VISCOELASTIC (NON-FICKIAN) DIFFUSION

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This review paper deals with mass transport in macromolecular materials. The study of mass transport through polymeric composite materials for example has applications in a variety of areas such as coatings, packaging and gas separations, to name just a few. Here we discuss several models for diffusion as well as several experimental techniques. In particular, we discuss models for case II diffusion, from a continuum mechanics point of view as well as via a mesoscopic theory. Variables such as temperature, molecular structure and mechanical deformation, affecting mass transport are also discussed.

Cette revue porte sur le transport de matière dans les matériaux macromoléculaires. L'étude du transport de masse dans les matériaux composites polymériques par exemple a des applications dans divers domaines, comme l'enrobage, l'emballage et la séparation de gaz, pour en nommer quelques-uns. Nous examinons ici plusieurs modèles pour la diffusion ainsi que plusieurs techniques expérimentales. En particulier, nous examinons des modèles pour la diffusion de type II, du point de vue de la mécanique des milieux continus et à partir d'une théorie mésoscopique. Des variables influant sur le transport de masse, telles la température, la structure moléculaire et la déformation mécanique, sont également étudiées.

Keywords: diffusion, viscoelastic systems, nanocomposite membranes

New uses for polymers and other synthetic materials have revolutionized entire industries and created new ones. In this contribution, we review the mass transport of small molecules through polymeric materials. Such transport is associated with many applications, such as gas separation, protective clothing, packaging, coating, drug delivery, etc. The process in which small molecules penetrate polymers and resins is very complex and so far not a single theoretical framework or mathematical model has been able to provide a complete explanation of this phenomenon.[1-3] Complexities associated with the transport mechanisms are associated with the physical properties of the polymeric materials. Polymer chains rearrange to accommodate small molecules; the polymer may swell as in the case of drug delivery for example. The degree and the time scale of the swelling greatly affects the kinetics of drug release.

One can consider the mass transport process to include three steps. Small solvent molecules are first absorbed on the surface of the polymeric material. Then the molecules diffuse through the polymer and finally, the solvent molecules desorb on the downstream surface of the polymer.[4, 5] The duration and intensity of these steps is influenced by several factors such as the polymer and permeant structures, temperature, mechanical deformation, solvent-polymer interaction, pre-contamination of the barrier material, presence of fillers, etc.[1, 6] Many of these factors affect the mass transport process through a substantial time scale associated with structural changes of the polymer, as in the case of plasticization for example, where the polymer changes from a glassy to a rubbery state when the local solvent volume fraction exceeds some threshold value. When diffusion occurs in the rubbery state, large segments of the polymer participate due to chain

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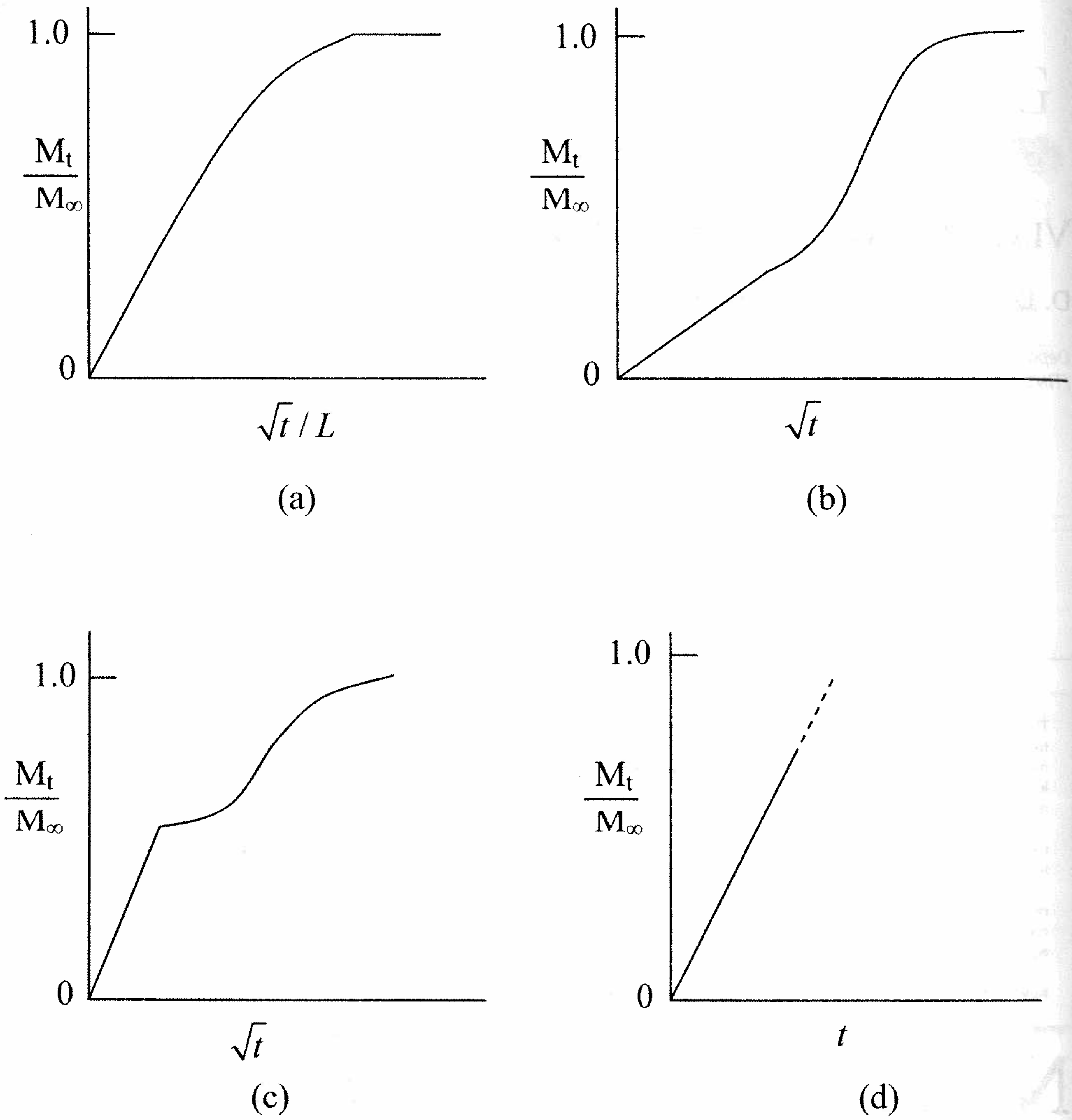

Figure 1. Different classes of non-Fickian sorption: (a) classical, (b) sigmoidal, (c) two-step, (d) Case II

rotations, translations as well as vibrations. Basically, a larger internal void space is more readily accessible. However, in the glassy state, polymers are usually hard or brittle and chain motion is limited. There is less free volume than in the case of rubbery polymers. It has also been shown that polymeric materials at a temperature below the glass transition temperature (T_g) may be in a state of non-equilibrium, with properties generally characterized as being time dependent. Correspondingly, the diffusion of small molecules through glassy polymers becomes rather complex.

Several diffusion models have been proposed for modelling mass transport processes. A model described by Fick's laws (Equations 1–2), is frequently used because of its simplicity and mathematical tractability. This is also known as Case I or Fickian diffusion.

$$J = -\rho D \frac{\partial c}{\partial x} \tag{1}$$

$$\frac{\partial c}{\partial t} = -\frac{\partial J}{\partial x} \tag{2}$$

Fick's first law (Equation 1) assumes that the flux (J) through a unit area of material is proportional to the concentration (c) gradient measured normal to the material, where the constant of proportionality is known as the diffusion coefficient (D).[7] Fick's second law (Equation 2) relates the concentration change as a function of time to the change in flux with respect to position. A fundamental criterion for Fickian diffusion is that the surface concentration attains its equilibrium value immediately upon a change in conditions and remains constant through the sorption process, i.e., in a resin matrix system the polymer chain segments at the surface must instantaneously reach saturation. Although Fickian diffusion theories have been thoroughly developed, most of the polymer-solvent systems do not obey such a simplified description.[8, 9] A general discussion of the Faraday Society on swelling and shrinking held in 1946 noted that in some polymer systems sharp boundaries, which moved linearly with time, existed between the swollen and unswollen regions. Twenty years later, Alfrey[10] characterized this process as "Case II" diffusion or sorption.

Fickian diffusion is rarely observed for the transport of a liquid through a glassy polymer.[11, 12] In the case of non-Fickian diffusion, a sharp front, which separates the dry polymer from the swollen polymer, is assumed to move linearly with time.[10] If the mass uptake M can initially be represented by

$$M = k\,t^{n} \qquad (3)$$

where t is the time and k and n are constants, then Fickian sorption corresponds to $n = 1/2$. Case II sorption is associated with $n = 1$. Anomalous sorption is characterized by: $1/2 < n < 1$. Figure 1 shows different classes of non-Fickian sorption.[13, 14] For one dimensional integral sorption experiments, Case II diffusion has the following phenomenological features: (1) a sharp boundary front that separates the highly swollen region from a dry, typically glassy region, is developed; (2) the sharp front moves into the polymer with a constant velocity causing the amount of fluid absorbed to increase linearly with time; (3) a small Fickian "precursor" exists in the dry region ahead of the front; and (4) there is an initial induction time, during which the sharp boundary is established near the film surface.[15]

The transport of a penetrant into a polymeric material can also be explained in terms of thermodynamics and kinetics.[16] The former is usually labelled as solubility or swelling and the latter as diffusion. The general question of solubility is usually formulated in terms of a solubility parameter, in a manner similar to that originally proposed by Hildebrand.[17] The phenomenon of swelling is closely related to solubility. However, identical or nearly identical Hildebrand solubility parameters do not necessarily result in swelling. A more appropriate way to measure the solubility can use the Hansen parameters, which divide the Hildebrand parameter into three parts: a dispersion force component, a hydrogen bonding component, and a polar component. The molecular dimensions of the permeant molecules must be small enough to enter the lattice network of the polymer. As the network is swollen by the sorption of the solvent, the network chains assume an elongated configuration and an elastic restrictive force develops in opposition to the ongoing swelling. A state of equilibrium is reached when the elastic restoring force of the network chains exactly balances the osmotic pressure driving the penetrant into the polymer.[18] The basic theory developed by Flory to account for the swelling of lightly cross-linked rubber, although useful for qualitative predictions, cannot completely account for the swelling of semi-crystalline thermoplastic resins below the glass transition temperature (T_g).[19]

Deviations from Fickian diffusion arise as a consequence of the finite rates by which changes in polymer structure occur in response to stresses imposed upon the material before and during the sorption-desorption process. If the polymer is partially crystalline or contains fillers, the transport process is markedly dependent upon the degree of crystallinity or the properties of the fillers.[20, 21] In addition, the polymer may exhibit solvent (or more appropriately penetrant) induced crystallization and show orthotropic swelling that further increases the complexity of the process.[22, 23]

THEORETICAL MODELLING

Models Based on Fick's Laws

Most of the theoretical studies used to model the diffusion process are based on Fick's laws. That is to say that the rate of transport through a unit area is proportional to the concentration gradient measured normal to the area. The easiest assumption is that the proportionality (diffusion coefficient D) is constant. A frequently used assumption is that the surface concentration immediately attains its equilibrium value and remains constant through the sorption process.

Numerous investigators have attempted, unsuccessfully, to develop a unified theoretical framework that could explain and model non-Fickian diffusion and its associated swelling.[1, 24] Frisch[25] and Crank[7] were among the first researchers to attribute non-Fickian transport to time-dependent mechanisms within a polymer. Crank and Park[26] proposed a history dependent diffusion coefficient that contained a term that instantaneously changed with concentration to an equilibrium value. That model was able to predict many of the features of non-Fickian diffusion, but did not predict the sharp front. Their approach introduced the concept of differential swelling stresses at the boundary due to expansive and compressive forces of the swollen and non-swollen regions. Frisch[27] suggested that a polymer below its T_g must possess history-dependent diffusion coefficients and experience time-dependent changes in surface concentration in order to maintain sorption-equilibrium at its boundaries. These time dependencies are intrinsically related to the relaxation times for molecular rearrangement in the polymer.

Long and Richman[28, 29] proposed that the concentration of solvent at the polymer surface does not instantaneously reach its equilibrium value. They assumed that the diffusion process can be divided into two stages, as a result of molecular relaxation. The first stage ("initial state") involves molecular rearrangements that can occur almost instantaneously. The second stage is a slower process, leading to a final equilibrium. Thus, the diffusion process consists of two parts: the absorption due to the concentration gradient set by the initial surface concentration and that due to penetrant transport as a result of the time-dependence of the surface concentration. This theory explains some non-Fickian diffusion behaviour, such as the "two-stage" sorption process. This concept introduced the relaxation idea of rather than a discontinuous jump or change in the diffusion coefficient as expressed previously by Crank.

Petropoulos and Roussis[30] extended the work of both Crank and Park and of Long and Richman by using activity rather than concentration. They applied the relaxation term to the bulk of the material rather than just to its surface.

Models for Case II Diffusion through Polymeric Materials

The preceding theories involved Fick's laws, along with assumptions on the boundary conditions and on the diffusion coefficient. The interaction of the penetrant and polymer and the physical properties of the polymer were not considered.

Thomas and Windle[31–33] made a major advance in the understanding of non-Fickian diffusion. Their model suggested that the diffusion process is strongly coupled to the mechanical response of the polymer. As the penetrant diffuses into the polymer, it creates an osmotic pressure. Initial swelling at the surface then creates space for additional penetrant and the plasticizing action of the penetrant causes a viscous creep. The accumulation of the solvent at the surface initiates a solvent shock wave that propagates into the membrane.[34] This model establishes that the creation of the surface sites is not an instantaneous process; it predicts an induction period. The rate at which the penetrant is absorbed must be compatible with the swelling rate controlled by the creep deformation of the surrounding polymer. The creep deformation depends on both the osmotic pressure (that causes the swelling) and the viscoelasitity of the polymer. Thomas and Windle's model represents a coupling between the osmotic pressure driven viscous response and Fickian diffusion. Their model qualitatively predicts most characteristics of Case II diffusion. However, they did not consider the effect of external stress (or strain).

Thomas and Windle's contribution stimulated much research dealing with Case II diffusion.[35–39]

In contrast to Fick's laws, which state that the flux is a linear function of the concentration gradient, linear irreversible thermodynamics suggested that the flux can be expressed in terms of a linear combination of chemical potential, temperature gradients as well as stress distributions. An equation for the flux for a binary mixture with one component (the polymer) having memory, was derived by Durning and Tabor[40] via non-equilibrium thermodynamics. Vrentas et al.[41] observed substantial changes in transport properties with fluid content, especially near the glass transition.[42] Fu and Durning[15] proposed a non-linear regime where polymer strains remain small but the transport properties vary significantly with composition.

Wu and Peppas[43, 44] focused on two kinetic processes governing Case II diffusion. One involves the kinetics of solvent penetration and the other involves highly non-linear material deformation. They characterized the process by a diffusion Deborah number, a ratio of mechanical to diffusion relaxation times. A relatively large Deborah number is associated with sorption processes controlled by mechanical relaxation.

Since Case II diffusion is associated with plasticization, Rossi et al.[45] and Friedman and Rossi[46] proposed a phenomenological model assuming that two different physical processes take place. The first one, solvent transport, is controlled by Fick's laws. The diffusivity, however, is different in the glassy and in the plasticized regions. The second process involves the transition from the glassy to the rubbery state. The kinetics of this transition sets an upper limit on the rate at which the material can be plasticized. That is to say that the velocity of the plasticization front separating the glassy and plasticized regions is bounded.

Rossi et al.[47–49] also tried to explain the sigmoidal (or S-shape) behaviour of the diffusion process. They incorporated the volume change due to swelling with Fick's laws and they concluded that for a simple model system, Fick's law of diffusion is valid.

The principles leading to non-Fickian diffusion are still under discussion, but it is widely accepted that possible polymer swelling plays an important role. During the swelling process, the polymer is deformed because of osmotic stress. Some researchers have considered the transport of the penetrants to be driven by both molecular diffusion and by a stress associated with swelling.[24, 37, 50–52] Most of these models modified the classical Fickian diffusion equation to account for the effect of stress. In addition, a constitutive equation to account for the time evolution of stress has to be introduced. The modified transport equation then becomes

$$\frac{\partial c}{\partial t} = D\nabla^2 c + E\nabla^2 \sigma \qquad (4)$$

In Equation (4), D and E are the molecular and elastic diffusion coefficients that are associated with concentration and stress, respectively. Note that if E is zero, Equation (4) simplifies to Fick's second law of diffusion. The initial approach proposed by Edwards and Cohen[52] has been extended to provide analytical expressions for flux versus time. These flux expressions involve dimensionless parameters that provide information as to whether the transport is either stress controlled or driven by molecular diffusion. Maxwell, Voigt and Jeffrey type models, similar to those used in linear viscoelasticity, have been used to relate the stress to time and concentration.[15, 24, 38, 52–57] For example, Chan Man Fong et al.[24] used this approach to introduce Equation (5), relating stress, concentration and time via a Jeffrey's type model.

$$\frac{\partial \sigma}{\partial t} + \beta\sigma = \nu_1 \frac{\partial c}{\partial t} + \nu_2 \frac{\partial^2 c}{\partial t^2} \qquad (5)$$

Hinestroza[56] extended this approach by using a more strict mathematical procedure. The simultaneous solution of Equations (4 and 5) yields an expression for the flux as follows:

$$J(t) = (-\gamma_1 Lc\beta)\left\{\begin{matrix} -1 + \\ \displaystyle\sum_{s=1}^{\infty}(-1)^s s\pi \left[\begin{matrix} \left[\dfrac{2}{\pi s}\dfrac{(\lambda_1 - 1)(\gamma_3\lambda_2^2 - \lambda_2)}{\left(1+\gamma_3(\lambda_1\lambda_2) - \gamma_3(\lambda_1+\lambda_2)\right)}\right] e^{-\lambda_1 t} + \\ \left[\dfrac{-2}{\pi s}\dfrac{(\lambda_2 - 1)(\gamma_3\lambda_1^2 - \lambda_1)}{\left(1+\gamma_3(\lambda_1\lambda_2) - \gamma_3(\lambda_1+\lambda_2)\right)}\right] e^{-\lambda_2 t} \end{matrix}\right] \end{matrix}\right\}\Bigg|_{x=1} \qquad (6)$$

where

$$\lambda_1 = \frac{W + \sqrt{W^2 - 4s^2\pi^2\gamma_1 V}}{2V} \qquad (7)$$

$$\lambda_2 = \frac{W - \sqrt{W^2 - 4s^2\pi^2\gamma_1 V}}{2V} \qquad (8)$$

and

$$V = 1 + s^2\pi^2\gamma_2\gamma_3 \qquad (9)$$

$$W = 1 + s^2\pi^2(\gamma_1 + \gamma_2) \qquad (10)$$

In Equations (9) and (10), W and V are function of γ_1, γ_2 and γ_3 which are given by

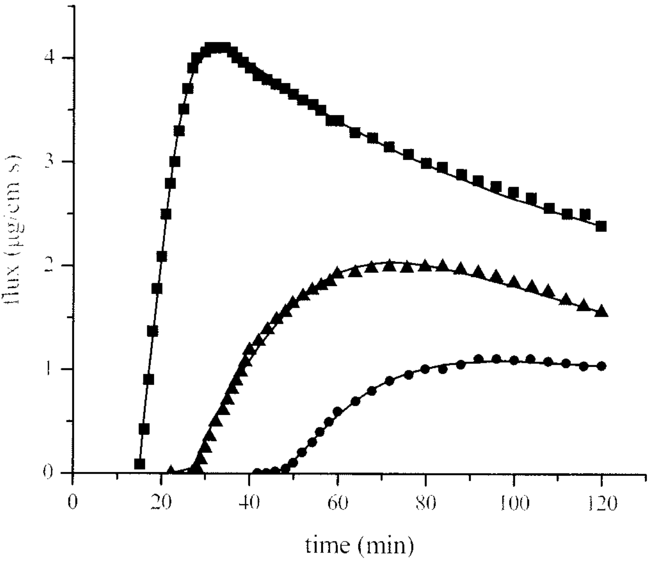

Figure 2. Permeation of organic solvents through PVC at 303 K: (■): dichloromethane (DCM), (▲): trichloroethylene (TCE), (●): benzene, (—): model predictions (Equation 6)

$$\gamma_1 = \frac{D}{l^2\beta} \tag{11}$$

$$\gamma_2 = \frac{E\nu_1}{l^2\beta} \tag{12}$$

$$\gamma_3 = \frac{\nu_2\beta}{\nu_1} \tag{13}$$

Here, β can be considered to be an inverse relaxation time. The ratio between parameters γ_1, and γ_2 provides an indication as to whether the transport is stress controlled or driven by molecular diffusion. Liu et al.[58, 59] used a dimensionless time (a Deborah number) that characterizes the relaxation of the polymer. Figure 2 shows quantitative agreement between experimental data and the theory. Even though this model fits the experimental data, it is based on continuum mechanics and does not consider the polymer-solvent interaction.

Since mass transport through glassy polymers involves non-equilibrium states, one needs to extend the thermodynamics to describe irreversible processes.[60] More recently, an emerging mesoscopic theory has been used to model non-Fickian diffusion processes.[34, 61–64] This method uses the Hamiltonian formulation together with Poisson brackets to derive the governing equations for reversible process. In addition, a dissipation bracket accounts for irreversible processes and the governing equations for the diffusion process can be obtained. Also, a conformation tensor (m) has been introduced to account for the structural changes of the polymer due to swelling or other external stress effects, in addition to the concentration of the penetrant and the flux state variables. One of the advantages of applying this mesoscopic theory is that the governing equations automatically satisfy the laws of thermodynamics. The governing equations for one-dimensional diffusion process are[34, 63, 65]

$$\rho\frac{\partial c}{\partial t} = -\frac{\partial J}{\partial x} \tag{14}$$

$$J = -\rho D\left(\frac{\partial c}{\partial x} + \Gamma_{11}\frac{\partial m_{11}}{\partial x}\right) \tag{15}$$

$$\frac{\partial m_{11}}{\partial t} = \frac{J}{\rho(1-c)}\frac{\partial m_{11}}{\partial x} - m_{11}\frac{\partial}{\partial x}\left(\frac{J}{\rho(1-c)}\right) - 2\lambda m_{11}\frac{\partial\varphi}{\partial m_{11}} \tag{16}$$

where φ is the Helmholtz free energy density, Γ_{11} is a component of tensor Γ, which relates the elastic and mixing parts of the free energy of the system. Equation (14) is Fick's second law. Note that Fick's first law has been generalized. Equation (15) shows that the flux is driven by the concentration gradient, but also by a conformation tensor gradient, which accounts for the polymer internal structural change. The time evolution of the conformation tensor is given by Equation (16). An expression of a balanced osmotic stress can also be obtained via this method. In dimensionless form, Equation (15) becomes

$$J = -\frac{1}{\sqrt{m_{11}}}\left(\frac{\partial C}{\partial X} + \Pi\frac{\partial m_{11}}{\partial X}\right) \tag{17}$$

The dimensionless parameter Π reflects the importance of the polymer internal structural change in a diffusion process. When a Maxwell-type model is used to calculate the free energy, another dimensionless time appears in the governing equations. This dimensionless time (a Deborah number, De) is the ratio of the polymer relaxation time to the diffusion time. Equation (17) also includes the effect of a moving boundary, via the $\sqrt{m_{11}}$ term.

Using the GENERIC approach, El Afif et al.[64] also successfully modelled the diffusion of two component fluids through polymeric membranes. Instead of just one Deborah number as for a one component system, the mixture solvent system is described by four dimensionless times due to cross-coupling effects.

Theories for Diffusion through Polymer Composites

Polymeric filled systems are used in a variety of applications as a result of their good physical and barrier properties. The diffusion of small molecules through the composite membrane involving distribution of impermeable objects is an important problem. By assuming different geometries of the impermeable objects, a diffusion coefficient D can be obtained.[66, 67] The expression for D involves the "droplet" volume fraction and accounts for the effect of the "filter." The situation is very different for a membrane containing impermeable platelets with high aspect ratio oriented perpendicular to the diffusion direction. Aris[68] proposed an expression for the diffusion coefficient of a composite. The equation contained terms accounting for the resistance to diffusion due to (1) the tortuosity introduced by the particles and (2) the spaces between adjacent "flakes" in the same horizontal plane. Cussler et al.[69] and Perry et al.[70] also proposed equations for the flux through barrier membranes containing flakes. Falla et al.[71] showed the effect of the tortuous paths caused by the presence of flakes, using Monte Carlo calculations for diffusion across the membrane.

A tortuosity theory has also been used to describe the effect of layered particles on the diffusion process. Bharadwaj[72] modelled the barrier properties of polymer-layered silicate nanocomposites. He proposed an equation involving the relative permeability of the polymer-silicate nanocomposite. It included a tortuosity factor, defined as the ratio of the shortest distance that a penetrant must travel to the shortest distance that it would have travelled in the absence of the layered silicate. It is expressed in terms of the length, width and the volume fraction of clay particles. He also addressed the effect of particle orientation and state of delamination. This tortuosity theory does however not explain the non-Fickian behaviour occurring in some diffusion process.

Transport processes through polymeric composites depend on composition, miscibility and phase morphology. Due to the complex internal structure, there is no single model that can provide a complete explanation of the transport process.

El Afif et al.[73–75] applied a General Equation for the Non Equilibrium Reversible and Irreversible Coupling (GENERIC) formalism to investigate the isothermal mass transport of a simple fluid through a blend of two immiscible Newtonian polymers. They chose two state variables to account for the size and shape of the polymer-blend interface. One is an interfacial internal density (Q) and the other is an interfacial orientation tensor density (**q**). A non-linear formulation that addressed the effects of the diffusion/interface coupling on the mass transport and on the morphology of the interface was derived. The obtained mass flux equation included a new term that accounts for the viscoelastic contribution of the interface, which may lead to non-Fickian behaviour. Liu[76] applied a similar method to investigate mass transport through polymer-clay nanocomposites. The state variable chosen to account for the nanocomposite internal complex interfacial structure was an area tensor (**A**), which was first proposed by Wetzel and Tucker.[77] The area tensor can be related to the (Q, **q**) model interpretation. A conformation tensor (**m**) is also included to characterize the effect of polymer internal structural changes. A set of governing equations can be obtained by applying the Hamiltonian/bracket formalism or a more generalized GENERIC formalism. The time evolution of concentration is as in Fick's second law. In a one dimensional situation, Fick's first law is extended as follows,

$$J_s = -\rho D\left(\frac{\partial c}{\partial x} + \mathrm{E}_{11}\frac{\partial m_{11}}{\partial x} + \Lambda_{\beta\gamma}\frac{\partial A_{\beta\gamma}}{\partial x}\right) \tag{18}$$

In dimensionless form, two dimensionless numbers Σ and Θ appear. Σ relates the polymer elasticity and the mixing properties of the solvent and the polymer-clay nanocomposite systems. Polymer swelling leads to $\Sigma \le 0$. Θ is a quantity relating the complex interface to the mixing properties. In the case of polymer swelling, $\Theta \ge 0$. Thus, for swelling polymers, the elasticity of the polymer matrix and the existence of complex interfaces will decrease the mass flux.

The time evolution of the polymer internal structural change, characterized by the conformation tensor **m**, can also be expressed by Equation (16). The corresponding free energy density φ is the one for the polymer-clay/solvent system. Here a dimensionless time ($\mathrm{De_m}$) is related to the polymer relaxation.

The change of area tensor **A** can be modelled by the following equation:

$$\frac{\partial A_{ij}}{\partial t} = \frac{J_s}{\rho(1-c)}\frac{\partial A_{ij}}{\partial x} + A_{1j}\partial_i\left(\frac{J_s}{\rho(1-c)}\right) + A_{1i}\partial_j\left(\frac{J_s}{\rho(1-c)}\right)$$

$$-\frac{1}{A_{kk}}A_{1\beta}A_{ij}\partial_\beta\left(\frac{J_s}{\rho(1-c)}\right) - \lambda^{A}_{\alpha\beta ij}\frac{\partial\varphi}{\partial A_{\alpha\beta}} \tag{19}$$

Another dimensionless time ($\mathrm{De_A}$) appears when Equation (19) is written in dimensionless form. This Deborah number is associated with the interface relaxation time. Deborah numbers $\mathrm{De_m}$ and $\mathrm{De_A}$ characterize the physical properties of the polymer as well as the type of diffusion process. Figure 3 shows quantitative agreement between this model (Equations 16, 18, 19) and experimental data.

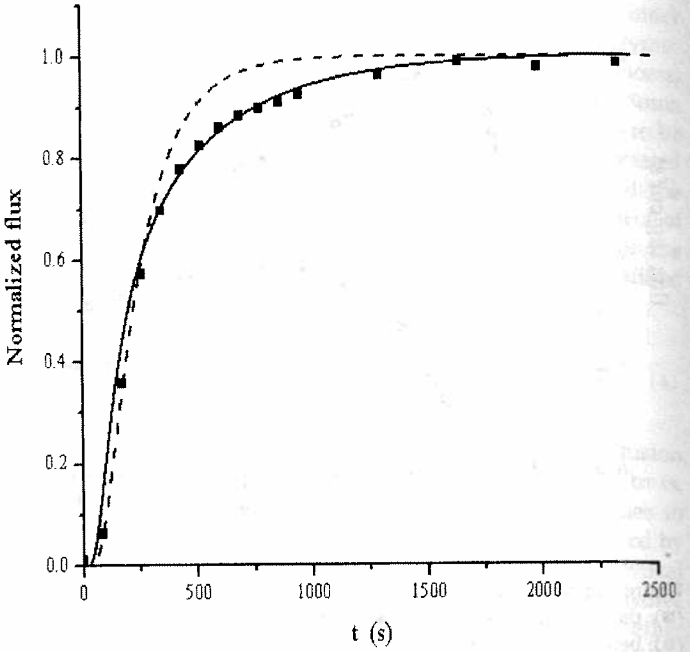

Figure 3. Normalized flux versus time for DCM through pure PDMS: (■): experimental data, (·): prediction of Fick's laws, (—): prediction of Equations (16, 18, 19)

EXPERIMENTAL TECHNIQUES

Although there are several standardized tests to measure permeation such as those of the American Society for Testing and Materials (ASTM F739), The British Standard Institution (BSI EN 369) and the International Organization for Standardization (ISO 6529), these permeation test methods, and their reporting requirements are not completely defined and continue to evolve. The EPA (Environmental Protection Agency) method 9090 also establishes procedures for evaluating membrane chemical resistance, but its results are more qualitative than quantitative.[78] The ASTM F739 standard has been used in most of the published work in this area.[14]

ASTM F739 Method

The ASTM test method F739 was first introduced in 1981 and subsequently revised in 1985, 1991, 1996 and 1999 by the ASTM F23 committee. It provides specifications for the design of a test cell and for the evaluation and documentation of barrier effectiveness of chemical protective clothing materials (CPC) when exposed to liquid or gaseous materials.[79] The materials intended for evaluation are flat samples cut from finished CPC or from materials intended for use in the manufacture of CPC.[78] For low volatility and low aqueous solubility compounds such as oil mixtures and heavy pesticides a solid absorbent collection medium is frequently used.[80] Silicone rubber sheets are used since they adsorb hydrophobic compounds and desorb them using common desorption solvents.[81] Filter paper, polyester, rayon, gauze and cotton have also being reported as appropriate solid absorbent collection media.[82] However, there has not yet been a consensus about the accuracy of permeation results using solid collection media since the effect of surface contact and

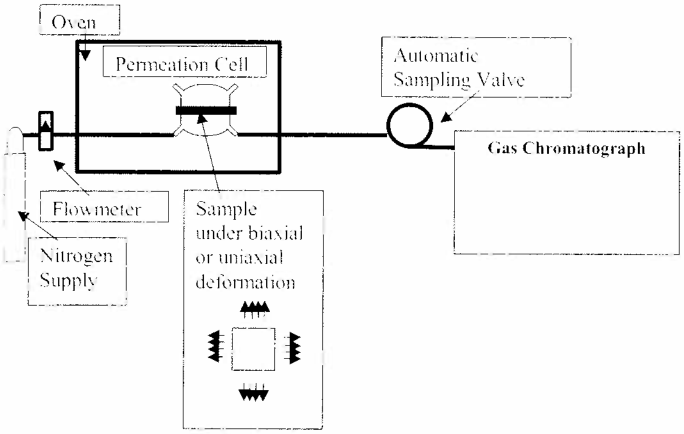

Figure 4. Experimental set-up for an open loop ASTM F739 permeation method

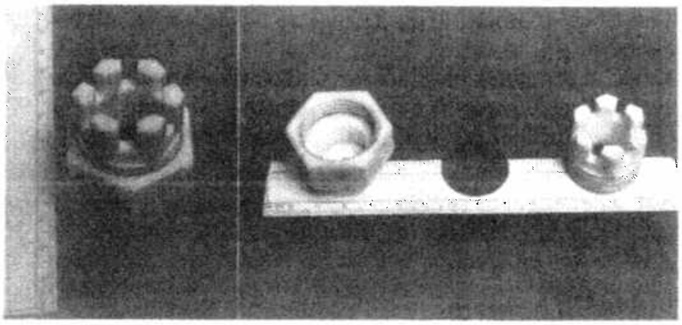

Figure 5. A gravimetric cell used in single component permeation experiments

adsorbance capacity has not been thoroughly studied.[83] Novel methods such as the splash method have been reported to produce results comparable to ASTM F739 but they have not been fully developed and further validation is required.[84]

The ASTM F739 test method establishes that the CPC sample should be conditioned at ambient temperature and relative humidity, its thickness measured and clamped into the cell so that the outer surfaces of the sample can be exposed to the test chemical. After clamping the sample inside the permeation cell, the collection medium contacting the inner surface can be then monitored. The cell temperature, test duration, analytical method, and system of configuration (i.e., open or closed-loop) are reported along with the results of the test.[14]

The breakthrough time (BT) and the steady-state permeation rate (SSPR) are the most common indices of permeation resistance used to assess the suitability of a particular CPC material for a particular chemical challenge. The BT is generally defined as the time that the challenge chemical is first detected at the downstream (inner) surface. The dependence of the BT on the sensitivity of the analytical method employed during testing led to the establishment by the ASTM F23 committee of a normalized BT. The SSPR is reached when the variables affecting permeation have reached equilibrium and the rate of permeation no longer changes with time. The normalized BT and the SSPR determined from the permeation test represent standardized measures of permeation resistance that can be used to compare CPC materials.

In the case of volatile solvents, the desorption process is accompanied by evaporation, permitting the use of a gaseous collection medium. However, if the permeant is not efficiently removed from the collection chamber after evaporation, the concentration of the permeant in the collection medium can reach saturation. In addition for solvents with a low vapour pressure, complete evaporation from the inner surface of the test sample may not occur. Both of these situations can lead to the accumulation of the permeant at the inner surface of the test sample, which decreases the solvent concentration gradient within the CPC sample and reduces the permeation rate. The apparent SSPR measured under these conditions would be artificially low, resulting in an overestimation of the barrier effectiveness. Thus, the collection medium chosen for testing must have a high capacity for the permeant. As a rule of thumb, it has been recommended that the concentration of the permeant in the collection medium be maintained below 20% of saturation.[85, 86]

One of the main problems of the ASTM F739 method is that it requires an expensive assembly that includes in addition to the permeation cell, an analytical instrument such as a FTIR or a gas chromatograph, a system of valves for sampling and a data acquisition system.[87] Figure 4 shows the experimental set-up used to determine BT and SSPR using the open-loop mode of the ASTM F739.

Other Experimental Methods for Permeation

The gravimetric method has been considered a valuable method to test protective clothing materials and to determine BT and SSPR. This method is based on the principle that when a chemical is brought into contact with the outside surface of the material, the product will diffuse into the material and reach the internal surface, to then evaporate. When the chemical evaporates, there is a loss of weight that can be detected by a balance. In this manner, the BT and the permeation rate of the chemical across the material can be determined.[88, 89] The necessary components for carrying out gravimetric studies are a specially designed permeation cell made of a light-chemical resistant material with a chamber to hold the chemical, a system to attach the sample to the cell, a balance, and a support for installing the cell on the balance. Several cells have been designed to perform gravimetric studies.[90–92]

Figure 5 shows a photograph of a gravimetric permeation cell developed by Guo et al.[92] that could be used to determine the permeation rates of vapours and liquids though polymeric materials. However, the gravimetric technique has several disadvantages. It can only be used with volatile solvents due to the limited airflow environment surrounding the gravimetric cell inside the balance. In addition, permeation of mixtures of solvents cannot be studied using this technique since the balance records the total weight loss of the mixture.

Alternative methods to determine permeation parameters and diffusion coefficients have also been examined. A modified thermomechanical analyzer (TMA) was used to determine the dimensional changes during a swelling experiment of polyethylene in chlorobenzene. Assuming a constant coefficient of hygroelasticity both the diffusion coefficient and the SSPR were determined.

Park et al.[86] proposed a novel experimental procedure that employs a confined double compartment method (CDCM) to analyze permeation of dilute volatile organic compounds (VOC) aqueous solutions, giving concentrations changes in both compartments. Deionized water was used as the collection medium in order to directly evaluate mass transport information; this is an improvement over previous methods since partition coefficients in the aqueous and vapour phase are different. Incorporating these two sets of concentration changes, the partition coefficients were calculated directly and the diffusion coefficients were estimated using the partition-diffusion model.

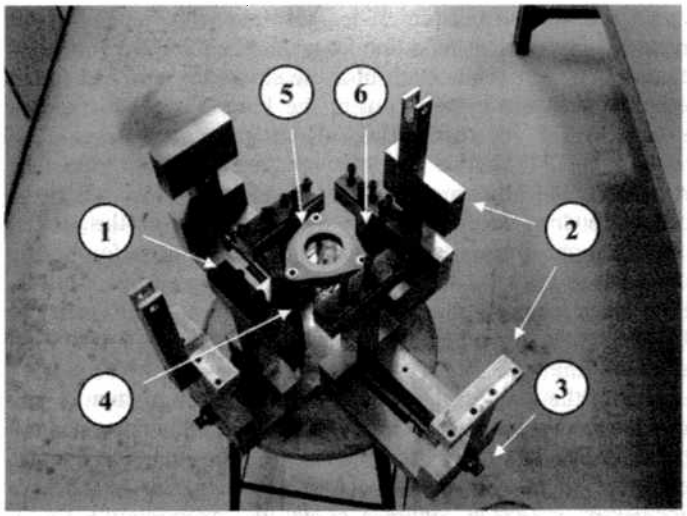

Figure 6. Apparatus for elongating polymeric membranes. (1) Mobile heads, (2) Fixed heads, (3) Screw system, (4) Inlet and outlet ports of the permeation cell, (5) Bottom hemisphere of the permeation cell, (6) Test sample location

The effects of partition and diffusion coefficient of aqueous concentration and of geomembrane thickness, tension and type could then be investigated. However, this method is not able to separate the contribution of each component of a mixture.

Permeation information can also be obtained from sorption experiments. Khinnavar and Aminabhavi[93] recently improved the sorption experimental technique. In this technique circular (disc-shaped) geomembrane samples of 2.00 cm diameter were conditioned in vacuum at 25°C for 48 h. The samples were then exposed to the respective liquids inside screw tight test bottles containing about 15–20 ml of the respective solvents maintained at the desired temperature. The test bottles were placed inside an oven for precise temperature control. After placing the samples inside the oven, weight determinations were recorded at suitably selected time intervals by removing the samples and wiping the surface solvent drops using filter paper. The samples were then placed on a top loaded balance to measure the mass uptake. Weights were measured until samples attained an equilibrium sorption and the weight did not change significantly over a period of one or two days.[94] Although this technique provides reliable data for single component permeation, it is not feasible for studying mixtures of chemicals.

In the case of permeation through geomembranes, concerns have been raised regarding the ability of the existing permeation tests to simulate the actual conditions the geomembrane liners are exposed to in a landfill.[95] In order to evaluate a material's response to out-of plane loading, as would occur during an uneven settlement of supporting soils, a multiaxial test was developed by Barret and Stessel.[96] The comprehensive test system for geomembranes (CTS) attempts to duplicate the structure of landfill surrounding the geomembrane, and the effects of wastes placement through the application of cyclic displacement. The mechanical simulation of landfill conditions is combined with the introduction of fluids that may be present in landfill leachate resulting in the ability to test the effects of chemical exposure with simultaneous loads.[97]

Hinestroza et al.[98] reported an experimental technique that allowed for the study of the effect of external mechanical deformation on permeation of organics through polymeric materials. Their experimental technique allowed for real time monitoring of single components as well as mixtures. Their technique used a F739 permeation cell mounted in the centre of an aluminium frame. Acetone and hexane experiments were used as permeants through carbon filled natural and butyl rubber membranes. The membranes were elongated uniaxially 20%, and 40%, as well as in the biaxial mode by 20 x 20% and 40 × 40%. Figure 6 shows the aluminium frame and the permeation cell used in their experiment. New monitoring techniques have also been investigated. For example, an aluminium cell chamber equipped with quartz windows to perform UV on-line measurements of the membrane under permeation was proposed by Moody.[99] The cell requires a sample of only 10 microliters, and provided the possibility of testing UV degradation in-situ with permeation experiments.

A new simple technique using room temperature fluorescence quenching of an indicator compound, penetrant, on filter paper was proposed by Pal et al.[100] The technique demonstrates high sensitivity, reproducible results and simplicity, but has the disadvantage of having a discrete sampling protocol, and the restriction that the permeant must quench penetrant fluorescence.

New techniques to measure permeation are continuously developed as researchers try to find a method suitable for specific permeants, barrier materials and operating conditions.

FACTORS AFFECTING THE MASS TRANSPORT PROCESS

Effect of Temperature on Permeation

The estimation of permeation parameters involves the determination of both the diffusion and solubility of a penetrant into the polymeric membrane. Solubility is determined by many factors including the chemical nature of the polymer and the penetrating species, hydrogen bonding, dipole interactions, molecular size and shape of the permeating species, etc. All these factors are influenced by temperature.[101, 102] Molecules come to rest at equilibrium positions and can move from one position to another if sufficient energy is supplied to the region in which such motion occurs. The energy is used to separate polymer segments, allowing the permeating species to move. This process is temperature dependent and is characterized by an activation energy.[103]

A strong dependence of permeation upon the temperature was evident from the experimental data for the permeation of toluene and trichloroethane through neoprene, butyl and nitrile rubbers.[104] The values for energy of activation for permeation (E_p) and for the energy of activation for breakthrough time (E_t) are determined via semi-log plots of flux versus the reciprocal of absolute temperature, according to the following Arrhenius-type relationships.

$$J = J_0 \exp(E_P / RT) \tag{20}$$

$$t_B = t_{Bo} \exp(E_t / RT) \tag{21}$$

The activation energy for permeation (E_P) seems to be more dependent on the polymer type than on the permeant.[105] However more experimental data are required for verification. The apparent activation energy for breakthrough time seems to be more dependent on the transported chemical type rather than on the polymer matrix.[103] A comparison of the activation energy of permeation (E_P) and activation energy for breakthrough times (E_t) reveals that for each polymer/chemical pair studied, $E_t > E_P$.

An Arrhenius-type relation also relates temperature and solubility of the solvent in the polymer:[106, 107]

$$S = S_0 \exp\left(\frac{-H_s}{RT}\right) \tag{22}$$

where S is the solubility and H_s is the heat of sorption. H_s can be positive or negative. When the heat of sorption is positive, the sorption process is endothermic, and sorption increases with increasing temperature.[106, 107] When the sorption process is exothermic (heat of sorption is negative), the sorption decreases with increasing temperature.[108]

The equation relating permeability to temperature is:

$$P = D \times S = P_0 \exp\left(\frac{-E_P}{RT}\right) \tag{23}$$

where P is the permeability, $P_0 = S_0 \times D_0$.

Effect of Permeant and Polymer Structure on Permeation

In the absence of significant interactions between solvent molecules and polymeric chain segments, sorption and diffusion follow a Fickian mechanism. Deviations from the Fickian mechanism are attributed to variations in the response of the polymer chain segments to a swelling induced by the presence of solvents.[109] The molecular structure of the permeating gas or liquid is an important factor in permeation. Liquid permeation depends on the molecular size of the liquid, that is to say: molecules such as pentane permeate more rapidly than larger molecules such as decane.[110] Molecular shape is also an important factor. Streamlined shapes such as p-xylene permeate more rapidly that the bulky o-xylene.[111] Guo et al.[112] analyzed the effect of molecular structure on diffusion of organic chemicals through rubber. They found that the rate of diffusion showed a clear dependence on solvent structure. The effect of molecular size and shape was characterized by an effective molecular volume. The value of this effective volume was calculated from the effective molecular diameter that was obtained by applying a weighting function over three perpendicular dimensions of the solvent molecule. That is:

$$d_{eff} = 0.6\, l_{\min} + 0.3 l_{mid} + 0.1 l_{\max} \tag{24}$$

where d_{eff} is the diameter of an effective sphere and the l_{min}, l_{mid} and l_{max} are the dimensions of the molecule in three orthogonal directions.

The use of this effective volume allowed for the prediction as well as the correlation of the diffusion coefficients of a solvent-polymer system using the properties of the pure polymer and the solvent. Figure 7 shows excellent agreement between the diffusion coefficient at zero solvent concentration and the effective volume for the solvents, based on d_{eff} as the sphere diameter.

The polarity of the liquid also plays an important role in permeation. For example, non-polar liquids such as toluene permeate more rapidly than the polar aniline in non-polar polymeric membranes such as polyethylene.[113] The latter effect is reversed in the case of polar membranes. The permeability of polymers is determined by many structural and morphological properties of both the polymer matrix and the permeating species. Theoretical attempts to correlate any or all of these properties with gas or liquid permeation have not been entirely successful.[114]

Mass transport through complex structured polymeric materials is not accurately described by Fick's laws. The diffusion process can be considered in the light of the free volume theory, which considers the creation as well as the size distribution of space required for the motion of the diffusing molecules. Thus the diffusion process relies heavily on the ease and degree of chain packing, it is related to the free volume and to the density.[115] The creation of space depends on the segment chain mobility and on the cohesive energy of the polymer. In addition, diffusion process will be affected by the degree of crystallinity and of crosslinking as well as by additives, such as fillers.[26]

The fact that a polymer may swell when in contact with penetrant solvent is an important issue. As the solvent penetrates into the polymer, the polymer network assumes an elongated configuration and elastic restrictive forces develop opposing the swelling process. A state of equilibrium is reached when the elastic restoring force of the network balances the osmotic pressure driving the penetrant into the polymer. The viscoelastic properties of the polymer play a very important role in this process, as they control the polymer response to the change in configuration. The time scale of the polymer relaxation is associated with the type of diffusion process. When the characteristic time of diffusion is much larger than the polymer relaxation time, the diffusion process is referred to as Case I (Fickian) diffusion. If the characteristic diffusion time is much smaller than the polymer relaxation time, one deals with Case II diffusion. Anomalous diffusion is characterized by the fact that the diffusion and relaxation times are comparable.[10, 116]

Though anomalous diffusion occurs mostly in glassy polymers near their glass transition temperature, it can also occur under conditions far from the glass transition.[56, 117] It is assumed that the solvent can be absorbed into the polymeric material before the polymer chains have a chance to completely relax. The polymer then experiences structural rearrangements. This rearrangement and reorientation may lead to rejection of some

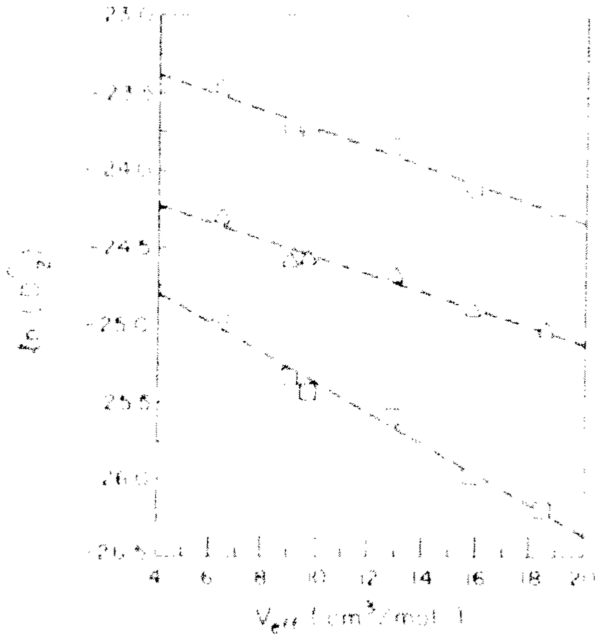

Figure 7. Relation between D_{12}^0 and V_{eff} for the diffusion of six solvents in natural rubber at different temperatures: (□) 293.2 K, (△) 313.2 K, (O) 333.2

of the solvent from the polymer. This partial exclusion of the penetrant will be more pronounced when the characteristic time of diffusion is smaller than the polymer relaxation time.

According to the free-volume theory,[26] diffusion in polymers occurs as small molecules travel through available spaces (holes) between polymer chains. The total free volume of the polymer and small molecules is larger than that of the polymer alone. This extra free volume allows for easier segmental motion of the polymer chains. Consequently, the diffusion of the molecules is enhanced as their local concentration increases. As mentioned in Introduction, this effect is called plasticization.[118] As the amount of solvent increases, a softening of the glassy polymer can be expected. When the solvent concentration exceeds a threshold value, the material changes from a glassy to a rubbery state. The diffusion coefficient in the plasticized region is significantly larger than the diffusion coefficient in the glassy region.[119]

In some cases, the presence of solvent can lead to polymer crystallization.[120] The ordered crystalline structure then rejects the solvent that was absorbed prior to its formation. A maximum in the diffusion curves is also to be expected.[121–123]

Mass transport through polymers with complex internal structures has also been reported in the literature. Unnikrishnan and Thomas[124] reported on the effect of fillers on the transport process through natural rubber. They found that as the size of carbon black particles decreased, the restriction to the overall chain mobility and flexibility of polysulphidic linkages increased. Thus, the permeation decreased with smaller filler particles. Permeation experiments on semi-crystalline polymers were also performed. The crystalline regions are considered impermeable to the penetrant solvent molecules, which diffuse and absorb only in the amorphous regions. There is usually a decrease in mass transport through polymers with increasing crystallinity due to a reduced amorphous fraction. Also the diffusing molecules are subjected to a more tortuous path due to the presence of impermeable crystallites.[125]

Composite polymeric materials are frequently associated with very complex structures.[126] Polymer-clay nanocomposites have recently been the subject of several investigations because of the impressive improvement on the mechanical, thermal, flame resistance, as well as barrier properties of such composite materials.[127–130] The high aspect ratio silicate clays lead to a significant increase in tortuosity for the diffusing molecules. In most cases, increased barrier properties have been reported.[128, 131, 132]

Drozdov et al.[133] performed sorption experiments of water molecules in vinyl ester/montmorillonite nanocomposite materials. They found that water transport in the neat vinyl resin is Fickian, but it becomes anomalous (non-Fickian) with increasing clay content. They attributed this non-Fickian behaviour to the immobilization of water molecules on the surfaces of the hydrophilic clay layers. Even though the diffusivity is significantly decreased due to the increased in tortuosity, the total mass uptake by the polymeric matrix increased, likely due to the clustering of water molecules. Similarly, it has been reported that the diffusivity of water through montmorillonite -poly(ε-caprolactone) nanocomposites decreased compared to mass transport in pure polymer, although the sorption increased.[125, 134, 135] The authors attributed this to a lower degree of crystallinity of the filled polymer matrix. They also observed that the diffusivity and sorption of dichloromethane vapour followed a similar trend with increasing clay content. The difference in the sorption properties of water and dichloromethane lies in the different interaction between the solvent and hydrophilic character of the silicate platelets.

One unexpected result was obtained with transport through a high free-volume, glassy PMP-fumed silica (FS) system.[136] It was found that the penetrant permeability coefficient increased substantially with increasing concentration of the nanoscale fumed silica, but the gas and vapour uptake in the PMP/FS was essentially unaffected. This increase in diffusivity is likely related to the increase in free volume in the PMP, induced by the fumed silica particles. Thus the clay particles not only increase the length of the diffusion path, they also trap hydrophilic solvent, and affect the crystallinity[137] and crosslinking.[138] The dominant effect of the addition of nanoclay particles is to substantially reduce mass transport.

Recently, Liu[76] performed permeation experiments involving dichloromethane (DCM) through poly(dimethylsiloxane) (PDMS)/clay nanocomposite membranes. He observed that the diffusion of DCM through pure PDMS is non-Fickian, but becomes more Fickian-like with increasing clay concentration in the PDMS matrix. He attributed this transformation to the reduced polymer chain mobility resulting from a higher clay concentration. That is to say that the apparent diffusion coefficient decreases due to an increase in tortuosity.[76]

Permeation of Mixtures

Some of the basic test methods described for the permeation of single components can be used to study the permeation of mixtures. These methods must frequently be adjusted to identify the species that have permeated through the membrane. The analysis of the permeant on the downstream side is required, due to the selective nature of the polymeric membranes, which result in species dependent transmission rates.[139] Analytical tools such as gas chromatography,[140] FTIR or GC mass spectroscopy for organics and atomic absorption for inorganics are often used to detect, identify and quantify the permeant.[141]

August and Tatsky[142] measured the transmission rates of six solvents through a 1.0 mm thick HDPE geomembrane. They used an apparatus consisting of two compartments separated by the geomembrane. The upper compartment contained the solvent mixture, the composition of which was held constant, and the lower compartment was partially evacuated. The permeation vapours were removed from the downstream (bottom) compartment, frozen in a cooling trap, and analyzed by gas chromatography.[143] Other experiments with mixtures showed that permeation of organics from a dilute solution could be substantially higher than would be expected from their reduced concentration.[144, 145] For example, even though the ratio between the concentrated toluene and the dilute solution was 1000:1, the ratio between the permeation rates through the geomembrane was 20:1.[146] The results from this work and similar experiments with gasoline and HDPE geomembranes indicate that the strong selectivity by the geomembrane may lead to very different permeation rates for the components of mixtures.[139, 147–149] The results from these studies allow one to conclude that significant quantities of an organic can permeate through a geomembrane due to selective permeation, even when the organics are present at low concentration.

Britton et al.[145] estimated the partition and diffusion coefficients of eight compounds in a HDPE geomembrane using the ASTM F739 standard. The solution used was an equi-molar mixture of eight compounds. The immersion/weight method was used to estimate the solubility coefficients of the penetrants. Park and Nibras[148] investigated diffusion and partition coefficients of dilute aqueous solutions of volatile organic compounds in high density polyethylene geomembranes. Their technique consisted of placing each geomembrane in a bottle filled with a particular solution. The weight gain of the geomembranes was measured and used to calculate the partition coefficient. However, they could not determine a relationship between partition and diffusion coefficients with concentration.

Nelson et al.[150] performed experiments using two component solvent mixtures. On the one hand, for cases involving the transport of chloroform and toluene through neoprene, the total permeation rates of the mixture were directly proportional to the volumetric concentration of each solvent. This observation is surprising since the neoprene was reported to be extremely swollen after the test. On the other hand a mixture of pentane and tri-chloroethylene through a polyethylene glove material exhibited pronounced synergism and showed that permeation rates of mixtures cannot be accurately predicted if the only information available is the permeation rate of only one component.

Permeation experiments were also performed for binary mixtures of hexane and acetone through natural and butyl rubber.[55] A change in selectivity as a function of deformation (stress enhanced transport) was observed. The initial concentration of the solution is also an important factor.

Effect of Mechanical Deformation on Permeation

Only a limited number of reports have appeared dealing with the effect of either external or residual stress on the transport of fluids in polymers. Treloar[151, 152] analyzed the effect of tensile stress on the swelling of rubber. His work noted that strained rubbers absorbed more fluid than the non-strained material.[153]

Wong and Broutman[154, 155] measured the diffusion of water in graphite-epoxy tensile bars and noted that stress levels up to 25% of the ultimate stress caused an increase in the diffusion coefficient, but had little effect upon the solubility.

Marom and Broutman[156] measured water diffusion at 95°C into fibreglass and graphite epoxy composites in stressed and unstressed states. They reported that stress enhances both the diffusion rate and the solubility. The diffusion coefficients differed by a factor of about 2 for the stressed and unstressed composites, while the solubilities showed an increase of only 10–20%.

Williams[157] discussed the effect of drawing on the transport of gases and vapours in polymers. He found that during cold drawing, plastic deformation reduces the number of sorption sites and increases the activation energy for diffusion. The changes in sorption and transport properties were a direct consequence of the denser packing and ordering of the tie molecules in the amorphous region as a result of the drawing process.

Gent and Liu[158] studied the sorption of liquids through fine threads of cis-polyisoprene and investigated the effect of tensile strain and penetrant molecular weight on the transport. They noted that the diffusion coefficient was essentially independent of the strain for extensions up to 300% but the degree of swelling increased by more than 100% for the same strain. The solubility data of this study were in agreement with the theory described by Treolar.

Orientation caused by the cold drawing of crystalline polymers can improve the physical properties as well as the barrier properties of these materials.[157] As fibres stretch, the molecules become more oriented and tend to crystallize. In turn, the fibres could become stronger, tougher, and somewhat more elastic than non-oriented fibres. High molecular symmetry and high cohesive energy between chains, require a fair degree of polymer crystallinity, which results in high tensile strength and high modulus of the fibres. An increase of the crystalline domain in linear low density polyethylene has been observed using wide angle x-ray diffraction (WAXD) when the polymer films were uniaxially and biaxially oriented.[159] Xiao et al.[160] reported stress-enhancement of permeation rates in polyvinyl chloride geomembranes, but observed the opposite effect with high-density polyethylene geomembranes (HDPE). They attributed this difference to irreversible structural changes of the HDPE. This is consistent with the results of Choy et al.,[161] who found that high draw ratios induce structural changes in polyethylene. The HDPE film is gradually transformed into a fibrillar structure, substantially reducing the number of sorption sites. Drummond et al.[162] used atomic force microscopy (AFM) to study structural changes due to external deformation. Not surprisingly, they reported that the initial extension caused the crystalline regions to orient along the draw direction. Further drawing produced a more defined fibrillar structure. Thus, for semi-crystalline polymers, such as polyethylene, the drawing process leads to a small increase in crystallinity, i.e., a change in crystallite size and shape that can affect the tortuosity and consequently the diffusion. Also, a change in chain mobility in the amorphous phase can also affect the diffusion.[163, 164] The orientation of the crystalline regions will also change during drawing. The orientation was viewed as decreasing the amount of excess free volume, bringing the polymer closer to equilibrium conditions.[165]

The effect of an externally applied stress on the diffusion and solubility and swelling of eight organic solvents in poly aryl ether ether ketone (PEEK) was investigated by Wolf and Fu.[16] This study found that the solubility and rate of diffusion, into the resin are greatly increased by the application of a stress. All eight fluids studied—benzene, toluene, methylene chloride, chloroform, carbon disulfide, methanol, acetone and water—were associated with stress enhanced diffusion, solubility and swelling. These results are particularly striking as the solubility is markedly increased and the time to reach saturation is reduced when the applied stress exceeds a critical value. For example, at 22°C the solubility of toluene into a 29% crystalline PEEK increased from 9% to almost 40% upon the application of a tensile stress of 35 MPa. Furthermore, the time required for a 0.25 mm thick membrane to reach the saturation value was reduced from thousands of hours to less than ten hours. This study associated for the first time a stress enhanced diffusion, solubility and swelling with a critical stress value that depended upon the crystallinity of the material, the particular penetrant, and the

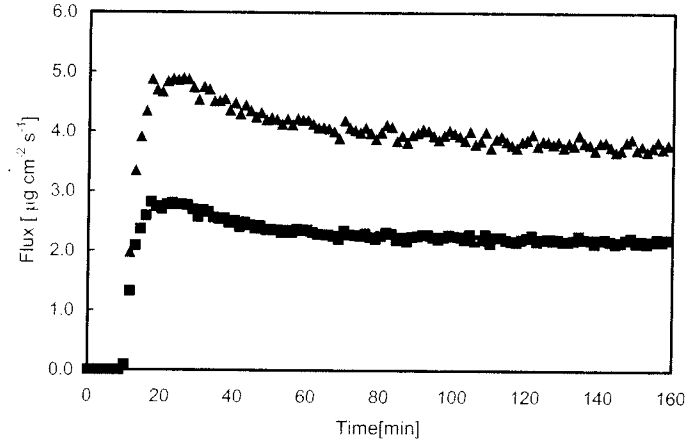

Figure 8. Flux versus time for an equivolumetric mixture of hexane and acetone through a natural rubber membrane. (■) Hexane, (▲) Acetone

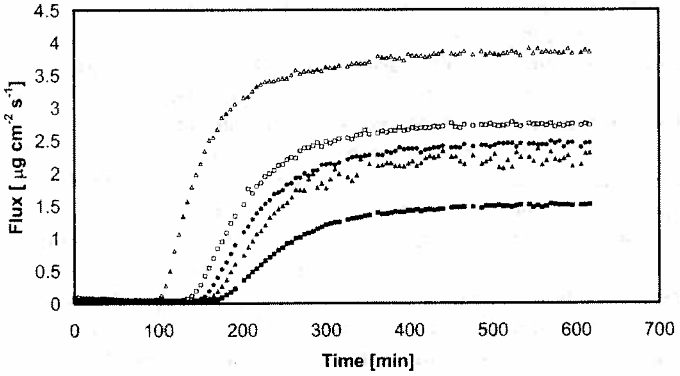

Figure 9. Flux versus time for the permeation of TCE through a Serrot LD400 LLDPE geomembrane at various uni and biaxial deformations. (■) 0%, (▲) 10%, (●) 20%, (□) 10 x 10%, (△) 20 x 20%

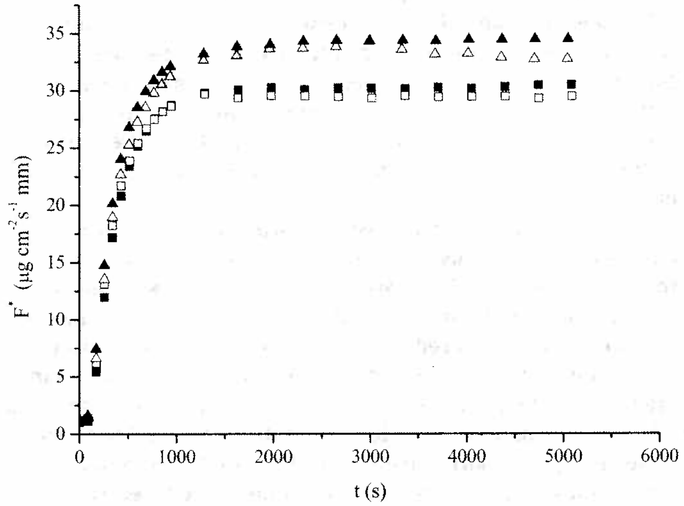

Figure 10. Thickness-normalized flux (F^*) versus time (t) for the permeation of DCM through PDMS with 1 wt.% nanoclay as a function of mechanical deformation. (■) 0%, (□) 5%, (△) 10%, (▲) 15%

temperature. Although the samples were elongated only uniaxially, Wolf and Fu found that the sorption of aromatic hydrocarbons and chlorinated solvents obeyed non-Fickian transport, characterized by three regions: an induction period, a limiting solubility, and a diffusion region. Both the induction period and the limiting solubility were strongly affected by the external stress while the diffusion rate was a weak function of stress.[16]

Other studies reported that external stress, either uniaxial tensile stress or fabrication residual stress, produced an enhanced equilibrium solubility and an accelerated rate of diffusion,[158, 166] however none of these studies performed the permeation or solubility experiments when the membranes were in the deformed state.

Recently, Hinestroza et al.[98] reported on an experimental technique that allowed for the study of the effect of external mechanical deformation on the permeation of organics through polymeric materials. This will be further discussed.

A decrease in breakthrough times with elongation was noted for the permeation of acetone and hexane through carbon filled natural and butyl rubber membranes. Figure 8 shows the flux versus time profile of an equi-molar mixture of acetone and hexane through a natural rubber membrane elongated biaxially (40 × 40%). The decrease in breakthrough time was also correlated with the decrease in membrane thickness. An increase in steady state permeation rates with elongation was also reported.

Additional permeation experiments were performed using trichloroethylene and methylene chloride through linear low density polyethylene geomembranes. Figure 9 shows the flux versus time profiles of methylene chloride (MEC) through a LLDPE geomembrane. Breakthrough times were reported to decrease with elongation. Steady state permeation rates increased with elongation. However, the increase in permeation rate in the case of the LLDPE was not as dramatic as the one experienced with rubber membranes. The difference was attributed to the fact that LLDPE is a semicrystalline material. It was assumed that the mechanical deformation may have decreased the actual permeation area by elongating the crystalline domains.[56]

Liu[76] investigated the mechanical deformation effect on the diffusion process of dichloromethane (DCM) through poly(dimethylsiloxane) (PDMS)/clay nanocomposite membranes. The extension of the membrane will not only decrease the thickness of the membrane, (enhancing the diffusion process), but will likely also pack the polymer chains (decreasing the free volume), which can decrease the diffusion coefficient. At small deformation, the decrease of free volume resulted in a decrease in permeation flux. At high deformation, the decrease in thickness of the membrane enhanced the diffusion process (Figure 10).

CONCLUSIONS

The transport of small molecules through polymeric materials is a very complex process that can be influenced by many factors, such as temperature, chemical nature of the diffusing molecules, the physical properties of the polymer, the interaction of the (small) solvent molecules with the polymer, the external mechanical deformation, the complex internal structure of the polymer, etc. A fundamental understanding of mass transport phenomena in membranes is essential in order to produce materials with improved barrier properties.

After more than sixty years of intense pure and applied research work, substantial progress has been made leading to a better understanding of non-Fickian diffusion processes. The current flurry of activities involving polymer-based nanocomposite systems, for applications such as controlled drug delivery, protective clothing, further suggest the need for more intense investigations of the non-Fickian diffusion process through systems with complex interfaces.

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