gennes, P. G. *Europhys. Lett.* **1995**, *32*, 391.

(2) See, for example: Thomas, N. L.; Windle, A. H. *Polymer* **1978**, *19*, 255. Nicolais, L.; Drioli, E.; Hopfenberg, H. B.; Caricati, G. *J. Membr. Sci.* **1978**, *3*, 231. Thomas, N. L.; Windle, A. H. *Polymer* **1981**, *22*, 627. Gall, T. P.; Lasky, R. C.; Kramer, E. J. *Polymer* **1990**, *31*, 1491.

(3) Samus, M. A.; Rossi, G. *Macromolecules* **1996**, *29*, 2275.

(4) Carslaw, H. S.; Jaeger, J. C. *Conduction of heat in solids*; Oxford University Press: Oxford, 1959; p 75.

(5) Namely,

$$\mathrm{erfc}(z) = \frac{1}{\sqrt{\pi}}\int_z^\infty \mathrm{e}^{-t^2}\,\mathrm{d}t$$

(6) See, for example, ref 4, p 282*ff*.

(7) The simplified picture of ref 1 implies a discontinuous jump for the solvent volume fraction from $\tilde{\phi}$ to Φ at $t = \tau_0$. This reflects the assumption that, for a rubbery polymer, equilibrium is reached at the boundary of the polymer occupied region as soon as polymer comes in contact with the solvent. This assumption could be relaxed, but this implies introducing additional phenomenological parameters.

(8) A similar crossover to a transport limited regime is predicted by a model for case II diffusion put forward previously: Astarita, G.; Sarti, G. C. *Polym. Eng. Sci.* **1978**, *18*, 388. For a mathematical analysis of this model see: Fasano, A.; Meyer, G. H.; Primicerio, M. *SIAM J. Math. Anal.* **1986**, *17*, 945.

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