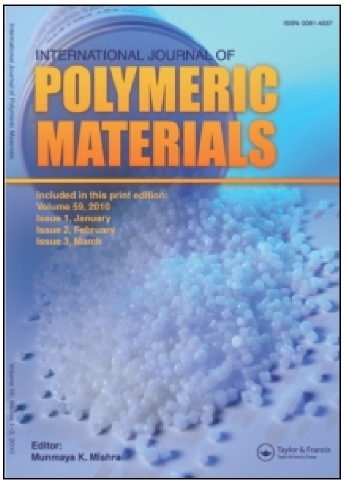

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Diffusion in Polymers with Varying Accessibility

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This paper considers the problem of describing quantitatively the process of diffusion in polymers attended with plasticization of their amorphous phase. A consequence of such plasticization is that the volume accessible for the penetrant molecules continuously increases during the course of their sorption. Assuming that the rate of the relaxation processes is far greater than that of diffusion, an equation has been generated to describe sorption in a matrix with varying accessibility. The numerical solution of this equation using the experimental data for a polyamide-water system demonstrates that sorption in the matrix with increasing accessibility is slower than sorption in a hypothetical matrix with constant accessibility equal to the portion of the amorphous phase. At the same time, the concentration of the penetrant in the former case proves higher in any point of the polymer specimen. The results obtained are important for calculating the rate constants for chemical reactions that in a polymer matrix are proceeding in the diffusion-kinetic mode.

KEY WORDS Diffusion, polymers, accessibility

1. INTRODUCTION

In describing the kinetics of chemical reactions between the functional groups of macromolecules and low-molecular-weight substances penetrating the polymer matrix, account should be taken of the "accessibility" of the functional groups. It is known that in the course of diffusion the penetrant dissolves not in the entire volume of the polymer but only in a certain portion thereof. Thus in partly crystalline polymers the penetrant dissolves only in the amorphous regions. Hence, its concentration C should be determined using an equation:

$$C = \frac{\underline{m}}{\underline{n}V} \tag{1}$$

where $\underline{m}$ is the mass of the sorbed substance, V is the geometrical volume of the polymer specimen, and n is the accessible portion of the volume (accessibility).[1] Accessibility has been found to depend on temperature as well as on the mass and chemical nature of the penetrant,[2-4] therefore the coefficient $\underline{n}$ in Equation (1) does not necessarily coincide with the portion of the sample which is amorphous phase. Specifically, it may be greater than that if the penetrant breaks up the structure of the crystalline phase, or smaller if sorption takes place from vapor with activity below unity. Since quantitation of the kinetics of chemical reactions in polymers requires knowledge of penetrant concentration, it is worthwhile to consider a diffusion equation describing the sorption of a penetrant in a polymer matrix whose accessibility changes during the process.

2. RESULTS AND DISCUSSION

Let us consider the dependence of polymer accessibility on the mass of sorbed substance, and then take account of this phenomenon in deriving the diffusion equation. Using $H \rightarrow D$ isotopic exchange, we have experimentally determined the accessibility of amido groups in a polycaproamide film for water molecules as dependent on water vapor activity in the milieu.[1] The relevant data presented in Figure 1 demonstrate that for each equilibrium water content in the polymer (curve 1) there is a specific accessible volume of the specimen (curve 2). Turning now to the nonstationary process of diffusion, it becomes clear that if there is a profile of water mass along the diffusion coordinate there must also be a profile of accessibility, which changes with time as the sorption equilibrium is approached. In a polymer specimen, for every geometrical cross-section perpendicular to the diffusion vector there is its own accessibility and, accordingly, its own effective cross-section of diffusion. Thus, water sorption proceeds in a medium where the diffusion cross-section varies with the diffusion coordinate and time. In any cross-section of the specimen (except its surface) the accessibility changes from a certain initial value corresponding to that at zero concentration of the penetrant[5] to a limit value corresponding to the accessibility at equilibrium penetrant concentration as determined from Figure 1.

Now we shall develop a diffusion equation that takes into account the dependence of the accessibility on penetrant mass. For simplicity we assume that the rate of change in accessibility in any cross-section of the polymer is far greater than the rate of change in the mass of the sorbed substance in this cross-section owing to

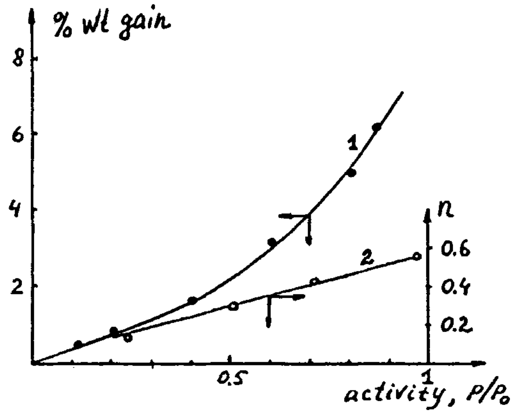

FIGURE 1 Dependences of water uptake and accessibility on water vapor activity at 25°C (polycaproamide film). (1) Weight gain, wt percent; (2) matrix accessibility.

diffusion. The case of comparable rates requires special analysis which would complicate the form of the diffusion equation without, however, altering the gist of the matter.

For the unidimensional case the equation sought can be obtained in a conventional way by considering the diffusant masses $\underline{\Delta Q}_1$ and $\underline{\Delta Q}_2$ that have passed through two neighboring unequal cross-sections $\underline{\Delta S}_1$ and $\underline{\Delta S}_2$:

$$\underline{\Delta Q}_1 = -D\frac{\partial C}{\partial \underline{x}}\underline{\Delta S}_1\underline{\Delta t}$$

$$\underline{\Delta Q}_2 = -D\frac{\partial C}{\partial \underline{x}}\underline{\Delta S}_2\underline{\Delta t}$$

Using the obvious relationships

$$C_2 = C_1 + \frac{\partial C_1}{\partial \underline{x}}\underline{\Delta x}$$

$$\underline{n}_2 = \underline{n}_1 + \frac{\partial \underline{n}_1}{\partial \underline{x}}\underline{\Delta x}$$

$$\frac{\underline{n}_1}{\underline{n}_2} = \frac{S_1}{S_2}$$

and finding the limit difference ($\underline{\Delta Q}_1 - \underline{\Delta Q}_2$) at $\underline{\Delta x} \to 0$, we obtain

$$\frac{\underline{dC}}{\underline{dt}} = D\left[\frac{1}{\underline{n}(\underline{c})}\frac{\partial \underline{n}}{\partial \underline{x}}\frac{\partial C}{\partial \underline{x}} + \frac{\partial^2 C}{\partial \underline{x}^2}\right] \tag{2}$$

In Equation (2) the concentration pertains only to the accessible volume. This concentration would be higher than the one obtained by solving the equation

$$\frac{\underline{dC}}{\underline{dt}} = D\frac{\partial^2 C}{\partial \underline{x}^2} \tag{3}$$

that describes the process of diffusion into a constant-accessibility matrix where $\underline{n} = \text{const} = \underline{n}_{\max}$.

For a more graphic interpretation of the sense of the equation just obtained, let us look at Figure 2 which schematically depicts a section through the thickness of the polymer specimen with superimposed mass and accessibility profiles for an

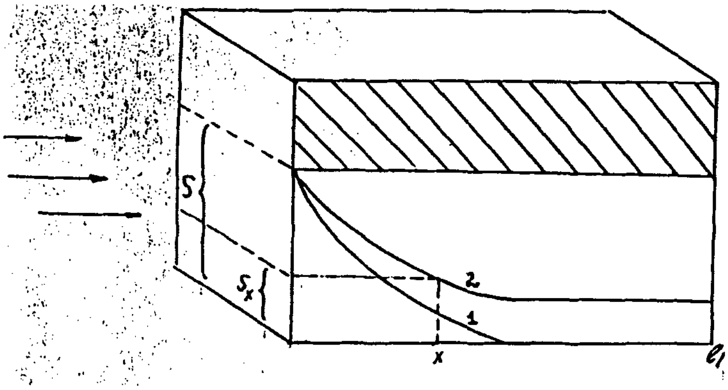

FIGURE 2 Schematic representation of the profiles of penetrant mass (1) and matrix accessibility (2) developing in the process of sorption. S and S_x are respectively the diffusion cross-sections at the specimen surface and at a distance x from the surface. The hatched area pertains to the volume of the specimen inaccessible under the given conditions.

arbitrary time of sorption. Thus with Equation (2) the penetrant concentration at distance x from the specimen surface is calculated as

$$C_x = \frac{\Delta m_x}{S_x \Delta x}$$

whereas with Equation (3) we have

$$C_x^* = \frac{\Delta m_x}{S \Delta x}$$

Obviously $C_x > C_x^*$ since $S_x < S$.

In the numerical solution of Equation (2) it is necessary to express the derivative $\partial n/\partial x$ in terms of $\partial n/\partial C$. This can be done using the experimental curve for the dependence of accessibility on penetrant mass, which can be approximated by an analytical function $m = f(n)$. Solving the equation

$$C = \frac{m}{V} = \frac{f(n)}{n \cdot V_0}$$

we can analytically or roughly estimate the function $n = \varphi(C)$. Substituting the expression for the derivative

$$\frac{\partial n}{\partial x} = \frac{\partial n}{\partial C} \cdot \frac{\partial C}{\partial x}$$

into Equation (2), we obtain

$$\frac{dC}{dt} = D\left[\frac{1}{\varphi(c)} \cdot \frac{\partial n}{\partial C}\left(\frac{\partial C}{\partial x}\right)^2 + \frac{\partial^2 C}{\partial x^2}\right] \tag{4}$$

Equation (4) can only be solved numerically, with the values $1/\varphi(\underline{c})$ and $\partial\underline{n}/\partial C$ calculated from the dependence $\underline{n} = \varphi(C)$.

To illustrate with a specific example the influence of accessibility on the diffusion rate and on the difference in the penetrant concentrations obtained with Equations (3 and (4), we shall make use of the data presented in Figure 1. In describing the process of diffusion of water at a vapor activity of 0.5 into a polymer film (equilibrium water capacity 2%, maximal accessibility 0.3), to a good approximation the dependence of the accessibility on the penetrant mass can be considered linear. During sorption, in each point of the polymer volume the accessibility would be changing from approximately 0.05 to 0.3 (the value 0.05 is the hypothetical accessibility at zero penetrant concentration, whereas at the polymer surface the accessibility is assumed equal to 0.3). In such a case the function $\underline{\varphi}(C)$ can be analytically expressed as

$$\underline{n} = \underline{\varphi}(C) = \frac{0.05}{1 - 6.72\cdot 10^{8} C}$$

which can further be used in the numerical solution of Equation (4).

Table I presents the data generated with Equations (3) and (4) for the distributions of water concentration along the diffusion coordinate for three moments of time.

Comparison of the distributions demonstrates that when accessibility is taken into account, the penetrant concentration in all cross-sections of the specimen proves to exceed the "conventional" one given by Equation (3). This excess depends on the diffusion time and on the distance from the specimen surface; in the specific

TABLE I

Distribution of relative penetrant concentrations through the thickness of polymer film (50 μm) for different times of sorption. The values of C and C^* have been calculated with Equations (4) and (3), respectively; $D = 10^{-13}$ m²/sec, $C_0 = 3.72\cdot 10^{-6}$ mole/dm³, for Equation (3) $\underline{n}$ = const = 0.3

Depth, μm	3.3 min		16.7 min		33.3 min	
	C/C_0	C^*/C_0	C/C_0	C^*/C_0	C/C_0	C^*/C_0
5	0.685	0.478	0.884	0.747	0.989	0.978
10	0.252	0.129	0.712	0.502	0.838	0.672
15	0.048	0.021	0.519	0.317	0.747	0.540
20	0.005	0.0026	0.362	0.199	0.672	0.448
25	—	—	0.295	0.153	0.642	0.422

TABLE II

Kinetics of water sorption by the polymer film. The values $\underline{m}_\infty$, $\underline{m}_t$, and $\underline{m}_t$ are respectively the equilibrium penetrant mass and the current masses calculated by Equations (4) and (3)

Relative mass	3.3 min	16.7 min	33.3 min
$\underline{m}_t/\underline{m}_\infty$ (Equation 4)	0.13	0.30	0.46
$\underline{m}_t^*/\underline{m}_\infty$ (Equation 3)	0.20	0.45	0.63

example considered here the C/C^* ratio changes from 1 to 2 in going from surface to center.

Although the current concentrations in the varying-accessibility matrix are always higher than in the constant-accessibility matrix, the rate of sorption turns out to be lower; Table II shows the respective kinetic data obtained with Equations (4) and (3). It should be noted that the change in accessibility during sorption is concurrent with plasticization of the matrix, which is known to be attended by an increase in the diffusion coefficient for the penetrant. Plasticization would not affect the pattern of the differences in concentrations but would influence the sorption kinetics. For other polymer–penetrant systems the extent of the difference in concentrations would be determined by the particular values of the diffusion coefficient, film thickness, and the form of function $\underline{n} = \varphi(C)$.

Attempts at linearizing the sorption curve generated by Equation (4) in the coordinates of the known analytical solution of Equation (3) and calculating the effective diffusion coefficient yield a value that is underestimated almost by half as compared with the one used in solving Equation (4). This signifies that if a change in accessibility takes place in a sorption experiment but is not accounted for, the resulting calculations may be erroneous.

Allowance for accessibility is especially important in the quantitative description of the processes of diffusion combined with chemical reactions, since the raction rate equation includes the penetrant concentration. Clearly in polymer–sorbate systems exhibiting plasticization the accessible volume is certain to change during sorption. Ignoring the change in accessibility and using equation of the type

$$\frac{\partial C}{\partial \underline{t}} = D\frac{\partial^2 C}{\partial \underline{x}^2} - W_{\text{chem}}$$

(where W_{chem} is the rate of the chemical reaction) would result in overestimation of the reaction rate constant calculated from the experimental data. This in its turn would lead to incorrect conclusions about the relationship between the polymer supramolecular structure and the reactivity of its functional groups, and would be a source of errors in predicting the useful life of polymer items.

3. CONCLUSION

(i) A diffusion equation is proposed for describing the sorption of a low-molecular-weight substance by a polymer with varying matrix accessibility.

(ii) Diffusion into a matrix with increasing accessibility is slower whereas the penetrant concentration in the polymer is higher than in the case of a constant-accessibility matrix.

(iii) The effect of elevated penetrant concentration in the varying-accessibility matrix must be accounted for in calculating the rate constant for chemical reactions that in polymers proceed in the diffusion–kinetic mode.

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