Chapter 2 Background of Diffusion Models

As an introduction to the need for relationships such as those described in the previous section, a brief review of the current models relating diffusivity to structural properties of a penetrant-polymer system is given below. The significant results as well as shortcomings of each diffusion model will be discussed.

The models that have been developed to describe diffusion in polymers typically fall under two major categories: (1) *molecular models* that analyze the specific penetrant and polymer chain motions together with the pertinent molecular forces, and, (2) "*free-volume*" models that attempt to relate diffusion coefficients to the free volume of the polymer system, a phenomenological approach.

2.1 Molecular Models

Molecular models are commonly based on the assumption that fluctuating "holes" or microcavities exist within the polymer matrix. At equilibrium, these "holes", may be described by a definite distribution within the polymer. Therefore, the diffusion of a penetrant depends greatly upon the concentration of holes that are large enough to accommodate the penetrant molecule. A penetrant molecule may exist in a hole of sufficient size and can "jump" into a neighboring hole once it acquires sufficient energy. This concept of acquiring a "sufficient amount of energy" is justified by the Arrhenius behavior of diffusion coefficients that has been observed experimentally (equation 1) [1].

(1) $D=D_o \exp(-E_a/RT)$

where E_a = apparent activation energy of diffusion,
D_o = a pre-exponential constant,
R = the gas constant, and
T = the absolute temperature.

One of the first molecular models of diffusion in polymers was proposed by Meares[2]. According to this model, the activation energy of diffusion was directly related to the square of the penetrant diameter. Furthermore, the primary step in diffusion was governed by the energy required to separate the polymer chains to form a cylindrical tube through which the penetrant could "jump" from one position to another. The relationship proposed by Meares is given by:

(2) $E_d= \pi/4\, \sigma^2\, N_A\, \lambda\, (CED)$

where E_d is the activation energy of diffusion, σ is the collision diameter of the penetrant, λ is the diffusional jump length, and CED is the cohesive energy density of the polymer. It is important to mention that this model assumes that the penetrant could be described by a spherical geometry, without any regard to other shape possibilities. It also neglects any polymer-penetrant interactions that may potentially influence the diffusion process.

Another model proposed by Brandt[3] utilized a more detailed description of the polymer structure to estimate E_d. An activated state of diffusion was defined when two polymer chains bend symmetrically creating a "passageway" for the penetrant molecule. Hence, a "cooperative" process between neighboring polymer chains is essential for penetrants unable to pass through existing inter-chain spaces. The activation energy, E_d, is defined as consisting of an intramolecular contribution, E_i, and an intermolecular contribution, E_b.

$$E_d=E_b+E_i \tag{3}$$

E_i results from the internal resistance to chain bending, and E_b from the repulsion experienced by the bent chain segment due to its neighboring chains.

Application of this model to experimental data resulted in a nonlinear dependence of E_d with the square of the collision diameter of the penetrant, σ^2. This is in contrast to the model of Meares where a linear dependence is predicted between E_d and σ^2. Brandt also suggested that an activation energy of diffusion is not necessary for penetrants small enough to diffuse through the existing free-volume between the polymer chains. Furthermore, he found that E_d was not proportional to the cohesive energy density of the polymer. The diffusion process is described in terms of polymer chain energetics, assuming that polymer-penetrant interactions are negligible.

Another model by Dibenedetto and Paul[4] was the first to more accurately predict the nonlinear behavior of E_d with σ^2. However, it neglects any interactions between the polymer and penetrant. In this model, the polymer is considered to be a homogeneous continuum, consisting of Avogadro's number of "center segments". A center is defined as a polymer repeat unit and is subject to a cylindrically symmetric potential field formed by four nearest-neighbors. The activation energy is defined as the potential energy difference between the "normal" state in which the four neighboring centers are at equilibrium positions, and the "activated" state in which they are separated by a cylindrical void. In other words, activation energy is described as the potential energy difference in the partial breaking of the bonds between the four "center" polymer segments. This idea is similar to the use of a cohesive energy density as described by Meares. A dissolved penetrant molecule is assumed to exist within a void or cell created by a bundle of four parallel polymer segments. Coordinated rotations and vibrations of these polymer segments result in another cylindrical void adjacent to the penetrant molecule. This is followed by the displacement of the penetrant molecule into the newly created cylindrical void. The energy required to compress the surrounding polymer chains in order to form this void is not accounted for.

2.2 Free Volume Models

Free volume models differ from molecular models in the fact that they do not consider diffusion as a thermally activated process. Instead, it is assumed to result from random redistributions of free volume voids within a polymer matrix. A detailed review of the free volume models is given in the text by Crank and Park[5] and by Lefebvre, et al[6].

The free volume models reviewed here are based upon the theories of Cohen and Turnbull[7,8] that describe diffusion as occurring when a molecule can move into a void larger than a critical size, V_c. Voids are formed during the statistical redistribution of free volume within the polymer. Free volume of the polymer, V_f, is defined as $V_f = V - V_s$, where V is the specific volume, and V_s is the specific molecular volume due to steric size and thermal vibrations. The probability that "n" polymer segments, of average free volume, V_f, may form a void larger than the critical size, V_c, is given by:

$$\text{Probability} \propto \exp[-\gamma\, V_c/V_f] \tag{4}$$

where γ is an overlap factor ($\gamma \cong 1$, for most polymers). Thus, the theory of Cohen-Turnbull defines diffusion using an "activation volume", $\gamma\, V_c$, and can be written as:

$$D = D_o \exp[-\gamma\, V_c/V_f] \tag{5}$$

This theory was originally developed for the self-diffusion of a penetrant in an ideal liquid of hard spheres. It is not applicable at temperatures far below the T_g where chain motions virtually cease or at high temperatures where an activation energy term may be necessary.

Vrentas and Duda[9,10,11] modified the theories of Cohen and Turnbull to enable the prediction of diffusivity from free volume parameters of a polymer and penetrant. An important feature of this modification is the allowance for a fundamental penetrant molecular jump that involves only part of the molecule. It introduces the concept of *specific shape* of the penetrant molecule, which was not accounted for in any of the models discussed above. However a major limitation of their predictions is the requirement of extensive information on the systems studied. For example, in order to calculate the diffusivity of a penetrant in a polymer, information on the temperature dependence of their density and viscosity, as well as solubility data, and at least three values of diffusivity at different temperatures are necessary. Vrentas and Duda[11] have also reported the deficiencies of the model in describing diffusion in glassy polymers, relaxing polymers and crosslinked polymers.

Another free volume model by Fujita[12] relates the thermodynamic diffusion coefficient, D_T, to the fractional free volume of the polymer, V_f, by

(6) $D_T=RTA_d \exp(-B_d/V_f)$

where A_d and B_d are characteristic parameters for a selected polymer-penetrant system. V_f can be evaluated as a function of temperature, for a pure polymer using the expression,

(7) $V_f(T) = V_f(T_r) + \alpha\ (T-T_r)$

where $V_f(T_r)$ is the fractional free volume of the pure polymer at a reference temperature T_r (usually T_g), and α is the free volume expansion coefficient. Although Fujita's model does not include a parameter that is a direct measure of polymer-penetrant interactions, it indirectly accounts for energetics through the V_f term, which is defined as:

(8) $V_f = V_f(T_r) + \gamma(T) * \phi$

where ϕ = volume fraction of the penetrant, $\gamma(T)$ = a parameter that is incorporated to describe the plasticizing efficiency of a penetrant molecule at a given temperature. The energetics is assumed to be contained in this parameter, $\gamma(T)$. This model still lacks the ability to describe size and shape effects of the penetrant. For instance, it assumes that the molecular weight of a polymer segment involved in a unit "jump" of a penetrant is equal to that of the penetrant. Furthermore, it has proven[13] to be insufficient in predicting penetrant diffusion coefficients that are largely independent of concentration, due to its over-estimation of the critical hole size.

Pace and Daytner[14,15,16] have developed an elaborate statistical mechanical model describing the diffusion of low molecular weight (simple) penetrants. This model considered the possibility of a penetrant moving in two distinct ways: (a) along the axis of a "tube" formed by parallel polymer chains, and (b) perpendicular to the axis of a "tube" between two polymer chains separated enough to permit passage of a penetrant molecule. Since (b) was considered to be the "rate-limiting step", the activation energy of diffusion was found to be proportional to the diameter of a penetrant, the inter-chain cohesion and stiffness of the polymer. Although this theoretical formulation possesses a high degree of mathematical complexity and molecular details, it has limited practical utility for many systems. This limitation results from the fact that it assumes simple, spherical penetrant geometries, and that the energetics of diffusion are largely determined by the inter-chain cohesion, while polymer-solvent interactions are not considered. Therefore, deviations from this theory exist for higher molecular weight (complex) molecules.

All of the diffusion models discussed so far, lack the ability to accurately describe the diffusion process in terms of size, shape, and chemical nature of the penetrant. For example, many of these models were derived based upon spherical geometries, which are usually applicable only to low molecular weight penetrants. The effects of specific interactions between the polymer and penetrant have often been ignored. Those diffusion models that do consider chemical structure often ignore some of the other physical factors described earlier. A brief review of a few studies pertaining to the influence of *size*, *shape*, and *specific interactions* of the penetrant in the diffusion behavior will be discussed in the next section.

2.3 Literature on Diffusion: Effects of Size, Shape, and Chemical Nature

The role that the molecular size of a penetrant plays in the diffusion process has been thoroughly investigated by many researchers. The earliest effort dates back to the work of Einstein and Stokes[17]. They proposed a model for an ideal solution, wherein, an inverse proportionality exists between diffusivity (D) and radius of a spherical penetrant. This model has limited utility in describing polymer-penetrant systems since a polymer matrix can only be reservedly regarded as a highly viscous liquid.

It has been shown[18,19] that a power law relationship exists between diffusivity and molecular weight of a penetrant. Factors such as shape and polymer-penetrant energetics are assumed to be included in a pre-exponential front factor. However, studies by Möller and Gevert[20] have also shown that deviations from the "universal" power law occur in strongly interacting systems. Another shortcoming of this formulation is that it does not contain a parameter that accounts for the influence of temperature on the diffusion process.

Detailed analyses of size effects are often carried out using linear alkane penetrants due to their limited energetics. A strong decrease in diffusivity of alkyl penetrants with increasing molecular weight (or molar volume) has been observed for many different polymer-types.[21,22,23]

In a study on alkyl penetrants (C_{12}-C_{32}) by Koszinowski[22], correlations between diffusion coefficients and activation energies of diffusion were attempted in view of the molecular model proposed by Einstein. However, the model proved to be insufficient over the range of molecular weights studied (C_{12}-C_{32}). A change in diffusion mechanism above a critical penetrant mass was also observed.

Aminabhavi and Phayde[21] have observed the role of shape and chain flexibility in the diffusion of alkyl penetrants through miscible polyolefin blends. The results of this study should however, be viewed with caution since no detailed analysis of the penetrant shape and mechanism of diffusion is given. Furthermore, the effects of shape and isomerism were not accounted for.

The diffusion of linear alkanes through poly(isobutylene) was investigated by Prager and Long[24]. The diffusion coefficients were found to decrease linearly with an increase in the number of carbon atoms. Branching of the alkanes rather than molecular length was observed to dominate the transport properties of the penetrant. A subsequent study involving larger, linear alkanes and cyclic alkanes[25] showed that the diffusion coefficients of cyclic alkanes were lower than those of their linear counterparts by a factor of 3. Furthermore, as the degree of branching in the linear alkanes increased, their diffusion behaviors approached those of the cyclic species. Thus, the significance of penetrant shape was clearly observed yet no qualitative relationship between shape and transport was proposed.

Chen and Edin[26] studied the diffusion of low molecular weight alkanes in glassy polymers, while varying temperature, penetrant size, and polymer structure. Diffusion coefficients were analyzed in terms of the Meare's molecular model and the Eyring transition-state theory. Correlations were developed between diffusivity, activation energy of diffusion, and square of the penetrant diameter. The behavior exhibited by the various polymers was explained in terms of their cohesive energy densities. This interpretation was reasonable since the penetrants utilized could be assumed to be spherical. Furthermore, the use of alkanes minimized any chemical interactions that may have occurred.

Kulkarni and Mashelkar[27] have performed similar analyses on a variety of polymeric matrices. Diffusion coefficients were found to exhibit an inverse dependence on molecular weight of the *n*-alkanes, indicative of a linear, segmental mechanism. Branched isomers, however, deviated dramatically from this linear dependence, implying that the mechanism of transport could be varied by changing the shape of the penetrant. A similar inverse dependence was observed for higher molecular weight alkanes (*n*-hexadecane and *n*-dodecane) in rubbery polymers.[28] These findings fortify the idea that even large *n*-alkane penetrants could diffuse in a linear fashion, by means of segmental motions.

The transport of a series of alkanes (pentane to hexadecane) through miscible blends of ethylene-propylene random copolymers and isotactic polypropylene have been investigated.[29] Diffusion and activation parameters were evaluated, and their dependencies on penetrant size, shape, and chemical nature were discussed. Diffusivity was found to decrease with increasing molecular weight and cross-sectional area of the penetrant. The solubility data were interpreted using Flory-Huggins interaction parameters. However, no formal attempts were made to relate the interaction parameter, χ, to the resulting transport behavior, which was assumed to occur via linear, segmental motions. Similar observations were made on the diffusion of alkanes through a tetrafluoroethylene/propylene copolymer[30]. It should be mentioned that all of the above studies failed to develop qualitative relationships isolating the contributions of each variable.

Recent studies on the transport of organic esters through a fluoroelastomer membrane[31,32] demonstrated the predominance of chemical effects. With increasing molecular weight of the esters and/or the number of ester functionalities, the diffusivity (D) was found to depend more on chemical nature than on molecular size of the penetrant. This behavior was explained in terms of solvation of the polymer matrix that gives rise to increased chain mobility. However, in order to describe these results completely, the role of size and chemical nature of the penetrant need to be quantified.

The diffusion behaviors of linear alkanes, linear alcohols and substituted phenols in polyolefins were compared by Koszinowski[33]. The alkanes followed the expected behavior based on molecular weight, while the alcohols and substituted phenols always exhibited lower diffusion coefficients than the corresponding alkanes due to their tendency for penetrant clustering. However, as the number of carbon atoms increased, both the alcohols and phenols approached the behavior of the alkanes as a result of increased shielding of the –OH group. The linear alkanes were thus considered as being an upper limit for the transport behavior of polar, alcohol penetrants.

Similar observations were made from a study on the diffusion of hindered phenols in low density polyethylene by Möller and Gevert[20] using a "film-stacking" FTIR method of analysis. The penetrants used were comprised of a series of antioxidants containing a 3,5-di-*tert*-butylphenyl structure with an ester branch. The length of the hydrocarbon segment of the branch was varied by addition of methylene units. Although the diffusion was found to occur via linear segmental motions, it exhibited gross deviations from a purely molecular weight-based argument. Larger increases in the activation energy of diffusion per addition of a methylene group were found for the hindered phenols as compared to literature values for *n*-alkanes. The FTIR data was used solely to provide transport coefficients and no chemical information was extracted. Aminabhavi and Khinnavar[34] have demonstrated that the effects described above are compounded by an increased hydrogen-bonding ability of the polymer in their study of the diffusion of aliphatic alcohols in polyurethane, nitrile-butadiene rubber, and epichlorohydrin membranes.

Transport of dialkyl phthalate plasticizers in poly(vinyl chloride) was investigated by Mauritz *et al*.[35] and Storey *et al*.[36] in order to correlate penetrant structure to the observed behavior. They attempted to develop a penetrant shape-dependent, free-volume based diffusion model that would utilize theoretical conformational analysis. The proposed relationship was similar to that of Cohen-Turnbull and was based upon evaluating the probabilities of an adjacent hole formation and a subsequent successful jump. The diffusion process was described in terms of the free volume available, the temperature of the process, the molecular weight of the penetrant, and its aspect ratio. Energetics were incorporated through the free volume term in accordance with the ideas of Fujita and Kishimoto[12]. Attempts by Mauritz and Storey to incorporate the effects of size, shape, and specific interactions were theoretically sound. However, the predicted diffusion coefficients were 2-3 orders of magnitude higher than the experimental ones. The need for an activation energy term, as in the theories of Macedo-Litovitz[37], may be essential to predict diffusivities of the same order of magnitude as experimental results. Furthermore, the inclusion of penetrant energetics within the free volume term needs to be more reflective of the actual, dynamic process that occurs during diffusion.

The above discussion demonstrates the need for a more detailed description of the roles that size, shape, and specific interactions play in the resulting diffusion behavior of a penetrant within a polymer matrix. Many of the models assume simple, spherical geometries for the penetrant that may not be applicable to higher molecular weight penetrants. The importance of the interactions between polymer chains has been demonstrated by Meares and Pace. However, polymer-penetrant energetics are often ignored, even though experimental data suggest otherwise. The Vrentas-Duda formalism possesses parameters describing all the three variables. Yet, the difficulty of its use makes it highly impractical for most applications.

The current study attempts to develop correlations which may form the basis of a model of diffusion, encompassing the effects of all three variables- size, shape, and specific interactions. Furthermore, these qualitative relationships may prove to be highly useful in predicting the transport behavior of a given penetrant/polymer combination.

Endnotes

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