Molecular diffusion in polymeric systems

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Abstract – Molecular diffusion of polymer chains and low molecular
weight constituents and impurities can be an important process in the
formation and application of polymer composites. Molecular diffusion
in polymer systems is a complex process which can be a strong function
of temperature, concentration, polymer molecular weight and polymer
morphology. During the last decade, significant advances have been
made in understanding the fundamentals of molecular migration in
polymeric systems and in predicting and correlating diffusion
coefficients of such systems. The main objective of this paper will
be to review these recent advances which can serve as precursors for
the development of basic theories to describe diffusion through
polymer composites. Emphasis will be placed on the description of
molecular diffusion in a binary system consisting of a polymer and a
low molecular weight solvent or penetrant at the limit of high polymer
concentration. The influence of temperature, concentration as well as
polymer and penetrant characteristics on the molecular migration
process will be considered. Also, the influence of the glass
transition temperature and the complications associated with the
coupling of molecular diffusion and polymer chain relaxation will be
discussed.

INTRODUCTION

The molecular migration of low molecular weight substances in polymers can be an impor-
tant process in the formation, processing, and application of polymeric materials. The
importance of this mass transfer process is perhaps most prominent during the reaction of
low molecular weight monomers to form polymers. The rate at which a polymerization
reaction proceeds is often controlled or strongly influenced by the molecular diffusion
of monomers, initiators, long-chain radicals, dead polymer chains, or low molecular
weight condensation products. In many commercial polymerization reactors, sharp gradi-
ents in monomer concentration often occur and rates of molecular diffusion influence the
rate of polymer formation and product characteristics such as molecular weight. Also,
volatile residuals which remain in the polymer after its initial formation must be
removed to control product properties as well as to meet health, environmental and safety
regulations. These polymer devolatilization processes can involve molecular diffusion of
the low molecular weight materials from polymer melts or solid particles.

The formation of composites by condensation polymerization is often controlled by the
molecular diffusion of the low molecular weight condensation products of the material.
In this case, we have a coupling of a polymerization reaction and a devolitalization
process. The formation of the low molecular weight condensation product is controlled by
the polymerization reaction and its removal is controlled by molecular diffusion in the
reacting polymeric medium. Both the rates of reaction and diffusion will be influenced
by several variables such as concentration, temperature, and polymer morphology.

Molecular diffusion can play an important role in the formation and dissolution of vapor
bubbles in polymers. In situations involving composites, formation of bubbles is
detrimental, while the initiation and control of such phase change processes is desirable
in the formation of cellular polymer foams.

Molecular diffusion can have a significant role during the application of polymer
products. In some applications such as barrier films, controlled release devices and
membrane separators, molecular diffusion is the key property which determines a product's
utility. Often the presence of impurities such as moisture is more critical during the

fabrication of a polymer part than during its utilization. However, the solution and migration of impurities such as water can play a dominant role in the utilization of composites since small concentrations of impurities can influence the binding between the filler material and the polymer matrix.

During the formation and processing of polymeric materials such as composites, molecular diffusion often takes place in a polymer liquid or melt, whereas the utilization of polymeric materials can depend upon the migration of small molecules which are dissolved in a solid or glassy polymer matrix. In the next section, diffusion in amorphous polymers above the glass transition temperature will be considered. The third section will consider mass transfer in the glassy state and the coupling of molecular migration and the relaxation of the polymer matrix. Finally, the potential role of these recently developed concepts for the development of basic theories to describe diffusion in polymer composites will be discussed.

DIFFUSION IN POLYMER MELTS AND SOLUTIONS

In polymerization processes, the diffusion of materials such as monomers and condensation products usually takes place in a polymer solution at temperatures above the glass transition temperature, T_g, of the system. In this region, the diffusion process usually follows classical diffusion theory and anomalous behavior which is unique to polymeric systems is not observed. As shown in the following section, anomalous or non-Fickian behavior is most often associated with glassy polymers. Although anomalous behavior can occur at temperatures above T_g, such observations are unusual. Consequently, the basic parameter required to describe mass transfer above T_g is the diffusion coefficient as defined by classical diffusion theory. Many advances have been made in predicting this coefficient from basic molecular properties for gases, vapors, and liquid systems consisting of non-polymeric materials. Unfortunately, these developments are not useful when one molecular species in the system is a high molecular weight polymer chain or network. Measurements of the diffusion coefficients in polymer-solvent systems show that these coefficients can be complex functions of many variables including temperature, concentration, molecular weight, and polymer morphology such as crystallinity, crosslink density, and orientation. In recent years, significant advances have been made for predicting and correlating diffusion coefficients in relatively simple systems consisting of a single solvent and an amorphous, non-crosslinked polymer. These advances will be reviewed and it is readily evident that they can serve as precursors for the analysis of systems consisting of more complex polymer morphology and heterogeneous systems such as composites.

The most appropriate theoretical procedure for describing diffusion in a polymer solution depends upon the relative polymer concentration in the solution. The various concentration regions are shown schematically in Figure 1. The solid line in this figure is the characteristic behavior of the diffusion coefficient of a polymer in a good solvent over the complete concentration range at a particular temperature, pressure and molecular weight. This diagram shows the general behavior of such systems; the actual range of the various zones depends on the characteristics of the particular polymer-solvent system. As indicated, the mutual binary diffusion coefficient sharply increases with solvent concentration and often exhibits a maximum value in the concentrated region when the polymer-solvent system is miscible over the complete range of concentration. In the infinitely dilute limit, the polymer molecules are widely dispersed in the solvent so that there are no interactions between the individual polymer chains. Analysis of
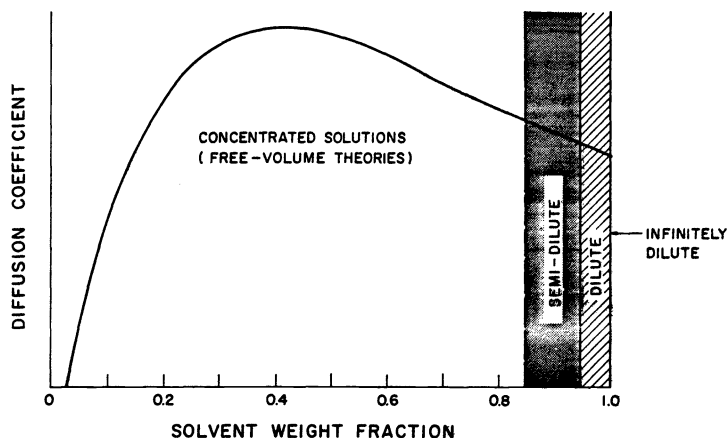

Fig. 1.   Schematic Diagram of Distinct Concentration
          Regions for Diffusion in Polymer-Solvent Systems
          Above the Glass Transition Temperature.

transport processes at this limit can readily be based on statistical mechanical calculations since the statistics of each polymer chain is not influenced by the presence of the other chains. The best method presently available for predicting the mutual diffusion coefficient at infinite dilution is the Kirkwood-Riseman theory (ref. 1) which is based on a consideration of the hydrodynamic friction between an unperturbed polymer chain and a solvent. This theory is limited to the theta condition for linear flexible chain polymers and it provides for a varying amount of hydrodynamic interaction between the segments of the isolated polymer chains. This theoretical formulation has been extended for the prediction of diffusion coefficients in non-theta solutions by utilizing thermodynamic theories to predict the linear expansion factor for a polymer chain in a good solvent (ref. 2-4).

In the dilute concentration region, the polymer molecules begin to interact hydrodynamically with each other; however, the domains of the individual polymer molecules do not overlap. The diffusivity in this dilute region can be approximated as a linear function of concentration, and statistical mechanical theories (ref. 5-11) have been developed to predict this concentration dependency which is related to the hydrodynamic interaction of the polymer chains. Depending on this interaction and the thermodynamics of the solution, these theories show that the diffusivity can either increase or decrease with polymer concentration in this region. A number of investigators have compared theoretical predictions with experimental data in this region, but these comparisons are somewhat inconclusive due to the lack of consistent data (ref. 5,7,12,13).

Once the domain of the individual polymer chains start to overlap, the system enters the semidilute region. This region extends to the concentration where the chain dimensions become independent of concentration. In this semidilute region, there exists intermolecular entanglements which can be expected to produce cooperative dynamic modes which are characteristics of a network. Hence, a semidilute solution may be pictured as a transient network structure. Diffusional transport in such systems has been analyzed using scaling laws (ref. 14,15). These laws do not predict the actual values of diffusion coefficients, but can be used to predict the exponents in simple power laws obeyed by various polymer properties in the limit of high polymer molecular weight. A reptation theory has been used in conjunction with a scaling law (ref. 16,17) to predict the concentration and molecular weight dependency of the polymer self-diffusion coefficient in the semidilute region. Transport in the concentrated region is generally considered too complex to analyze rigorously using molecular mechanics because of the numerous degrees of freedom and a complex intramolecular and intermolecular interaction. This is unfortunate since most of the problems of practical significance involve diffusion in the concentrated region.

Analyses of diffusional transport in the concentrated region have been carried out using either approximate molecular theories or the free-volume theory of transport. The most comprehensive molecular theory for this region has been proposed by Pace and Datyner (ref. 18,19). This approximate molecular theory is limited to a relatively narrow solvent concentration region of approximately 0 to 10% volume fraction solvent. The only theories available which can predict diffusional behavior over the complete concentrated region are based on free-volume concepts.

Cohen and Turnbull (ref. 20) first proposed that molecular diffusion in liquid systems can be described by a theory based on free-volume concepts. They proposed that the volume of a liquid could be considered to consist of two components. First, there is the actual volume occupied by the molecules and surrounding these molecules is free-volume space which is continuously being redistributed by the random thermal fluctuations of the fluid. Volume changes associated with changes in temperature are related to changes in this free volume, while the occupied volume is considered independent of temperature. If a molecule is to migrate in the liquid, a free-volume hole of sufficient size must appear adjacent to the molecule. Consequently, molecular diffusion is due to the jumping of molecules into free-volume holes caused by the random fluctuation of the local density. In the Cohen-Turnbull theory, the self-diffusion coefficient in a pure liquid is related to the probability that a hole of critical size will be formed by random fluctuations in free volume. A number of investigators have modified this original theory (ref. 21-24), and a generalized theory developed by Vrentas and Duda (ref. 12,25-27) has been shown to be very useful for predicting and correlating mutual binary diffusion coefficients in concentrated polymer-solvent solutions. In this theory, the free volume of the liquid is considered to consist of two distinct populations as shown in Figure 2. The redistribution of one segment of this free volume referred to as the interstitial free volume involves a high activation energy and this free volume does not play a significant role in molecular migration processes. Only a fraction of the free volume, the hole free volume, is considered to be capable of being redistributed without energy constraints and it is this free volume which forms the cavities for molecular migration. Although this hole free volume cannot be measured directly, the free-volume parameters required to predict this volume can be obtained from correlations of viscosity versus temperature data for pure polymer and solvent liquids. By assuming additivity of free volumes, the hole free volume in a polymer solution can be predicted from pure component viscosity and density data.
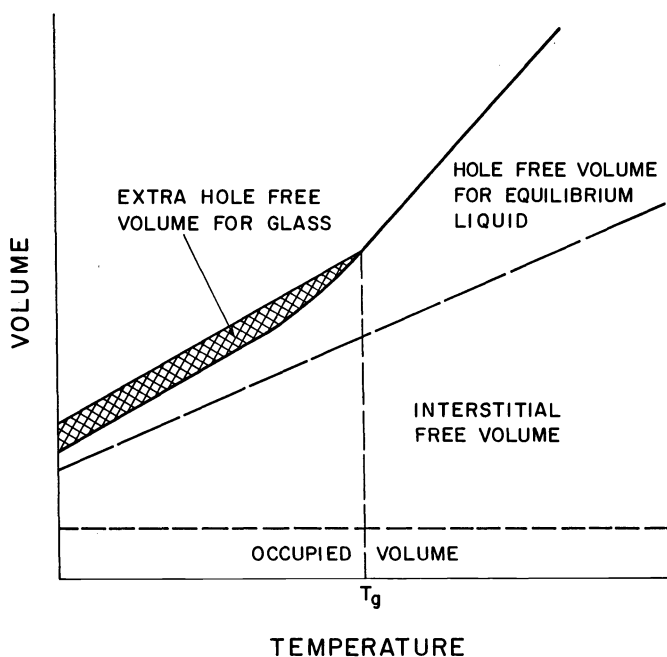
Fig. 2. Volume-Temperature Behavior of an Amorphous Polymer.

In the Vrentas-Duda theory, free-volume concepts are used to predict the self-diffusion coefficients of the polymer and solvent and these predictions are coupled with solution thermodynamic information to predict the mutual binary diffusion coefficient as a function of temperature and concentration. A basic concept in the theory is that the polymer moves by the migration of segments of the polymer chain. A key parameter in the theory is the relative size of the free-volume holes required to accommodate these segments in respect to the holes needed for solvent migration.

In essence, this development permits the prediction of binary diffusion coefficients from pure component density and viscosity data and thermodynamic information for the binary solution. Comparison of theoretical predictions with experimental measurements for several systems has shown that this theory can predict diffusion coefficients over a broad range of temperature and concentration in concentrated polymer solutions. The accuracy of these predictions is greatly enhanced if a few diffusivity measurements are available to determine a few key parameters in the theory. Consequently, the principle utility of the free-volume theory of transport for polymer-solvent diffusion is that the self-diffusion coefficient of the solvent and the mutual binary diffusion coefficient can be predicted over wide temperature and concentration ranges using only a small amount of diffusivity data (ref. 26).

The predictive capabilities of the Vrentas-Duda theory are illustrated in Figure 3 where the symbols represent diffusivity measurements. The predicted lines in this figure are based on the utilization of pure component data and details of the predictive procedure are available (ref. 26,28). In addition to density and viscosity data, the solubility parameters of the toluene and polyvinyl acetate were used to predict the interaction parameter in the Flory-Huggins theory to predict the thermodynamic behavior of this solution. Finally, diffusivity measurements for other solvents in polyvinyl acetate were utilized to estimate the size of the jumping unit of the polymer chain. Unfortunately, theoretical predictions are not always as accurate as shown in Figure 3, and for most cases a few diffusivity data points are required. Figure 4 shows the correlative capabilities of the free-volume theory. In this correlation, a regression analysis of all the data points was performed to determine three parameters in a theory which are difficult to determine without some diffusivity data (ref. 29).

The trends shown in Figures 3 and 4 are typical for most solutions of a good solvent. At low solvent concentrations, a small increase in the solvent weight fraction will cause a very significant increase in available free volume and a correspondingly large increase in the diffusion coefficient. The sensitivity of the diffusion coefficient to the solvent concentration will increase as the temperature approaches the glass transition
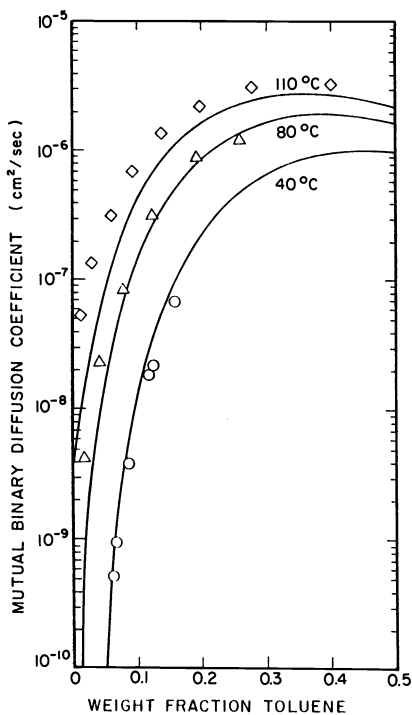
Fig. 3. Free-Volume Theory Predic-
tions for Toluene-Polyvinyl
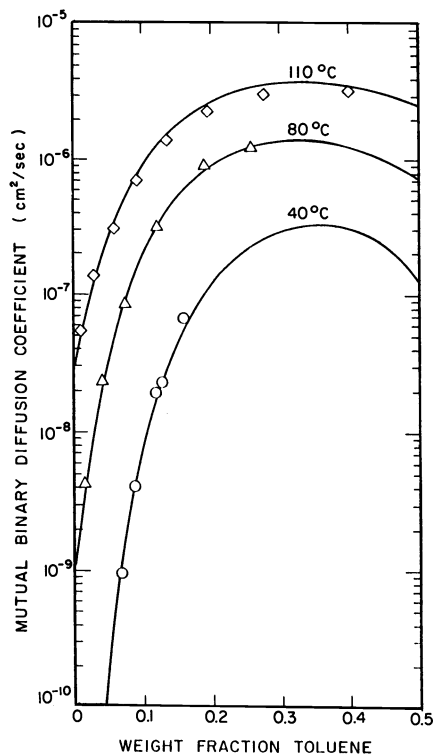Acetate System.

Fig. 4. Free-Volume Theory Correla-
tion of Diffusivity Data for
Toluene-Polyvinyl Acetate Systems.

temperature of the polymer (ref. 30). The diffusivity becomes more independent of
concentration as the temperature increases and as the molecular size of the solvent
decreases (ref. 30). As the solvent concentration continues to increase, the coupling of
the self-diffusion process and the solution thermodynamics can cause a maximum in the
diffusivity versus concentration relationship for solutions of good solvents. This
free-volume formulation has been shown to be applicable up to concentrations of
approximately 70 weight percent solvent (ref. 26).

DIFFUSION IN POLYMERIC GLASSES

When the temperature of a polymer melt is lowered, the random motion of the chains
naturally slows down. To maintain a thermodynamic equilibrium state, the volume of the
melt must decrease with the decreasing temperature as indicated in Figure 2. If the rate
of the molecular rearrangement to cause this densification is slow compared to the rate
of cooling, a non-equilibrium or glassy state will be formed. This process is analogous
to the formation of a super-saturated solution in which the rate of cooling is faster
than the rate of crystallization required to maintain an equilibrium state. As Figure 2
indicates, the temperature where the glassy state appears is referred to as the glass
transition temperature, T_g, and below this temperature the volume of the system is higher
than the equilibrium state. Consequently, a glassy system has more free volume than the
corresponding equilibrium state at the same temperature. The transition to a glass
occurs over a range of temperature and it depends upon the rate of cooling. Similarly,
the amount of extra free volume in a glassy material depends upon how the glass was
formed. Rapid cooling will induce higher extra free volume, and in principle the system
could be maintained as an equilibrium liquid at all temperatures if the cooling rate were
infinitely slow. At low temperatures, such an equilibrium liquid would exhibit
qualitative characteristics such as brittleness similar to a glassy material. The
fundamental mechanisms for molecular processes such as diffusion would be the same for an
equilibrium liquid independent of temperature, and theories developed to describe
diffusion in polymer melts could be extrapolated to describe molecular migration in an
equilibrium liquid at low temperatures where molecular motions have become relatively
slow. Consequently, the free-volume theories described in the previous section could in
principle be used to predict and correlate diffusion at any temperature as long as an
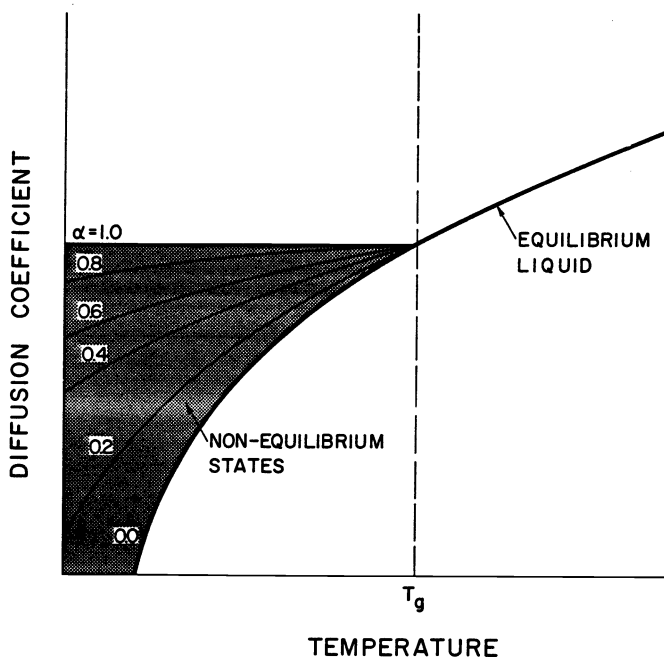equilibrium state is maintained.

Fig. 5. Schematic Diagram of Diffusivity Behavior in the Vicinity of the Glass
Transition Temperature as Predicted by the Free-Volume Theory. The Fraction
of the Volume at T_g Which Is Available for Molecular Transport in the Polymer
Glass Is Equal to α.

A logical extension of the free-volume concepts developed to describe diffusion above the
glass transition temperature is   based on the premise that the same free-volume rela-
tionship will apply below T_g if the excess free volume of a glass is considered available
for molecular transport. Such a theory has been developed to describe molecular diffu-
sion in a polymer glass (ref. 31), and this formulation includes one extra parameter
which indicates the amount of excess free volume in the glass. The general characteris-
tics of this free-volume description of diffusion in the glassy state are presented in
Figure 4. If an equilibrium liquid is maintained at all temperatures, the theory
predicts a continuous relationship between the diffusion coefficient and temperature and
there is a smooth transition as the temperature is lowered below T_g. However, since the
hole free volume decreases with decreasing temperature, this theory predicts that the
diffusion coefficient will become quite small at low temperatures. In Figure 5, the
parameter α indicates the fraction of the hole free volume available in the system at T_g
which is frozen into the material and consequently is available at temperatures below T_g.
This figure shows the two extreme cases. If the amount of hole free volume was maintain-
ed constant below T_g ($\alpha = 1$), then the diffusion coefficient would be a constant below
this transition.   At the other extreme, if no extra hole free volume existed below T_g,
the diffusion coefficient would follow the relationship describing diffusion in an
equilibrium liquid ($\alpha = 0$). As this figure indicates, the free-volume theory predicts
that a break will occur in the diffusivity vs. temperature relationship in the vicinity
of T_g. This is in contrast to many common perceptions that molecular motion essentially
stops at T_g and there would be a correspondingly precipitous drop in the diffusion
coefficient. Behavior predicted by the free-volume theory is consistent with experimen-
tal observations. It has been shown that there is a break in the diffusivity vs. tempera-
ture relationship in the vicinity of T_g and the diffusion process in the glassy state is
actually faster than that which would be projected from measurements above the glass.

Several characteristics of the free-volume theory for glassy polymeric materials are not
illustrated in Figure 5. Calculations based on this modified free-volume theory (ref.
31) indicate that the magnitude of the break in the diffusivity vs. temperature relations-
hip at a given α or excess free volume will increase as the molecular size of the solvent
molecule increases. Similarly, this formulation indicates that the diffusion process
will be faster in glasses which are obtained by rapid quenching. Although all the predic-
tions of the free-volume theory developed to describe diffusion in the vicinity of the
glass transition are in qualitative agreement with the available experimental measure-
ments, the quantitative predictions of this theory have not been validated.

A quantitative comparison of experimental measurements and theoretical predictions in the
glassy state is quite difficult since there are many complexities associated with the

glassy state which are usually not important in systems above T_g:

a. The free volume and other molecular characteristics of a glass are not a unique function of state variables such as temperature, pressure and composition which uniquely define an equilibrium state. Two investigators conducting experiments on a glassy polymer at identical temperatures could observe quite different diffusional behavior since the amount of free volume in a glass will be a function of the history of the formation of the material.

b. The state of a glassy material at a fixed temperature is not fixed for there is always a thermodynamic driving force which is causing the material to relax to the equilibrium state. Consequently, as a glassy material ages, it will densify and the rate of a diffusion process will decrease with time.

c. In the relaxation process described in the above paragraph, it was implicitly assumed that the time required to make a diffusion measurement was short compared to this relaxation process and a diffusion measurement could be obtained at a fixed state or a fixed value of α. On the other hand, in many diffusion processes, the addition of a small amount of solvent or penetrant will accelerate the relaxation of the glassy material and studies of diffusion will involve mechanisms based on the coupling of molecular migration and the relaxation of the polymer chains.

   The coupled relaxation-diffusion process described in paragraph (c) results in experimental measurements which are not consistent with classical diffusion theories. Consequently, many studies of diffusion in glassy polymeric materials have resulted in the observation of anomalous behavior. This coupled diffusion-relaxation process can distort experimental measurements and many types of anomalous behavior have been reported (ref. 24,32-35). The most common examples are that the measured diffusivity as well as solubility are not unique functions of the state of the system as described by the temperature, pressure and concentration, but appear to depend on non-state variables such as time and the dimensions of the material being investigated. At the present time, there does not exist a general theory which can be used to analyze all the various types of mass transfer phenomena which have been observed for polymer-solvent systems. However, anomalous effects in polymer-solvent diffusion can be anticipated by comparing the rate of diffusion to the rate of rearrangement of polymer molecules (ref. 36,37). The nature of diffusional transport in polymer-solvent systems can be ascertained by defining a diffusion Deborah number, as the ratio of a characteristic relaxation time of the fluid, to the characteristic time of the diffusion process. Details concerning the calculation of this diffusion Deborah number are presented in the literature (ref. 37).

In cases where the diffusion Deborah number is small (approximately less than 0.1), the molecular relaxation is much faster than the diffusion transport, conformational changes in the polymer structure appear to take place instantaneously, and the diffusion process involves what is essentially a purely viscous binary mixture in which an equilibrium state exists at all points in the diffusion field. This is diffusion in the classical sense, and this process, which is called viscous diffusion, involves application of the familiar diffusion equation with a mutual diffusion coefficient. All the diffusion theories presented in this paper are limited to this classical diffusion regime. When the diffusion Deborah number is large (> 10), there is essentially no time variation of the polymer structure during the diffusion process. Such a process is characteristic of diffusion into thin samples of glassy polymers at temperatures significantly below T_g. In this diffusion process, a diffusing solvent molecule is moving through a material which effectively has the properties of an elastic solvent, and the classical diffusion formulations will be applicable. Also, since the diffusing species does not change the structure of the glassy material, the diffusion coefficient is usually essentially independent of concentration.

In cases where the Deborah number is of the order of unity, the processes of molecular relaxation and diffusive transport occur in comparable time scales. Since the rearrangement of polymer chains and the movement of solvent molecules takes place simultaneously, this type of diffusional behavior has been referred to as viscoelastic diffusion. Anomalous or non-Fickian phenomena that have been observed in the study of diffusional transport in polymer-solvent systems are associated with this viscoelastic regime. Many studies near and below T_g occur in this coupled relaxation-diffusion regime. However, it should be pointed out that anomalous behavior is not unique to the glassy state. Deborah numbers of the order of unity can exist at essentially any temperature depending upon the relative magnitude of variables such as polymer chain relaxation, diffusion coefficient, and sample dimension. Anomalous behavior due to coupled diffusion-relaxation processes have been observed at temperatures as high as 60°C above T_g.

Although this coupling of diffusion and relaxation during diffusional transport in polymer-solvent systems has been described in detail by a number of investigators, no

general theory has been developed to describe this coupled phenomena. This is unfortunate, since many practical applications involving diffusion in polymer materials, particularly glasses, occur in the viscoelastic diffusion region. The coupling of polymer chain relaxation and solvent migration influences the overall mass transfer process by influencing the molecular migration mechanism and the dynamic solubility at a phase interface.

In conclusion, the diffusional behavior in glassy polymeric materials is a complex process which is not fully understood. The free-volume formulation which gives the predictions illustrated in Figure 5 is only applicable for cases of small Deborah number where the molecular relaxation process is fast compared to the diffusion process. This formulation is based on a particular assumption concerning the nature of the extra free volume in a glassy material. Figure 5 is based on the approximation that the extra free volume is indistinguishable from the free volume of an equilibrium liquid in its availability to facilitate molecular migration. However, some experimental measurements of gas sorption and glassy polymers have led to theoretical interpretations in which the extra free volume of a glassy material is considered to be different in nature from the free volume that would exist in an equilibrium liquid.

In the sorption of simple gases in glassy polymers at low pressures, it would be expected that the sorption isotherm is given by Henry's law in which the concentration of the solvent in the polymer is directly proportional to the gas pressure. Correspondingly, the diffusion process should follow the classical theory of diffusion in the elastic diffusion regime and the diffusivity should be independent of concentration. However, several investigators (ref. 38-42) have reported a non-linear sorption isotherm and a concentration-dependent diffusion coefficient. One explanation of these observed data is that there exists two distinct molecular populations of the solvent in the polymer. One population is dissolved directly into the polymer matrix and follows a Henry's law sorption behavior. A second population is sorbed into microvoids or holes which are associated with the extra hole-free volume of a glassy polymer and this sorption follows a Langmuir model of sorption. This dual-mode sorption mechanism results in a non-linear sorption isotherm, and the basic concept of two molecular populations can be used to predict a concentration-dependent diffusivity (ref. 38,39). This dual mode theory of sorption and transport has been described in detail in several reviews (ref. 40-42).

DIFFUSION IN POLYMER COMPOSITES

The preceding sections present an overview of molecular diffusion in homogeneous polymer systems. Transport in a heterogeneous medium such as a composite is greatly complicated by the morphological structure of the phase domains. The most common approach is to assume that the transport in phase domain within a composite is analogous to transport in a homogeneous sample of that phase at the same state as defined by temperature, pressure, and concentration. This is a reasonable assumption if the size of the phase domains is large compared to the size of the penetrant and if transport along phase boundaries is insignificant. Information concerning transport in the individual phases is then coupled with a model of the composite morphology to predict and correlate transport in the composite. A limiting condition which is valid for many composites is that transport in one phase is insignificant so that its role is to act as a barrier. Under these conditions, penetrant molecules must migrate around the impermeable phase and hence a tortuosity is introduced. In contrast, the rates of transport in both phases may be comparable such as in the case of polymer-polymer composites.

The appropriate model for the morphology of the composite depends upon the degree of randomness of the material. Systems can be perfectly ordered such as regular arrays of spheres, elipsoids, cylinders, etc., or layered structures. Transport in such heterogeneous media can be modeled by solving the appropriate transport equations in the regular geometry phases with appropriate boundary conditions at the phase boundaries. Basically, there are two classes of transport processes which can be considered, steady-state permeation and transient or unsteady-state sorption. Barrer (ref. 43) has presented an excellent review of the solutions available for transport in regular heterogeneous media.

At the other extreme, we have transport in random and chaotic systems, with random arrangement of randomly shaped phases. Models of such systems are naturally statistical in nature and recent theoretical advances to describe transport in such disordered media are the Effective Medium Theory (ref. 44), percolation theory (ref. 45), and phase distributions represented by Voronoi tessellations (ref. 46). Ottino and Shah (ref. 47) have presented a review of the recent advances for describing transient sorption and permeation in disordered systems. These authors show that the effective diffusivities obtained by sorption and permeation experiments can differ significantly, particularly for systems close to but below the percolation threshold.

Most of these studies have dealt with the two limiting morphologies, regular structures or completely random systems. Unfortunately, the variety of morphologies is enormous and many systems of practical interest fall between the perfectly ordered and perfectly random states. Not only have the available studies focused on the limits of perfectly ordered and perfectly disordered systems, but there is no complete mathematical theory for the classification of the degree of disorder.

As indicated above, it is possible that the bulk properties of the polymer in a composite are not equivalent to the corresponding properties of a homogeneous sample of the polymer. Differences can be anticipated when the polymer domains are small. For example, the free volume in a small polymer domain can be influenced by the constraints of the surrounding phase boundary. There is some evidence (ref. 48) that the free volume and diffusivity in the amorphous domains of a crystalline polypropylene increase at a high crystalline volume fractions. Such interactions can be determined by comparing the effective diffusivity in a composite containing a non-conducting filler with the diffusion coefficient in a homogeneous polymer sample. Although the effective diffusivity in a composite can be significantly less than the diffusivity in the homogeneous polymer, the influence of temperature and concentration on the diffusivity will be the same for both cases if the free volume is not influenced by the size of the polymer domains. For example, Wright (ref. 49) has shown that the influence of temperature on the diffusion of water in cast epoxy resin is similar to the temperature dependency of the effective diffusivity in epoxy composites of carbon fibers even though the values of the effective diffusion coefficients are almost an order of magnitude less.

In conclusion, coupling of recent advances for describing transport in disordered heterogeneous systems and the availability of theories to predict diffusion coefficients in homogeneous polymers should lead to an improvement in our understanding of molecular diffusion in polymer composites.

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