# Permeation of carbon dioxide and water vapour in plasticized poly(vinylchloride)–starch blends: anomalous behaviour

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A method is presented for studying anomalies in the diffusion of gases and vapours in dense polymer films in the transient regime. It was applied to the diffusion of $CO_2$ and water vapour in plasticized-poly(vinylchloride)(PVC)–potato-starch blends. The apparent diffusion coefficient of $CO_2$ in plasticized PVC remains constant in the transient regime, while that of water vapour first increases, passes through a maximum and then finally decreases to a constant value. The anomalous process observed for water vapour permeation in the transient regime can be explained by the interaction between the diisooctylphthalate (DIOP) plasticizer and the deformation of the polymer network due to stresses generated by the starch particles swelling. For water vapour in the stationary regime, the diffusion coefficient decreases and sorption coefficient increases when the starch content increases. There is a strong increase in both sorption and diffusion coefficients when pure PVC is replaced by DIOP-plasticized PVC.

**(Keywords: plasticized-PVC–starch blends; permeability; anomalous permeation)**

## INTRODUCTION

Understanding of the diffusion of gases and vapours in polymers is of great importance for controlling the permeability of these components in films used in packaging, protection coating or in membrane-based separations. It is well known that the diffusion of condensable gases and vapours in many polymers, particularly polymers in the glassy state, is ‘anomalous’, i.e. the process cannot be adequately described by Fick’s law. A review of anomalous phenomena that may occur during sorption and desorption of vapours in polymers has been given by Crank and Park[1]. The anomalies were generally attributed to the time-dependences of sorption and diffusion properties. A general mathematical analysis of transport in glassy materials based on irreversible thermodynamics has been given by Frisch[2], who considered time-dependent phenomena to have resulted from the relaxation of internal degrees of freedom. Rational thermodynamics developed more recently[3,4] are, in principle, suitable for describing such phenomena not only for diffusion, but also for reaction in polymers, since they are not limited by linearity or closeness to equilibrium. The linearized version of the theory applied to the mixture of a fluid and a polymer solid has led to equations for anomalous diffusion of gas in a polymer[5]. Crank[6] has set up a model in which the diffusion coefficient increases in a second stage due to the relaxation processes in the glassy state of the polymer. The model, which was capable of producing anomalous sorption and desorption curves of some solvent-vapour–polymer systems, assumed that the rate of increase in the diffusion coefficient at constant concentration obeys the first-order law.

Whatever the nature of the anomalies, the first problem is the determination of the apparent change in the sorption or the diffusion properties. The most generally used method is based on the measurement of the sorption kinetics in a quartz-spring balance[1]. Park[7] also measured the permeation rates as a function of time by accumulating the permeated species during successive periods of time. This procedure is suitable for films whose properties change rather slowly with time and which are relatively permeable to the species considered.

In this paper a dynamic permeation method is described, which enabled a fast change in permeability with time to be monitored, particularly the change that occurs before steady-state permeation is reached. With the assumption of constant concentration of the permeant at the membrane upstream face[1], at least in the transient regime, the variation with time of an apparent diffusion coefficient determined from the permeability at different times provides a way of quantitatively measuring the departure of the permeability from ideal Fickian

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behaviour. A better insight into the polymer–penetrant system during the transient permeation process could then be obtained from the variation of this departure with time in the transient regime. The method also provides opportunities to ascertain whether or not the diffusion process is Fickian with constant diffusion, and to obtain the value of the diffusion coefficient when it again becomes constant. Without such an analysis of the transient regime, the simplified method of determination of the diffusion coefficient from the time at which the permeation flux reaches half the value at steady state[8–10], which postulates that the diffusion is Fickian with constant diffusion coefficient, should not be used.

In the first part of the paper, the theoretical framework of the 'thermodynamics' origin of the time-dependence of the permeation flux and the calculations that lead to the apparent diffusion coefficient are described. In the second part, results concerning plasticized-PVC–potato-starch blends are reported and discussed. These polymer blends have been used in the manufacture of artificial leather in Czechoslovakia.

## THEORY

### *Thermodynamics*

Many phenomena may affect the course of permeation, including modification of the solubility or diffusivity of the permeant, e.g. interactions between the permeant and the polymer network, reorganization of the material structure (relaxation, crystallization, phase segregations), deformation of the polymer network due to stresses generated by differences in swelling in the volume of the polymer, micro-crack formation or healing. However, they are difficult to observe directly because of space and time scales on which they occur. Not only may they affect the properties of the permeant in the polymer material, but also the driving force of the transport in the membrane.

Here, the permeation flux of a pure component, in the framework of rational thermodynamics, is expressed as a function of the gradient of the chemical potential, the deformation tensor gradient and the gradient of an internal parameter $\beta$, which represents the influence of structural changes in the materials[5]:

$$J = L\left(\frac{\delta\mu}{\delta C}\right)\frac{\delta C}{\delta x} + L\left(\frac{\delta\mu}{\delta B}\right)\frac{\delta B}{\delta x} + L\left(\frac{\delta\mu}{\delta B}\right)\frac{\delta\beta}{\delta x} \qquad (1)$$

where $J$ is the density of permeation flux, $L$ is Onsager's coefficient, $\mu$ is the chemical potential, $C$ is the concentration of permeant, $B$ is the deformation tensor, $\beta$ is the structure-related internal parameter and $L(\delta\mu/\delta C)$ corresponds to the diffusion coefficient, i.e. the mobility of the permeant due to a gradient in chemical potential.

Equation (1) is valid for isothermal permeation without external fields and inertial forces, and for an isotropic material in undistorted reference (infinitesimal deformation). Therefore, transport through micro-cracks, which represents the heterogeneity in the material, is not included in this equation. The first term corresponds to the 'generalized' Fick law (diffusion flux due to a gradient in the chemical potential) and the last two terms express the influence of the deformation of the polymer network and the structural changes on the permeation flux. If the contribution of these two terms is important, the transport deviates from that described by Fick's laws and becomes anomalous. The last term is related to the structure of the polymer, e.g. to the formation of interaction complexes between the polymer and the permeant, while the second term is related to the deformation of the polymer network whether it is isotropic or not. Depending on the variation on the chemical potential with these parameters, it makes a negative or positive contribution through these terms to the overall flux to make the transport non-Fickian.

### *Calculations of the apparent diffusion coefficient as a function of time by the dynamic permeation method*

The departure from Fickian diffusion gives a quantitative measurement of the transport due to non-equilibrium situations in potentials other than the chemical potential.

A convenient method for determining the Fickian diffusion coefficient is the dynamic measurement of diffusivities through polymer films[7,8]. It is based on the continuous measurement of the rate of permeation of a permeant into the gas flowing past one side of the membrane, when a step change in partial pressure of the penetrant is imposed on the other side. An inexpensive thermal conductivity detector, a semiconductor detector and a flame ionization detector are suitable for continuously monitoring the permeation rate. The calculation method proposed by Felder *et al.*[8], which requires a numerical integration of the response data, can give a precise determination of the diffusion coefficient when the diffusion is Fickian. For Fickian diffusions through flat sheets, Fick's second law:

$$\frac{\delta C(t,x)}{\delta t} = D'\frac{\delta^2 C(t,x)}{\delta x^2} \qquad (2)$$

can be solved to yield, in the case of constant diffusivity $D'$ and boundary conditions $C(0,x)=0$, $C(t,l)=0$ and $C(t,0)=C_1$:

$$J = (D'C_1/l)\left[1 + 2\sum_{n=1}^{\infty}(-1)^n \exp(-D'n^2\pi^2 t/l^2)\right] \qquad (3)$$

where $J$ is the apparent permeation flux at the time $t$, $l$ is the membrane thickness, $t$ is the elapsed time and $C_1$ is the concentration at the membrane upstream face, which is assumed to be constant. The alternative solution for the same boundary conditions is:

$$J = (4D'C_1/\pi^{0.5}l)(l^2/4Dt)^{0.5}\sum_{m=0}^{\infty} \times \exp[-(2m+1)^2 l^2/4D't] \qquad (4)$$

The diffusion coefficient can be deduced by the curve-fitting method over the complete response in time or estimated by different techniques[10]. Nevertheless, it is difficult to determine whether the deviations from those curves are due to experimental error, or the difficulty caused by the nonlinearity of equation (4), or to a violation of the assumptions of the diffusion model.

We propose a method for calculating the apparent diffusion coefficient, whose variation with time can be attributed to the non-Fickian terms, whatever the physical origin of the phenomena is. Equation (3) can be rewritten as:

$$r = J/J_s = 1 + 2\sum_{n=1}^{\infty}(-1)^n \exp(-D'n^2\pi^2 t/l^2) \qquad (5)$$

where $J_s$ is the steady-state permeation flux (at large time $t$) and $r$ is the reduced value of flux at the considered time $t$:

$$J_s = D'C_1/l \tag{6}$$

When all the terms with $n > 1$ in the series can be neglected, equation (5) reduces to

$$D'\pi^2 t/l^2 = -\ln[(1-r)/2] \tag{7}$$

Equation (7) permits computation of the 'apparent' diffusion coefficient $D'$ with less than 2% error at times for which $J > 0.46J_s$[8]. For the calculation of early-time diffusion coefficient, more terms in the series should be considered. With the second and third terms of the series taken, equation (7) can be rewritten as:

$$D'\pi^2 t/l^2 = -\ln[(1-r)/2 + q - p] \tag{8}$$

where the terms $q$ and $p$ are defined, respectively, by:

$$q = \exp\{4\ln[(1-r)/2]\} \tag{9}$$

$$p = \exp\{9\ln[(1-r)/2]\} \tag{10}$$

The series in equation (4) converges more quickly, so all the terms with $m > 1$ can be neglected for the computation of $D'$ at times for which $J < 0.97J_s$[8].

By using the same reduced parameters as above, the corresponding expression for (4) is:

$$r = [4/(2\pi)^{0.5}](l^2/2Dt)^{0.5}\exp(-l^2/4Dt) \tag{11}$$

or

$$2\ln[r(2\pi)^{0.5}/4] = -u + \ln u \tag{12}$$

where

$$D' = l^2/2ut \tag{13}$$

For the computation of 'apparent' diffusion coefficients $D'$ either by equations (8) or (13), the reduced flux $r = J/J_s$ is calculated at each instant $t$ and the equations (8) and (13) are solved to yield $D'$. If the values of $D'$ obtained from both equations are identical and constant in the whole transient period, the diffusion process is Fickian with the constant diffusion coefficient given by these equations.

If the transport is not Fickian, or the diffusion coefficient is not constant, equations (8) and (13) will no longer give the same, constant values for $D'$, which are no longer the value of the diffusion coefficient. They correspond to the values that the diffusion coefficient would take at the considered time in order to meet the obtained value of the reduced flux. If they are higher at a certain time than the stabilized value of $D'$ obtained when the polymer comes to a relaxed state, this would mean there was a positive contribution to the permeation flux from other terms at that time. Therefore, the variation of the value of $D'$ as a function of time may give some information about the dynamics of permeation, since it represents the deviation of the actual permeation from the Fickian behaviour in the transient regime. An example of this situation is given in *Figure 1*: the actual diffusion pattern does not fit the ideal curves computed from equations (3) and (4) and the $D'$ values correspond to the cross-points at different time.

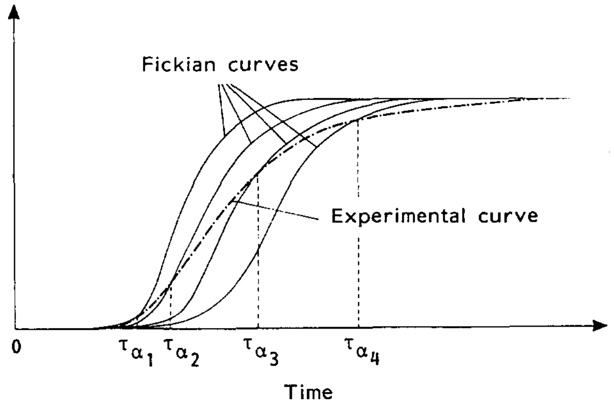

**Figure 1** Diagram of permeation flux *versus* time as obtained experimentally for anomalous diffusion and ideal Fickian flux curves computed with different values of diffusion coefficient

## EXPERIMENTAL

### *Membranes*

The plasticized membranes were made by mixing diisooctylphthalate (DIOP) plasticizer with potato starch (of specific surface area 0.19 $m^2 g^{-1}$) with poly(vinylchloride) (PVC) (Vestolit B7021 from Germany) at 180°C and storing the blend under low atmospheric pressure (to minimize bubble formation) for 24 h before hot calendering. They were about 100 $\mu$m thick and free from volatile substances. The films obtained were slightly translucent.

The pure PVC film was prepared by slow evaporation of PVC solution-cast on a glass plate at room temperature. Its thickness was 3 $\mu$m.

### *Procedure*

The membrane was clamped in a cell and suddenly put into contact with a gas or vapour source at constant pressure in order to obtain a step concentration. The permeant emanating from the downstream face of the membrane was carried away by a stream of hydrogen to a thermal conductivity detector[11], the output from which was recorded until a stable signal was obtained[11]. All experiments were made at 25°C at the partial pressure of 101.325 kPa for $CO_2$ and 3.167 kPa for water vapour (saturation pressure at 25°C).

The permeation flux of the film for water vapour and for $CO_2$ was calculated from the steady-state value by using appropriate calibration curves of the detector. The permeability coefficient was obtained from the equation:

$$P = Jl/\Delta p \tag{14}$$

where $J$ is the permeation flux, $P$ the permeability coefficient, $l$ the membrane thickness, and $\Delta p$ the difference in partial pressure between the upstream and downstream compartments.

## RESULTS

### *Diffusion of water vapour in pure PVC*

The apparent diffusion coefficient of water vapour through this film is constant over the whole transient period and corresponds to the constant Fickian diffusion coefficient of $1.5 \times 10^{-14}$ $m^2 s^{-1}$. It should be noted that the pure PVC film was prepared by solution casting, while the plasticized film was made by calendering.

### *Diffusion of water vapour in PVC plasticized by DIOP*

Values of apparent diffusion coefficient computed from the flux of permeation through the 100:80 PVC–DIOP film at various times are plotted as a function of time together with equation (13) in *Figure 2*. It can be seen that the apparent coefficient first increases rapidly with time to a maximum of $2.5 \times 10^{-12}\ m^2\ s^{-1}$ at about half of the steady-state flux value of $J_s$ ($t = 100$ s), then decreases progressively to a stable value of $D' = 1.3 \times 10^{-12}\ m^2\ s^{-1}$ at $t = 650$ s. No change in diffusivity is observed after this time to times much longer than that of the 99% steady-state flux value (900 s). The stabilized value is found to be consistent with the value given by Thomas[12] for plasticized PVC ($1.7 \times 10^{-12}\ m^2\ s^{-1}$ at 30°C).

### *Diffusion of water vapour in DIOP-plasticized PVC–potato-starch blends*

*Figure 3* shows the details of the variation of the apparent diffusion coefficient as a function of time for the 100:80:5 PVC–DIOP–potato-starch blend. The apparent diffusion coefficient achieves its maximum at $t = 231$ s with a shoulder at 565 s, where the corresponding diffusion coefficients are, respectively, $6.4 \times 10^{-12}\ m^2\ s^{-1}$ and $4.6 \times 10^{-12}\ m^2\ s^{-1}$. It decreases next to the constant value of $4 \times 10^{-12}\ m^2\ s^{-1}$ at 800 s and remains constant for the rest of the experiment.

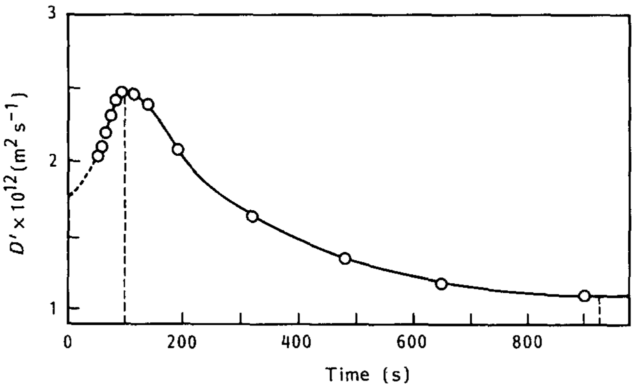

**Figure 2** Variation of diffusion coefficient as a function of time in the transient regime for the permeation of water vapour through the 100:80 PVC–DIOP membrane

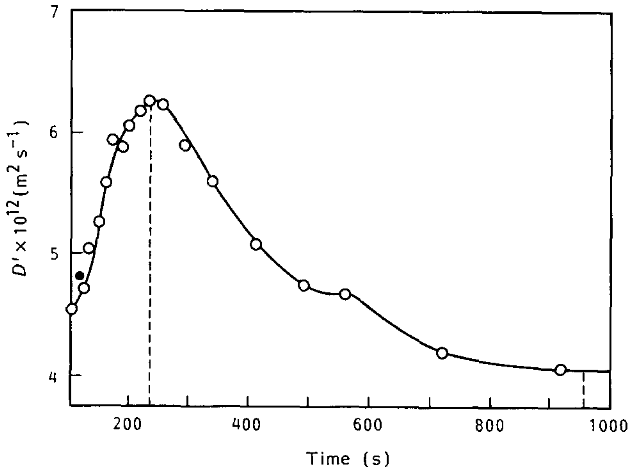

**Figure 3** Variation of diffusion coefficient as a function of time in the transient regime for the permeation of water vapour through the 100:80:5 PVC–DIOP–potato-starch blend

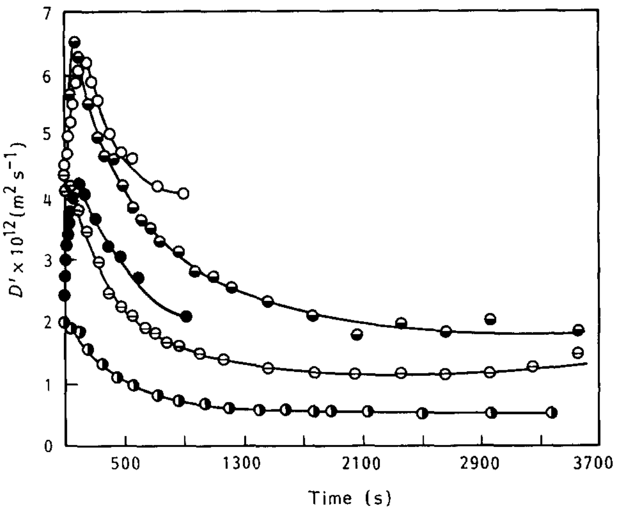

**Figure 4** Influence of the amount of potato starch in the PVC–DIOP–potato-starch blends on the plots of diffusion coefficient *versus* time (◑ 5, ⊖ 10, ● 20, ◒ 30 and ○ 40 mass% of potato starch in the 100:80 PVC–DIOP polymer)

**Table 1** Values of steady-state diffusion coefficient of water vapour in PVC–diisooctylphthalate (DIOP)–potato-starch blends of different composition

| Composition (mass%) | | | $D' \times 10^{12}$ |
|---|---|---|---|
| PVC | DIOP | Starch | ($m^2\ s^{-1}$) |
| 100 | 0 | 0 | 0.015 |
| 100 | 80 | 0 | 1.30 |
| 100 | 80 | 5 | 4.01 |
| 100 | 80 | 10 | 1.93 |
| 100 | 80 | 20 | 1.52 |
| 100 | 80 | 30 | 1.24 |
| 100 | 80 | 40 | 0.52 |

The time dependences of the diffusion coefficient obtained with the blends containing different amounts of added potato starch are shown in *Figure 4*. For the blends containing up to 20% by mass of potato starch (the mass portions of PVC and DIOP are kept at the same levels of 100% and 80%, respectively), the plots of apparent diffusion coefficient *versus* time have the same pattern with a maximum at about 250 s. For higher contents of potato starch in the blend, the diffusion coefficient starts at a high level and decreases steadily with time to a constant value at long time. The stabilized values of the diffusion coefficients shown in *Table 1* decrease when the starch content increases. On the other hand, the values of diffusion coefficient calculated from equations (8) and (13) are generally similar (*Table 2*).

### *Diffusion of $CO_2$ in pure PVC*

The apparent diffusion coefficient does not depend on time in the transient regime and is equal to $6 \times 10^{-14}\ m^2\ s^{-1}$ for the solution-cast film.

### *Diffusion of $CO_2$ in DIOP-plasticized PVC*

The dynamic permeability of $CO_2$ was measured with the same membrane sample as above. The plot of apparent diffusion coefficient as a function of time (*Figure 5*) is practically constant ($D' \approx 2.3 \times 10^{-11}\ m^2\ s^{-1}$). The

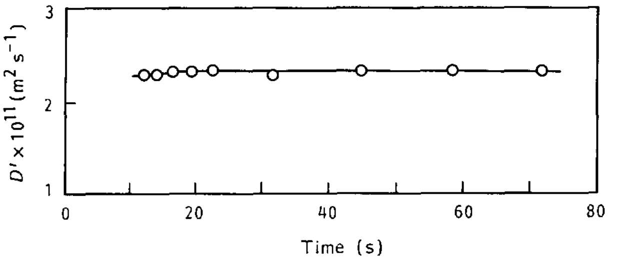

**Figure 5** Variation of diffusion coefficient as a function of time in the transient regime for the permeation of $CO_2$ through the 100:80 PVC–DIOP membrane

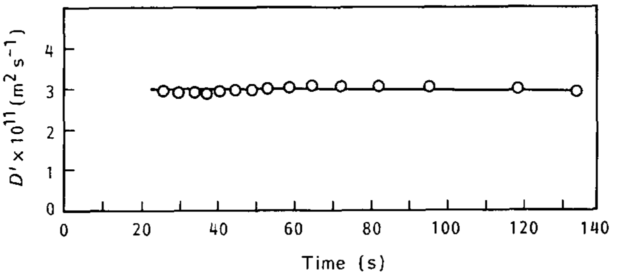

**Figure 6** Variation of diffusion coefficient as a function of time in the transient regime for the peremation of $CO_2$ through the 100:80 PVC–DIOP membrane

**Table 2** Values of steady-state diffusion coefficient of carbon dioxide in PVC–DIOP–potato-starch blends of different composition, as calculated from equations (8) and (13)

| Composition (mass%) | | | $D' \times 10^{11}$ ($m^2$ $s^{-1}$) (equation (8)) | $D' \times 10^{11}$ ($m^2$ $s^{-1}$) (equation (13)) |
|---|---|---|---|---|
| PVC | DIOP | Starch | | |
| 100 | 0 | 0 | 0.0065 | 0.0065 |
| 100 | 80 | 0 | 1.30 | 1.30 |
| 100 | 80 | 5 | 2.96 | 3.00 |
| 100 | 80 | 10 | 2.70 | 2.70 |
| 100 | 80 | 20 | 3.10 | 3.12 |
| 100 | 80 | 30 | 2.91 | 2.96 |
| 100 | 80 | 40 | 3.13 | 3.12 |

diffusion of $CO_2$ in PVC plasticized by DIOP then satisfies the assumption of Fickian diffusion with constant diffusion coefficient.

### *Diffusion of $CO_2$ in PVC–DIOP–potato-starch blends*

*Figure 6* shows that the diffusion coefficient of $CO_2$ is practically constant. The constant values vary slightly with potato-starch content, but the variation seems to be due to small changes in the properties of the prepared membranes (*Table 2*). The diffusion coefficient values obtained from both equations (8) and (13) are identical within the experimental error range (*Table 2*): $(2.9 \pm 0.2) \times 10^{-11}$ $m^2$ $s^{-1}$ for the starch content ranging from 5 to 40 parts. Therefore, it can be concluded that the diffusion process is completely Fickian with constant diffusion coefficients.

## GENERAL DISCUSSION

It appears that the diffusions of $CO_2$ and water vapour through plasticized PVC blended with potato starch show different behaviour in the transient regime. The diffusion of $CO_2$ is Fickian, while that of water vapour is anomalous. It is well known that the diffusion of water in many glassy polymers is not Fickian, which is due to the fact that water molecules are small and have the strong ability to form hydrogen bonds between themselves or with the polymer. Aggregation of sorbed water in hydrophobic materials may occur and leads to a decrease in diffusion coefficient.

If the diffusion is Fickian, but is concentration-dependent, e.g. the diffusion coefficient increases exponentially with the local concentration of the permeant in the polymer, as generally observed for organic-vapour–polymer systems[13], but also for water–ionomer membrane systems[14], the values of calculated apparent diffusion coefficients would steadily increase in the transient regime, since the penetrant content at any point of the membrane would increase with time (until the steady rate is reached).

Such a steady increase in the diffusion coefficient was not observed in our experiments. Instead, in all cases, the apparent diffusion coefficient tends towards a constant $D'$ value later in the transient regime. This indicates a negligible concentration dependence for both $CO_2$ and water vapour. There is, therefore, negligible 'plasticizing' effect of penetrant molecules on their diffusion in the network. The behaviour observed is consistent with the fact that, unlike in the cases cited above[13,14], the PVC matrix does not show such a significant swelling by $CO_2$ or by water vapour.

The anomalous diffusion observed for the dynamic permeation and the proposed method of calculation needs to be discussed in more detail. The diffusion anomalies can be classified into three types according to their characteristic features[14–16]: sigmoid, for the general shape of the sorption curves; two-stage sorption, in which there is a first stage of rapid uptake of vapour to a pseudo-equilibrium, followed by a slower approach to a final true equilibrium in a second stage; advancing boundaries (case II), in which a sharp boundary of penetrant is observed. It should be emphasized that this generally accepted classification is essentially based on characteristic behaviour in sorption-rate measurement.

**Table 3** Values of the apparent diffusion coefficient $D'$ calculated at various times during the transient regime by using equations (8) and (13) for the system of water vapour and the 100:80:5 PVC–DIOP–potato-starch blend

| $t$(s) | $r$ | $D' \times 10^{12}$ ($m^2$ $s^{-1}$) (equation (8)) | $D' \times 10^{12}$ ($m^2$ $s^{-1}$) (equation (13)) |
|---|---|---|---|
| 103.5 | 0.017 | 4.55 | 6.38 |
| 123.0 | 0.046 | 4.72 | 5.71 |
| 130.5 | 0.074 | 5.04 | 5.70 |
| 148.5 | 0.131 | 5.27 | 5.60 |
| 159.9 | 0.179 | 5.58 | 5.76 |
| 168.0 | 0.246 | 5.95 | 6.04 |
| 187.5 | 0.303 | 5.88 | 5.93 |
| 198.9 | 0.360 | 6.09 | 6.12 |
| 214.5 | 0.417 | 6.18 | 6.19 |
| 231.0 | 0.474 | 6.26 | 6.27 |
| 253.5 | 0.531 | 6.23 | 6.23 |
| 292.5 | 0.589 | 5.91 | 5.91 |
| 337.5 | 0.646 | 5.62 | 5.62 |
| 412.5 | 0.703 | 5.07 | 5.07 |
| 489.0 | 0.760 | 4.76 | 4.76 |
| 561.3 | 0.817 | 4.68 | 4.68 |
| 723.3 | 0.874 | 4.21 | 4.20 |
| 918.3 | 0.931 | 4.08 | 4.03 |

In fact, the situation is different in transient permeation and transient sorption. The sorption measurements give the integrated vapour take-up, the variation of which as a function of time depends on the driving force. As the driving force for diffusion decreases progressively, once the vapour reached the centre of the film, the rate of sorption also decreased, whatever the physical phenomenon, and misinterpretation may be made in these conditions. In transient permeation, provided the concentration in permeant in the downstream side of the membrane is kept very low, the driving force remains constant during the experiments.

The anomalous diffusion observed is obviously not of the case II type, for which the permeation rate would be very low when the diffusion boundary is still in the membrane, but once the front reaches the downstream face, the permeation rate (and therefore the apparent diffusion coefficient) would increase rapidly to the steady state.

The model developed by Long and Richman[17] to account for two-stage sorption does not seem to be suitable for our cases either. Based on microradiographic determination of concentration distributions as a function of time, these authors have proposed a model in which the surface concentration increases with time due to a slow rearrangement of polymer chains. It transpires that, with this model, we would obtain an apparent diffusion coefficient that increases with time; this increase would occur in two steps, as observed in transient sorption, when the diffusion down the initial gradient is complete before there is any significant increase in surface concentration.

Crank[15] has suggested a model in which the surface concentration is held constant, but the diffusion coefficient is a function of time, to account for sigmoid and some pseudo-Fickian types of sorption curves. First, the diffusion coefficient immediately increases at the step increase in the penetrant concentration at the surface, then slowly drifts in a second stage towards an equilibrium as a result of the relaxation process characteristic of the glassy state.

Our results can be qualitatively explained in a similar way. Based on our thermodynamics approach the first stage corresponds to a change in polymer structures and a strong deformation of the polymer network. As a consequence, the second and the third terms in equation (1) increase with time from a nil value, leading to a growing positive deviation from the ideal diffusion law (equation (1)). The deformational and structural changes gradually extend through the membrane thickness and the diffusion coefficient curves reach an extremum. The position of the extremum (*Figure 4*) varies with the relative rates and amplitudes of these processes.

In a further stage, the deformational and structural changes gradually approach a balance, i.e. the second and third terms in equation (1) tend to vanish. This stage corresponds to the relaxation of the strained network and is reflected by a decrease in diffusion coefficient (*Figure 4*).

We postulate that there could be a third stage, which may be related to a slow relaxation of larger segments of chains (reorganization of chains). This stage corresponds physically to the slow relaxation considered by Crank[15], which leads to a further increase of the diffusion coefficient with time. Such a situation was not observed in the systems presented in this paper, but is observed in other systems, depending on the natures of the penetrant and the polymer.

Although no physical picture can be directly drawn from the results, the analysis of the variations of $D'$ with time for different membrane–permeant systems on the basis of their physicochemical properties might give a better insight into the behaviour of polymers in permeation.

It seems important to us to emphasize once again that the apparent diffusion coefficient $D'$ is equal to the true diffusion coefficient only for Fickian diffusion with constant diffusion coefficient, e.g. for diffusion of $CO_2$ in all films studied, and water in pure PVC. In the other cases, $D'$ is simply a measure of the deviation from the ideal Fickian behaviour and its values include all the contributions to the permeation.

The Fickian permeation observed for all the films and $CO_2$ gas indicates that this gas behaves similarly to permanent gases at the pressure studied. The much higher diffusion coefficient obtained with the DIOP-plasticized film compared with the unplasticized film may be attributed to the presence of the plasticizer, which imparts a higher segmental mobility (or a higher free volume) to the polymer material.

The fact that the diffusion of water vapour through pure PVC is Fickian, while that through the plasticized films is anomalous, would mean that the presence of this plasticizer is the cause of the anomalies. It should be noted that the plasticizer is compatible with the polymer, so that any phenomenon affecting the DIOP molecules would affect the behaviour of the polymer–plasticizer system. The DIOP molecule possesses an ester group, which is a strong hydrogen-bond acceptor[18]. In the presence of water, the carbonyl group will bind with water to form a hydration complex. As a result, when the film is put into contact with the water vapour, the contribution of the last term in equation (4) (change in the chemical potential with the change in internal structures) would increase with time to a maximum and then would decrease down again to zero as the diffusion progresses because of the saturation of the ester sites. The experimental curve (*Figure 2*) depicts such a change in the apparent diffusion coefficient.

With increasing starch content, the curves of $D'$ *versus* time show a similar pattern to that for the plasticized PVC film up to 20% of starch (*Figure 4*). For blends containing 30 and 40% starch, the early increase in $D'$ practically disappears and $D'$ decreases steadily to approach a constant value. One can also notice the decrease in the steady-state value of $D'$ with the increase in starch content (*Figure 4*).

In order to interpret the results, two features should be borne in mind: the heterogeneity of the blends of starch with plasticized PVC due to the incompatibility of the two polymers (as shown in *Figure 7*); the affinity of starch to water due to the presence of hydroxyl groups in the glucopyrannose monomer units. The intrachain hydrogen bonds make the starch chain insoluble, at least at low temperature (starch is gelatinized in hot water).

The results obtained with the blends may be explained as follows. The dispersed starch grains tend to absorb water and swell. Since they are embedded in the plasticized PVC matrix, their swelling would result in a compression stress in the material. The driving force for the swelling, the energy of mixing (mainly the enthalpic term due to hydrogen-bond interactions), would be

**Table 4** Values of steady-state permeation and sorption coefficients (STP conditions) of $CO_2$ and water vapour in PVC, plasticized-PVC and PVC–DIOP–potato-starch blends of different composition

| Composition (mass%) | | | $P \times 10^{16}$ ($CO_2$) ($m^3\ m\ m^{-2}\ s^{-1}\ Pa^{-1}$) | $P \times 10^{15}$ (water) ($m^3\ m\ m^{-2}\ s^{-1}\ Pa^{-1}$) | $S \times 10^5$ ($CO_2$) ($m^3\ m^{-3}$ film $Pa^{-1}$) | $S \times 10^2$ (water) ($m^3\ m^{-3}$ film $Pa^{-1}$) |
|---|---|---|---|---|---|---|
| PVC | DIOP | Starch | | | | |
| 100 | 0 | 0 | 0.009 | 0.12 | 1.38 | 0.008 |
| 100 | 80 | 0 | 3.40 | 7.12 | 1.47 | 0.548 |
| 100 | 80 | 5 | 3.08 | 8.29 | 1.04 | 0.207 |
| 100 | 80 | 10 | 3.05 | 8.95 | 1.13 | 0.461 |
| 100 | 80 | 20 | 3.05 | 9.16 | 0.97 | 0.602 |
| 100 | 80 | 30 | 3.01 | 10.10 | 1.03 | 0.814 |
| 100 | 80 | 40 | 3.11 | 9.87 | 0.99 | 1.90 |

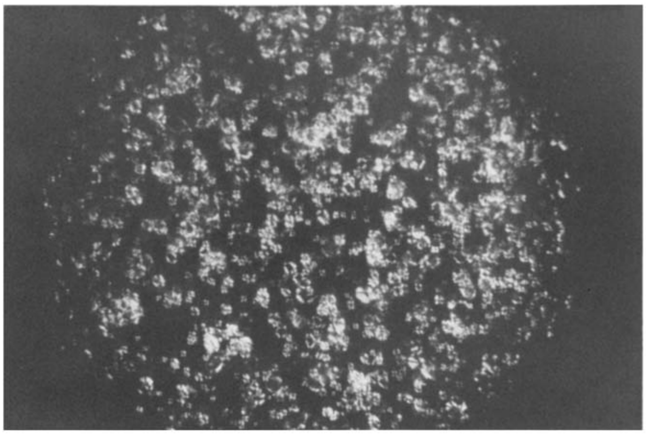

**Figure 7** Photograph taken under cross-polarized light with an optical microscope of the 100:80:20 PVC–DIOP–potato-starch blend. The bright spots correspond to the starch particles (magnification: 228×)

gradually counterbalanced by the elastic resistance of the polymer as the swelling progresses. This results in a decrease in the free volume of the polymer and the appearance of a deformation-related term $[L(\delta\mu/\delta B)\ \delta B/\delta x \neq 0]$. In the starch phase there should be a contribution of the term connected with the change in the starch structure due to hydration. At low starch content, the contribution due to the DIOP plasticizer prevails because of its high content. At high starch content, the contribution arising from the starch swelling becomes significant and screens out the influence of the water sorption on DIOP: the early increase in the permeation curve is masked by the negative contribution due to starch swelling.

In all cases of anomalous permeation studied, the shift towards a constant $D'$ value in the second part of the transient regime would indicate a relaxation of the phenomena arising from the sudden contact with water vapour. If this constant $D'$ value is assumed to be the value of the diffusion coefficient in the steady-state regime, then the sorption coefficient $S$ could be derived from the permeability coefficient $P$ by using the relationship:

$$S = P/D \qquad (15)$$

Although it may appear speculative, the assumption of the plateau value of $D'$ (i.e. the value corresponding to a negligible deviation from Fickian behaviour) to be the diffusion coefficient in the steady-state regime should be correct. Indeed, this is equivalent to the value obtained by extrapolating the linear part of the curve of accumulated amount of the permeant in the downstream compartment *versus* time to the $x$-axis in the time-lag method[15], since the linear part of the time-lag method corresponds to the plateau in our transient permeation method. In comparison, the method using a point in the transient regime (time at which a finite fraction of the steady-state flux is reached[7,8,10]) gives an incorrect value of the diffusion coefficient when the coefficient is not constant, or when there are other contributions like those outlined in this paper.

*Table 4* gives the values of the permeability and sorption coefficients in the steady-state regime for different membranes and permeants. The permeability, diffusion and sorption coefficients of $CO_2$ through DIOP-plasticized membranes do not change significantly with starch content if the usual fluctuations observed in the properties of solid materials made from different batches are taken into account. The weak influence of incorporated starch particles in the polymer matrix may be explained by the low starch content (less than 20%) and also by the intrinsic permeability of the starch phase (*Tables 2* and *4*).

The diffusion and the sorption coefficients of water vapour are affected by the starch content: the diffusion coefficient decreases, and the sorption coefficient increases, when the starch content increases. However, the behaviour of the pure PVC and the plasticized PVC cannot be deduced from that of the blends. The plasticizer greatly improves the diffusion coefficient of both permeants (*Tables 1* and *2*) due to the increase in the mobility of polymer segments; it does not change the sorption of $CO_2$, but it strongly enhances that of water. These results are consistent with our interpretation of the anomalous diffusion of water (and normal diffusion of $CO_2$) on the basis of strong interactions between water and the DIOP plasticizer, since the extent of sorption of a species (water in this case) by a material somehow reflects its interactions with the material. The decrease in the diffusion, and the increase in the sorption, with increasing starch content suggest that starch particles would act as fillers that increase the length of the mean diffusive pathway, but they are not inert fillers in the sense that they make the overall sorption higher, and they may contribute to the overall diffusion. The latter point might be important for blends containing a high proportion of starch. It was shown in acid digestion of starch dispersed in polyethylene that, above a certain threshold (31%), there is a percolation through the starch phase[19]. In a similar way, there could be a strong increase in water permeation due to percolation at sufficiently high starch content.

In conclusion, the proposed method for observing time-dependence phenomena in diffusion in polymer materials offers an interesting alternative to the study of diffusion in polymers. Subtle differences in the behaviour of plasticized-PVC–potato-starch blends to water-vapour penetrant were detected in this way. On the basis of the rational thermodynamics, the additional flux of permeation of water may be attributed to the interactions between water molecules and DIOP molecules. The starch phase would contribute negatively to the transient permeation flux due to a compression effect on the PVC matrix upon swelling. Further experiments in different conditions are needed to obtain a better insight into the diffusion mechanism in glassy polymers

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