Diffusion and relaxation in glassy polymer powders: 1. Fickian diffusion of vinyl chloride in poly(vinyl choride)

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A model is presented for diffusion-controlled sorption in polymer powders consisting of uniform spherical particles. Gravimetric sorption-rate data for vinyl chloride in PVC powders are found to obey this Fickian model for certain types of samples over limited ranges of vinyl chloride pressure increment or temperature. Superficially similar deviations from the model are caused by particle non-uniformity and by the onset of a relaxation-controlled transport mode. These two causes can be distinguished by appropriate choice of sample type and experimental conditions. A simple modification of the model satisfactorily accounts for the effect of particle non-uniformity upon sorption kinetics for conditions under which transport is diffusion-controlled. The use of powder samples in vapour-sorption experiments seems to afford several advantages over conventional film specimens, including more convenient measurement of the very low diffusivities characteristic of the glassy state, and more definitive separation of the contributions of diffusion and relaxation processes to the overall transport mechanism.

INTRODUCTION

The complex transport behaviour of organic vapours and liquids in glassy polymers has been studied extensively for over twenty years and reviewed by several authors[1-4]. It is now widely agreed that transport involves both a diffusion process, controlled by a concentration gradient, and a relaxation process, controlled by a time-dependent response of the polymer to a swelling stress. As the relative contributions of these two processes change and interact, a wide range of behaviours can be encountered. The observed effects may vary not only with the particular polymer/penetrant system considered, but also with the range of vapour activities or concentrations covered in specific experiments. Rogers[3] has pointed out, for example, that sorption vs. time curves may be pseudo-Fickian, sigmoid, or two-stage as the penetrant concentration is increased. Alfrey *et al.*[5,6] consider simple Fickian diffusion (sorption initially linear with $t^{1/2}$) and Case II sorption (linear with t) as limiting cases representing domination by diffusion and relaxation, respectively. Hopfenberg and Frisch[7] have suggested that virtually the entire range of possible behaviours may be expected in a given system when a sufficient range of temperatures and penetrant activities are investigated. Hopfenberg[8] has also pointed out, however, that at the low temperatures and activities where simple Fickian behaviour in the glassy state might be expected, experimental times become prohibitively long with conventional polymer film samples.

Recently, Vrentas, Jarzebski and Duda[9] have proposed a diffusive Deborah number, $(DEB)_D$, as a criterion for predicting whether transport is diffusion- or relaxation-controlled. This dimensionless number is defined as:

$$(DEB)_D = \frac{\lambda_m}{\theta_D} \qquad (1)$$

where λ_m is a mean relaxation time and θ_D a characteristic diffusion time given by L^2/D, with L the sample thickness and D the diffusion coefficient. In this treatment, then, the sample dimension becomes an important factor, in addition to composition and temperature, in determining the transport properties to be anticipated. When λ_m and θ_D are similar in magnitude, anomalous diffusion (involving both Fickian and relaxation processes) is probable. For $(DEB)_D \ll 1$, rubbery-state or viscous Fickian diffusion is expected, while for $(DEB)_D \gg 1$, elastic, or glassy-state Fickian diffusion may occur. Vrentas *et al.* thus suggest adding the Deborah number criterion to the temperature-activity diagrams of Alfrey[5] or Hopfenberg and Frisch[7] for a more general prediction of the type of transport behaviour to be anticipated.

A recent study[10] of transport in the system vinyl chloride/PVC employed powdered polymer samples instead of the film specimens almost universally used in previous vapour-sorption work on polymers. In powder samples, diffusion paths may be reduced by orders of magnitude below the practical limit in films, and it is thus feasible to investigate transport behaviour at high values of $(DEB)_D$. The anticipated, but little studied range of glassy-state Fickian behaviour, and the interesting transition from Fickian to anomalous transport, can thus conveniently be studied.

This paper considers the diffusion of vinyl chloride monomer (VCM) in a variety of PVC resin powders. A model for Fickian diffusion in a system of small, uniform spheres is presented, and it is shown that sorption data obeying this model are obtained within certain limits of sample type and VCM activity. Superficially similar deviations from the model are caused by particle non-uniformity and by a contribution from relaxation-controlled transport. Experimental methods for distinguishing these effects are presented.

Subsequent papers in this series will consider other vapour/polymer powder systems and extend these studies to situations (larger particles and higher vapour activity) where relaxation-controlled transport becomes an increasingly important factor.

EXPERIMENTAL

Materials

Polymer samples used in this study included a number of commercial and experimental PVC homopolymers made by suspension-, mass-, and emulsion-polymerization techniques. All were used in the powder form obtained directly from the polymerization process by normal recovery and drying procedures. Particle structures were characterized by optical and electron microscopy and by nitrogen-adsorption surface area measurements. A few measurements were also made on a sample of rigid PVC film. Specific samples are described where pertinent in the body of the paper.

Equipment and procedures

The measurements reported here were made with a recording Electrobalance (Model RG, Cahn Division, Ventron Instruments Corp., Paramount, California). The balance was mounted in a glass vacuum chamber with connections to a source of VCM vapour and to vacuum pumps. PVC samples were suspended from the balance in a light aluminium pan near the bottom of a 40 cm Kovar hang-down tube, which was surrounded by a circulating liquid jacket for temperature control. Sample weights were from 100 to 500 mg; use of the balance at 1 μg sensitivity thus could detect weight changes as small as 2 ppm. The normal procedure was to evacuate the balance chamber until the sample reached constant weight, then admit VCM vapour to a selected pressure and record weight change with time on a strip-chart recorder (Hewlett–Packard 7100B). Pressures were measured to ±0.1 mmHg with a strain-gauge transducer and digital voltmeter. Because of the large vapour volume and small sample size, sorption caused negligible change in pressure after an addition of VCM vapour.

The diffusion equations used in analysing the data assume that changes of pressure, and consequently of surface concentration, are made instantaneously. This condition can be closely approached for increases of pressure; by bringing a small vessel to a measured VCM pressure, then quickly opening this vessel to the balance chamber, pressure could be increased to a predetermined value in a few tenths of a second. Such sharp decreases in pressure, especially to zero, are not so easily achieved. Using oil diffusion and mechanical pumping, liquid nitrogen traps, and large vacuum lines, pressure could be reduced from, say, 200 mm to ~30 μm in one minute. In most experiments, the half-evacuation time was considerably less than the half-desorption time, so no corrections were made for the non-instantaneous pressure change. The response of the balance and recorder provided useful data beginnning within 3 to 5 sec after a pressure change.

MODEL FOR FICKIAN DIFFUSION IN UNIFORM-SPHERE POWDERS

Comparison of experimental data with Fick's Law requires a solution of the diffusion equation appropriate to the sample geometry and experimental boundary conditions. The simplest geometry for powders is a collection of spherical particles of uniform size. This condition can in fact be closely approached in PVC powders prepared by emulsion polymerization. Consequently, as a model to approximate Fickian sorption of VCM by PVC resins, we have used Crank's solution[11] for the non-steady-state diffusion in a sphere in the case of uniform initial concentration through the sphere, a constant concentration at the surface, and constant D. The equation for this case is:

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-4Dn^2\pi^2 t/d^2) \qquad (2)$$

where M_t is the weight of penetrant entering or leaving the sphere in time t after an instantaneous change in surface concentration, M_∞ is the total weight change after infinite time at the new surface concentration, n is the series of integers, D is the diffusion coefficient, and d is the diameter of the sphere.

The following assumptions are implicit in applying equation (2) to VCM sorption or desorption experiments on PVC powders.

(1) Diffusion obeys Fick's laws.

(2) D is constant over the concentration range covered by the experiment.

(3) The solution for a sphere is applicable to a sample consisting of many spherical particles of uniform size; i.e., diffusion occurs in each particle independently, with no interparticle diffusion.

(4) The PVC powder does, indeed, consist of uniform-sized spherical particles.

(5) At the start and end of the experiment, the VCM concentration is uniform through the particles.

(6) The VCM concentration at the particle surface is always at equilibrium with the surrounding vapour phase.

(7) At time zero, the VCM pressure is instantaneously changed to a new value, thus immediately changing the surface VCM concentration of the particles.

(8) The VCM concentration in the particles is zero initially in the case of sorption starting at zero VCM pressure, and zero finally for desorptions to zero pressure.

(9) There is no concentration gradient in the vapour phase, and no surface layer effect; i.e., transport is limited only by diffusion within the PVC particles.

If all these assumptions are valid, then equation (2) will describe the weight gain (or loss) as a function of time in a VCM sorption (or desorption) experiment. This equation predicts that the time required for a given fraction of the ultimate weight change to occur is independent of the initial or final VCM concentration (or pressure), and is proportional to the ratio d^2/D. This ratio, then, can be determined by fitting equation (2) to the experimental data, but evaluation of D requires independent determination of the particle diameter.

To test the agreement between experimental data and the model, two graphical representations of equation (2) are useful. As shown in *Figure 1*, a plot of M_t/M_∞ (or of M_t) against the square root of time is initially nearly linear, then

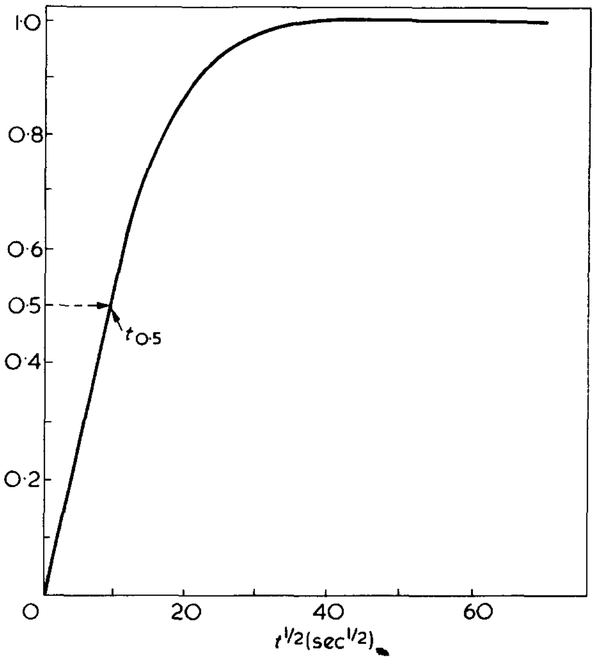

Figure 1 Plot of M_t/M_∞ vs. $t^{1/2}$, calculated from equation (2) with $d^2/D = 10^4$ sec

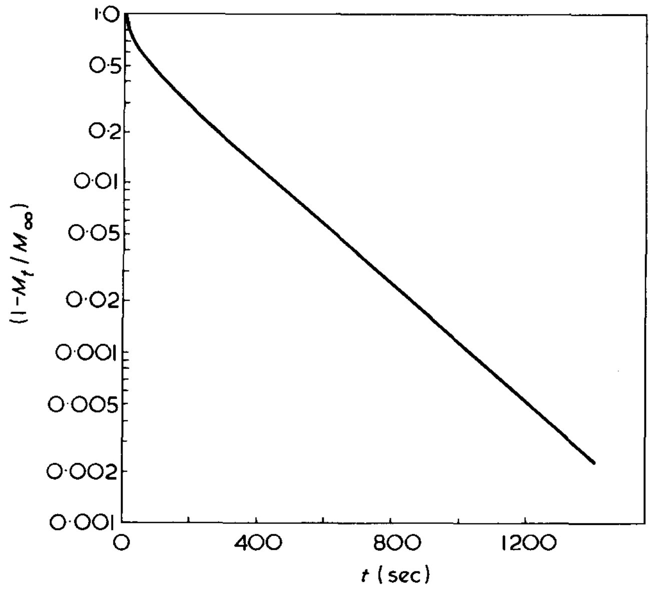

Figure 2 Plot of log$(1 - M_t/M_\infty)$ vs. t, calculated from equation (2) with $d^2/D = 10^4$ sec

bends over to approach a well-defined limit. A plot of log $(1 - M_t/M_\infty)$ vs. t, as in *Figure 2*, shows initial curvature, then approaches a straight line. Each of these plots also offers a means of evaluating d^2/D from experimental sorption data. From equation (2) it can be shown that $t_{0.5}$, the time at which $M_t/M_\infty = 0.5$, or the 'half-sorption time', is

$$t_{0.5} = 7.66 \times 10^{-3} \frac{d^2}{D} \tag{3}$$

for t in sec, d in cm, and D in cm^2/sec. Thus $t_{0.5}$ may be interpolated from a plot of M_t/M_∞, or of M_t, vs. $t^{1/2}$ and d^2/D evaluated by equation (3). Alternatively, d^2/D may be obtained from the limiting slope of the $\log_{10}(1 - M_t/M_\infty)$ vs. t plot:

$$\text{Slope} = -\frac{4\pi^2 D}{2.303 d^2} \tag{4}$$

The determination of d^2/D from half-sorption time depends mainly on the data in the early stages of sorption, while the log$(1 - M_t/M_\infty)$ method emphasizes the later-stage data.

FICKIAN, UNIFORM-SPHERE BEHAVIOUR IN VCM/PVC SORPTION

Sorption and desorption rate data for VCM in a wide variety of PVC powder samples have been obtained at temperatures from 25°to 110°C and VCM pressures from zero to 700 mm. The experimental data thus extend well below and above the glass transition temperature of PVC ($T_g \cong 85°C$). Relative VCM pressure, $P_{rel} = P/P_0$, where P_0 is the saturated vapour pressure, ranged from zero to a maximum of 0.23 at 25°C (where $P_0 = 3000$ mm) and to a maximum of 0.04 at 110°C ($P_0 = 19\,200$ mm). The form of the M_t vs. $t^{1/2}$ curves was found to depend both upon the type of PVC sample used and upon the pressure range and temperature of the experiment. Curves closely fitting the Fickian, uniform-sphere model, equation (2), are found under limited conditions of VCM pressure or temperature, but only for samples which closely approximate the 'uniform-sphere' requirement.

'Uniform-sphere' PVC samples

By emulsion polymerization, it is possible to prepare PVC powders which consist of spherical particles of diameters from approximately 0.1 to 1 μm, with very narrow size distributions. The M_t vs. $t^{1/2}$ curve from a typical VCM sorption experiment on one such monodisperse sample is shown in *Figure 3*. The experimental data conform very well to the curve calculated from equation (2) using the d^2/D value obtained from the half-sorption time and equation (3).

In the case of PVC resin powders made by suspension or mass polymerization, the gross particles (roughly 100 μm diameter) seen at low optical magnifications are neither spherical nor uniform in size. Electron microscopy has shown, however, that these gross particles are agglomerates of primary particles (~1 to 5 μm diameter) which are approximately spherical and fairly uniform in size within a given resin sample. This observation suggested application of the uniform-sphere model to sorption data on the suspension- and mass-polymerized PVC resins. *Figure 4* shows an illus-

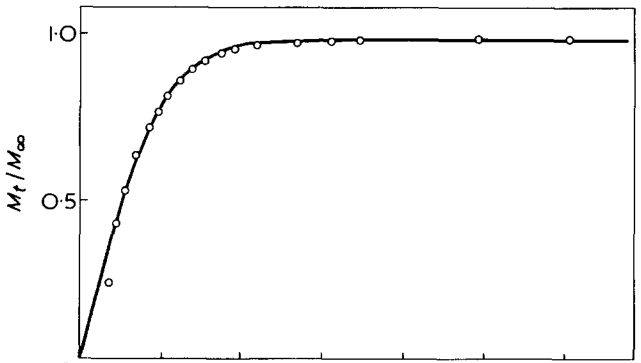

Figure 3 Plot of M_t/M_∞ vs. $t^{1/2}$ for VCM sorption by 0.44 μm emulsion PVC, 23°C, $P_{rel} = 0 \rightarrow 0.0037$. ○, Experimental; —— equation (2) for $t_{0.5} = 7.3$ sec

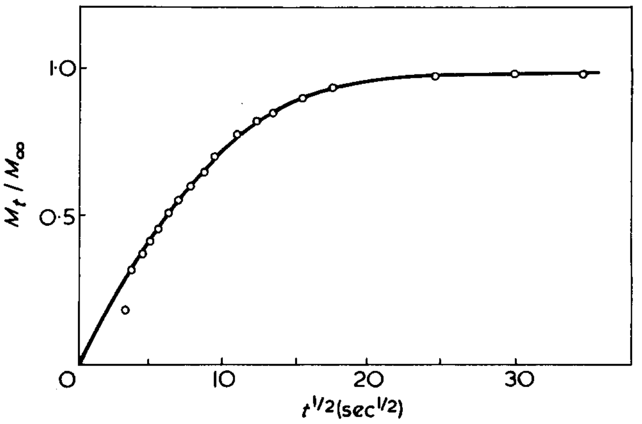

Figure 4 Plot of M_t/M_∞ vs. $t^{1/2}$ for VCM sorption by suspension-polymerized PVC, 40°C, $P_{rel} = 0 \rightarrow 0.0048$. ○, Experimental; ——— equation (2) for $t_{0.5}$ = 38.4 sec

trative M_t vs. $t^{1/2}$ curve from a VCM sorption experiment on a suspension-polymerized PVC; the agreement of the data with equation (2) shows that the uniform-sphere model is an adequate approximation for this particular sample. The degree of agreement with the model, however, varies considerably among different samples of mass and suspension types of PVC. It will be shown below that such variations among samples can be related to the uniformity of their particle structure.

Temperature and VCM pressure conditions for Fickian behaviour

For samples of known uniform-sphere particle structure (monodisperse emulsion PVCs), VCM sorption or desorption data fitting equation (2) are obtained only within certain conditions of VCM pressure and temperature. At temperatures below T_g, such simple Fickian behaviour is observed only for sorption runs covering very small increments of VCM pressure (P_{rel} increments of 0.01 or less), and for desorption runs to zero pressure. Above T_g, equation (2) is obeyed in sorption or desorption runs over the full P_{rel} range covered by the data. Experiments outside these conditions invariably lead to slow changes in sample weight continuing long beyond the time required to reach equilibrium according to equation (2). This sort of deviation from the Fickian uniform-sphere model will also be discussed below.

Determination of diffusion coefficient

When the PVC sample and experimental conditions produce data fitting the Fickian, uniform-sphere model, the ratio d^2/D is most readily determined from the half-sorption time. Sorption or desorption experiments are run to diffusion equilibrium to establish M_∞, then the time, $t_{0.5}$, at which $M_t = 0.5\ M_\infty$, is read from an M_t vs. $t^{1/2}$ plot, or directly from the recorder trace of weight vs. time. D is then calculated via equation (3) from $t_{0.5}$ and d.

The particle diameters used in calculation of D were determined from N_2 adsorption surface area measurements. For spheres of density ρ, the surface-to-weight ratio is $6/\rho d$, thus for PVC ($\rho = 1.4$):

$$\bar{d}_s = 4.29/S_g \qquad (5)$$

where S_g is the specific surface area in m^2/g and $\bar{d}_s$ is surface-average particle diameter in μm. This measure of particle size agrees reasonably well with electron microscopy for both emulsion PVCs and the primary particles of suspension resins.

Diffusion coefficients determined by this procedure for emulsion, suspension, and mass PVC resins are in good agreement. This result indicates that the rate-controlling factor in VCM diffusion is the dimension of the primary particles in each case, not the agglomerate size in suspension or mass resins. Use of the agglomerate size in calculating D from sorption data would increase D by several orders of magnitude; this factor appears to account for the discrepancy between our results and those reported by Wolf and Kreter[12]

Temperature dependence of D

The diffusion coefficient for VCM in PVC has been determined from half-sorption or -desorption times at temperatures from 25° to 110°C. It was necessary to use samples of differing $\bar{d}_s$ in different temperature ranges, since $t_{0.5}$ becomes inconveniently long at low T when $\bar{d}_s$ is relatively large, while $t_{0.5}$ is too short to measure accurately at the higher Ts when $\bar{d}_s$ is small. For the determination of D, only data closely approximating the Fickian, uniform-sphere model were used; these data therefore covered low VCM pressures and VCM in PVC concentrations up to ~2 mg/g.

Results of these measurements are presented as an Arrhenius plot in *Figure 5*. The agreement among samples is good; most of the scatter may be attributed to uncertainty in $\bar{d}_s$. Since these samples covered the molecular weight range found among commercial PVCs, it does not appear that D varies significantly with molecular weight in this range. The value of D also appears to be insensitive to the type of PVC resin, as emulsion, suspension, and mass resins give very similar results. The straight line of *Figure 5* indicates an activation energy for diffusion of 17 kcal/mol. The equation of this line:

$$D = 3.7\exp(-17\,000/RT) \qquad (6)$$

may be used to estimate D over the temperature range of the data.

Concentration dependence of D

In comparing results of sorption and desorption runs on the same sample and over a similar VCM pressure increment, it was generally observed that desorption was somewhat slower than sorption. *Figure 6* illustrates this effect for a representative set of sorption and desorption data, plotted as M_t vs. $t^{1/2}$. Consequently, values of D calculated from

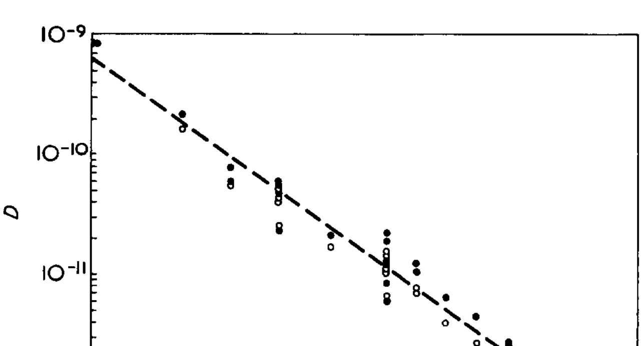

Figure 5 Plot of log D vs. $1/T$ for VCM diffusion in PVC powders: ●, sorption; ○, desorption

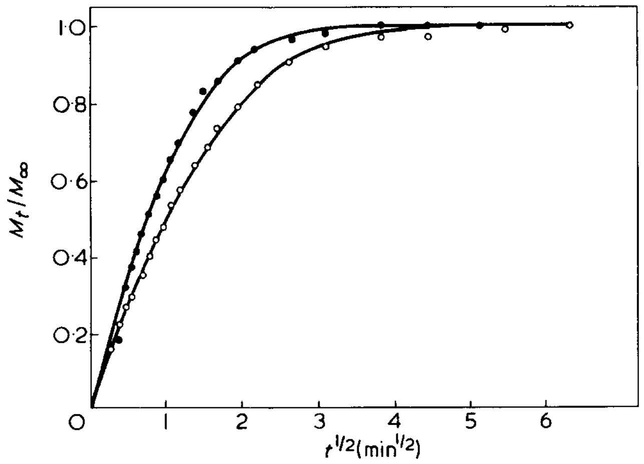

Figure 6 Plot of M_t/M_∞ vs. $t^{1/2}$ for VCM sorption and desorption by suspension PVC, 40°C, $P_{rel} = 0 \rightarrow 0.005 \rightarrow 0$. ●, Sorption; ○, desorption

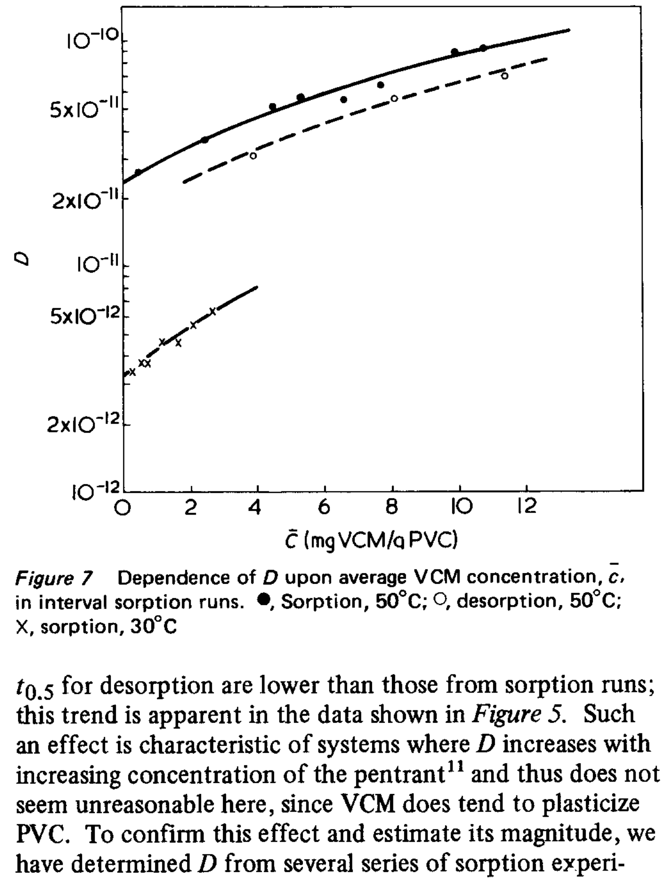

Figure 7 Dependence of D upon average VCM concentration, $\bar{c}$, in interval sorption runs. ●, Sorption, 50°C; ○, desorption, 50°C; X, sorption, 30°C

$t_{0.5}$ for desorption are lower than those from sorption runs; this trend is apparent in the data shown in *Figure 5*. Such an effect is characteristic of systems where D increases with increasing concentration of the pentrant[11] and thus does not seem unreasonable here, since VCM does tend to plasticize PVC. To confirm this effect and estimate its magnitude, we have determined D from several series of sorption experiments in which the VCM pressure was increased in successive steps ('interval sorption' experiments). Results of such runs at 30° and 50°C are shown in *Figure 7* as plots of D vs. $\bar{c}$, where $\bar{c}$ is the average VCM concentration in the PVC during each step. The data clearly show a steady increase in D with increasing VCM concentration. However, over the concentration range from zero to 2 mg/g, the change in D is hardly greater than the experimental uncertainty in D determinations for different resin samples (*Figure 5*).

Results on rigid PVC film

For sorption by a plane sheet or film, the relation analogous to equation (3) for spheres is:

$$t_{0.5} = 0.049 \frac{l^2}{D} \tag{7}$$

where l is the film thickness[11]. From the D values obtained on powder samples, equation (7) predicts inconveniently long experimental times for measurements on films of any reasonable thickness. Yet it does seem important to establish whether or not the D values determined in resins would also apply to fused PVC items. For this purpose, VCM sorption measurements were made on a sample of experimental extruded rigid PVC film which contained 2.5 % w/w of a tin stabilizer as the only additive. Sections of thickness 0.005 cm were used in VCM sorption experiments over a pressure interval of 0 to ~100 mm at 25°, 70°, and 90°C. The initially linear M_t vs. $t^{1/2}$ plots, shown in *Figure 8*, indicate Fickian diffusion behaviour. Only at 90°C was equilibrium reached within the time available. For the other temperatures, M_∞ and $t_{0.5}$ were estimated by assuming the equilibrium amount sorbed would be similar to that sorbed by powder samples. The estimated values of D at 25°, 70°, and 90°C were 3.1×10^{-12}, 8.0×10^{-11}, and 5.4×10^{-10} cm²/sec, respectively. These values are somewhat higher than the average Ds for pure resin powders (see *Figure 5*), suggesting slight plasticization by the stabilizer. Yet the order-of-magnitude agreement indicates that the pure-resin D values should be applicable, to a fair approximation, in estimating VCM migration rates from rigid PVC products. Other support for this approximation has recently been obtained from the good agreement between observed VCM migration rate into water from PVC pipe and the predictions of a model based on pure resin diffusivity values[13].

These few measurements on PVC film demonstrate an important experimental advantage to the use of fine polymer powders instead of sheet or film specimens: the measurement of very low diffusion coefficients can be brought into an experimentally convenient time-scale with powder samples. For example, the half-sorption time for a 0.005 cm film with $D = 10^{-12}$ cm²/sec is about 14 days; but for a powder of 1 μm particle diameter and the same D, $t_{0.5}$ is only 76 sec.

DEVIATIONS FROM FICKIAN, UNIFORM-SPHERE MODEL

It was noted above that sorption or desorption vs. time data fitting equation (2) are obtained only when both the

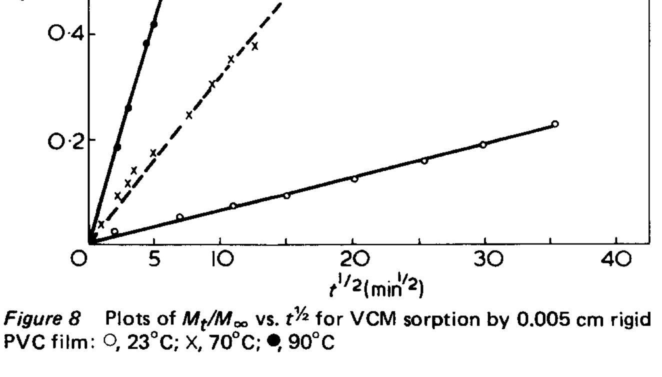

Figure 8 Plots of M_t/M_∞ vs. $t^{1/2}$ for VCM sorption by 0.005 cm rigid PVC film: ○, 23°C; X, 70°C; ●, 90°C

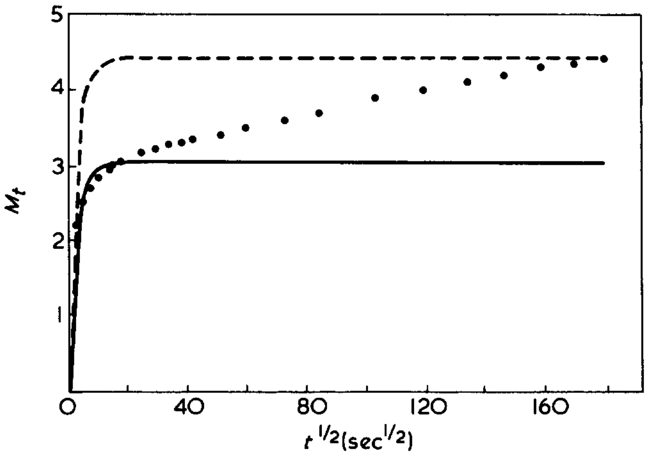

Figure 9 Deviation from equation (2) due to non-Fickian sorption; M_t vs. $t^{1/2}$ for VCM sorption by 0.44 μm monodisperse emulsion PVC, 30°C, P_{rel} = 0.02 → 0.05. ●, Observed; —— and – – –, equation (2)

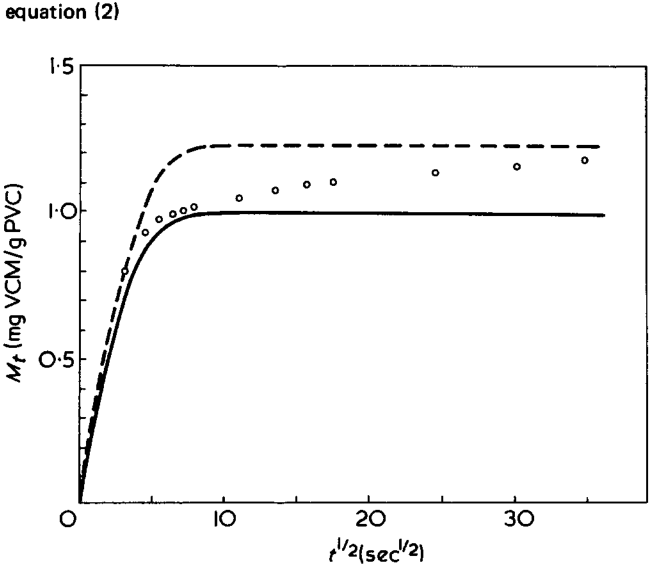

Figure 10 Deviation from equation (2) due to particle non-uniformity; M_t vs. $t^{1/2}$ for VCM sorption by commercial suspension PVC, 90°C, P_{rel} = 0 → 0.015. ○, Observed; —— and – – –, equation (2)

PVC sample and the VCM pressure range of the experiment meet certain requirements. Experiments outside either set of requirements lead to weight changes which continue long beyond the equilibration time predicted by the model for the appropriate values of d^2/D. While the results are superficially very similar, it is possible to distinguish clearly two independent causes of this behaviour: particle non-uniformity and non-Fickian diffusion.

Distinction between particle non-uniformity and non-Fickian effects

These two effects can be separated by appropriate choices of sample and experimental conditions. For example, for a monodisperse emulsion PVC (whose sorption–time curve over a small VCM pressure increment fits equation 2), deviations from the model in sorption over a larger pressure increment cannot be attributed to particle non-uniformity; thus a contribution of a non-Fickian diffusion process is indicated. Conversely, when slow equilibration is observed in sorption over a small VCM pressure increment (one which gives data fitting (2) for a monodisperse sample), the deviation from the model can be attributed to particle non-uniformity. Similarly, slow equilibration in sorption or desorption at $T > T_g$ (where the model is obeyed for uniform-particle samples) is also evidence for particle non-uniformity.

Figures 9 and *10* show examples of sorption–time runs in which the deviation from the Fickian, uniform-sphere model can clearly be attributed to particle non-uniformity, in one case, and non-Fickian diffusion in the other. The similarity of the experimental curves shows that these sorption data alone would be insufficient to distinguish the cause of the deviation; the particle structure and pressure increment must also be considered.

By suitable experimental design, then, it is possible to use sorption–time data unambiguously to obtain information about either particle non-uniformity or about the non-Fickian diffusion process. Both sorts of experiment will be discussed further in the following sections.

EFFECT OF PARTICLE NON-UNIFORMITY

Results on commercial resin samples

Sorption or desorption curves on many commercial suspension- and mass-polymerized PVCs, run over small VCM pressure increments, give M_t vs. $t^{1/2}$ plots approximating the uniform-sphere Fickian model. However, when the same data are plotted as $\log(1 - M_t/M_\infty)$ vs. t, emphasizing the later stages of sorption or desorption, substantial deviations from equation (2) are apparent. *Figures 11* and *12* compare the two types of plot for a sorption run at 90°C from vacuum to 200 mm VCM pressure (P_{rel} = 0.015) for a representative mass-polymerized PVC. Since the high temperature and small pressure increment tend to eliminate any non-Fickian contribution, the deviation from equation (2) may be attributed to particle non-uniformity.

Previous knowledge of mass- and suspension-PVC particle structure is consistent with a possible effect of non-uniformity on rate of VCM removal. It has long been recognized that certain resins contain a small portion of non-porous particles often identified with 'fish-eye' problems. These particles are detectable by their clear appearance under a low-power, optical microscope, in contrast to the opaque, white appearance of porous particles. They are believed to arise from excessive knitting-together of primary particles during polymerization to form solid PVC regions which may be as large as the gross agglomerated particles of the resin, i.e., up to about 100 μm. Now if this dimension, rather than the few-micron primary particle diameter, is the controlling

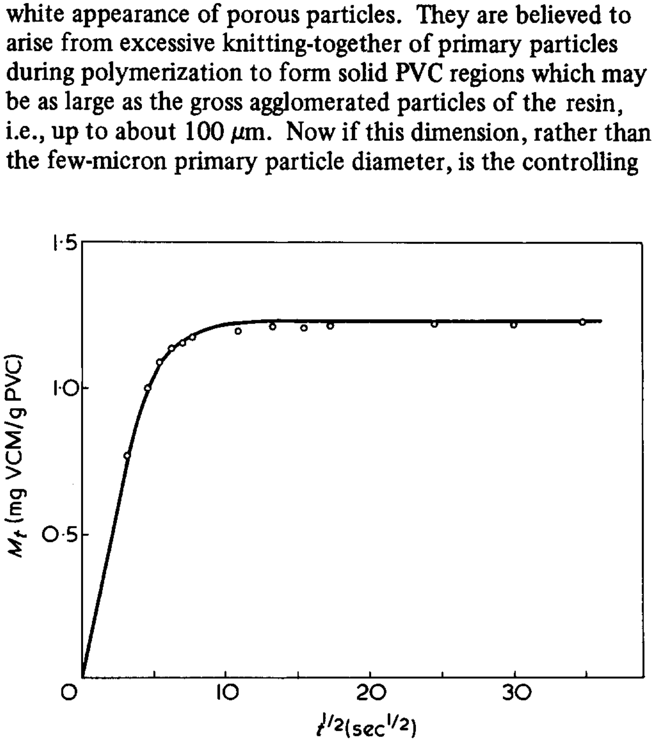

Figure 11 Plot of M_t vs. $t^{1/2}$ for VCM sorption by commercial mass-polymerized PVC, 90°C, P_{rel} = 0 → 0.015. ○, Observed; ——, equation (2) for $t_{0.5}$ = 6.2 sec, M_∞ = 1.23 mg/g

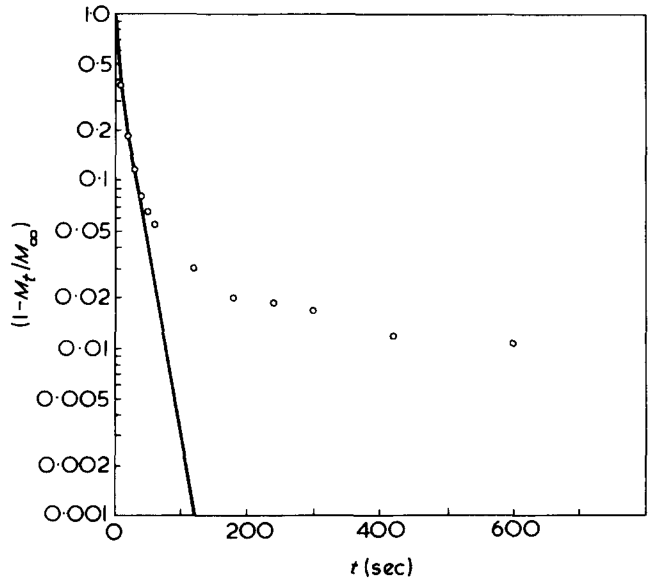

Figure 12 Same data and curve as *Figure 11*, plotted as $\log(1 - M_t/M_\infty)$ vs. t

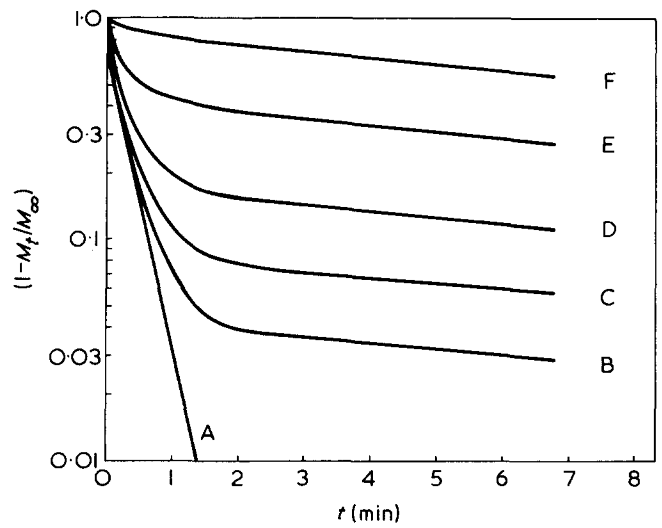

Figure 13 Curves calculated from equation (8) for uniform and mixed particle sizes, with $D = 2 \times 10^{-10}$ cm^2/sec. A, 100% 4 μm particles; B, 95/5 % w/w 4 μm/40 μm; C, 90/10; D, 80/20; E, 50/50; F, 100% 40 μm

factor in rate of sorption, then the non-porous particles will sorb VCM much more slowly than the porous ones. The presence of a few such particles in an otherwise porous resin thus could well account for slow sorption or desorption of the last fraction of the total VCM.

Model for non-uniform particles

The effect of a non-uniform particle size can be predicted through equation (2) by simply adding the curves calculated for various particle sizes in proportion to their weight fraction in the sample. Thus we may write:

$$1 - \frac{M_t}{M_\infty} = \frac{6}{\pi^2}\sum_i X_i \sum_{n=1}^{\infty} \frac{1}{n^2}\exp(-4Dn^2\pi^2 t/d_i^2) \qquad (8)$$

where X_i is the weight fraction of particles having diameter d_i. To illustrate, the curves shown in *Figure 13* have been calculated by applying equation (8) to hypothetical mixtures of 4 and 40 μm particles for desorption of VCM at 90°C ($D = 2 \times 10^{-10}$ cm^2/sec).

Experimental confirmation of the model for non-uniform particles has been obtained through measurements on two resins of different average primary particle size ($\bar{d}_s = 1.9$ μm, and $\bar{d}_s = 20$ μm) and on a deliberate 90/10% w/w mixture of the two. The results shown in *Figure 14* agree well with the form of the calculated curves of *Figure 13*. The VCM desorption curves for many commercial suspension and mass PVC resins are also in qualitative agreement with their relative non-porous particle content judged from microscopy.

It thus appears that the effect of non-uniform particle size upon the Fickian sorption of a vapour by a polymer powder can be modelled rather simply through equation (8). The consistency between experimental data and this model suggests, moreover, that vapour sorption measurements may be a useful method for obtaining information about the particle-size distribution of polymer powders. From calculated sorption–time curves for mixtures of two particle sizes (e.g., *Figure 13*) it is seen that the slope and level of the curve at the longer times are dependent on the size and weight fraction, respectively, of the larger particles. Similarly, the curves at short times reflect the size and weight fraction of the smaller particles. It seems clear that the presence of more than two sizes in the population would cause a more gradual change in slope. In principle, an experimental sorption time curve seems to contain the information needed to derive a weight-fraction particle size distribution for a polymer powder. Extraction of the size distribution by fitting equation (8) to the experimental data, however, may be a formidable task. A prerequisite for this technique, of course, would be the demonstration that the chosen experimental conditions produce Fickian behaviour with a sample known to have a uniform particle size; without this evidence, it might be impossible to distinguish particle-size distribution effects from a contribution of non-Fickian sorption.

NON-FICKIAN DIFFUSION EFFECTS

Even with monodisperse, emulsion-PVC samples, sorption experiments below T_g and covering VCM P_{rel} increments greater than about 0.01 show a much slower approach to

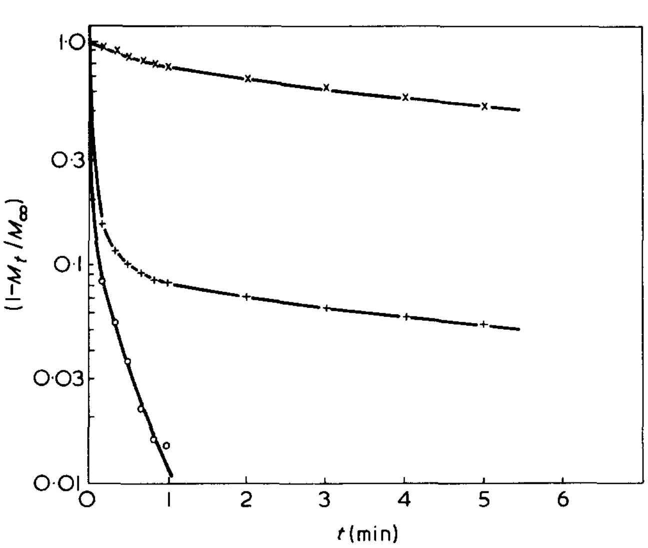

Figure 14 Experimental $\log(1 - M_t/M_\infty)$ vs. t curves for uniform and mixed particle sizes, 90°C. ○, $\bar{d}_s = 1.9$; ×, $\bar{d}_s = 20$ μm; +, 90/10 % w/w 1.9 μm/20μm

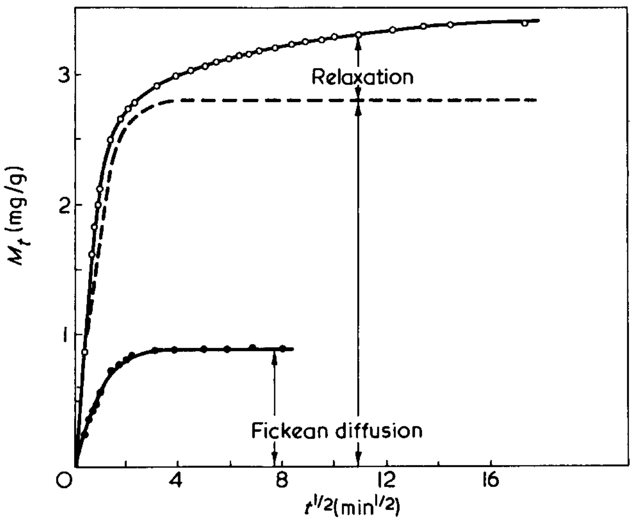

Figure 15 Schematic separation of diffusion and relaxation contributions to VCM sorption by suspension PVC, 50°C. ●, P_{rel} = 0 → 0.002; O, P_{rel} = 0.002 → 0.019

equilibrium than predicted by the Fickian uniform-sphere model. It is suggested that this behaviour represents the onset of a non-Fickian, relaxation-controlled mode of sorption superimposed on the Fickian diffusion, as indicated in *Figure 15*. A somewhat similar 'two-stage' sorption process has been observed by Bagley and Long[14] for the sorption of acetone by ethyl cellulose and by Fujita[2] for several other systems. Their interpretation also seems applicable to the VCM/PVC system; in the early stage of sorption, the VCM concentration gradient provides the major driving force and the transport process is dominated by Fickian diffusion. When the concentration of VCM resulting from this process is sufficient to develop a significant swelling stress, the slow response of the glassy polymer to this stress produces gradual swelling of the polymer structure and permits additional sorption. This swelling–relaxation process may continue even after the Fickian process has produced a virtually uniform concentration of VCM through the polymer; in this event, the contribution of Fickian diffusion becomes negligible, and the later stage of sorption is dominated by the relaxation-controlled process.

In the fine PVC powders studied here, the short diffusion paths result in equilibration times as short as a few minutes for the Fickian diffusion process. Thus this stage may be essentially complete before appreciable stress-relaxation has occurred. The net result is a first stage which is nearly pure Fickian diffusion and a second stage which is almost entirely relaxation-controlled.

In desorption experiments to a non-zero VCM pressure in VCM/PVC powder systems, a contribution of the relaxation-controlled process also is indicated, as the approach to desorption equilibrium may be very slow[15]. In desorptions to zero VCM pressure, however, the sample weight follows the Fickian curve to a rapid 'equilibrium' of zero VCM content. Resorption experiments[15] have provided evidence that volume relaxation of the PVC continues as a slow process even in the absence of sorbed VCM. It appears that, under vacuum, all of the sorbed VCM escapes by the rapid Fickian process, but volume-relaxation is not necessarily completed during desorption. This behaviour closely parallels the observations of Barrer, Barrie, and Slater[16] in studies on ethyl cellulose.

In contrast to the two-stage sorption behaviour in the glassy state, sorption and desorption experiments conducted above T_g appear to follow simple Fickian diffusion kinetics over the VCM pressure range of the present data (P_{rel} = 0 to ~0.05). Thus, in the rubbery state, the relaxation process seems sufficiently rapid to be complete within the time scale of the Fickian diffusion stage.

This study of the VCM/PVC system indicates that vapour-sorption experiments on polymer powder samples in the glassy state offer a significant advantage over similar experiments with film samples, in that diffusion and relaxation effects may be conveniently separated. The short diffusion times encountered with fine powders permit the attainment of 'diffusion equilibrium' before appreciable relaxation occurs. The extent of first-stage sorption then reflects the state of the polymer essentially unperturbed by penetrant-swelling; this has proved to be a useful technique in assessing the effects of prior polymer history on the properties of glassy PVC[15]. The rate of sorption in the first stage is principally controlled by the Fickian process and, therefore, may be used to estimate a true diffusion coefficient even when the total sorption does not follow the Fickian model. Furthermore, since the second-stage sorption is almost entirely relaxation-controlled, the kinetic and equilibrium parameters describing the slow relaxation processes can be obtained from long-time sorption data. With film specimens, in contrast, diffusion times and relaxation times are often comparable, hence separation of relaxation from purely Fickian diffusion is often impossible.

Further studies on vapour sorption in glassy polymer powders and mathematical treatments of the data to separate diffusion and relaxation rate constants will be reported in the near future.

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