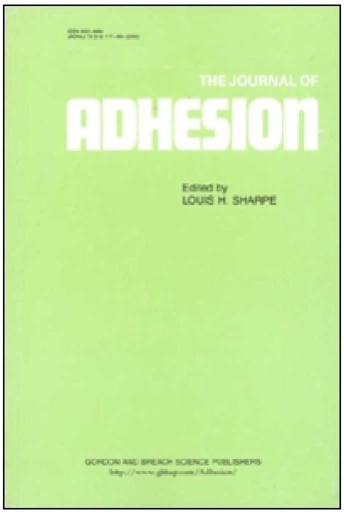

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A Model for the Diffusion of Moisture in Adhesive Joints. Part I: Equations Governing Diffusion

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A methodology is proposed to relate the diffusion coefficient of small penetrant molecules in polymers to temperature, strain, and penetrant concentration. The approach used is based on well-known free volume theories. It is assumed that the transport kinetics is governed by the constant redistribution of the free volume, caused by the segmental motions of the polymeric chains. An expression for the diffusion coefficient is inferred from the temperature, strain, and penetrant concentration dependence of the free volume. The stress dependence of solubility is predicted from the Hildebrand theory. It is shown that the resulting constitutive equations exhibit many features desirable for joint durability studies. Finally, a non-Fickian driving force arising from differential swelling is included in the governing equations.

KEY WORDS Diffusion; polymer (or adhesive); stress-assisted diffusion; free volume; solubility; dilatational strain.

INTRODUCTION

Moisture may enter a bond by diffusion through the adhesive, through the adherends or by moving along an interphase region. If one assumes that water molecules have the same degradative effect on the adhesive and interphase region, regardless of their migration path, then it becomes of ultimate concern to be able to understand and to predict the kinetics of moisture ingression *via* the

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different paths. This paper investigates an important mode of moisture intrusion into a joint: bulk diffusion through the adhesive.

Earlier work has demonstrated that the diffusion rate in a polymer can be increased by a number of factors such as temperature, stress and damage. In particular, "non-Fickian" kinetics, often associated with a sharp diffusion front, has been attributed to a strong dependence of the diffusion coefficient on concentration and/or moisture-induced damage. Externally applied stresses, residual stresses, and swelling stresses are known to affect diffusion rate. These various features (with the exception of damage) are reviewed in light of their usefulness to the specific problem of moisture diffusion in adhesive joints. Although damage can significantly enhance moisture ingression, it is reasonable to exclude it from this preliminary investigation because joints in service in moist environments are normally loaded to a small fraction of their ultimate breaking strength (dry), thereby minimizing damage arising solely from the applied load.

In Part I, the theoretical background leading to the equations governing diffusion will be reviewed in detail. Although the key concepts underlying the proposed theoretical treatment have been studied by several other workers, some novelty is introduced in the mathematical formulation of the constitutive relations. One of the major objectives of this study is to offer a treatment unifying both the diffusion behavior and the mechanical behavior into a single phenomenological model. It will be shown that the unified approach not only facilitates the description of the coupling between diffusion and stress relaxation, but also leads to a common material characterization. Many workers have recognized the importance, in the case of polymers, of the interdependence between the diffusion process and stress relaxation. Unfortunately, the solutions proposed to date have either dealt with specific boundary value problems or have failed to include in one single treatment, all the known forms of coupling. It follows that the solutions offered were often severely restricted in their conditions of applicability. By contrast, this treatment is meant to be as general as possible, and to be implemented in a finite element code. Unlike closed form solutions, the Finite Element Method can deal with almost any kind of boundary value problem of interest to designers. In the field of adhesion engineering, our goal is to provide designers with a general computational method to predict moisture intrusion into adhesive bond lines or into composite matrices, when they are subjected to a combination of external loading and internal swelling.

Part I is introductory and thus should be appraised only in the context of the entire work. In particular, Part I is not sufficient to understand fully the effect of stress and stress relaxation on diffusion. The constitutive relations for the mechanical behavior and swelling behavior are discussed in Part III.

GENERAL FORM OF THE EQUATION GOVERNING DIFFUSION

Let us consider a binary mixture consisting of a penetrant of small size (*e.g.*, water) permeating a polymer. The polymer is isotropic, amorphous and can be in either the glassy, leathery or rubbery state. It is natural to assume that the small penetrant molecules are much more mobile than the polymeric macromolecules. It follows that mass transport in this system can be described in terms of one flux only, namely that of the penetrant, because the polymer can be considered as a fixed reference. In general, the mass flux of penetrant can be separated in four components, each corresponding to a class of thermodynamic driving force.[1] Each driving force gives rise to small perturbations in the random walk of the diffusing species. Assuming the driving forces are uncoupled, and the departure from randomness small, the resulting macroscopic fluxes are additive:

$$\mathbf{J} = \mathbf{J}^C + \mathbf{J}^T + \mathbf{J}^\sigma + \mathbf{J}^\Phi \tag{1}$$

where: $\mathbf{J}^C$ = Fickian mass flux (entropy driven)
$\mathbf{J}^T$ = thermally-driven mass flux
$\mathbf{J}^\sigma$ = stress-induced mass flux
$\mathbf{J}^\Phi$ = forced mass flux (driven by an external force)

(Bold characters will represent vectorial quantities throughout this paper)

The Fickian flux arises as a result of concentration gradients and is given by:

$$\mathbf{J}^C = -D\,\nabla C \tag{2}$$

where: D = diffusion coefficient
C = penetrant concentration
∇ = gradient operator

Expression (2) is known as Fick's First Law as long as D is a constant or a function of C only. It will be shown later that the diffusion coefficient is a function of temperature and stress (or strain) as well:

$$D = D(C, T, \sigma) \tag{3}$$

where: T = temperature
σ = stress.

The thermal flux is driven by temperature gradients and is known as the Soret Effect:[1]

$$\mathbf{J}^T = -\frac{D^T C}{RT}\nabla LnT \tag{4}$$

where: D^T = thermal diffusion coefficient

Thermal diffusion becomes a significant component of the overall flux when an adhesive undergoes frequent temperature fluctuations. Sudden variations in external temperature give rise to temperature gradients internally which may persist for a long time, especially when the structure has a low thermal conductivity.

The stress-induced flux is produced by a non-uniform stress field[2] and is given by:

$$\mathbf{J}^{\sigma} = -\frac{DC}{RT}\nabla W_p \tag{5}$$

where: R = the gas constant
W_p = potential energy function

There is no general form for W_p. It is a function of the local entropy change of the penetrant when the polymer is subject to a stress (strain) field. Since the stress distribution within a joint is rarely uniform, proper attention should be given to this effect *a priori*. Furthermore, if the adhesive tends to swell by a large amount in the presence of the penetrant, $\mathbf{J}^{\sigma}$ could conceivably become quite large because differential swelling across the adhesive is generally constrained by stiff adherends, leading to large pressure gradients internally, under either sorption or desorption processes. A possible form for W_p will be suggested in this article.

The forced diffusion flux is of importance in cases when the penetrant molecules are subject to an external force field (*e.g.*, electrical or inertial). In an adhesive joint, such a field may exist locally in the region known as the interphase. Close to a hydrophilic oxide layer, the intermolecular field experienced by a water molecule can be more intense than in the bulk polymer. This disparity is expected to cause local perturbations in the diffusive flux. It should be noted that, in this article, $\mathbf{J}^{\Phi}$ refers to a component of the flux arising from any external force field, with the exception of stress fields. The effect of stress fields is already incorporated in the $\mathbf{J}^{\sigma}$ component of the flux.

Let us now consider the total flux $\mathbf{J}$. Since conservation of mass must be satisfied, we must have:

$$\frac{\partial C}{\partial t} = -\nabla \cdot \mathbf{J} \tag{6}$$

where t is time, leading to the final governing equation:

$$\frac{\partial C}{\partial t} = \nabla \cdot \left\{ D(C, T, \sigma)\left[\nabla C + \frac{C}{RT}\nabla W_P\right] + \mathbf{J}^T + \mathbf{J}^{\Phi} \right\} \tag{7}$$

In the remaining discussion, the problem will be reduced to that of diffusion in a medium of uniform temperature and in the absence of an external force field ($\mathbf{J}^T = \mathbf{J}^{\Phi} = 0$). Expression (7) shows that the effect of stress is twofold: (1) stress field gradients give rise to a thermodynamic force ∇W_p and (2) stress also affects the mobility of the penetrant, quantified here by the diffusion coefficient. The effect of stress on mobility does not disappear in a uniform stress field, although the stress-induced driving force does vanish.

At this point, it is useful to recall that polymeric adhesives are viscoelastic in nature. Thus, our governing equation is valid instantaneously only. Stress and stress gradients need to be updated constantly in order to account properly for the rheology of the material. The problem of the coupling between the diffusion boundary value problem and the viscoelasticity boundary value problem will be addressed in more detail in Part III. For the time being, we simply need to keep in mind that the governing equation is implicitly time dependent on the right hand side of the equation.

A thorough literature review[2–7] led us to conclude that expression (7) contains many of the known features necessary for modelling non-Fickian transport in the absence of damage. These features are:

1. The history dependence of the diffusion coefficient, in this case, through the coupling with the viscoelastic response,
2. The effect of a non-uniform stress distribution, and
3. The concentration dependence of the diffusion coefficient. (Although listed as a source of anomalous behavior, this concentration dependence does not, in fact, violate Fick's Second Law in its most general form).

Note that the proposed governing equation is by no means the only possible theoretical model. It simply contains provision for important features often found in separate theories, but not in a unified approach.

The stress dependence of the solubility (accompanied here by an implicit time dependence) has also been identified as a source of non-Fickian behavior.[7–9] This difficulty can be addressed in the framework of a numerical analysis, by normalizing the concentration with respect to the saturation level at the current time step, and by providing an adequate model for the stress dependence of solubility. Such a model will be discussed later in this article.

A MODEL FOR THE DIFFUSION COEFFICIENT BASED ON THE COHEN–TURNBULL THEORY

The purpose of this section is to establish a general theory for predicting the diffusion of small molecules in polymeric materials. Particular attention will be devoted to the temperature dependence, stress dependence and penetrant-concentration dependence of D.

The Cohen–Turnbull model

The Cohen–Turnbull model[10,11] was originally developed to describe self-diffusion in an ideal liquid made of hard spheres, but it has been extended to concentrated solutions and undiluted polymers. The model is based on the idea that molecular transport occurs by the movement of molecules into voids with a size greater than some critical value. Voids are formed by the statistical redistribution of the free volume. Free volume is defined as:

$$V_f = V - V_0 \tag{8}$$

where: V = specific volume
V_0 = occupied volume

Furthermore, it is assumed that:

1. Free volume is continually redistributed with time, and that no local free energy is required for redistribution. As a result, distribution is random.
2. Molecular transport occurs by the movement of diffusing molecules into voids of at least their molecular size, which are formed as a result of the random redistribution of free volume.

In the case of the self diffusion (or viscous flow) of a polymer, the molecular jump representation must be replaced by the concept of segmental rearrangements which can occur whenever the surrounding free volume reaches some critical value V_c. In other words, in order for a portion of the polymeric chain to take a new conformation, the "cage" formed by nearest neighbors must reach a critical size.

The probability that n increments of free volume of average size V_f would accumulate into a void of size V_c is proportional to $\exp\left(-\theta\frac{V_c}{V_f}\right)$, where θ is an overlap factor arising from the fact that the same void is available to more than one molecule. In the case of viscous flow, critical volume V_c must be large enough to allow a local rearrangement of the chain conformation, whereas in the case of the diffusion of a small penetrant, V_c must be large enough to allow a local molecular jump of the penetrant. Thus V_c is a characteristic of the polymer only in the case of self diffusion (or viscous processes) and V_c is a characteristic of a given polymer-penetrant pair in the case of the diffusion of a small penetrant molecule. From the form of the probability distribution, it follows that the diffusion coefficient contains an activation volume term:

$$D = D_0 \exp\left(-\theta\frac{V_c}{V_f}\right) \tag{9}$$

Equation (9) implies that the free volume is the only parameter involved in describing transport phenomena. This theory is not sufficient, however, at temperatures too low relative to the glass transition temperature T_g, when motions of the chains within the free volume are too slow. Nor does it apply at very high temperatures where activation energy barriers must be overcome.[13] Note that in the framework of the Cohen–Turnbull theory the free volume is not the true free volume in the geometric sense, but only that portion of the total free volume which can be redistributed with no local change in free energy. It follows that the occupied volume V_c defined here is not the hard-shell volume, but a larger quantity which can be changed by a stress field (*i.e.*, the occupied volume is compressible).

The Macedo–Litovitz and Vrentas–Duda theories

Macedo and Litovitz[12] introduced an expression for the self-diffusion coefficient very similar to that of Cohen and Turnbull, except that it contains an activation energy factor:

$$D = D_0 \exp\left(-\frac{E}{RT}\right) \exp\left(-\theta \frac{V_c}{V_f}\right) \tag{10}$$

It was postulated that, in addition to the minimum hole-size requirement, an energy barrier must be surmounted. When inverted, expression (10) describes a viscosity. The obtained form is virtually identical to a known extension of the WLF equation including an Arrhenius-like temperature dependence.[13] In the glassy state (non-equilibrium), the temperature dependence predicted by the elementary WLF equation is known to be incorrect and an Arrhenius temperature dependence has been widely reported. This finding is consistent with expression (10) and will be the object of further discussion later.

Vrentas *et al.*[14] developed a constitutive behavior for the self diffusion in polymers based on Eq. (10). Their treatment of the free volume is more complex than the one used in this work. In addition to the free volume treatment of Cohen and Turnbull, the Flory–Huggins polymer solution theory and some aspects of the entanglement theory of Bueche are employed. An average free volume $\bar{V}_f$, as well as an average critical volume $\bar{V}_c$, are defined for the binary mixtures sorbent (subscript 1)-polymer (subscript 2):

$$\bar{V}_f = k_{11}\omega_1(k_{21} + T - T_{g1}) + k_{12}\omega_2(k_{22} + T - T_{g2}) \tag{11}$$

$$\bar{V}_c = \omega_1 \hat{V}_1^* + \omega_2 \xi \hat{V}_2^* \tag{12}$$

where: ω_i = mass fraction of component i;
T_{gi} = glass transition temperature of component i;
k_{11}, k_{21} = free volume parameters for the solvent;
k_{12}, k_{22} = free volume parameters for the polymer;
ξ = ratio of the critical molar volume of the penetrant jumping unit to the critical molar volume of the polymer jumping unit
$\hat{V}_i^*$ = specific critical hole free volume of component i.

In the limit, when the mass fraction of penetrant is small, $\bar{V}_f$ and $\bar{V}_c$ become mainly polymer dependent and the above approach becomes equivalent to the one shown herein. Our simpler approach, in which the free volume of the mixture is dominated by that of the polymer, is very reasonable because polymers with a large moisture solubility are not suitable for the structural adhesive applications with which we are concerned.

Extension of the Doolittle theory to the problem of diffusion of small molecules

Doolittle proposed an empirical equation relating polymer viscosity to the free volume, which was found to apply to polymers in their rubbery range.[13] Fluidity F, the inverse of viscosity, is given by:

$$F = A^{-1} \exp\left(-B \frac{V - V_f}{V_f}\right) \tag{13}$$

where A and B are empirical constants. The parallelism between Eqs. (9) and (13) is striking. This was explained earlier by the fact that the elementary process for viscous flow and the elementary process for sorbent diffusion are identical. In order to prove that Eqs. (9) and (13) are identical mathematically, one can use Einstein's equation for the diffusion coefficient and Stokes' equation for the friction constant. According to Einstein's equation for the diffusion coefficient:[15]

$$D = \frac{kT}{f_n} \tag{14}$$

where: D = diffusion coefficient
k = Boltzmann constant
T = temperature
f_n = friction constant

Equation (14) holds for any thermally-driven process governed by the three-dimensional random walk of diffusing species. Stokes' equation states that the friction constant is proportional to viscosity:[15]

$$f_n = \lambda\eta \tag{15}$$

As reviewed by Ferry,[13] the work of Rouse and Bueche demonstrated that Eq. (15) holds for polymers and that the proportionality coefficient λ is a function of density, molecular weight, and molecular geometry.[13] In this case, f_n is a measure of segmental frictional resistance. Combining (14) and (15) yields:

$$D = \lambda^{-1}kTF \tag{16}$$

And we find a diffusion coefficient of the form:

$$D = \mu T \exp\left(-\theta \frac{V - V_f}{V_f}\right) \tag{17}$$

where μ is a material constant. Let η and η_0 be the viscosities of the polymer and f and f_0 the fractional free volumes at a given temperature T and a reference temperature T_0, respectively. (The fractional free volume is defined as the ratio V_f/V). Doolittle, in his work on the viscous flow of polymers, showed that:[13]

$$Ln\frac{\eta}{\eta_0} = B\left(\frac{1}{f} - \frac{1}{f_0}\right) \tag{18}$$

where B is the empirical constant mentioned earlier. Assuming that f changes linearly with temperature,

$$f = f_0 + \alpha_0(T - T_0) \tag{19}$$

and combining with expression (18) leads to the well known WLF equation for the shift factor a:

$$Ln\,a = -\frac{\frac{B}{f_0}(T - T_0)}{\frac{f_0}{\alpha} + T - T_0} \tag{20}$$

The WLF equation concerns itself with the viscoelastic response. It was noted earlier that, in general, the critical hole size V_c for the local rearrangement of a polymer segment is not the same as the critical hole size for penetrant jump. It can be seen in expression (9) that a change in V_c can be expressed mathematically by varying θ, with V_c remaining constant. Noting that θ and B are inversely related, it is now possible to extend conveniently the above results to the diffusion of a penetrant of small size, simply by replacing B by B^D, a numerical parameter inversely related to the minimum hole size for the jump of a small penetrant molecule.

By combining expressions (14), (15) and (18) a diffusion counterpart of the Doolittle equation is found:

$$D = \frac{D_0}{T_0} T \exp\left\{-B^D\left(\frac{1}{f} - \frac{1}{f_0}\right)\right\} \tag{21}$$

Derivation of the constitutive equation for the diffusion of a penetrant of small size

Several investigations in the field of rheology have suggested that free volume is a good unifying parameter to describe changes in the time scale of material response. In the WLF equation, the effect of temperature was incorporated by stating that the fractional free volume was a linear function of temperature in the rubbery range. Likewise, the effect of stress and solvent concentration can be introduced by stating as a first approximation that the fractional free volume is a linear function of the dilational stress component and the solvent concentration. Knauss and Emri[16] used this concept to develop a nonlinear viscoelastic constitutive behavior centered on free volume effects. They postulated that the change in fractional free volume due to each variable was additive:

$$f = f_0 + \alpha\,\Delta T + \varepsilon^f_{kk} + \gamma C \tag{22}$$

where: α = coefficient (volumetric) of thermal expansion of the free volume
γ = coefficient (volumetric) of swelling
ε^f_{kk} = volume dilatation of the free volume due to external loads

However, as pointed out by Knauss and Emri, it is more appropriate to state that the free volume depends on the temperature history, strain history and swelling history if we are to extend this concept to the glassy range. Thus f should be written in the form of a sum of convolution integrals:

$$f = f_0 + \alpha(t) * dT + \varepsilon^f_{kk}(t) + \gamma(t) * dC \tag{23}$$

at first, we will limit ourselves to the simpler case where α, and γ are time independent and Eq. (23) reduces to (22). These assumptions are known to be correct above T_g where the system is always close to thermodynamic equilibrium. The linearity in concentration is unlikely to be obeyed with solvents reaching high concentrations. For this reason, it will be assumed that the change in free volume due to the solvent is better described by:

$$\Delta f = \gamma C^N \tag{24}$$

Expression (22) then becomes:

$$f = f_0 + \alpha\,\Delta T + \varepsilon^f_{kk} + \gamma C^N \tag{25}$$

The exponent N must be considered as an adjustable parameter relating to the occurrence of non-zero volume change on mixing. Substituting (25) in (21) yields an expression for the diffusion coefficient:

$$D = \frac{D_0}{T_0}\,T \exp\left\{\frac{B^D}{f_0}\,\frac{\alpha(T - T_0) + \varepsilon^f_{kk} + \gamma C^N}{f_0 + \alpha(T - T_0) + \varepsilon^f_{kk} + \gamma C^N}\right\} \tag{26}$$

Although there are eight parameters in this theory, each has a precise physical significance. Subscript 0 on any variable refers to a reference temperature T_0. In order to use B^D, f, and α from the WLF theory, it is convenient to use $T_0 = T_g$. The domain of validity of equation (26) is the same as that of the WLF equation, that is, roughly: $\{T_g, T_g + 100\}$.

As pointed out previously, an activation energy must be introduced if one wishes to extend (26) above $T_g + 100$. This temperature range however, is not considered in the current discussion.

Extension to the glassy state, physical aging

Expression (26) was originally derived for small penetrant molecules and for temperatures corresponding to the rubbery range of the material. Local motions of the main chains or of the side groups, as well as Brownian motions of the penetrant molecules, are known to persist in the glassy state as well. A list of possible local chain motions is given in Reference 13. Since such local segmental rearrangements can drive the diffusion of small penetrant molecules, the phenomenological model derived earlier still applies in principle below the glass transition temperature, except for the temperature dependence. The reason that the temperature term is not valid any more is that α describes the dilatation of the free volume above T_g only. (α is equal to the difference between the volume thermal expansion coefficient of the specific volume and that of the occupied volume). Below T_g, the fractional free volume is much less temperature-dependent (although it is still time-dependent due to aging). It has been shown by Matsuoka *et al.* that the abrupt change in the temperature dependence at the glass transition can be explained by using the Adam–Gibbs' formula for the relaxation behavior.[17] The Adam–Gibbs' formula expresses the shift factor in terms of the configurational entropy of the polymer, rather than in terms of the free volume. The configurational entropy is used as a measure of the size of the cooperatively-rearranging region and seems to give a better description of the state of the polymer below T_g than the free volume. This entropy-based approach leads to an Arrhenius-like equation if the entropy is frozen at some value, as in the rapidly quenched glassy state, or leads to a Vogel–Fulcher-like equation (same as WLF) above T_g. In order to remain consistent with the above results as well as with expression (10), the following form is proposed for the diffusion coefficient below T_g:

$$D = D_g \exp\left(-\frac{\Delta H}{RT}\right) \exp\left\{\frac{B^D}{f_g} \frac{\varepsilon^f_{kk} + \gamma C^N}{f_g + \varepsilon^f_{kk} + \gamma C^N}\right\} \qquad (27)$$

where: ΔH = activation energy
R = the gas constant

Expression (27) states that the free volume continues to govern the effect of stress and swelling below the glass transition temperature, implying that these forces act primarily on very local volumetric properties such as the critical void size. By contrast, temperature appears to affect motions over larger volumes encompassing cooperative segmental motions. The Arrhenius temperature dependence shown in expression (27) has been observed experimentally on numerous penetrant-polymer systems below the glass transition temperature.[7] Often, the Arrhenius form is also used above T_g, with an activation energy differing from that below T_g. This is simply due to the fact that the WLF equation can be mathematically fitted as an Arrhenius equation by using an apparent activation energy.

Of course, f is not the same at, and below, the glass transition temperature. Thus, expression (27) by itself gives an incomplete description of the material behavior. This apparent inconsistency is dealt with by introducing physical aging into the model. We will see that the use of a shift factor (acceleration factor) is phenomenologically equivalent to having a reduced ε^f_{kk}.

In the rubbery state, equilibrium is reached very rapidly in response to variations in temperature, stress, and penetrant concentration. This is due to the fact that the free volume response is quasi-instantaneous under these conditions. By contrast, a material in the glassy state is not in thermodynamic equilibrium and the response of the free volume to changes in external conditions is delayed. For this reason, a time-dependent diffusion coefficient containing hereditary integrals is more promising for the glassy range. Expression (27) is still valid instantaneously, however, and can be used in an iterative numerical scheme. Glassy polymers have a volume enthalpy and entropy which are larger than they would be in the equilibrium state. This metastable (or supercooled) state causes the free volume to collapse slowly with time until equilibrium is reached. The phenomenon is known as physical aging.[18]. Successful diffusion modelling in the glassy range must incorporate this important effect.

Struik[18] proposed a simple method to incorporate aging into existing constitutive equations. The time-dependent reduction of the free intermolecular space causes relaxation processes to take place over a longer time. Thus, an acceleration factor was defined in order to relate actual time to effective time:

$$d\lambda = a(t)\, dt \qquad (28)$$

where: λ = effective time
t = actual time
$a(t)$ = acceleration factor

The acceleration factor may also be defined in terms of molecular mobility $M(t)$:

$$a(t) = \frac{M(t_e + t)}{M(t_e)} \tag{29}$$

where: t_e = aging time at the start of service life or testing
t = service life or test time

Struik proposed the following power law for the acceleration factor:

$$a(t) = \left(\frac{t_e}{t_e + t}\right)^{\mu} \tag{30}$$

where μ is a constant and $0 \leq \mu \leq 1$. Expression (30) was derived theoretically and confirmed by long-term experiments.[18] We conclude that expression (23) can be readily modified to incorporate aging, by replacing actual time t by effective time λ in the integral symbols. Moreover, we have established from the above discussion that λ is related to t by:

$$\lambda = \int_0^t \left(\frac{t_e}{t_e + \xi}\right)^{\mu} d\xi \tag{31}$$

At this stage, it must be noted that there exists a secondary transition temperature T_∞ in the glassy range below which physical aging ceases, due to extremely low molecular mobility. It follows that the above treatment no longer applies below T_∞. Adamson[19] has proposed both a conceptual model and an experimental method to estimate the free volume in the entire glassy region, including the truly glassy region below T_∞. Further, his data confirm that the free Volume Theory of molecular mobility—with some minor revisions—still explains observed sorption behavior in the glassy domain. It is true that the physics of free volume is basically incorrect in a non-equilibrium state such as the glassy state. However, it still remains that the basic concepts of the theory are extremely helpful in deriving correct predictive models for the behavior under stress. As demonstrated by Knauss,[16] in the field of viscoelasticity these models can be valuable tools for life prediction, in spite of their inherent imperfection.

A POTENTIAL FIELD FUNCTION FOR THE STRESS-INDUCED DIFFUSION FLUX

It was shown earlier that stress (strain) can affect the diffusion rate in two ways: (1) by altering the mobility of the penetrant and (2) by producing an extra driving force. By relating the diffusion coefficient to strain, we addressed the mobility effect. We must now establish a theoretical background to estimate the magnitude of the stress-induced driving force. A primary cause for this driving force in a joint is uneven swelling in the direction of the moisture flux. Uneven swelling gives rise to pressure gradients along constrained bond lines. In contrast to fluids, *e.g.*, where pressure energy is dissipated, viscoelastic solids (adhesives) will store some elastic energy, causing the chemical potential of the penetrant to be changed. The potential energy function introduced in expression (5) is a measure of this free energy change.

Various forms have been suggested for the potential field function W_p by workers interested in the diffusion of interstitials in stressed metals,[20,21] in the stress-induced diffusion of macromolecules,[2,22] and in the stress-assisted diffusion of small penetrants in polymers.[9] In each case, the method consisted of finding the entropic potential of the diffusing species under the stress conditions of interest. For the problem of transport of small penetrant molecules in polymers, we will take the free energy of mixing of a sorbent (subscript 1) with a polymer (subscript 2), for our entropic potential function. From the Flory–Huggins theory,[23] we know that the chemical potential of the sorbent is given by:

$$\mu_1 = \mu_1^0 + RT[\chi_1 v_2^2 + Ln\, v_1 + v_2] \tag{32}$$

where: v_1 = volume fraction of penetrant
v_2 = volume fraction of polymer
χ_1 = Flory–Huggins interaction parameter

Let V_1 and V_2 be the volume of penetrant and polymer, respectively, in the binary mixture. The fractional free volume may then be defined as:

$$f = \frac{V_f}{V_2} \tag{33}$$

Using the same notation as in the section dealing with diffusivity, and assuming that the penetrant tends to fill the available free volume, the volume of penetrant may be approximated by:

$$V_1 = V_2 f \tag{34}$$

The volume fraction of polymer under stress may be approximated by:

$$v_{2\varepsilon} = \frac{1}{1 + f_0 + \varepsilon_{kk}^f + \gamma C^N} \tag{35}$$

Likewise, the volume fraction of penetrant under stress (before the system has recovered to an equilibrium state) may be approximated by:

$$v_{1\varepsilon} = \frac{f_0 + \gamma C^N}{1 + f_0 + \varepsilon_{kk}^f + \gamma C^N} \tag{36}$$

Since the formation of extra "holes" in the presence of mechanical deformation does not affect the sum of all pair-wise interaction energies between the polymer and the penetrant molecules, the enthalpy term in expression (32) is unchanged under stress. Thus the chemical potential μ_1^{ε} of the penetrant in a strained polymer is given by:

$$\mu_1^{\varepsilon} = \mu_1^0 + RT\left[\chi\left(\frac{1}{1 + f_0 + \gamma C^N}\right)^2 + Ln\left(\frac{f_0 + \gamma C^N}{1 + f_0 + \varepsilon_{kk}^f + \gamma C^N}\right) + \frac{1}{1 + f_0 + \varepsilon_{kk}^f + \gamma C^N}\right] \tag{37}$$

The excess chemical potential of the penetrant with respect to the unperturbed state is given by:

$$\delta\mu_1^{\varepsilon} = RT\left[Ln\left(\frac{1+f_0+\gamma C^N}{1+f_0+\varepsilon_{kk}^f+\gamma C^N}\right)+\frac{1}{1+f_0+\varepsilon_{kk}^f+\gamma C^N}-\frac{1}{1+f_0+\gamma C^N}\right] \quad (38)$$

$\delta\mu_1^{\varepsilon}$ is the excess entropic potential of the diffusing species under stress, and can be taken as our potential field function W_P.

Rearranging expression (38) and noting that $f_0 \ll 1$, $\varepsilon_{kk}^f \ll 1$ and $\gamma C^N \ll 1$ in all polymer-penetrant systems of interest in this study (small strains, minimal swelling), it immediately follows that:

$$\nabla W_P \simeq -RT\,\nabla\varepsilon_{kk}^f \quad (39)$$

and the stress-induced flux is:

$$\mathbf{J}^{\sigma} \simeq +DC\,\nabla\varepsilon_{kk}^f \quad (40)$$

Note that ε_{kk}^f is related to the trace of the stress tensor by an instantaneous compressibility. Thus, to some extent, $\nabla\varepsilon_{kk}^f$ is analogous to a pressure gradient. However, in contrast to pressure, which can only be positive, strain or stress may be positive or negative, leading to an increase or decrease of the chemical potential. Therefore, the excess chemical potential defined earlier is an algebraic quantity.

Consider a polymer constrained between two rigid adherends held at a fixed distance. If the polymer tends to swell in the presence of moisture, ε_{kk}^f, which is the mechanical component of free volume dilatation, becomes negative and more so as the concentration of penetrant increases (See Part III for the constitutive relations describing the hygro-mechanical behavior). Thus ∇C and $\nabla\varepsilon_{kk}^f$ have opposite signs and the two corresponding fluxes are of the same sign, leading to accelerated moisture penetration. This prediction is consistent with a number of results reported in Reference 7.

THE STRESS AND TEMPERATURE DEPENDENCE OF SOLUBILITY

The stress (strain) dependence of solubility must be addressed if one wishes to obtain correct concentration predictions. In this section, Peterlin's approach[24] will be used to evaluate the solubility S in relation to temperature and stress. It will be shown that the predicted sensitivity of S to stress is an order of magnitude lower than the sensitivity of the diffusion coefficient to stress and that an Arrhenius-type of relation is obeyed for temperature. Once again, the free volume concept will prove to be extremely helpful in deriving the constitutive equations.

Peterlin[24] used the Hildebrand treatment of the thermodynamics of polymer-solvent mixtures, in which the entropy of mixing appears as a function of the fractional free volumes of the polymer (f_2) and of the penetrant (f_1). The mixture is treated as a two-component van der Waals liquid whose entropy is proportional to the logarithm of the volume available for kinetic movement, which is assumed to be equal to the free volume of the mixture.[23] Assuming that the resultant free volume fraction of the two-component system can be obtained by a linear rule of mixtures,

$$f = v_1 f_1 + v_2 f_2 \tag{41}$$

the following expression for the chemical potential of the penetrant was obtained:

$$\mu_1 = \mu_1^0 + RT[\chi_1 v_2^2 + v_2^\varepsilon + Ln(1 - v_2^\varepsilon)] \tag{42}$$

where:

$$v_2^\varepsilon = \frac{f_2 v_2}{f_1 + (f_2 - f_1)v_2} \tag{43}$$

Expression (42) is another form of the Flory–Huggins equation shown in the previous section. (The same notation is used). Note that f_2, the free volume fraction of the polymer, is equal to the f_0 parameter introduced earlier and that the free volume fraction f_1 of a low molecular weight penetrant is generally larger than f_2. The chemical potential of the sorbent in the vapor phase is given by:

$$\mu_1 = \mu_1^0 + RT\,Ln\frac{P}{P_T} \tag{44}$$

where P/P_T is the activity of the vapor in terms of partial pressure. At equilibrium, the chemical potential of the sorbent in the vapor phase must be equal to the chemical potential of the sorbent dispersed in the polymer. Expressing this equality and assuming small sorption (v_2 close to 1), gives:

$$v_1 = \frac{f_2 P}{f_1 P_T}\exp[-(1 + \chi_1)] \tag{45}$$

By definition, solubility in weight fraction can be expressed as:

$$S = \frac{\rho_1 v_1}{P \rho_2 v_2} \tag{46}$$

where: ρ_1 = density of the sorbent
ρ_2 = density of the polymer

It follows that solubility is related to the polymer free volume fraction by:

$$S = \frac{f_2 \rho_1}{f_1 \rho_2 P_T}\exp[-(1 + \chi_1)] \tag{47}$$

The fractional free volume appears as an entropic quantity measuring the probability for the creation of a sorption site. Thus, by changing the free volume of the polymer component, stress acts predominantly on the entropy of the system (see expressions (42) and (43)). According to our notation, the free volume fraction of the polymer under strain is given by:

$$f_2 = f_2^0\left(1 + \frac{\varepsilon_{kk}^f}{f_2^0}\right) \tag{48}$$

where: $f_2^0 = f_0$.

Substituting expression (48) into (47) yields our final result for the strain dependence of solubility:

$$S = \frac{f_0 \rho_1}{f_1 \rho_2 P_T} \exp[-(1+\chi_1)]\left(1 + \frac{\varepsilon^f_{kk}}{f_0}\right) \tag{49}$$

Now, from the Flory–Huggins theory, we know that the interaction parameter is related to the heat of mixing ΔH_1 by:

$$\chi_1 = \frac{\Delta H_1}{RTv_2^2} \tag{50}$$

Substituting (50) in (49), and noting that v_2 is close to 1, yields an Arrhenius type of temperature dependence:

$$S = S_A \exp\left(-\frac{\Delta H_1}{RT}\right)\left[1 + \frac{\varepsilon^f_{kk}}{f_0}\right] \tag{51}$$

where: S_A = constant.
ΔH_1 = activation energy for solubility (enthalpy of mixing).

Note that in the case of a vapor in contact with the polymer, the activation energy for solubility also contains the heat of condensation of the vapor. This is due to the fact that, in the Hildebrand theory, the reference state of the two unmixed components is the liquid state.

Thus, according to this treatment, the relative change in solubility due to stress is equal to the mechanical dilatation of the free volume normalized to the initial free volume fraction:

$$\frac{\delta S}{S_0} = \frac{\varepsilon^f_{kk}}{f_0} \tag{52}$$

where: S_0 = solubility under zero strain for a fixed temperature.

An alternate and more direct treatment of the strain dependence of solubility is to assume immediately that the solubility is proportional to the total fractional free volume of the polymer. This model is based on the assumptions that (1) once equilibrium sorption is achieved, sorbent molecules fill all the available free volume, including the strain-induced free volume, and that (2) swelling is negligible:

$$S = \frac{S_0}{f_0}(f_0 + \varepsilon^f_{kk}) \tag{53}$$

which is obviously equivalent to expression (52). It will be shown in Part II that the above result agrees quite well with data collected on the carbon dioxide-low density polyethylene system, but that lack of agreement is found in the case of water in Ultem 1000.

The relative change of the diffusion coefficient due to a small strain will be determined in Part II. It will be shown that:

$$\frac{\delta D}{D_0} = \frac{B^D}{f_0^2} \varepsilon^f_{kk} \tag{54}$$

Recalling that B^D is close to 1 and that f_0 is quite small (0.03), we conclude that diffusivity should be more sensitive to strain than solubility, by one or two orders of magnitude. Also, note that diffusivity is much less affected by strain in the rubbery range than in the glassy range. This property may be attributed to the larger free volume in the rubbery range to the virtual incompressibility of rubbers.

CONCLUSION

A comprehensive model for the isothermal diffusion of gases and vapors in polymers has been discussed. All our results can be summarized in a system of three governing equations:

$$\frac{\partial \bar{C}}{\partial t} = \nabla \cdot \{D(\varepsilon^f_{kk}C)[\nabla \bar{C} - \bar{C}\nabla \varepsilon^f_{kk}]\} \tag{55}$$

$$\bar{C} = \frac{C}{S_0[1 + \beta_S \varepsilon^f_{kk}]P} \tag{56}$$

$$D(\varepsilon^f_{kk}C) = D_0 \exp\left\{\frac{B^D}{f_0}\frac{\varepsilon^f_{kk} + \gamma C^N}{f_0 + \varepsilon^f_{kk} + \gamma C^N}\right\} \tag{57}$$

where: $\bar{C}$ = normalized concentration
S_0 = solubility in the reference state
β_S = experimentally or theoretically-determined coefficient
P = vapor pressure
D_0 = diffusion coefficient in the reference state
ε^f_{kk} = dilatation of the free volume
γ = coefficient of swelling expansion
f_0 = reference fractional free volume of the polymer
B^D = parameter inversely related to the critical void size

It is now firmly established that the diffusion boundary value problem of interest in joint durability studies is highly non-linear and is coupled with the mechanical response of the polymer. The fully-coupled solution for a number of boundary value problems will be given in Part III, using finite element analysis. Note that Eqs. (55) to (57) are implicitly time dependent. It follows that the above closed-form representations are incorrect when not properly coupled, in some iterative scheme, with the equations describing the viscoelastic response. (Convolution notations, as in expression (23), could be used, but would only add confusion with no real gain in rigor).

In Part II, experimental diffusion data on a number of polymer-penetrant systems will be used to validate the diffusivity and solubility models developed in this section. Particular emphasis will be placed on the effect of stress (strain) on the transport rate.

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