JOURNAL OF MATERIALS SCIENCE 30 (1995) 916–922

Modelling the behaviour of gas bubbles in an epoxy resin: evaluating the input parameters for a diffusion model using a free-volume approach

J. R. WOOD
Casali Institute of Applied Chemistry, The Hebrew University, Jerusalem, Israel
M. G. BADER
Department of Materials Science and Engineering, University of Surrey, Guildford, UK

Models based on a mass-diffusion theory successfully represent the growth and collapse of gas bubbles in an epoxy resin. A quantitative evaluation of the steady-state diffusion equations requires values for the diffusion coefficient and the solubility of the mobile species within the resin precursor. These parameters are affected by changes in temperature and/or pressure, and they are generally not measured as part of a processing schedule. Models have been evaluated that predict the temperature dependence of the gas diffusion coefficient in the resin. A free volume approach describes the viscosity of the resin successfully at temperatures of up to 100 K above the glass-transition temperature. At higher temperatures, a thermal-energy-barrier approach is more appropriate. A direct correlation between the viscosity of the resin and the gas diffusion coefficient is proposed which is considered to be applicable to any gas/resin system where specific component interactions are negligible and the solute concentration is sufficiently low that it does not affect the free volume of the medium.

1. Introduction

When thermosetting resins were first introduced as matrices for composites, empirical methods were used to determine the process variables (temperature/pressure–time profiles). Such methods have several disadvantages; they are restricted to small ranges of the process variables, they cannot be generalized for different materials and geometries, and last, but not least, they are expensive and time consuming. The shortcomings of empirical methods can be eliminated by the use of scientifically valid models which provide a means of establishing the optimum values for the processing variables. Process control can be a predictive or an interactive technique where quantitative models allow simulation and prediction of the effects of the controllable variables – composite formulation, fabrication pressure, temperature and time. The ultimate aim of such control is to produce void-free composites of the specified dimensions with the optimum degree of cure of the resin. This depends on a complex interaction involving heat transfer, resin flow and chemical reactions. Once the material and processing inter-relationships have been identified it is possible to establish the optimum values of these processing variables as well as facilitating the real-time control of the manufacturing operation. Most practical processes. (for example, autoclave curing of prepreg or resin transfer moulding (RTM)) require that the matrix resin should be a liquid of low viscosity, typically less than 1 Pa s, during the critical infiltration and consolidation stages of the process.

Many of the material and processing parameters play an active role in more than one model, that is the temperature influences both the kinetics of the curing operation and the flow of the resin (Fig. 1). Resin flow is controlled by the viscosity of the resin (which is of critical importance to composite processing) and by the consolidating pressure. These factors affect the infiltration of the reinforcement and the macroscopic consolidation of the laminate. The viscosity is also important since it is related to the resistance of the medium to molecular motion, which controls both self-diffusion and diffusion of any dissolved species. During the curing process, the viscosity increases, until, at gelation, both flow and diffusion effectively cease. Molecular-transport processes, up to the point of gelation, are critical to the production of void-free composites.

2. Bubble behaviour

Bubbles present within the resin will grow, or collapse, according to the concentration of the mobile species, the temperature and the hydrostatic pressure in the resin during the cure cycle. Bubble behaviour is influenced by such changes in accordance with the ideal-gas-law equations and by the diffusion of mobile species across the bubble/resin interface; that is, gaseous species in the bubble diffuse into the resin or dissolved gases in the resin diffuse into the bubble. An increase in temperature or a decrease in pressure will cause the gas within the bubble to expand, resulting in

0022–2461

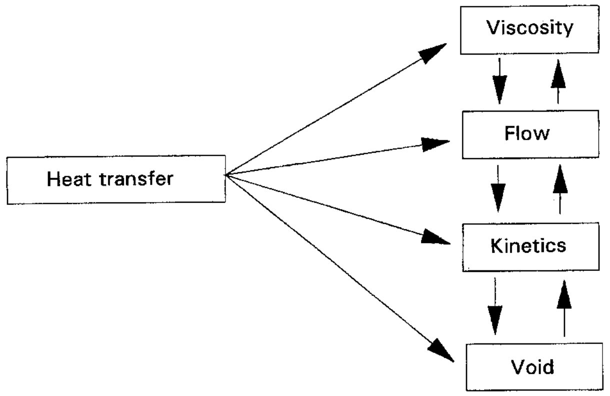

Figure 1 A flow diagram of some interactive processes.

bubble growth, and vice-versa. Changes in pressure and temperature can also have a pronounced effect on the solubility of mobile species in the resin, which may influence not only the magnitude of the driving force for diffusion but also the direction of the concentration gradient. Since an increase in temperature also causes an increase in the diffusion coefficient, mass transfer of molecularly mobile species will also increase, resulting in more-rapid bubble growth or in collapse, depending on the direction of the diffusion gradient relative to the host bubble [1].

Models based on mass-diffusion theory have been investigated [1, 2], and it is considered that entrapped bubbles can be collapsed or suppressed from growing by manipulating the process variables during the curing operation; that is, it is possible to influence bubble behaviour by changing the processing temperature and pressure. To implement these models successfully, a number of input parameters and their respective interactions with the process variables need to be evaluated before it is possible to predict the growth or collapse rate of gas bubbles in the liquid resin. These material parameters include the diffusion coefficient and the solubility of the mobile species in the liquid resin, they are functions of temperature and/or pressure. Since a model is only as successful as the accuracy and *availability* of the input data, it is beneficial to have relationships that can predict these input parameters and/or their interaction with the changing process variables from fundamental data on materials or from more accessible physical quantities. The rationale behind the investigation is that such relationships and the input parameters required for a void model can then be translated to other systems or process options, with minimal additional characterization of materials. By minimizing empiricism it is also easier to confront the problem that there is no universal cure cycle since it is necessary to determine an optimum schedule within a processing window dictated by the heat transfer, cure and consolidation processes.

This paper deals specifically with how the diffusion coefficient of a non-condensible gas within a liquid polymer may be related to the viscosity of the polymer medium and how the temperature dependence of the latter can be predicted from independent physical quantities.

3. Transport phenomena

The viscosity of a resin system is extremely temperature dependent, initially decreasing sharply as the temperature is raised and then rapidly increasing as cross-linking reactions lead to gelation of the resin (Fig. 2). Although the viscosity, and its relationship with temperature, is generally a parameter that is measured in composite processing, it is still necessary to represent the interaction mathematically before it can be used in a predictive model. Although this can be totally empirical (using mathematical regressions to fit experimental interactions) it is more advantageous to use models that have some physical basis to take into account different resin systems or cure cycles.

An Arrhenius relationship is often used to describe the temperature dependence of the viscosity where each molecule is considered to occupy an equilibrium position, thus requiring a definite energy of activation, ΔE_η in order to pass to another position. This energy is regarded as consisting mainly of the energy required for the formation of a *hole* into which the molecule can pass in its motion from one equilibrium position to the next [3]. Viscous flow, however, is not a simple thermally activated process in polymers since the viscosity is sensitive to the extra free volume made available by thermal expansion as well as the extra violence of kinetic agitation [4].

The free volume is the unoccupied space which arises as a result of inefficient packing of molecules. Fox and Flory [5] have suggested that above the glass-transition temperature T_g a decrease in the temperature of a polymer will be accompanied by a decrease in the free volume which continues until the T_g is reached. At this temperature the free volume attains a characteristic value which remains constant as the temperature is further reduced. The glass-transition temperature can then be pictured as a specific volume change due solely to an increase in free volume. As the polymer is cooled towards its glass-transition temperature there is an enormous increase in the viscosity so that the chemical structure is of secondary importance to the non-specific vitrification phenomenon.

In terms of the migration of molecules (whether solute or solvent), transport is affected by the free

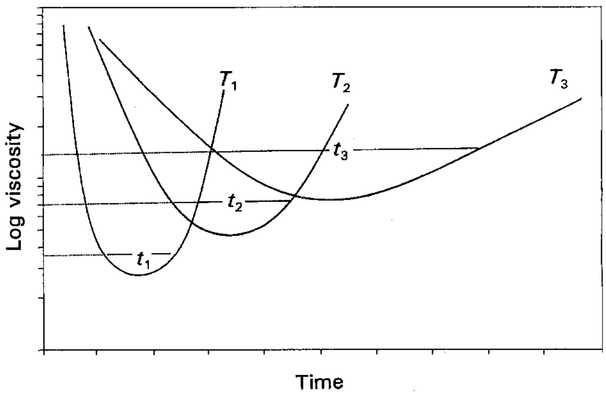

Figure 2 Schematic viscosity–time profiles for different temperatures where $T_1 > T_2 > T_3$.

volume, and the viscosity of a liquid can be related to the number of "holes", or more realistically to this free volume. This is demonstrated by the fact that the temperature dependence of the viscosity of a liquid is significantly lower at constant volume than at constant pressure, indicating that the volume facilitates molecular motions and that most of the thermal expansion at constant pressure goes into providing extra free volume [6]. This temperature dependence can be expressed in a linear form, where $f(T)$ is the free volume fraction at a temperature T, and $f(T_g)$ is the free-volume fraction

$$f(T) = f(T_g) + \alpha(T - T_g) \qquad (1)$$

at T_g which is considered to have the universal value 0.025 for all polymers [7]. The parameter α is the difference in the respective volume-thermal-expansion coefficients above and below the glass-transition temperature; this is deemed to have a universal value of $4.8 \times 10^{-4}\,K^{-1}$.

The free-volume theory can be reconciled with the thermal-activation approach, which is concerned with raising the energy of a flowing molecule over a potential energy barrier, by considering that the activation energy is made up of two contributions, the work required to make a hole for the molecule to jump into and the work required to free it from its immediate environment. The former is generally much larger than the latter in non-polar liquids and it is found to be almost constant for a large number of liquids. At higher temperatures ($\gg T_g$) a simple activation-energy approach should prevail while as the temperature is decreased towards T_g this is no longer valid since the energy of activation becomes dependent on the availability of a suitable hole for a segment to move into rather than being representative of the potential-energy barrier to rotation. Empirically, it has been noted that polymers that are still stable at temperatures in excess of $100\,K^{-1}$ above their glass-transition temperatures obey an Arrhenius relationship [8].

The diffusion of penetrating molecules in a liquified polymer also requires rearrangement of the relative molecular conformations within a mixture, and the behaviour is closely related to the rheological properties of the medium. However, it must be emphasized that the molecular and segmental motions are somewhat different for the two processes, especially when diffusion is compared to the bulk viscosity of the medium. For the diffusion of small molecules only relatively local co-ordination of segmental motions are involved. In viscous flow processes, there is an actual displacement of the matrix molecules, requiring more co-ordination of these segmental motions [9].

4. Materials characterization

The resin investigated in this study was a commercial unmodified bisphenol-A/epichlorohydrin resin (Shell 828) that had an epoxide group content of 5.128 mol kg^{-1} [10]. Using the relation $M_n = 2000$/epoxide content [11, 12] this corresponds to an average molecular weight of 390 g mol^{-1}. The density of the resin was measured and it was found to agree with the manufacturer's specifications (1160 kg m^{-3} at 298 K) and it was not found to change significantly over the temperature range of interest (293–373 K).

The viscosity of the resin was measured using a simple falling-sphere method and it was found to be extremely temperature dependent having a room temperature value (293 K) of 23–26 Pa s (Fig. 3). This method was limited to a temperature of 353 K at which point the sphere velocity was too high to attain consistent readings. A capillary-tube method was used for the higher-temperature (lower-viscosity) data [13]. The tube was calibrated against glycerol, which had a known viscosity (1.5 Pa s at 293 K). The resin was sucked into the capillary tube and one end was temporarily sealed to allow the resin to reach the required temperature. The seal was then broken and the flow time for the resin to pass through the tube under gravity was measured and correlated to the viscosity. All measurements were within ± 10% of the mean value. The diffusion coefficient of nitrogen in the resin, determined from bubble-dissolution rates, was found to increase by over three orders of magnitude for the temperatures measured (313–425 K) and it did not show any discrete change in its mechanism (Fig. 4). Details of the method of measuring the diffusion coefficient are described elsewhere [1, 2, 14].

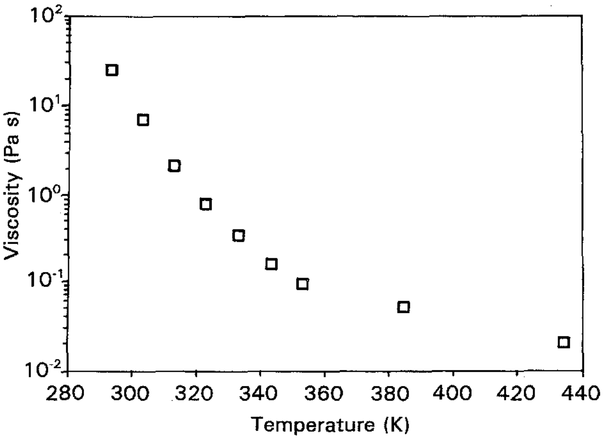

Figure 3 The temperature dependence of resin viscosity.

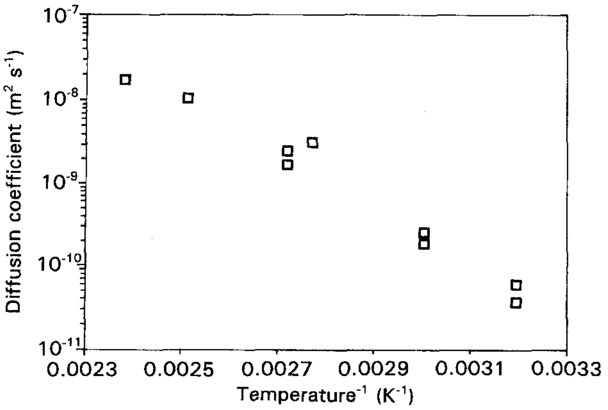

Figure 4 An Arrhenius plot showing the temperature dependence of the diffusion coefficient of nitrogen in resin.

5. Viscosity–high-temperature regime

If it is supposed that n molecules forming a liquid are bound to each other by bonds adding up to a total energy of nU, then to vaporize a single molecule would require an energy $U/2$, since each bond is shared between two other molecules provided the rest of the molecules join up so as to leave no hole in the liquid. If a hole is left, the vaporization of a single molecule will require an energy U. The return of a molecule from the single state to a hole prepared for it would result in the liberation of an energy $U/2$, and therefore the energy required to make a hole of molecular size in a liquid without vaporization of the molecule is $U - U/2 = U/2$. It follows that the energy required to make a hole in the liquid large enough for a molecule is the same as that required to evaporate a molecule without leaving a hole. This latter quantity is related to the latent heat of vaporization, H_v, and so the energy of activation for viscous flow, E_η, which is required for the provision of a suitable hole, should also be related to the heat of vaporization.

In reality, the activation energy for viscous flow is much smaller than this. In fact, experimental evidence has shown that liquids fall into well-defined groups. For molecules that have spherical fields of force, such as tetrachloromethane and benzene, H_v/E_η is about 3 whereas the ratio is approximately 4 for asymmetric molecules [15].

The resin molecule is a long molecule even before the polymerization reaction and it will not have a spherical field of force. The space required for it to flow by segmental motion is only a fraction of that occupied by a single molecule. If the solubility parameter, δ, of the resin is known, it is possible to calculate the notional molar energy of vaporization, ΔE, for a resin molecule using the relationship,

$$\delta = \left(\frac{\Delta E}{V}\right)^{1/2} \tag{2}$$

where V is the molar volume [16].

For the range of temperatures in the processing route, the enthalpy of vaporization and the energy of vaporization are approximately equivalent. The solubility parameter has been estimated from molar attraction constants and Hansen parameters to give $\delta \approx 20.45(\mathrm{J\,cm^{-3}})^{1/2}$ for this system [17]. The molar volume can be calculated from the density and the molar mass to give $\Delta E \approx 140\,\mathrm{kJ\,mol^{-1}}$. Using the empirical ratio $H_v/E_\eta = 4$ gives an activation energy for viscous flow of $E_\eta \approx 35\,\mathrm{kJ\,mol^{-1}}$.

Liquids that are held together by hydrogen bonds show an activation energy for viscous flow that changes markedly with temperature; for example, glycol, glycerol or water. The energy of activation of such substances consists not only of the fraction of the enthalpy of vaporization to break what may be termed *physical bonds* but also the energy to break hydrogen bonds, which must be broken when the liquid flows. As the temperature is raised the number of hydrogen bonds diminishes because of the thermal movements of the molecules, and the energy of activation will therefore decrease; that is, the larger is the number of hydroxyl groups, the more complex are the number of hydrogen bonds and the greater is resistance to flow [18].

The resin molecules used in this study had a hydroxyl group on their backbone which could interact with other hydroxyl groups on other resin molecules. Such interactions are thermally labile and this will partly explain any change in the activation energy for viscous flow, E_η, with increasing temperature along with the increasing free volume. If it is assumed that such interactions as hydrogen bonds are broken at temperatures where the viscosity is governed by thermal activation, then the cohesive energy density δ^2 will be lower than it was at room temperature. Removing the hydrogen-bonding component from the solubility parameter and applying the same treatment as before decreases the activation energy for viscous flow from 35 to $29\,\mathrm{kJ\,mol^{-1}}$ [17]. Even if some H-bonds are stable, this semi-empirical approach indicates that at high temperatures an Arrhenius relationship will describe the temperature dependence of the viscosity and that the activation energy will be in the range 29–35 $\mathrm{kJ\,mol^{-1}}$.

The absolute rate theory [19] states that the flow process is dependent on the height of the energy barrier, ΔE_η, the number of times the barrier is attempted, υ, and the flow volume, V_0.

$$\eta = \frac{kT}{\upsilon V_0} \exp\left(\frac{\Delta E_\eta}{R_g T}\right) \tag{3}$$

where, R_g is the universal gas constant and T is the absolute temperature.

These pre-exponential parameters are not known, but order of magnitude estimates can be made. If it is assumed that the number of times a resin molecule (or part of a resin molecule) attempts the barrier is inversely related to its vibrational frequency, then a value of 10^{13} s for υ is appropriate for this temperature range in a simple liquid [15]. The flow volume can be considered simply as a spherical volume which is related to the mean jump distance. The jump distances that are believed to occur in liquids are in the range 0.2–0.5 nm, or about one eighth of the volume of a polymer molecule [6]. If a value of 0.3 nm is taken, then the pre-exponential factor is 3.6×10^{-6} Pa s, at 293 K. This value will not change much over the temperature range considered. This Arrhenius relationship is compared with the free-volume theory and the experimental data in the next section.

6. Viscosity–low-temperature regime

At temperatures where free-volume effects are more significant than the molecular chemistry (as T_g is approached) the viscosity can be mathematically represented using the basic form of the Williams–Landelan–Ferry (WLF) equation [7] which is in the form of a shift factor, a_T, and is simply the ratio of the viscosity at a temperature T, relative to that at a reference temperature, T_0. The expression is given by

$$\log a_T = \frac{-C_1(T - T_0)}{C_2 + T - T_0} \qquad (4)$$

where T_0 is a reference temperature and C_1 and C_2 are constants characteristic of T_0 and, to a lesser extent, the polymer.

If the reference temperature is the glass-transition temperature of the polymer, T_g, then C_1 and C_2 take the values 17.44 and 51.6, respectively, which are considered to be *universal constants* [7]. This assumes that the glass-transition temperature is an "iso-free volume" state.

Hence a plot of $(T - T_0)/(-\log a_T)$ versus $T - T_0$ should be linear with a slope $1/C_1$ and with an ordinate intercept of C_1/C_2. Fig. 5 shows a plot of this type with reference temperature of 293 K for the experimental data. This value was chosen since it was the lowest temperature measured and it had the least scatter. A linear regression has been used to find the best-fit line through the low-temperature points. The two high points were not used in the regression as these temperatures were well in excess of the applicability of the free-volume theory and they would be better represented by an energy-barrier approach.

The data falls on a good straight line giving $C_1 = 7.69$ and $C_2 = 125.58$. These values can now be used to determine T_g using the inter-relations

$$C_{1T_g} = \frac{C_1 C_2}{C_2 + T_g - T_0}$$

$$C_{2T_g} = C_2 + T_g - T_0 \qquad (5)$$

Substituting the empirical and the universal constants into both equations yields values for T_g of 223 K and 219 K, respectively. These values for the T_g determined from the viscosity are comparable to those values calculated from the semi-empirical molecular-mass dependence of epoxy prepolymers [20] where,

$$T_g = 377.5 - \frac{6x10^4}{M_n} \qquad (6)$$

and M_n is the molar mass of the polymer.

Equation 6 gives a value of 223 K for T_g. The viscosity at T_g, determined from the WLF equation and the viscosity at 293 K (≈ 25 Pa.s), is 2.74×10^{11} Pa s, which is in agreement with many polymer systems [21].

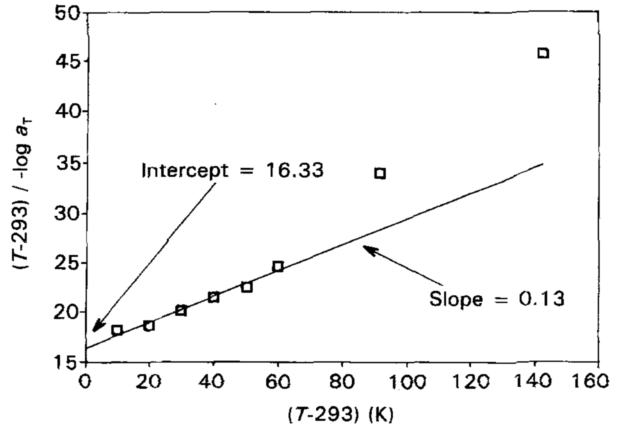

Figure 5 WLF plot for the viscosity of the resin with reference temperature of 293 K.

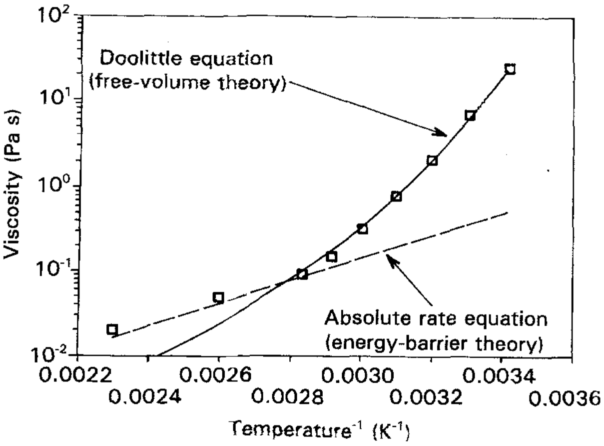

Figure 6 Viscosity data/Doolittle equation (Equation 7) ($B_\eta = 0.98$, $\eta_0 = 1.36\times10^{-6}$ Pa s). Absolute rate equation (Equation 3) ($E_\eta = 29$ kJ mol^{-1}, $kT/(vV_0) = 3.6\times10^{-6}$ Pa s)).

The viscosity can also be represented by Doolittle's semi-empirical equation [22].

$$\eta = \eta_0 \exp\left(\frac{B_\eta}{f(T)}\right) \qquad (7)$$

where B_η and η_0 are constants and $f(T)$ is the temperature dependence of the free volume (Equation 1). Fitting this equation to the viscosity data using the universal constants and $T_g = 223$ K, it was found that B_η was 0.98 which is very close to the accepted value of unity.

In fact, if the Arrhenius relationship (predicted by the absolute rate theory) is also applied it can be clearly seen that it begins to represent the data where the free-volume theory begins to fail (Fig. 6), although the pre-exponential constant is too speculative to allow a confident quantitative estimate of the point at which it becomes the dominant mechanism. This may not be too much of a problem for most composite systems since the resin will have begun to gel before the free-volume theory breaks down completely. It should be noted that at the gel point the processes of eliminating bubbles and laminate consolidation will effectively cease.

7. Comparison of viscosity and diffusion data

Many attempts have been made to predict the diffusion coefficient and/or its dependence on temperature from molecular considerations. Although expressions based on such models would seem to offer the advantage that the necessary parameters should be predictable from the inherent properties of the penetrating molecule and the resin, all models to date have one or more *adjustable parameters* except for some specific systems over limited temperature ranges [23, 24]. Models based on the free-volume theory have a definite advantage in that they can relate other measurable parameters such as the viscosity to the diffusion coefficient. As the viscosity of the resin is a required and generally known parameter, a correlation between the diffusion coefficient of molecules in the medium and the rheology is extremely valuable. One can modify the Doolittle equation (Equation 7) by noting that the diffusion coefficient is inversely proportional to the frictional resistance in accordance with molecular friction-theory [25], that is diffusion and viscous flow will be governed by the same frictional constant. In a very crude approximation one may say that this is proportional to the viscosity of the medium so that

$$D = D_0 \exp\left(\frac{-B_d}{f(T)}\right) \qquad (8)$$

The pre-exponential constant is a parameter that depends on the size and shape of the penetrant molecule. The parameter B_d can be interpreted as the efficiency of the use of the available free volume in the diffusion process [26].

It is interesting to compare the ln(viscosity) and diffusion-coefficient versus $1/T$ graphs. To make this comparison quantitative the temperature dependence is often expressed in terms of an activation energy. If the WLF equation (Equation 4) is used, it can be seen that the activation energy for viscous flow can be represented by

$$\Delta E_\eta = \frac{R_g d(\ln a_T)}{d(1/T)} \qquad (9)$$

Therefore, differentiating the generalized form of the WLF equation gives

$$\Delta E_\eta = \frac{2.303 R_g C_1 C_2 T^2}{(C_2 + T - T_0)^2} \qquad (10)$$

It is apparent that the activation energy for viscous flow is not a function of $(T - T_0)$ alone, and thus it is not surprising that although there is a universal a_T-function there is no universal ΔE. As one cannot compare "activation energies", apart from at a specific temperature (comparison with experimental data is difficult with the need to draw tangents to the curve), it is more useful to consider Doolittle's equations (Equations 7 and 8) for the viscous and the diffusion process directly. Fig. 7 shows the application of the Doolittle equation for viscosity and the modified form for the diffusion coefficient with the experimental data. The coefficients B_d and B_η are both unity within experimental error. The ratio of the Doolittle coefficients B_d and B_η is therefore also unity, implying that the efficiencies in utilising the free volume by a mass-transport process relative to momentum transfer are similar. This is interesting in that one would expect that a small molecule, such as nitrogen, would diffuse much faster in a resin than the diffusion of a resin molecule required for viscous flow. This implies that the temperature dependence of the diffusion process is characterized by the mutual action between molecules of the resin and not of that between the dissolved nitrogen and the resin.

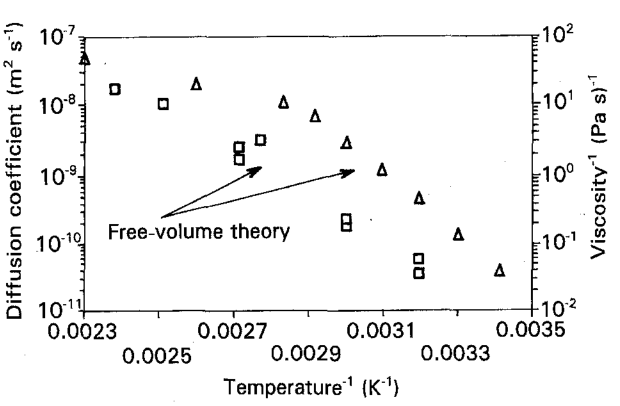

Figure 7 Free-volume theory applied to: △ the viscosity and (□) the diffusion data.

This interesting result can be considered in molecular terms. If the solute molecule is larger than the solvent then the motion of the solute cannot be described in terms of vibrations about an equilibrium position and displacements of the latter, instead, it must be described by Brownian motion. In this case it is clear that there will be a relationship between the viscosity and the diffusion coefficient of the solute. If the solute molecule is of comparable size to the solvent it will diffuse at the same rate as the solvent since the diffusive transport is completed only by the jumping of a neighbouring solvent molecule into the remaining void. This does not imply that a nitrogen molecule is of a comparable molecular size to a resin molecule. A semi quantitative argument states that polymers do not flow as single rigid units. Instead, small segments jump from one equilibrium position to another. The effective activation energy for diffusion is therefore not only a consequence of the transition of the diffusant to a new equilibrium position but also the motion of the resin into the initial position, that is the effective activation energy for diffusion must refer to the whole complex of particles participating in the transition, which for dilute solutions, as in the case of permanent gases in polymers, cannot markedly differ from that governing viscous flow. Hence, there will be closer relationship for low penetrant concentrations and large-size penetrants between the diffusion coefficient and the bulk viscosity.

8. Conclusions

It has been shown that the rate of diffusion of nitrogen gas in an epoxy resin is directly related to the viscosity of the resin, over the range of temperatures relevant to most practical composite processing operations.

This relationship is extremely fortuitous, since the gas diffusion coefficient in the resin is a necessary and more easily interpreted, but not readily available, parameter for prediction of bubble growth and collapse processes. It should also be applicable for any gas/resin system where the free volume is not significantly disturbed by the penetrating molecule, that is, at low penetrant concentrations. If the temperature dependence of the viscosity is known, T_g can be calculated and for this system it was found to agree relationship for epoxy prepolymers; that is, if the molecular weight of the resin is known then the temperature dependence of the viscosity can be predicted. Thus a knowledge of the viscosity of the resin and application of free-volume theory enables calculation of the temperature dependence of the diffusion coefficient for any temperature in the processing cycle.

The gas diffusion coefficient should also be predictable in a curing system where the viscosity is initially decreased by raising the temperature and then dramatically increases due to the cross-linking reaction. It will then be possible to determine the point at which the bubble is effectively "frozen" into the laminate and so to place limits on the time required to eliminate bubbles in the curing cycle. It must be remembered that the diffusion coefficient can only be as accurate as the model that predicts the viscosity; that is, if free volume theory applies over a limited temperature range in the processing cycle then this will also be the limit of the calculated diffusion coefficient. At higher temperatures the relationship between the viscosity and the diffusion coefficient may still prevail but the chemical structure of the polymer will play an increasingly important role in comparison to the non-specific vitrification phenomenon; that is, the viscosity can no longer be considered to be temperature dependent due to free-volume considerations alone. In this system, free-volume theory was found to be applicable over a wide temperature range above the calculated and predicted glass-transition temperature of the resin, that is, in a curing system, gelation of the resin will intervene before the free-volume theory breaks down for most processing options.

Acknowledgements

This work was carried out in the Department of Materials Science and Engineering at the University of Surrey with support from the SERC and Rolls Royce Plc.

1. J. R. WOOD, PhD thesis, University of Surrey, England (1992).
2. J. R. WOOD, and M. G., BADER, Proceedings of 8th International Conference on Composite Materials. Composites: Design, Manufacture and Application. (ICCM-8), Honolulu, edited by S. W. Tsai and G. S. Springer. (SAMPE, Covina, USA) paper no. 10-M, July (1991) 1–9.
3. H. EYRING, *J. Chem. Phys.* **4** (1936) 283.
4. S., GLASSTONE, "Textbook of physical chemistry" (MacMillan, London, 1948) p. 499.
5. T. G. FOX, and P. J. FLORY, *J. Phys. Chem.* **55** (1951) p. 221.
6. P. MEARES, "Polymers: structure and bulk properties", (Van Nostrand, London, (1965) p. 237.
7. M. L. WILLIAMS, R. F. LANDEL and J. D. FERRY *J. Amer. Chem. Soc.* **77** (1955) 3701.
8. J. M. G. COWIE, "Polymers: chemistry and physics of modern materials" (Intertext Books, Aylesbury, UK (1973) 201.
9. F. BUECHE, *J. Chem. Phys.* **20** (1952) 1959.
10. Shell Resins Epikote Technical Manual, E. P. 1. 1. 12, 3rd Edn (Shell, 1987).
11. H. BATZER and S. A. ZAHIR, *J. Appl. Polym. Sci.* **19** (1975) 585.
12. K. RAVINDRANATH, and K. S. GHANDI, *ibid.* (1979) 1115.
13. P. J. FLORY, *J. Amer. Chem. Soc.* **62** (1940) 1057.
14. J. R. WOOD, and M. G. BADER, Proceedings of the 9th International Conference on Composite Materials Composites: Modelling and Processing Science. (ICCM-9), edited by A. Miraveta (Univ. of Zaragoza and Woodhead, Zaragoza, Spain) Vol. 3 Madrid, 12–16 July (1993) Section 5, p. 567.
15. J. FRENKEL, "Kinetic theory of liquids" (Oxford University Press, 1946) p. 206 and p. 194.
16. J. H. HILDEBRAND, *J. Amer. Chem. Soc.* **38** (1916) 1452.
17. J. R. WOOD, and M. G. BADER, *J. Mater. Sci.* **29** (1994) 844.
18. G. C. PIMENTAL, and A. L. McCLELLAN, "The hydrogen bond" (Freeman, San Francisco, 1960) p. 212.
19. W. D. KINGERY, H. K. BOWEN, and D. R. UHLMANN, "Introduction to ceramics", (Wiley, New York, 1976) p. 704.
20. J. V. ALEMAN, *J. Polym. Sci.* **18** (Polymer Chemistry Edition), (1980) 2561.
21. F. W. BILLMEYER, "Textbook of polymer science" (Wiley, New York, 1962) p. 210.
22. A. K., DOOLITTLE, *J. Appl. Phys.* **22** (1951) 1471.
23. P. MEARES, *J. Amer. Chem. Soc.* **76** (1954) 3415.
24. W. W. BRANDT, *J. Phys. Chem.* **63** (1959) 1080.
25. F. BUECHE *J. Chem. Phys.* **20** (1952) 1959.
26. A. PETERLIN, *J. Macromolecular Sci. Phys. B* **11** (1975) 57.

Received 15 December 1993
and accepted 10 January 1994