

Kinetics of the formation of swollen surface layer in the system polyamide—formic acid

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Dedicated to Professor A. Blažej, DrSc, Dr.h.c, on his 50th birthday

The kinetics of the formation of swollen surface layer was studied in the system crosslinked and noncrosslinked polyamide (PAD)—formic acid. It has been ascertained that the transport process of the diffusion of formic acid into the solid sample of modified and nonmodified PAD formally obeys the Fick's law. Furthermore, it has been found that the value of the parameter n occurring in the equation $\delta = k t^n$ describing the time dependence of the total width of polymeric layer decreases with decreasing concentration of formic acid in the initial penetrant. The values of mean integral diffusion coefficients of formic acid in PAD are comparable with the values found by Doležel for other penetrants. The activation energies of interfacial diffusion for all samples investigated varied in the range 24—27 kJ mol⁻¹ while their values were not substantially affected by the amount of the bonded crosslinking agent — triphenyl phosphite.

Изучалась кинетика образования поверхностного набухшего слоя в системе сетчатого и не сетчатого полиамида (ПАД)—муравьиная кислота. Было найдено, что транспортный процесс диффузии муравьиной кислоты в твердые образцы модифицированного и не модифицированного ПАД формально подчиняется законам Фика. Дальше было найдено, что при понижении концентрации муравьиной кислоты в исходном пропиточном растворе понижается также значение параметра n -выступающего в уравнении, описывающем временную зависимость общей толщины набухшего слоя полимера, $\delta = k t^n$. Значения средних интегральных коэффициентов диффузии муравьиной кислоты в ПАД сравнимы со значениями для других пропиточных веществ, полученными Долежелом.

Энергии активации межфазной диффузии для всех изучаемых образцов располагались между 24 и 27 кДж моль⁻¹, причем на их значения не оказывало существенное влияние количество сшивателя — трифенилфосфита.

If a sample of solid polymer is in contact with liquid solvent, its surface instantaneously gets saturated with the molecules of solvent. The rate of penetration of the solvent molecules into the polymer in glass-state is primarily determined by their diffusion into the polymer sample. The total width of the swollen surface layer situated at interface depends on temperature, time, and thermal history of the polymer sample.

The diffusion of solvent molecules into a polymer in glass-state is frequently accompanied by the so-called "anomalous effects" the interpretation of which is problematic from the view-point of the general Fick's theory. This problem was studied by many authors [1—5].

Kwei et al. [5] investigated the diffusion of acetone in PVC by measuring the weight of samples and the depth of penetration of the solvent molecules. These authors analyzed their results on the basis of the general equation of diffusion respecting the Fick's mechanism as well as the so-called "case II" mechanism and obtained a very good agreement of the theory with experiments. We have also obtained a similar agreement by studying the diffusion of some other solvents (cyclohexanone, cyclopentanone, 1,2-dichloroethane, *N,N*-dimethylformamide, tetrahydropyran, and monohalogenated derivatives of benzene) into PVC [6]. A detailed study of the penetration of some solvents into PAD was carried out by *Doležel* [7—9] by the microscopic method involving the intensification of the contrast between solid and liquid phase by means of an organic dye. According to this author [7—9], the values of diffusion coefficients of 0.1—1.0 N hydrochloric and sulfuric acid in noncrosslinked PAD varied within the range 10^{-12} — 10^{-11} m² s⁻¹. *Doležel* [7—9] ascertained the essential fact that the activation energy of diffusion of the above penetrants is considerably dependent on the content of crystalline fraction in original polymer.

On the basis of equal approach as in [6], we present the results of kinetic study of the formation of swollen surface layer in the system crosslinked and noncrosslinked PAD—formic acid (concentration range 30—98.8 weight % in water) in this paper.

In all cases included here, the total width of the swollen surface layer linearly depends on the square root of time at a constant temperature. This fact has been expected by *Crank* [10] for such cases when the concentration dependence of diffusion coefficient is gradual. In the first approximation, it may be assumed that the surface concentration of the solvent molecules in the polymer—solvent interface does not change all the time. Thus, on the basis of the second Fick's law

$$\frac{\partial c}{\partial t} = D \left(\frac{\partial^2 c}{\partial x^2} \right) \quad (1)$$

and boundary conditions

$$\begin{array}{ll} t = 0; \quad c_1 = 0 & \text{for } x > 0 \\ c_1 = \text{const} & x = 0 \end{array} \quad (2)$$

$$\begin{array}{ll} t = t; \quad c_1 = \text{const} & \text{for } x = 0 \\ c_1 = 0 & \text{for } x \rightarrow \infty \end{array} \quad (3)$$

Crank has derived [10] the following solution of eqn (1)

$$c_1 = c_1^0 \operatorname{erfc} \left\{ \frac{x}{[2(Dt)^{1/2}]} \right\} \quad (4)$$

where c_1^0 is the concentration of solvent in the interface and other symbols have the usual meaning. By expanding the function $\operatorname{erfc}(x)$ into a series and omitting the higher terms of the expansion, we obtain the following expression for the time dependence of the total width of the swollen surface layer δ

$$\delta = (2Dt)^{1/2} \quad (5)$$

which was used by Doležel for the calculation of D [7—9].

The solvent molecules not only penetrate into the polymer, but also cause its swelling. Therefore, the position of the interface between liquid solvent and swollen polymer changes with time. This circumstance is not involved in the solution according to Crank. This problem may be solved by introducing a mobile coordinate system in which the outer interface between swollen surface layer and liquid solvent with a constant surface concentration c_1^0 is regarded as a reference plane.

The quantity D in eqn (5) may be considered to be the apparent diffusion coefficient which is independent of concentration (Fig. 1) in the initial time interval when the concentration of solvent in the polymer is low.

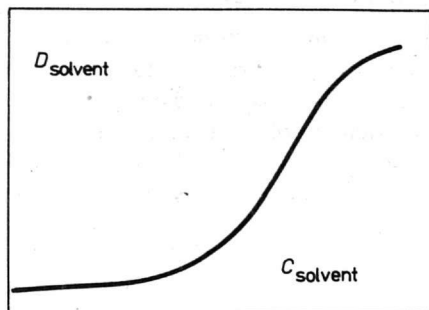


Fig. 1. Expected dependence of the diffusion coefficient of formic acid on its concentration in polymeric matrix.

Experimental

The width of the swollen surface layer was measured with a simple experimental equipment consisting of the following constituents: 1. microscope Meopta; 2. temperature controlled jacket of the measuring cell; 3. thermostatic cylinder; 4. thermostat; 5. light source. The size of polymer samples used for measurements was $6 \times 3 \times 0.25 \text{ mm}^3$. The samples were put between two plane-parallel glass plates which were so compressed with a constant pressure by means of the contiguous part of cell and two clamps that the diffusion of solvent was ensured only in the direction of the axis x while the sample was exposed approximately to equal pressure on either side perpendicular to the vector of flow.

Every sample thus adjusted was thermostated until the temperature was equal inside and outside the measuring cell. The adjusted cell was thermostated in a cylinder which was connected in series with the hole metallic jacket of the measuring cell into the temperature controlled circuit. Simultaneously, formic acid was thermostated in the glass insert placed in the temperature controlled jacket of the cell. The thermostating was accurate to $\pm 0.1^\circ\text{C}$. On reaching thermal equilibrium in the system, the measuring cell was put into the glass insert of thermostatic cylinder filled with HCOOH . As soon as the sample came into contact with the acid, a stop watch was set going and the width of the swollen surface layer was read in regular time intervals.

The following samples of crushed PAD produced in Chemlon, Humenné [11] were investigated:

— $\eta_{\text{meas}} = 1.852$ (1% solution in phenol—tetrachloroethane 1:3, 30°C), m.p. 224°C , flow index 5.5 g/10 min, content of low-molecular substances 0.53%.

— $\eta_{\text{meas}} = 1.794$ (determined under equal conditions), m.p. 224°C , flow index 6.9 g/10 min, content of low-molecular substances 2.1%.

The crosslinking of PAD with triphenyl phosphite was performed as follows: The samples of crushed PAD were dried in vacuum drier at $90\text{--}110^\circ\text{C}$ and at the pressure of 0.1 kPa for 50 h. After drying, CCl_4 (200 ml) was added to the polymer (1 kg) and the mixture was thoroughly shaken for about 1 min. Afterwards, triphenyl phosphite dissolved in CCl_4 was added in small portions to the partially cooled crushed material under constant stirring. After evaporating CCl_4 , the reaction mixture was held at 100°C for 1 h. The modified PAD was remelted at $260\text{--}280^\circ\text{C}$ and moulded in a multi-stage press into foils of 0.25 mm width.

Triphenyl phosphite was produced by CHZJD, Bratislava (b.p. 360°C or 235°C at 1.8 kPa).

Formic acid (Lachema, Brno, anal. grade, concentration of original sample 98.8 weight %) was diluted with distilled water to 30, 40, 60, and 80 weight % solutions.

The temperature dependence was measured in the interval $20\text{--}60^\circ\text{C}$ while each measurement was carried out at least three times. The individual measurements are marked by different points in corresponding figures. The selected sets of experimental data were processed by the method of least squares. The determination of D is burdened by the error $\pm 3\text{--}5\%$ and the values of activation parameters by the error $\pm 5\text{--}10\%$.

Results and discussion

The characteristic kinetic curves for the formation of swollen surface layer and interfacial diffusion in the systems noncrosslinked polyamide—formic acid and crosslinked polyamide—formic acid are arranged in Figs. 2—5. The observed spread of experimental points in the relations $\delta^2 = f(t)$ is occasionally due to fluctuation in the width of moulded foils or possibly to nonuniform distribution of aggregate structures in the whole volume of sample.

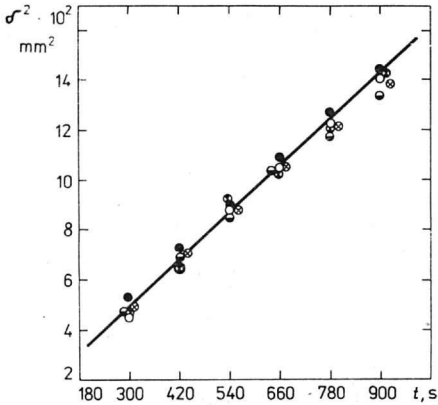


Fig. 2. Variation of δ^2 with t for noncrosslinked PAD swollen with HCOOH (98.8%) at 40°C (5 independent measurements).

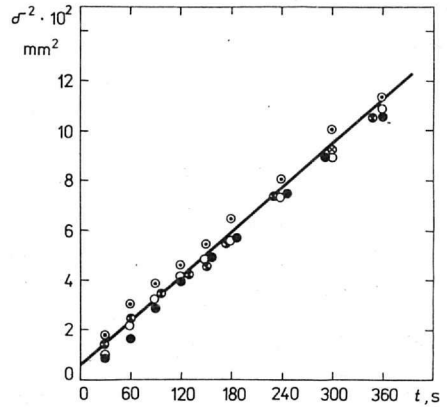


Fig. 3. Variation of δ^2 with t for noncrosslinked PAD swollen with HCOOH (98.8%) at 60°C (4 independent measurements).

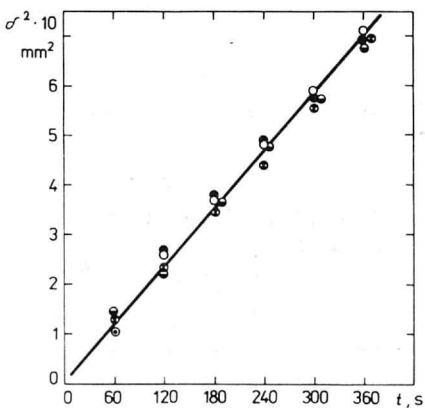


Fig. 4. Variation of δ^2 with t for crosslinked PAD containing 0.2 weight % of TPP and swollen with HCOOH (98.8%) at 50°C (4 independent measurements).

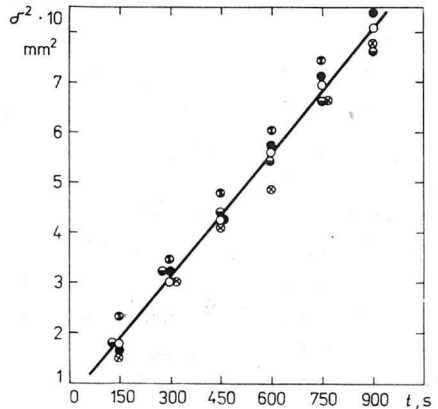


Fig. 5. Variation of δ^2 with t for crosslinked PAD containing 0.7 weight % of bonded TPP and swollen with HCOOH (98.8%) at 20°C (5 independent measurements).

It is remarkable that the diffusion of concentrated formic acid into non-crosslinked and crosslinked polyamide formally obeys the Fick's law and does not change with the concentration of bonded triphenyl phosphite at 20°C. Formally the same course as at 20°C was observed in the whole width of the temperature interval studied. A slight shift in the straight lines $\delta^2 = K t$ with respect to the origin of coordinate system observed in some cases is due to the nonperpendicularity of section of the investigated polymeric specimen and cannot, therefore, affect our statement concerning the formal mechanism of process.

As stated by many authors [6—9], the constant of proportionality is related to the mean integral diffusion coefficient D . The values of these coefficients have been calculated from eqn (5) and are listed in Table 1.

Table 1

Values of the mean integral diffusion coefficient D of formic acid (98.8%) in noncrosslinked polyamide

% TPP	$D \cdot 10^{11}, \text{m}^2 \text{s}^{-1}$				
	20°C	30°C	40°C	50°C	60°C
0	3.666	5.275	7.656	9.905	13.90
0.1	3.54	5.105	7.085	9.085	12.19
0.2	3.485	5.105	6.75	9.49	11.30
0.3	3.545	5.625	7.503	10.0	12.38
0.4	3.955	5.48	7.445	10.925	14.55
0.5	3.895	4.78	7.18	11.345	12.78
0.6	3.95	5.62	7.65	10.75	13.83
0.7	4.062	5.50	7.725	10.35	13.48

It may be stated unambiguously that the value of D increases with temperature while the absolute values in the investigated concentration region do not show any clear dependence on the amount of bonded TPP (Fig. 6). This statement is conformable to the general theory of diffusion processes in polymers. The character of transport processes in the system polymer—penetrant is, besides experimental conditions, considerably influenced by the character of both components constituting the investigated system. By introducing disturbances into the chains of macromolecules in the form of crosslinks, some motional properties of polymeric molecules are essentially affected. However, if the concentration of these defects is not high enough to change the motional state of the basic kinetic unit, *i.e.* statistic segment, it does not cause a change in the values of diffusion coefficients of low-molecular penetrants in a given matrix. The amount of TPP bonded in the investigated samples is relatively small and evidently occurs in the

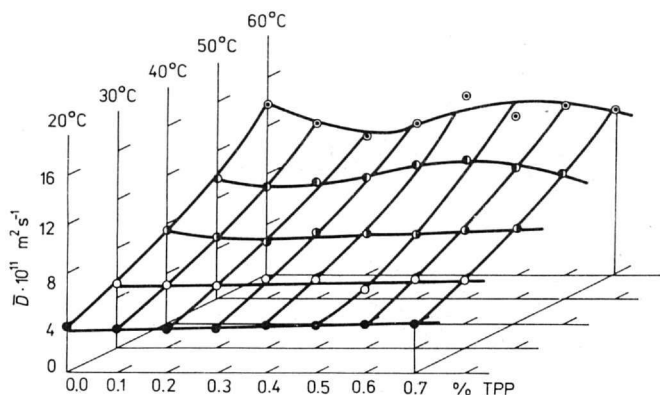


Fig. 6. Plot representing the dependence of the mean integral diffusion coefficient of 98.8% formic acid on temperature and amount of the bonded TPP.

concentration interval where the motional state of PAD segments does not considerably change.

The diffusion of solvent molecules into a polymer occurring in glass-state is frequently accompanied by the so-called "anomalous behaviour" preventing to use the Fick's laws for the quantitative description of transport phenomenon. This problem was thoroughly studied by *Alfrey* [12]. This kind of diffusion shows the following characteristic features:

— On introducing the solid polymeric sample into contact with liquid solvent, an intermediate swollen surface layer arises. This layer is distinctly separated from the remaining sample by a sharp boundary surface which is called by some authors, *Ueberreiter* [13—19], *Vasenin* [20], *Valko et al.* [21] "optical interface" in contrast to "interface" between the swollen surface layer and solution. This fact, however, is not an unambiguous criterion for estimation whether the process obeys or does not obey the Fick's laws.

— At temperatures deep below T_g of the unswollen polymer, the width of penetration, *i.e.* the weight increase, or the width of the swollen surface layer δ increases linearly with time which means that the rate of advance of the optical interface does not change with time. This case was called by *Alfrey et al.* [12] "case II transport". According to these authors, the gel layer of swollen polymer occurring behind the optical interface is in this case in the state of equilibrium swelling. As experimentally demonstrated by *Kwei* and *Zupko* [5], it holds for the ratio of the volumes of gel before (v) and after (v_0) swelling

$$\frac{v}{v_0} = \frac{\delta}{d} \quad (6)$$

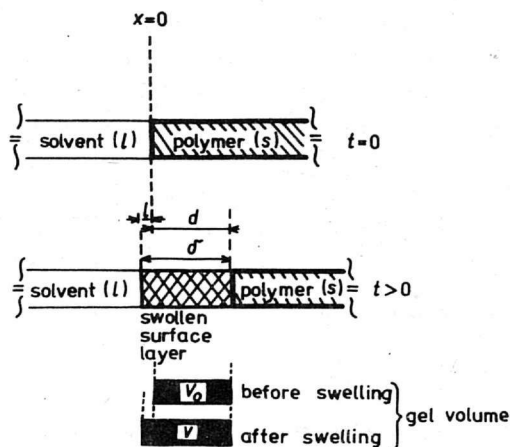


Fig. 7. Schematic representation of the course of swelling.

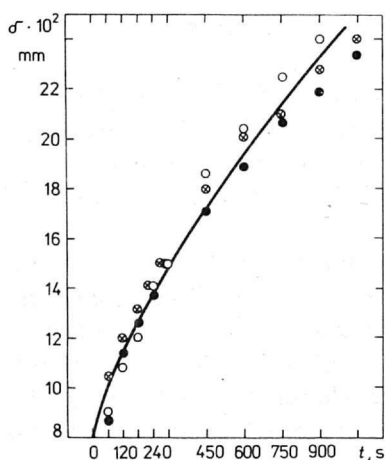


Fig. 8. Width of the swollen surface layer δ as a function of the time of swelling t of non-crosslinked PAD in 60% HCOOH at 25°C (3 independent measurements).

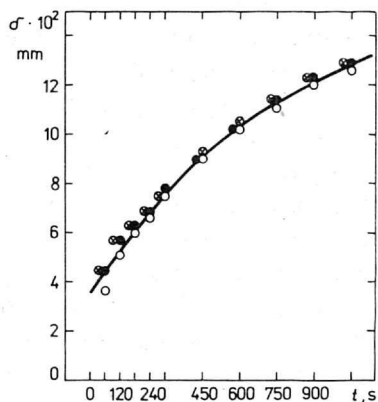


Fig. 9. Width of the swollen surface layer δ as a function of the time of swelling t of crosslinked PAD (0.5 weight % of TPP) in 40% HCOOH at 25°C (3 independent measurements).

where δ is the total width of the swollen surface layer and d is the distance to which the optical interface has advanced from a spatially fixed origin in the interface polymer—solvent at the time $t=0$.

Because of a large error accompanying the experimental investigation of the value of l which is in our case by decimal order smaller than δ and d , we focused our attention on the determination of the value of δ (Fig. 7).

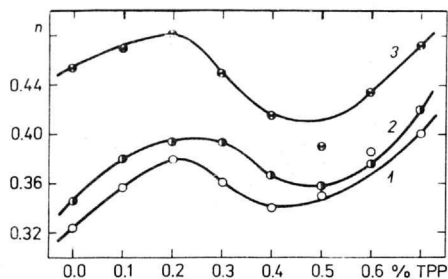


Fig. 10. Variation of the parameter n occurring in eqn (7) with the amount of bonded TPP for different concentrations of the penetrant (HCOOH) at constant temperature 25°C.
1. 40%; 2. 60%; 3. 80%.

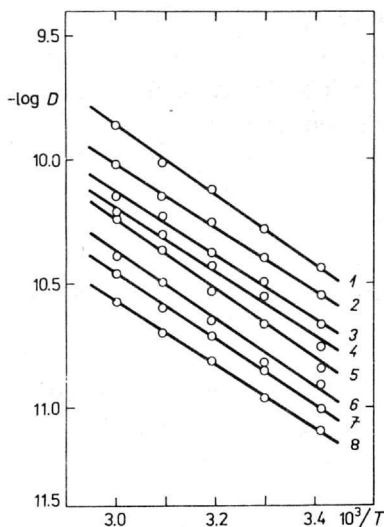


Fig. 11. Dependence of D on T in Arrhenius coordinates for 98.8% HCOOH and PAD containing different amounts of bonded TPP (weight %).
1. 0%; 2. 0.1%; 3. 0.2%; 4. 0.3%; 5. 0.4%; 6. 0.5%; 7. 0.6%; 8. 0.7%.

For easy understanding, the coordinate system y is shifted with respect to the axis x always by 0.1 unit beginning with curve 2.
 D is expressed in $\text{m}^2 \text{s}^{-1}$.

In none of the cases we found a linear dependence of the width of the swollen surface layer on time. The course of the function $\delta = f(t)$ (Figs. 8 and 9) is slightly curved and can be expressed in all cases by the equation

$$\delta = k t^n \tag{7}$$

where the constant n is a function of the concentration of HCOOH and for dilute solutions of HCOOH of the concentration of the bonded TPP, as well. It was expected that the value of n should decrease with increasing concentration of TPP. It is obvious from Fig. 10 that the value of n varies in the investigated concentration interval of TPP at 25°C according to the following semicubical parabola

$$n = ax^3 + bx^2 + cx + d' \tag{8}$$

where a, b, c, d' are empirical constants and x is the weight percentage of bonded TPP.

These facts necessitate a deeper theoretical analysis because of a possible

dissociation of HCOOH and selective bonding of the H_3O^+ and $HCOO^-$ ions to the chains of modified and nonmodified polyamide as well as of a possible formation of "quasi-phase" electric potentials between particular sublayers of the overall swollen surface layer.

A considerable part of polymeric materials which are widely used in technical practice may be regarded as heterogeneous systems. From the view-point of internal structure they may be divided into three main groups: 1. dispersed phase in continuum; 2. two or several phases permeating each other; 3. laminates.

Our case evidently belongs to the first group. It is known [11] that the material studied was neither purely crystalline nor purely amorphous but represented a system containing both phases. In general, it is assumed that the diffusion of low-molecular substance proceeds in purely crystalline regions much slower owing to high order of the system. The high values of the measured diffusion coefficients as well as the low values of activation energy for interfacial diffusion which are comparable with the corresponding values found for amorphous polymers, however, indicate that the process of swelling proceeds uniformly in a sample. Therefore, different driving forces (internal and external) which accelerate the diffusion in crystalline regions and retard the diffusion in amorphous regions must be in operation for a given penetrant. It seems that the decisive and most mobile component in the system is the ion H_3O^+ which is, because of its small volume, able to diffuse easily by the vacant mechanism even into the geometrically more or less perfectly arranged crystalline structures of polyamide.

It follows from Fig. 11 that the dependence of the mean integral diffusion coefficient on temperature may be described by a general equation of the type

$$D = D^0 \exp\left(\frac{-E_D}{RT}\right) \quad (9)$$

Table 2

Activation parameters E_D and D^0 for the formation of the swollen surface layer in the system HCOOH (98.8%) – (PAD crosslinked with TPP)

Weight % of bonded TPP	E_D kJ mol ⁻¹	$D^0 \cdot 10^6$ m ² s ⁻¹
0	26.7 ₂	2.12 ₀
0.1	24.7 ₀	0.91 ₀
0.2	24.2 ₅	0.74 ₉
0.3	25.0 ₂	1.08 ₅
0.4	26.6 ₀	2.12 ₂
0.5	25.0 ₆	1.16 ₀
0.6	25.5 ₈	1.44 ₁
0.7	24.6 ₀	0.97 ₆

The corresponding values of the calculated apparent activation energies of diffusion E_D and the pre-exponential factors D^0 as a function of the concentration of TPP are listed in Table 2. We can see that the activation energy varies in the range 24–27 kJ mol⁻¹ for all samples investigated, which is a value several times lower than the value expected. This result confirms the above-mentioned considerations.

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