Diffusion-relaxation coupling in polymers which show two-stage sorption phenomena

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The diffusion behaviour of swollen polymer films in interval sorption experiments cannot be explained satisfactorily by the available models for diffusion into polymeric materials, and compels us to accept that the state of the swollen polymer should be characterized not only by the state variables such as temperature and pressure but also by a 'degree of swelling'. The concept of activity parameter as an internal state variable is introduced as an yardstick for the degree of swelling and the rate of evolution of this has been related directly to the concept of relaxation time. Assuming a simple empirical constitutive rate equation for the physical process involved, asymptotic as well as the complete solution of the proposed mathematical model are developed and the results agree well with the available experimental data on two-stage sorption.

INTRODUCTION

The diffusion behaviour of low molecular weight solvents in glassy polymers cannot be described adequately by concentration-dependent diffusivity whenever the solvent causes swelling of the polymer[1–5,12]. This 'non-Fickian', behaviour can be attributed to changes in polymer structure induced by the solvent, and has often been related to stresses exerted by one part of the medium on another as diffusion proceeds[6–9].

Astarita and Sarti[10] have presented a phenomenological analysis of this problem which takes into explicit consideration the kinetics of the glassy → swollen secondary phase transition. They have considered the case of a semi-infinite slab of polymer, and, in spite of rather extreme simplifying assumptions, they have shown that the major characteristics of the so-called 'case-two transport' and 'anomalous diffusion' behaviours observed experimentally can be predicted. Astarita and Joshi[11] have relaxed some of the simplifying assumptions introduced by Astarita and Sarti, and have thus been able to explain quantitatively a variety of different sorption behaviours observed experimentally, and in particular the effect of sample dimensions.

However, not all experimentally observed behaviours can be explained by the still somewhat simplified model of Astarita and Joshi. In particular, Bagley and Long[13] have reported experimental observation on interval sorption of acetone in cellulose acetate films, which cannot be explained by the model discussed in reference 11.

The experiments by Bagley and Long can be concisely described as follows. The polymer film is first brought to equilibrium with acetone vapour at some vapour pressure p_o; the vapour pressure is then brought to a new value $p_1 (> p_0)$ and the weight sorbed is measured as a function of time. The experiment is then repeated with progressive increases of the acetone vapour pressure.

The weight vs. time behaviour observed for each interval sorption, is, qualitatively, as follows: an initial uptake where W is proportional to $t^{1/2}$ is observed, followed by an apparent equilibrium. This is in turn followed by a slow approach to final (and presumably true) equilibrium.

While such behaviour for the first sorption interval for which it is observed can be explained by Astarita and Joshi's model, by attributing the apparent equilibrium to glassy-phase saturation, the reproduction of the same behaviour for subsequent sorption intervals cannot: in Astarita and Joshi's model, once the polymer has undergone the glassy → swollen secondary phase transition, it can only behave as an ordinary material incapable of showing anomalous diffusion. Bagley and Long's experiments, however, force one to accept the fact that a satisfactory description of diffusion in polymers requires consideration of an additional complication, namely that a polymer is in fact capable of different 'degrees of swelling', so that in some sense to be made precise the state of the polymeric material cannot simply be described by stating whether it is glassy or swollen. The present work presents a formalization of this rather elementary physical concept.

MODELLING OF THE PHENOMENON

Consider a polymer sample which is uniformly at equilibrium with some external phase where the fugacity of a solvent is f_0. Suppose that at time $t = 0$ the fugacity of the solvent is brought to some new value f_1, and kept constant thereafter. This is in essence the description of the experiments of Bagley and Long discussed in the introduction.

Whenever phenomena of mass transfer between two phases are considered, it is always assumed that equilibrium prevails at the interface, say that the fugacity is continuous across an interface. The philosophical reasons for such an assumption are hard to pin down, but it has always been a successful assumption in mass transfer work and there seems to be no reason to reject it in the case where one of

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the phases is a polymeric material. Therefore, in the experiment described, the fugacity of the solvent in the polymeric phase at the interface may be assumed to be f_1 from $t = 0$ onwards.

This does not, however, necessarily imply that the concentration of solvent at the interface will be constant in time. Indeed, the relationship between fugacity and concentration of a component of a phase depends on the *state* of that phase; while in general the state is regarded as being uniquely determined by temperature and pressure, in the case of a swollen polymer an additional state variable needs to be considered, namely, the degree of swelling.

Let $c(t)$ be the concentration of solvent in the polymer at the interface at $t > 0$. An activity parameter ξ may be defined as follows

$$c = \xi f_1 \tag{1}$$

where ξ is a function of time, $\xi = \xi(t)$. The parameter so defined is presumably related to the degree of swelling; since there is no pragmatic reason to define the latter independently of the former, we may as well take ξ itself to be an appropriate yardstick of the state of the material.

As $t \to \infty$, the activity parameter ξ will approach some equilibrium value ξ_1^* corresponding to the fugacity f_1, say

$$\lim_{t\to\infty} \xi = \xi_1^* \tag{2}$$

Yet at $t = 0$ the activity parameter is the one corresponding to equilibrium under a fugacity f_0, say ξ_0^*:

$$\xi(t = 0) = \xi_0^* \tag{3}$$

If the rate of approach to the final value ξ_1^* is sufficiently slow, a time-dependent concentration of solvent at the interface will be observed.

Introduction of the parameter ξ is an example of a well known procedure of thermodynamic theory, namely, the theory of systems with internal state variables. Such theories have been studied in rigorous mathematical terms[14], and their usefulness in the description of polymer physics has been pointed out[15]. Typically, the thermodynamic theory of systems with internal state variables requires the introduction (in addition to the usual constitutive functions delivering the values of such thermodynamic quantities as entropy, pressure, etc.) of a constitutive function the value of which is the rate of change of the internal state variable. In the specific case considered here, one would need to introduce a constitutive function for the rate of change of the activity parameter say:

$$\frac{d\xi}{dt} = r(\xi) \tag{4}$$

where only ξ itself has been considered as an argument of the function $r(\bullet)$, since f_1, temperature and pressure are held constant in the experiment considered.

Equation 4 allows to define, though of course trivially, the equilibrium value ξ_1^*, as the root of the function $r(\bullet)$, say $r(\xi_1^*) = 0$. (The thermodynamic theory implies that, if $r(\bullet)$ is sufficiently smooth at $\xi = \xi_1^*$, then the affinity, derivative of free energy with respect to ξ is zero at $\xi = \xi_1^*$; this is irrelevant for the present problem).

In order to be able to make quantitative predictions, a specific form for the constitutive function $r(\cdot)$ needs to be assumed. The simplest such form is of course the linear one; say, consistently with the requirement that $r(\xi_1^*) = 0$, we may write:

$$\frac{d\xi}{dt} = \frac{\xi_1^* - \xi}{\theta} \tag{5}$$

where θ is the 'relaxation time' of the swelling phenomenon. Equation 5, subject to the boundary condition $\xi = \xi_0^*$ at $t = 0$, integrates to

$$\xi = \xi_1^* - (\xi_1^* - \xi_0^*) \exp(-t/\theta) \tag{6}$$

and hence from equation 1:

$$c = c_1^* - (c_1^* - c_{10}) \exp(-t/\theta) \tag{7}$$

where:

- $c_1^* = f_1 \xi_1^*$, is the *equilibrium* concentration of solvent corresponding to the fugacity f_1;
- $c_{10} = f_1 \xi_0^*$ is the concentration corresponding to the fugacity f_1 and to the activity parameter ξ_0^* (the latter corresponds to equilibrium under a fugacity f_0).

Long and Richmann[16] have measured the interface concentration of solvent in the polymer as a function of time, and report that equation 7 is indeed a good correlation of measured data. It seems therefore that there is no need to lay down constitutive assumptions more complex than the linear form given in equation 5.

Of course, in the experiment considered, while the *fugacity* of the solvent is constant in time, and equal to f_1, at the interface of the sample, it is not so within the sample itself. In fact, the concentration in the bulk of the sample at time $t = 0$ is $c_0^* = f_0 \xi_0^*$, and is therefore *different* from the concentration c_{10} that established itself at the interface at time 0. Hence, a diffusion phenomenon will start taking place since time $t = 0$ in the sample.

Before discussing the mathematical description of the diffusion phenomenon, a few elementary order-of-magnitude arguments can easily be presented. These allow to establish very simply two limiting asymptotic behaviours.

First consider the case where θ has a small value, say more precisely

$$\theta <\!<\!< X^2/D \tag{8}$$

where X is the half-thickness of the sample and D is the diffusivity of the solvent. If equation 8 is satisfied, the concentration of solvent at the interface will have approached its equilibrium value c_1^* before any appreciable amount of solvent has had time to diffuse into the sample. Correspondingly, one would observe an ordinary diffusion phenomenon under a steady driving force $c_1^* - c_0^*$, and the swelling-relaxation phenomenon needs not be considered at all. Indeed, this is the behaviour observed in practically all nonpolymeric materials, which are characterized by exceedingly short relaxation times.

Conversely, consider the case where θ is a very large number, say:

$$\theta >\!>\!> X^2/D \tag{9}$$

In this case, a diffusion phenomenon would proceed under a driving force $c_{10} - c_0^*$ up to complete saturation of the sample before the interface concentration of solvent changes appreciably from its initial value c_{10}. One would therefore observe an apparent saturation of the sample, followed by a very slow secondary uptake; the latter would simply be described by equation 7 which would now apply through the sample. This is in essence the experimentally observed behaviour reported by both Bagley and Long[13] and Long and Richmann[16] which cannot be explained by the Astarita and Joshi analysis[11].

It is interesting to observe that, if equation 9 is satisfied, and if the overall length of the experiment is larger than X^2/D but smaller than θ, one would not observe the slow secondary uptake, and one would attribute the plateau to equilibrium; in other words, c_{10} would be identified with the equilibrium concentration which it is not. These apparent equilibria, the values of which depend on the past history to which the sample has been subjected, have been observed experimentally[19] and discussed theoretically[18].

Since the asymptotic behaviours to be expected if either equation 8 or equation 9 hold can be obtained without a mathematical formulation of the diffusion-relaxation phenomenon, the latter needs to be developed only for those cases where the relaxation time θ and the diffusion time X^2/D are the comparable orders of magnitude. This is discussed in the next section.

MATHEMATICAL MODEL

Let θ_D be the diffusion time:

$$\theta_D = X^2/D \tag{10}$$

As discussed in the preceding section, a formal methematical model is required only when θ and θ_D are of comparable orders of magnitude. Such a mathematical model should describe both the concentration and the activity parameter field within the sample; the differential equations for the two fields are in principle coupled, since by the principle of equipresence[19] one would need to assume that the diffusivity depends on the activity parameter.

As a first approximation, one may neglect the latter effect and regard D as a constant. With this approximation the differential equation for the concentration field becomes uncoupled, and reduces to the ordinary diffusion equation. The boundary conditions are: at the sample's surface, equation 7; at time 0, $c = c_0^*$. In the special case where the sample has a plane geometry (e.g., a membrane), this problem allows a closed form solution, which has been given by Long and Richmann[16] who deduced equation 7 from direct experimental observations. The solution as given by Long and Richmann fits experimental data with satisfactory accuracy, thus showing that the assumption D = constant is not unreasonable one.

There are a few points about the analytical solution which deserve comment. Let W be the weight of solvent sobred per unit volume of the polymer sample; the analytical solution can be cast in the following form:

$$W = (c_1^* - c_0^*) f_D(t) - (c_1^* - c_{10}) \left[f_{DR}(t) - \frac{\tan\phi}{\phi}(1 - e^{-t/\theta}) \right] \tag{11}$$

where:

$$\phi^2 = \theta_D/\theta = X^2/D\theta \tag{12}$$

$$f_D(t) = 2 \sum_{N=1}^{\infty} \frac{1 - \exp(-a_N^2 t/\theta_D)}{a_N^2} \tag{13}$$

$$f_{DR}(t) = 2 \sum_{N=1}^{\infty} \frac{1 - \exp(-a_N^2 t/\theta_D)}{a_N^2 - \phi^2} \tag{14}$$

$$a_N = \pi \left(N - \frac{1}{2} \right) \tag{15}$$

The parameter ϕ is reminiscent of the Thiele modulus which emerges in the analysis of the effectiveness of porous catalysts. The function $f_D(t)$ is the ratio of weight sorbed to driving force which would emerge from the analysis of a purely diffusive process.

It requires tedious but straightforward algebra to convince oneself that, when $\phi \gg 1$, the whole term in square brackets on the RHS of equation 11 tends to zero [in particular, if ϕ approaches one of the a_N values, the leading term in the series which defines $f_{DR}(t)$ cancels out with the second term in the square bracket]. This implies that the whole process proceeds as an ordinary diffusion process under the driving force $c_1^* - c_0^*$, i.e., the relaxation does not manifest itself in any observable way.

Conversely, if $\phi \ll 1$, the function $f_{DR}(t)$ approaches the value of $f_D(t)$ at all times, and equation 11 becomes:

$$W = (c_{10} - c_0^*) f_D(t) + (c_1^* - c_{10})(1 - e^{-t/\theta}) \tag{16}$$

i.e., the process proceeds first as an ordinary diffusion under the *initial* driving force $c_{10} - c_0^*$, leading to an 'apparent equilibrium' this is followed by a slow first-order relaxation to the final equilibrium under the residual driving force $c_1^* - c_{10}$.

One may therefore conclude that the limiting behaviours predicted on an intuitive basis in the preceding section do in fact emerge as proper asymptotes of the analytical solution for the particular geometry (plane) for which such a solution is available. This gives support to the idea that such limiting behaviours will in fact be observed for any geometry.

It is, however, important to note that ϕ is only the square root of the θ_D/θ ratio, and that therefore the two limiting behaviours will in fact be observed *only* if the diffusion and relaxation times are widely different. When such is not the case, equation 11 shows that one cannot simply superimpose a diffusion term and a relaxation term in the calculation of the weight sorbed; diffusion and relaxation are coupled through the term in square brackets which contains both θ_D and θ.

Berens[20] and Berens and Hopfenberg[21,22] have presented an analysis of sorption in very fine polymer powders, where data are correlated by an equation which, in the notation of this paper, reads:

$$W = (c_{10} - c_0^*) f_D(t) + \sum_{i=1}^{\infty} (c_{1i}^* - c_{10})(1 - e^{-t/\theta_i}) \tag{17}$$

where $f_D(t)$ is the pure diffusion function appropriate to the spherical geometry. The equation proposed is based on the concept that there may be more than one relaxation process to be taken into account, each of them with a different relaxation time θ_i. From the viewpoint taken in this paper, Berens and Hopfenberg consider the case where only one internal state variable is not sufficient to determine the state of the material, so that instead of only the parameter ξ a set of parameters ξ_i needs to be considered. Furthermore they implicitly assume that the kinetics of evolution of all internal state variables are of the simple linear form of equation 5.

Several comments are in order concerning equation 17. First of all, unless the diffusion time θ_D is much less than the *smallest* relaxation time θ_i, equation 17 cannot be correct, since it does not allow for a diffusion–relaxation coupling term of the type of the term in square brackets on the RHS of equation 11. When the data that Berens and Hopfenberg correlated with equation 17 are examined, it turns out that several sorption curves do not exhibit a plateau region of apparent equilibrium, thus showing that in fact at least one of the relaxation times has an order of magnitude comparable to that of the diffusion time. Therefore, there is some doubt as to whether in fact equation 17 is appropriate for the analysis of such data except as essentially a curve-fitting procedure. Indeed, Berens and Hopfenberg do not claim any more than the latter.

Hopfenberg[24] has informed us that he has experimental evidence showing that swelling can be induced even at very low solvent activities, and has pointed out that this may justify the simple additivity implied by equation 17. An 'On-Off' mechanism triggering the swelling, is not easily accommodated from the viewpoint taken in this work, since whatever solvent is sorbed in the core of the sample and thus measured as part of the total weight increase, would still need to get to the core by diffusion.

Although equation 17 allows in principle for as many relaxation times θ_i as one wishes, in practice Berens and Hopfenberg do not need more than two, and often in fact only one, in order to correlate the data. It turns out that those sets of data which do exhibit an apparent equilibrium plateau can be correlated by using only one relaxation time: this of course corresponds to using equation 16 when it is predicted to hold, i.e., when $\phi \ll 1$.

The sets of data which require two relaxation times for correlation belong to two categories. The first one is that of sorption curves with no plateau, but with $dW/dt > 0$ at all times. For such sorption curves equation 17 does not seem to be appropriate (at least one of the θ_i's is of the order unity), and it is presumable that an equation of the form of equation 11, with $f_D(t)$ and $f_{DR}(t)$ appropriate to the spherical geometry, could correlate the data at least equally well.

The second category of data are sorption curves which go through a maximum, then decrease to a minimum and finally slowly approach saturation. Data of this kind do indeed suggest that at the very least two distinct relaxation processes are taking place, the faster one being towards a state with a *lower* solubility than the initial one.

The word relaxation, popular as it is, in fact is a confession of ignorance; it is commonly used to describe any time-dependent process, the physical nature of which is not understood[22]. In this paper we have tried to identify a specific physical process which causes a relaxation type of macroscopic behaviour, i.e., a first order rate of change of the degree of swelling, the latter being measured by the activity parameter ξ.

There is a rather old set of data[23] which is reminiscent of the Berens and Hopfenberg data quoted above, though there is no indication of a final approach to equilibrium after the minimum has been reached; in other words, the weight sorbed vs. time curve presents an overshoot of the equilibrium value. Mathematically, data of this type are easily correlated by the analysis presented, by simply allowing ξ_1^* to be *less* than ξ_2^*. Physically, this is rather surprising at first sight, since it is hard to believe that solubility decreases with increasing degree of swelling. One is therefore forced to look for other physical phenomena (Solvent induced crystallization, crazing of the glassy region relieved by additional sorption, and desorption of some originally present component, are possible candidates) in order to explain the data. In fact, both the first and the third physical phenomena have experimental support[25–27]. When experimental results, such as the Berens and Hopfenberg data quoted before, show final slow additional uptake of solvent after the overshoot, one needs to consider a degree-of-swelling slow phenomenon following whatever phenomenon is responsible for the initial overshoot, i.e., in mathematical terms, one needs at least two internal state variables.

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