QUANTITATIVE PROCESS MODELLING OF TRANSPORT
PHENOMENA AND BUBBLE DYNAMICS FOR POLYMER MATRIX
COMPOSITE MATERIALS

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To my father and mother.
Miss Elk  My theory by A. Elk. Brackets Miss, brackets. This theory goes as follows and begins now. All brontosauruses are thin at one end, much much thicker in the middle and then thin again at the far end. That is my theory, it is mine, and belongs to me and I own it, and what it is too.

Presenter  That's it, is it?

Monty Python's Flying Circus

16-11-72
ABSTRACT

The problem of porosity has been addressed in relation to process modelling of composite materials. The material and processing inter-relationships, critical to the production of a void-free laminate, have been investigated and it is considered that entrapped bubbles can be collapsed and nuclei can be suppressed from growing, or totally inactivated, by manipulating the process variables either prior to, or during the cure operation. As these processes are time dependent, models based on mass diffusion theory have been utilised which can predict the rate of growth and collapse of bubbles in the resin precursor. Models have been evaluated that predict the prerequisite driving force and diffusion coefficients and their respective interactions with the processing variables from the chemistry and rheological properties of the resin, using fundamental thermodynamic correlations and solubility parameter theory. Simple experimental methods have been developed to measure the model input parameters based on conventional techniques and bubble dynamics. The model relationships have been compared to the measured data and were found to successfully predict gas bubble behaviour for a range of gas concentrations, temperatures and hydrostatic pressures.

The presence of water in the resin has been investigated primarily to determine its effects on the behaviour of bubbles. The water-resin system exhibited an anomalous sorption isotherm under ambient conditions and the diffusion coefficient was found to be a function of temperature and water concentration. A thermodynamic analysis indicated that water was present in several forms; molecularly dispersed, associated and bound to the resin molecule. The growth of bubbles due to water diffusion for different conditions was found to be related to basic thermodynamic quantities and the diffusion coefficient of the molecularly dispersed component. Relationships have been also found between mass transport and momentum transfer phenomena for the gas and water-resin systems.

Experimental evidence and model predictions suggest that certain currently used composite processing practices are detrimental to the production of a void-free composite.
ACKNOWLEDGEMENTS

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1.5 POROSITY IN COMPOSITES

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The objective behind the processing of thermosetting matrix composite materials is to produce a void-free laminate 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 compaction. In order to process high performance structural laminates consistently, it is necessary to identify the material and processing inter-relationships which are critical in attaining a high quality composite part.

When composites were first introduced the process variables were selected by empirical methods. These have several disadvantages; they are restricted to small ranges of the process variables, can not be generalised for different materials and geometries and last but not least, 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 of the processing variables, as well as facilitating the real time control of the manufacturing process.

This chapter introduces the principles behind composite processing and reviews some of the fabrication techniques. It also introduces the problems associated with porosity and discusses the detrimental effects of voids on the mechanical properties of the final composite that have provoked this investigation.

1.1 PRINCIPLES OF COMPOSITE PROCESSING SCIENCE

In order to analyse the whole processing operation it is first necessary to separate the contributory factors into unit processes. The second stage is to develop quantitative models for each unit which allow simulation and prediction of the effects of the controllable variables; composite formulation, fabrication pressure, temperature and time. These unit models may then be incorporated into a master model which simulates the whole operation and allows processing schedules to be optimised. The final stage is to develop "expert systems" [Roberts (1987)] using these models which
may control the process interactively. The more important unit processes are discussed briefly.

1.1.1 Heat Transfer

Virtually all composite processing operations involve heating and cooling. Heat transfer often plays a dominant role because the polymers used as matrices and the reinforcement have low thermal conductivities and there is often a narrow interval between the process temperature and the temperatures at which unacceptable matrix degradation occurs. For these reasons the thermal properties of the composite often have a critical influence on the processing time and hence the production rate.

Although standard heat transfer equations may be used, empirical corrections are often required due to the inadequacies of methods for calculating thermal conductivities of multi-phase materials (fibre/air/resin) and undefinable boundary conditions [Thornburgh and Pears (1965)][Springer and Tsai (1981)]. The thermal characteristics of the system will also change during cure as well as the heat transfer between the layers of fibre, cloth or mat with applied pressure. Resin flow will change the heat capacity and conductivity of the porous plies throughout the cure schedule [Kenny and Nicolais (1988)].

Accurate prediction of the temperatures at all points within the moulding is of critical importance for all the subsequent unit models since many of the key parameters are temperature dependent. Figure 1.1 shows how heat can effect some of the critical processes which may play an active role in more than one unit model.

1.1.2 Cure Process

Thermosets are reactive systems which polymerise and crosslink when heated [Flory (1953)]. There are often competing chemical reactions, some of which are strongly exothermic, which may dominate at different temperatures [Hagnauer et al.(1982)] and may lead to over heating in thicker sections [Hanks et al.(1988)].
A typical thermoset is a pasty solid or viscous liquid at the start of the process. On heating its viscosity first drops, often dramatically, but then increases as the cure reactions proceed. It becomes effectively solid at the point of gelation although the curing reactions may continue for some considerable time [Sacher (1973)]. Modelling the curing process requires that the viscosity, the degree of cure and the rate of heat evolution are known at any time during the process and for all relevant thermal histories. It is generally not possible to develop the model directly from chemical kinetics and therefore experimental measurements must be made using thermal analysis and thermo-rheometry. Secondary factors, such as the effect of ageing of the polymer during storage and contamination by moisture absorption [Penn (1979)], should also be considered.

1.1.3 Consolidation

The liquid matrix must impregnate the reinforcement at some stage of the processing operation. The infiltrating resin can displace air, allowing wetting of the reinforcement. Consolidation of the pack is required to fully compact the composite which usually involves resin flow out of the laminate. Critical factors are the flow of liquids through porous media and the wetting characteristics of the fibre/resin system. Simple models based on the flow of a liquid through an array of cylindrical rods provide
some insight but do not give a quantitative match with experiment [Lindt (1986)]. The practical problem is to ensure that the process parameters allow sufficient time for full consolidation to occur before the matrix gels.

1.1.4 Bubble Kinetics

Porosity may be a consequence of inadequate infiltration or consolidation. It may also occur due to the formation of bubbles from volatiles such as dissolved or entrapped air, moisture or solvents in the system. It is necessary therefore to know the conditions under which bubbles nucleate, grow and collapse, which will be a function of concentration of the volatile, temperature and pressure.

Porosity may be eliminated if the resin hydrostatic pressure is sufficiently high to force the volatiles into solution [Loos and Springer (1983)]. They may ultimately diffuse out of the laminate after processing as the laminate comes to equilibrium with its environment. At this point it is important to distinguish between the pressure applied to the laminate pack and the actual hydrostatic pressure within the resin. In the autoclave process, consolidating pressures of 5-8 atmospheres (5.05x10^5-8.08x10^5 Pa) are often used but a vacuum is drawn beneath the sealing membrane. Under these circumstances the consolidating pressure is largely reacted against the solid-to-solid contact in the reinforcement and the actual hydrostatic pressure in the laminate resin is much less than one atmosphere [Lindt (1983)].

1.2 PROCESS CONTROL

Process control can be a predictive or an interactive technique. Figures 1.2 and 1.3 show the process model components and how each can be used to develop a cure schedule. Figures 1.4 and 1.5 show the current technology in autoclave closed-loop control. The basic requirements are first that a temperature-pressure/time profile be determined either by modelling or empirically. Secondly the means must be provided to monitor the critical parameters, generally pressure and temperature, as they
Figure 1.4 Autoclave Closed-Loop Control: Generation 1

Figure 1.5 Autoclave Closed-Loop Control: Generation 2
are fundamentally the only parameters that can be changed once the composite has been committed to the processing cycle. For well established processes it is often adequate to monitor these at fixed positions outside the moulding, it is however, more desirable to incorporate sensors within the component. Thermocouples may be easily incorporated into both tool and laminate whereas more expensive pressure transducers will usually be only set in the tool. Dielectric monitoring is especially useful for monitoring the cure process in thermosets and disposable micro-circuit devices are now available for this purpose [May et al. (1976)] [Yokota (1977)]. With effective monitoring it becomes possible to control the process variables (pressure, heating, cooling, etc.) which can maintain the process along the optimum path.

1.3 REVIEW OF FABRICATION PROCESSES

One of the principal attractions of composite materials is their ability to be tailored, so that their properties match the service requirements. This versatility also extends to the number of processing possibilities. Overall it must be borne in mind that the objective of any manufacturing process is to produce components which meet the design specification, may be produced at the required rate, are reliable, durable and cost effective.

It is beyond the scope of this work to classify all the processing alternatives as materials and production methods are becoming much more versatile and traditional boundaries are no longer maintained. One can however, make simplified classifications and these are discussed in the following.

1.3.1 Web Reinforcement Processes

In these processes the reinforcement has already been converted into an intermediate sheet or web form. This might be a woven cloth, a continuous or discontinuous random mat, a pre-impregnated warp sheet (prepreg) or sheet moulding compound. The main variations are the methods of resin impregnation which can occur
before or during moulding. In the former case, where the web is impregnated prior to moulding, the resin may be applied by heating the resin to reduce its viscosity or as a solution in a volatile solvent which is subsequently evaporated (figure 1.6). The standard method is to cast the resin onto a backing film (usually polyethene or paper) with the dimensions controlled by a doctor blade. The fibre web is then sandwiched between two layers of resin film and passed between heated rollers which impregnate the fibres with the resin (figure 1.7). This is usually carried out in a continuous process although drum winding methods can be used for small-scale operations. The solvent production method can lead to porosity in the final part if the volatile component is not fully removed, while melt impregnation is limited by the possibility of premature curing.

Once completed the impregnated sheet can then be stored (usually at low temperatures as both resin and curing agent are present) or used directly in contact or compression moulding processes, the former often in an autoclave.

Impregnation can also be effected during moulding by impregnation of dry reinforcement with the web laid into the mould and the resin applied manually or injected. Cure may be at ambient or elevated temperatures and with or without applied pressure. Compression moulding can also be done in this way although granular-solid matrix, which is easier to handle, can be used as well as liquid resins, with infiltration performed at elevated temperatures and pressures.

1.3.2 Direct Roving Processes

In these processes the reinforcement, in the form of a spool of continuous tow or roving, is converted directly into the component. There are three basic processes, the first of which is a variant of contact moulding.

1) Spray up: The reinforcement is fed into a special applicator head where it is chopped into short lengths (typically 25-50mm) and sprayed by an air jet onto the mould surface. Simultaneously another spray applies liquid resin so that both fibre and resin are delivered in the correct ratio at the mould surface.
Figure 1.6 Solvent Prepreg Process

Figure 1.7 Melt Impregnation Process
2) Filament winding: The continuous filament is wound onto a mandrel in layers to form the component. The resin can be applied by spraying the mandrel or by pre-impregnating the roving in a bath of liquid resin.

3) Pultrusion: Continuous reinforcement is pulled through a heated die. The matrix may be applied by passing reinforcement through a bath of liquid resin before entry to the die, injecting at the point of entry or by pre-impregnating as a separate operation.

1.3.3 Discontinuous Reinforcement-Moulding Compounds

In this case short fibres or particulate material may be made into sheet products but are often processed as moulding compounds for compression or injection moulding. These incorporate resin in the liquid form, as a pasty solid or as solid granules. The charge of pre-compounded material needs to be plasticised by heating before the moulding processes can occur.

1.4 AUTOCLAVE LAMINATING PROCESS

Some of the processes listed above are limited in terms of the geometry of the final part or the type of reinforcement used. For high performance structural applications where reliability, quality and durability are more critical than the cost, laminates are often based on pre-impregnated web or sheet (prepreg) and are processed in an autoclave [Dave et al (1987)] [Purslow and Childs (1986)]. These sheets consist of collimated sheets of fibre, or cloth, impregnated with a thermosetting resin which are laid-up in a prescribed orientation to form a laminate which is subsequently subjected to heat and pressure (positive and vacuum) within the autoclave chamber. Consolidation of the laminate occurs and the resin undergoes the chemical crosslinking reaction. This method allows precise control of the fibre orientation as well as controlling the fibre/resin fraction before processing.
A typical cure cycle is shown in figure 1.8. Initially the pack is bagged and the entire tool is moved into the autoclave chamber where a is vacuum drawn under the sealing membrane which remains throughout the whole cure schedule. The temperature is then ramped from ambient, resulting in a rapid decrease in the resin viscosity and the onset of exothermic chemical reactions (figure 1.9). At some point on the initial heating ramp the resin viscosity reaches a minimum and then begins to increase. Up to this point little consolidation should have occurred other than that associated with the wetting between the plies. At the temperature hold, the autoclave pressure is applied and laminate consolidation is initiated. One final ramp and hold is used to complete the cure before the whole chamber is cooled to ambient temperature by a cooling gas. For each laminate, resin system and its associated tooling there will be a particular combination of autoclave conditions which will produce a satisfactory laminate - there is no universal cure cycle.

The main advantage of the autoclave is that the pressure is applied by a gaseous environment (either air or nitrogen) which is heated and circulated. This encourages uniform heating and compression over the whole prepreg pack (often assisted by heating the mould) which gives greater control over the process variables to produce laminates with high dimensional tolerances and low porosity. However, as a processing route it is slow, since it involves the labour intensive lay-up of laminae, bleeder plies (to soak up excess resin), breather plies (for the removal of emanating gases) and release films (figure 1.10). Although sections of the process are becoming mechanised it is still an expensive method to produce a composite laminate and does not yield the part-to-part reliability that is required for the large complex structures currently on the drawing boards [Roberts (1987)]. One of the major problems in attaining this part consistency is the presence of voids in the final composite laminate [Tang et al.(1987)].
Figure 1.8 Cure Cycle Temperature/Time Profile

Figure 1.9 Cure Profile
1.5 POROSITY IN COMPOSITES

Voids in composites should be reduced to a minimum level as they lead to variability of the final part which can affect the mechanical properties. Apart from large cavities due to gross defects in the manufacturing operation, there are two basic types of void in composite materials:

i) voids along individual fibres (which may be spherical or be elongated parallel to the fibres and relate in diameter to the fibre spacing) typically in the range 5-20μm (figure 1.11).

ii) voids between laminae and in resin-rich pockets.

Such voids can be readily detected in polished sections and one method of determining the volume fraction of voids, $V_v$, is to make a quantitative analysis, using point counting techniques on micrographs (figures 1.12 and 1.13). This approach

Figure 1.10 Autoclave and Moulding Pack

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allows an evaluation of the type and distribution of voids but requires a large number of sections to be examined before a reliable value of $V_v$ can be determined. A more simple and commonly used method is based on density measurements. The volume fraction of voids is defined as,

$$V_v = 1 - (V_f + V_R)$$  \hspace{1cm} (1.1)

where $V_f$ and $V_R$ are the fibre and resin volume fractions, respectively. Hence,

$$V_v = 1 - (W_f / \rho_f + W_R / \rho_R)$$  \hspace{1cm} (1.2)

where $W_f$ and $W_R$ are the fibre and resin weight fractions and $\rho_f$ and $\rho_R$ are the fibre and resin density, respectively.

The volume fraction of voids in a composite can be subsequently calculated from the weight of the fibres and the weight of the resin in a known weight
Figure 1.12 Micrographs of Poor Composite - Dark regions are due to voids

Figure 1.13 Micrographs illustrating poor bonding and voids in a crossply laminate
of composite. However, since $V_v$ is determined from the difference between two relatively large values and the density measurements are not very reliable, the accuracy in determining $V_v(\%)$ is usually $\pm 0.5\%$.

Ultrasonic scanning techniques (C-scan) can also be used for the non-destructive examination of void distributions and delamination faults in composite materials [Angell and Markham (1980)]. The test sample is scanned by an ultrasonic probe and the attenuation of the ultrasonic signal by the material is measured to give a two or three dimensional image of the sample. This method is extremely useful in the quality control of sheet material (figure 1.14).

1.5.1 Origin of Voids

The most common cause of voids is the inability of the resin to displace all the air which is entrained between the fibres during impregnation or entrapped between the plies during the lay-up process. The rate at which the reinforcement passes

Figure 1.14 C-Scan of Multiply Laminate - Light Regions are voids and delaminations
through the resin (or the resin passes through the reinforcement), the viscosity of the resin and the wettability or contact angle between the resin and reinforcement surface are of the utmost importance since they will affect the removal of entrained air [Bascom (1965)]. Voids may also be caused by entrapped air bubbles in the resin, which are carried into the composite and not expelled, by dissolved air which desorbs during the temperature/pressure cycle or from volatile components of the resin formulation which are not completely removed during impregnation and which subsequently volatilise. Water may also be absorbed into the resin from humid air, as a consequence of the polar nature of the epoxy molecule and may act as a volatile, stabilising existing voids [Springer (1982)].

The occurrence of voids has been documented thoroughly in thick laminates and is often associated with the inter-ply regions [Browning (1990)]. Difficulties in the handling or lay-up procedures or use of excess bleeder plies in the pack can lead to air entrapment. There must also be porosity due to the fibre packing density since misaligned fibres will create spaces where resin is lost [Purslow and Childs (1986)]. A good quality laminate clearly requires that spaces between fibres should be completely filled with resin, which will depend primarily on the ability of the resin to infiltrate thoroughly the spaces between fibres.

Although the exact mechanism of void formation is not yet fully understood, in the most general case it can include mechanical entrapment as well as nucleation of stable bubbles in the resin phase. This is in agreement with the inter-ply porosity observations in that mechanically entrapped voids are likely to occur during the lay-up and the ply interface is a resin-rich region where bubbles can grow and coalesce. Although a reduction in void content can be attained by thorough degassing of the resin prior to impregnation and by utilising careful lay-up techniques [Paul and Thompson (1965)], the finite contact angle between the resin and reinforcement, which is indicative of non-perfect wetting, represents the inherent difficulty in producing a void-free structure.
1.5.2 Influence on the Mechanical Properties

Some of the early studies to determine the effect of voids on the mechanical properties of composite materials remain quantitatively inconclusive because of the inability to control other material parameters properly, such as resin content, while varying the void content [Broutman (1967)]. Although reliable relationships have not yet been found for relating void content to tensile or flexural strengths, their effect on the interlaminar shear strength and compressive strengths has been identified (see below) [Fried (1965)] [Hand (1965)]. Voids can also limit the durability of these materials by providing paths for environmental penetration into and through the composite [Ashley (1985)] [Browning (1978)] [Apicella et al. (1979)].

Experiments have shown a virtually linear relationship between the resin tensile strength and interlaminar shear strength [Paul and Thompson (1965)]. The presence of voids was found to limit the interlaminar shear strength whatever the tensile strength of the resin tested and a linear relationship was found between the void content and the reduction of the interlaminar properties, except at very low void levels. Similar empirical relationships have been found between void content and the compressive strengths and moduli [Fried (1965)]. From an evaluation of a large amount of experimental data Judd and Wright (1978) concluded that regardless of resin type, fibre type and fibre surface treatment, the interlaminar shear strength of a range of composite materials decreases by about 7% for each 1% of voids up to a total void content of about 4% (figure 1.15) [Angell and Markham (1980)].

While the average void content in most composites range from approximately 1% to 5%, the voids displace only resin, i.e. if the fibre volume fraction is 0.7 the resin volume fraction is 0.3, so for an average void content of 1%, 3.3% of the resin volume must be void and similarly for an average void content of 5%, 16.7% of the resin must be void. Furthermore, the void distribution is non-uniform and voids tend to collect, producing local regions of high void density. In these areas the shear transfer through the resin is effectively eliminated and thus initial failure, corresponding to a bundle fracture, is anticipated in the weakest of these small volumes, i.e. the
opportunity for the fibres in a small volume of a composite to behave like a bundle of unconnected fibres is introduced by the presence of voids [Rosen (1964)]. The transverse ply strength has been shown to be significantly affected by void content (figure 1.16) [Hull (1981)].
Figure 1.15 Reduction in Interlaminar Shear Strength with Increasing Void Volume Fraction

Figure 1.16 Variation in Transverse Tensile Strength with Void Content
# CHAPTER TWO

**NUCLEATION OF BUBBLES**

## 2.1 NUCLEATION THEORY

- 2.1.1 Heterogeneous Nucleation
- 2.1.2 Possible Sources of Nuclei
- 2.1.3 Pre-Pressurisation

## 2.2 PORE PENETRATION

- 2.2.1 Equilibrium Considerations
- 2.2.2 Kinetics of Pore Penetration

## 2.3 NUCLEATION OBSERVATIONS

- 2.3.1 Analysis of Nucleation Observations

## 2.4 SUMMARY
2. NUCLEATION OF BUBBLES

Apart from mechanical entrapment there are two fundamental processes involved in the formation of a bubble of visible size. They are nucleation and growth. The former seems to be rather ill-defined in terms of the processing of composite materials. No thorough analysis of the phenomenon has been found in the literature. The possibility of "nucleation" in a composite system, in conjunction with experimental observations is assessed in the following.

When a new phase is formed by a nucleation and growth process, it must start as a very small region and then increase in size. This may occur homogeneously (freely in the volume of the original phase) or heterogeneously (on surfaces or foreign particles) [Uhlmann and Chalmers (1966)]. Initially it has a high surface-to-volume ratio which tends to make it unstable because of its high surface energy. The pressure difference, $\Delta P$, across the bubble interface is given by the Laplace equation,

\[
\Delta P = \frac{2\gamma}{R} \quad \text{.... (2.1)}
\]

where $\gamma$ is the liquid/vapour interfacial tension and $R$ is the radius of the bubble.

Formation of a stable bubble requires a vapour pressure equal to the sum of the local hydrostatic pressure plus the pressure due to the surface energy, i.e. taking the surface tension forces for air/resin as 0.035 N/m (Section 6.1), it follows that a bubble 1mm in diameter is subject to a pressure of $1.4 \times 10^3$ Pa (0.0014 atm.) more than the resin around it, while a bubble of diameter 1µm would similarly be subjected to a pressure of $140 \times 10^3$ Pa (1.4 atm.). Unless the resin is saturated with dissolved gas to at least a corresponding amount the bubble will not be stable and will dissolve in the resin. Another way of looking at the Laplace equation (equation 2.1) is that application of external pressures, in excess of the pressure inside the bubble, will suppress bubble growth.
It is of interest to examine the effect of bubble size and the associated pressure, as dictated by equilibrium considerations, to construct an equilibrium map. This type of map is a simplification of the theory for determining inflation pressures required in the formation of structural foams. Gent and Thompkins (1969) related the effect of the elasticity of the medium as well as the surface tension forces to the critical inflation pressure. Although this has been shown to work well in the case of elastomeric foams it does require another input parameter, namely the shear modulus of the uncured resin, which is not readily available. It must also be remembered that in the case of a thermosetting resin there will also be a viscoelastic component since the viscosity will also play an important role in determining the inflation pressure. Unfortunately there does not seem to be a theory that relates the critical pressure for growth to the rheological properties of the fluid medium. The following map (figure 2.1) is based purely on the equilibrium considerations dictated by equation 2.1 and the curves indicate stable bubble equilibrium states for liquid resin pressures. Growth will take place above the lines and collapse below the lines for any given resin pressure. The region below the line \( P=0 \) represents the bubble pressure to overcome only the resin surface tension forces. As the resin pressure increases, higher total pressures within the bubble must be attained in order to create stable bubbles, with smaller bubbles requiring much higher pressures than larger bubbles due to surface tension forces. The question arises at this point as to how bubbles are ever nucleated if such high degrees of supersaturation are required even to stabilise them.

2.1 NUCLEATION THEORY

The rate of nucleation can be described by classical nucleation theory [Fisher (1948)]. It states that a definite quantity of work, \( W \), is associated with the thermodynamically reversible formation of a vapour bubble in the interior of a liquid. The probability of a nucleus being formed is reduced by the factor \( \exp(-W/kT) \), where \( k \) is the Boltzmann constant and \( T \) is the absolute temperature. If there are \( N \) similar places in the system where a nucleus could form and if \( N \) is sufficiently large then nuclei are expected to be found at some of them, i.e. the number of nuclei, \( n \), in the
system is given by \( n = N \exp(-W/kT) \). If the nucleus is very small and can form equally well at every place in the system, \( N \) can be expected to be the same order of magnitude as the number of atoms or molecules in the system. When the probability of forming a nucleus is the same everywhere, the system is in a state suitable for homogeneous nucleation.

The work of nucleation can be expressed as the net work of the formation of a cavity and the work required to fill it with vapour plus the work of formation of the liquid/vapour interface,

\[
W = \gamma A - (pV - PV)
\]

where \( P \) is the pressure of the liquid, \( \gamma \) is the liquid/vapour interfacial tension, \( A \) is the interfacial area, \( V \) is the volume and \( p \) is the vapour pressure.
Figure 2.2 Work required for reversible formation of a bubble of radius $R$ in a liquid under negative pressure

Figure 2.2 shows the relationship between $W$ and $R$ indicating that the condition for continued growth is that the radius should exceed $R^*$, the critical radius. The associated critical activation energy is given by,

$$W_{\text{max}} = \frac{16\pi \gamma^3}{3(p-P)^2} \quad \ldots \quad (2.3)$$

This equation for the work required to form a critical nucleus differs from that usually seen in standard texts on nucleation theory, which generally approach nucleation using the Gibbs free energy and deal with the formation of an incompressible phase, i.e. crystals, condensates etc. As a bubble is not incompressible it should be noted that the Gibbs free energy of formation and $(p-P)$ are not equivalent.
The rate of nucleation, \( \frac{dn}{dt} \), is therefore given by,

\[
\frac{dn}{dt} = BN \exp\left(-\frac{W_{\text{max}}}{kT}\right) \quad \text{.... (2.4)}
\]

where \( B \) is the frequency of encounters of a nucleus with atoms or molecules of the precipitating substance in the parent phase. \( B \) can be determined from the theory of absolute reaction rates, using \( kT/h \) as an order-of-magnitude estimate, where \( h \) is Planck's constant [Fisher (1948)].

It quickly becomes apparent that homogeneous nucleation theory is not directly applicable to a composite system. For any reasonable reduction of pressure, resin begins to foam and this phenomenon is utilised quite successfully in the degassing operation (sections 4.1 and 6.3.1). Degassing requires energy for the phase transition of dissolved gas or vapour to a nucleus of gas or vapour molecules. Since \( \Delta P \), the pressure difference across the bubble interface, is related to \( R^* \) by equation 2.1 it can be shown that for a reduction in pressure from 1 to 0.1 atmospheres, a typical vacuum drawn during degassing, the equilibrium bubble radius is \( = 7 \mu m \). Substituting this into equation 2.3 gives a very large value of \( W_{\text{max}}/kT \) which corresponds to a vanishingly small value for the rate of nucleation (equation 2.4). In fact the predicted radius is several orders of magnitude larger than that expected from molecular fluctuations [Frenkel (1948)]. Numerous calculations have been made on the theoretical strength of a pure liquid [Fisher (1948)], usually based on the formation of a spherical cavity with an interatomic radius, which indicate that pure liquids are not expected to fracture and form bubbles unless negative pressures (hydrostatic tensions) or substantial superheats are applied to the system.

This leads to the conclusion that under normal processing conditions homogeneous nucleation is not a realistic consideration and that there must be other factors that facilitate bubble formation.
2.1.1 Heterogeneous Nucleation

Homogeneous nucleation can be directly extended to include the presence of a substrate [Bankoff (1957)]. A surface effectively reduces the barrier to nucleation represented by the surface energy and a nucleus will preferentially form at these sites. When a nucleus forms on a substrate, in addition to the creation of the nucleus/matrix interface (as in homogeneous nucleation), some high energy substrate/matrix surface is replaced by lower energy substrate/nucleus surface, thereby resulting in a smaller surface contribution (figure 2.3).

The work of formation for a nucleus of critical size on a flat substrate is now,

\[
W_{\text{max}} = \frac{16\pi r^3}{3(p-P)^2} \frac{2+3\cos\theta - \cos^3\theta}{4}
\]

where \(\theta\) is the contact angle between the nucleus and the substrate.

Equation 2.5 shows that the thermodynamic barrier to nucleation on a substrate should decrease with increasing \(\theta\) and approach zero as \(\theta \to 180^\circ\). If such a contact angle were attained then the resin would not be able to tolerate any reduction in pressure without a nucleation event. Since the advancing contact angle of a commercial epoxy resin on an E-glass fibre surface (a major source of substrate in a composite system) is found to lie between 37° and 80°, depending on surface roughness [Bascom (1965)], it can be concluded that plane surfaces can also be eliminated from consideration. It is possible that some foreign microscopic debris has a contact angle with the resin that is conducive to a nucleation event for reasonable pressure reductions. An order of magnitude calculation does indicate that for nucleation to occur in the resin, for moderate pressure reductions, the contact angle \(\theta\) of the hemispherical cap on the plane substrate would have to be very close to 180°, i.e. the substrate must be virtually unwetted by the resin. This does not appear to be feasible since even in a model system, as in the case of water on paraffin (which is commonly considered not
to be wetted), the average contact angle is $95^\circ$ if quite smooth [Adam (1941)]. Although it is difficult, if not impossible, to determine the substrate available in a resin system a priori, it does seem a reasonable assumption that plane surfaces, whatever the nature of the solid material, are not responsible for the low nucleation threshold of a resin system.

Fibre surfaces can not be considered to be plane due to curvature but it has been shown that it is even more difficult for a liquid to pull away from a surface projection than from a plane surface [Bankoff(1957)] and correspondingly less difficult to pull away from a cavity. The latter will be discussed in more detail in the following section. It can be concluded that the macroscopic surfaces of the fibres do not act as nucleation sites for bubble formation in a composite system.
2.1.2 Possible Sources of Nuclei

It has already been mentioned that pure liquids can theoretically withstand high negative pressures and be heated well in excess of their boiling points without the onset of bubbling. This will only occur if the system is very clean [Galloway (1954)]. Ordinary liquids begin to cavitate at the point when the local pressure equals the vapour pressure of the liquid [Knapp (1958)]. Epoxy resins degrade before boiling but volatile components within the resin (dissolved gases, water, solvents, etc.) and impurities could act as weak spots which cause the system to rupture with small reductions in pressure, forming bubbles. Liquids generally contain a number of impurities only a few of which could be expected to produce a weak spot. These are known as cavitation nuclei and various forms have been proposed [Harvey et al. (1947)].

The physical state of a dissolved impurity is quite different from the undissolved one. The theory of solutions indicates that a dissolved impurity should have very little effect on the cavitation threshold of the base liquid, i.e. the impurity is dispersed molecularly throughout the system. This leaves undissolved solids, immiscible liquids and free gas as possible sources of weak spots in a composite system.

Undissolved solids are abundant in a commercial resin. The viscosity of liquid resins enables dust and other airborne particles to become entrapped along the processing route. For a moderately viscous resin exposed to the atmosphere, where solid particles will have a density in the range of 2-3 g/cm³, it can be concluded from Stoke's law that microscopic particles have a good probability of remaining in suspension.

A composite has numerous fibre/resin interfaces but the adhesive force across a well-wetted surface is high and even if the degree of wetting is poor, is still probably higher than the effective tensile strengths observed in normal liquids [Pease and Blinks (1947)]. Plesset (1969) has shown that for a wetted solid, rupture will occur at a location other than the particle and concluded that a wetted particle had a
greater adhesion for the liquid than the cohesion of the liquid for itself. This is in agreement with the earlier theoretical work of Bankoff (1957) for rupture at plane surfaces (Section 2.1.1). It can also be concluded that if the fibre/resin interface was inherently weak then it would be impossible to prevent the fracture of the resin and all composite systems would have impossibly high void contents, i.e. a void associated with every fibre/resin interface.

Resins need to be mixed with curing agents and often accelerators to initiate the crosslinking reaction. These liquids are not totally miscible with the resin. Experiments tend to indicate that the interface between immiscible liquids is not weak enough to explain the lack of tensile strength of a liquid [Weyl and Marboe (1949)]. This reduces the range of impurities, that can be considered responsible for the weak spots in a resin system, to undissolved gases and unwetted solids.

The Laplace equation (equation 2.1) indicates that the resin would have to be highly supersaturated with gas for a microscopic bubble to remain stable. In most process situations this is not the case and a gas bubble should collapse. This leads to the problem of why nuclei persist in a resin system.

The main theory to emerge is that of Harvey (1947) who, working on the formation of bubbles in blood, suggested that gas is entrapped in small crevices of unwetted particles. This seems a tenable concept in that it provides a means whereby the pressure in a gas bubble can be maintained lower than the pressure in the liquid so that the bubble will not collapse even when the liquid is unsaturated.

In the case of a conical cavity with a rounded bottom the radius of curvature of the meniscus continuously increases as the bubble grows from the apex to a macroscopic size, provided it is well wetted (figure 2.4). If the bubble is approximately spherical at the critical radius, the work of formation will be approximately given by equation 2.3, since for complete wetting $\theta=0^\circ$ in equation 2.5. It appears that a well-wetted cavity will not lead to significant reductions of the fracture pressure. If, however the cavity is poorly wet (say $\theta=90^\circ$) the situation is entirely
different (figure 2.5). The radius of curvature of the meniscus begins at a very small value at the apex, but rapidly becomes large, and may approach infinity, or a negative value after it has climbed a short distance up the walls. Hence, the cavity can now rapidly fill with vapour with this favourable radius of curvature. In order for the vapour to expand past the cavity it is necessary for it first to form a hemispherical cap at the mouth of the cavity. The radius of the cap is approximately the radius of the cavity mouth (exactly if \( \theta = 90^\circ \)) and the cavity will nucleate bubbles if its radius at the mouth is equal or greater than the critical radius \( R^* \).

This theoretical analysis applies equally well to wedge shaped crevices if the walls are well-wetted. Such crevices exist between fibres and tows in composite materials. Once again the theoretical fracture pressures are negative and well in excess of experimental observations. If the walls are non-wetted, the liquid can be torn away from an arbitrarily small area of the apex with very little expenditure of work, but the resulting vapour phase can not grow until the liquid-solid bond has been fractured along the entire length of the crevice. It seems that nucleation in the absence of a pre-existing vapour phase will normally take place at non-wetted cavities rather than crevices. One other possibility may be mentioned. If a well-wetted crevice contains a short section which is not wetted, the vapour embryo need not extend past the unwetted portion, and the crevice will act essentially as an unwetted cavity. Such contamination may occur through the deposit of minute quantities of grease and other organic materials from the air and this phenomenon is readily appreciated by the well known fact that a clean glass slide will no longer support a continuous film of water once it has been dried in air.

Fisher (1948) pointed out that if an unwetted cavity or crevice has a truly sharp apex (conical cavity), no finite pressure can force the liquid all the way into the depression (figure 2.6). It is evident that there is no problem of nucleating the vapour phase when the pressure is reduced. It appears that for bubble formation from non-wetted surfaces, nucleation proceeds from a pre-existing vapour phase rather than by tearing the liquid from a portion of the solid boundary. If the resin is saturated with air, it will have no tendency to rise into unwetted capillaries and essentially no
Figure 2.4 Successive Bubble Profiles - Wetted Cavity

Figure 2.5 Successive Bubble Profiles - Unwetted Cavity
reduction of pressure can be maintained. If the resin has been partially or totally degassed it will tend to rise into the capillaries until the partial pressure of air in the capillary space is in equilibrium with the dissolved air concentration. Since this is a diffusion process, it may require hours or even days depending on the temperature and the concentration gradient. Diffusion theory will be discussed in more detail in subsequent sections.

If the resin is degassed and has negligible vapour pressure at room temperature, at atmospheric pressure the vapour embryo pressure will eventually drop practically to zero, corresponding to a radius of curvature of approximately 1μm in steep walled unwetted cavities, i.e. ΔP=2γ/R for a bubble to remain stable indefinitely, without solution, on a lyophobic (solvent repelling) surface containing a cavity.

The vapour embryos will collapse completely in wetted cavities, and if the meniscus can not attain this critical radius of curvature as it advances in an unwetted cavity, the vapour phase will also disappear. If the cavity having a sharp apex is well wetted, the vapour phase will collapse until its radius of curvature is within an order of magnitude of the spacing between molecules in the liquid, so that the cavity is effectively nullified at the nucleation centre. It appears that a large contact angle is essential for the retention of effective vapour phase nuclei on a solid surface.

If the surface is not wetted, as in the case of resin and glass fibres [Bascom (1965)], or not wetted in spots, almost certainly there will be present some steep walled cavities which retain a vapour phase. These may be in an impurity particle or between individual fibres or

![Figure 2.6 An Unwetted Conical Cavity](image-url)
tows. If the liquid is now subjected to the slightest increase in temperature or decrease in pressure, the nucleus will begin to grow spontaneously, but can not leave the cavity unless the mouth of the cavity is equal to or greater than the critical radius. The radius of the largest unwetted cavity will subsequently determine the fracture threshold of the resin.

2.1.3 Pre-Pressurisation

If the system is subjected to pre-pressurisation then the radius of curvature of the meniscus will decrease in an unwetted cavity. There seems no reason however, why the vapour phase will not spontaneously grow again once the pressure is released. In other words pre-pressurisation should not affect the fracture pressure of the system [Harvey (1947)]. If the surface is well wetted, all vapour phases should eventually disappear, if the liquid is not saturated with dissolved gas to the same concentration. Dean (1944) found that, in the case of water, large tensile stresses could be sustained if the surfaces were allowed to stand in the presence of de-aerated water for some time. This indicates that if the same phenomenon is analogous for a liquid resin then an increase in fracture pressure could be attained by pre-pressurisation thus increasing the driving force for diffusion of the entrapped air into the resin. Another undeniable consequence of pre-pressurisation is that vapour embryos in partially wetted cavities will be collapsed.

Elimination of nuclei by means of pressurisation seems theoretically feasible in a composite system. Application of a positive pressure would not only collapse wetted and partially wetted cavities but would also aid the collapse of any bubbles that have been mechanically entrapped during the resin mixing operation or lay-up process. The rate of collapse will be dependent on the parameters that affect the diffusion process. Only non-wetted cavities in wedge shaped cracks or crevices will be oblivious to pressurisation.
2.2 PORE PENETRATION

Solid surfaces are rough and irregular and if the resin has not been forced to the bottoms of all cavities then on reducing the pressure, or heating the system, trapped vapour cavities will nucleate. If the resin has been forced to the bottom of all cavities and crevices a bubble will form at the apex of the severest cavity as dictated by equation 2.5. The fracture pressure is determined by combining equations 2.4 and 2.5 with an assumption that the fracture pressure is the pressure that causes a nucleation event in a reasonable time, e.g. one bubble in t seconds. Then \( \frac{dn}{dt} = \frac{1}{t} \) and equation 2.5 can be solved accordingly. From this it can be concluded that the fracture threshold of liquid resin is also dependent on how long one is willing to wait for the first bubble to appear. For a bubble to appear in a reasonable time, say \( 1/cm^2 s \), substantial negative pressures are required and therefore to increase the fracture threshold and prevent nucleation it is imperative that all cavities are flooded.

2.2.1 Equilibrium Considerations

Neglecting any diffusion process, penetration into any pore containing air will occur until the back pressure of entrapped air equals the capillary driving pressure [Packham (1983)]. This equilibrium situation for a cylindrical cavity can be expressed as the distance \( x \) penetrated into a pore of length \( l \) and radius \( r \), which for air entrapped under atmospheric pressure is,

\[
x = l (1 - \frac{P_a r}{\gamma \cos \theta + P_a r})
\]

where \( P_a \) is atmospheric pressure and \( \gamma \) and \( \theta \) are the liquid/vapour interfacial energy and contact angle, respectively.

Applying equation 2.6, figure 2.7 shows that a smaller pore will have a greater proportion of its length filled at equilibrium. Assuming a contact angle of zero,
the resin ($\gamma = 0.035 \text{ N/m}$) will penetrate 25% of a 1$\mu$m cylindrical cavity. Considerable penetration would be expected for pores less than 100nm although the equilibrium penetration decreases with increasing contact angle.

### 2.2.2 Kinetics of Pore Penetration

The discussion above assumes that equilibrium contact between the resin and the substrate is achieved. For the processing of composites, time is a critical parameter and it is therefore relevant to consider the kinetics of pore penetration.

The starting point for such a discussion is usually Poiseuille's law for the flow rate, $dx/dt$, of a Newtonian liquid of viscosity $\eta$ in a tube of radius $r$ under the influence of a pressure $P$,
If the driving pressure is taken to be the capillary pressure \((2\gamma \cos \theta / r)\) equation 2.7 can be integrated (assuming \(\theta\) and \(\eta\) are constant) to give the Washburn equation [Washburn (1921)] which shows the penetration, \(x_t\), is proportional to the square root of time,

\[
x_t^2 = \frac{r^2P}{8\eta}t \quad \ldots \quad (2.8)
\]

It can be concluded that for a liquid resin system, where viscosities are not extremely high (typically 11-15 Pa.s at 25°C (298K)), equilibrium penetration will be attained very quickly for a large range of contact angles and pore diameters.

This theory has also been extended for crevices in terms of adhesion of polymers to substrates [Cherry (1981)] but can equally apply for the conditions of gases trapped in crevices. This is an important consideration when dealing with a resin impregnating close-packed fibres. In this case, where the crevice between two fibres can be approximated to a groove with a sharp apex, it is possible to determine how long it would take the moderately viscous resin to fill these crevices.

Once again the starting point is the Laplace equation but in this case the radius of curvature of the resin is infinite in the plane perpendicular to the paper (figure 2.8),

\[
\Delta P = \frac{\gamma}{R} \quad \ldots \quad (2.9)
\]

where \(R\) is the radius of curvature and \(\gamma\) is the surface tension between the liquid and vapour phases.
It can be seen that $x_1 = R \cos(\theta - \alpha)$ so therefore,

$$\Delta P = \gamma \frac{\cos(\theta - \alpha)}{x_1}$$ .... (2.10)

If this pressure acts on an element $dx$ wide, as shown in the inset to figure 2.8, then if the resin behaves as a Newtonian liquid of viscosity $\eta$, and if the speed of vertical movement into the groove is $u$, then it can be shown that

$$\Delta Pdx = \eta y \frac{\partial u}{\partial x} - \eta y \left( \frac{\partial u}{\partial x} - \frac{\partial^2 u}{\partial x^2} \right) dx$$ .... (2.11)

or
\[ \frac{\Delta P}{y} = \eta \frac{\partial^2 u}{\partial x^2} \quad \text{... (2.12)} \]

which can be integrated remembering that \( x=0, \ \partial u/\partial x=0 \) and \( x=x_1, \ u=0 \). Hence,

\[ \Delta P(x^2-x_1^2) = 2y\eta u \quad \text{... (2.13)} \]

Now the mean velocity of the leading surface of the resin as it penetrates the groove is given by,

\[ u^* = \frac{\Delta P}{2y\eta} \int_0^{x_1} \frac{(x^2-x_1^2)}{x_1} \, dx = -\frac{\Delta P}{3y\eta} x_1^2 \quad \text{... (2.14)} \]

The negative sign arises because the centre of the liquid surface is actually moving upwards relative to the edges. Since \( dy/dt=u^* \) and \( x_1=x_0(1-y/y_0) \) and substituting for \( \Delta P \), gives

\[ \frac{dy}{dt} = -\frac{\gamma \cos(\theta - \alpha)}{3\eta} x_0 \left( \frac{1}{y} - \frac{1}{y_0} \right) \quad \text{... (2.15)} \]

which can be integrated,

\[ \frac{\gamma \cos(\theta - \alpha)}{3\eta} \frac{x_0}{y_0} = y_0 \log \left( \frac{y_0}{y_0-y} \right) \quad \text{... (2.16)} \]

It is apparent that equation 2.16 is an over-simplification of the phenomena of crevice penetration. It suggests that the crevice can never be filled but the time to fill 99% of it can be estimated. It also neglects the back pressure of air in
the crevice and also the fact that pressure may be applied to assist the penetrating resin. It does show that resin penetration between two adjacent fibres (fibre diameters range between 5-20µm) is very rapid, if it is assumed that the crevice between them is approximately V-shaped. Equation 2.10 also shows that the effective pressure when the crevice is half full is low and application of quite a small pressure will accelerate this penetration.

It can be concluded that penetration into pores or crevices of the size expected in a composite system will be rapid and the depth of penetration will be governed by equilibrium considerations. Even in the case of a prepreg system, where the resin is effectively solid at room temperature, penetration will occur quickly as the temperature is raised and the resin viscosity decreases. It must be remembered that, according to equation 2.16, the penetration time is finite, so reducing the pressure (drawing a vacuum) before the resin viscosity is lowered will encourage growth of the entrapped air before wetting of the fibres or pore penetration can take place. This is contrary to the typical cure schedule described in Section 1.4.

Equilibrium considerations are therefore critical as they fundamentally determine whether a cavity or crevice will be filled. Even with perfect wetting (θ=0°), the capillary back pressure will prevent penetration and any finite contact angle between the resin and substrate will exaggerate this effect.

These theories tie in with Bascom's observations (1965) of bubbles in glass strands as they emerged from a resin bath. By adding a surfactant to the epoxy resin, the contact angle was reduced to 0° and appreciable reductions in void density of over 50% were noticed without changing the viscosity. The same result was found for higher viscosities with similar contact angles but changing the strand speed by a factor of 100 had no effect on void density. This implies that the equilibrium penetration was attained rapidly but flooding of pores and crevices is governed by the contact angle and the surface tension forces as shown by equation 2.6.
Although addition of a surfactant would seem to provide a method of reducing void levels in the final composite, perfect wetting in itself is not sufficient to eliminate all voids. Such changes in the resin formulation to attain perfect wetting also may not be tolerated in terms of the final mechanical properties. It is reasonable to assume that in any closed-pore capillary there will be entrapped vapour which will prevent resin penetration. Such nuclei can grow in accordance with the perfect gas laws as the pressure is reduced or as the temperature is increased. Once the laminate has been committed to the cure operation, nullification of such nuclei can only be achieved by diffusion of the retained vapour into the resin. Once molecularly dispersed these vapours or gases will have no affect on the fracture threshold of the resin unless the system is subjected to hydrostatic tensions.

2.3 NUCLEATION OBSERVATIONS

A series of preliminary experiments were performed to investigate the problem of nucleation. Although many of the observations are explained in a qualitative fashion they can be related to the theories described in this chapter. The resin used and the preparation procedure is described in Section 6.1.

i) Resin that had been equilibrated with nitrogen gas at ambient pressure was placed in glass phials that had been cleaned rigorously and allowed to stand at elevated temperature until all suspended bubbles had been removed. This was done at atmospheric pressure and 333K. Some of the samples were placed in a steel pressure vessel and subjected to positive hydrostatic pressures. Pressure was applied from a nitrogen gas bottle which maintained an overpressure. Subsequent measurements showed that the overpressure did not affect the dissolved gas concentration, i.e. the applied pressure could be considered as a hydrostatic ram. The gauge pressures were 10, 20 and 30 atmospheres. The samples were left for an hour under pressure. All samples, including those that had been left at atmospheric pressure, were then placed in a vacuum oven at 333K. The oven was then evacuated slowly.
It was found that on evacuating the oven the samples that had been subjected to atmospheric pressure began to bubble before those that had been subjected to elevated pressures. All samples bubbled eventually and from the sides of the container. No obvious nucleation point was noted on subsequent examination. The samples exposed to 10 and 20 atmospheres began to bubble virtually simultaneously.

ii) An unwetted glass fibre tow was placed within a glass phial containing nitrogen-saturated resin. The samples were placed in the vacuum oven at 333K. Bubbles began to stream from the fibres as the oven was evacuated. The vacuum was released and the bubbling stopped. On reducing the pressure again the bubbling started from the same point. The temperature of the oven was then raised to 353K. The bubbling continued (although at a faster rate) and the vacuum was released. On reducing the pressure again the bubbling did not continue.

iii) Small squares of woven glass fibre cloth were placed in glass phials. Nitrogen-saturated resin was poured over the mat and the samples were allowed to stand at atmospheric pressure and 333K in the vacuum oven. Bubbles could clearly be seen nestling in the interstices of the cloth. On evacuating the oven these bubbles expanded causing break-up of the cloth. Other samples were allowed to stand under the same conditions for several days until no bubbles were visible. The cloth was considered to be wetted since it was now transparent. On reducing the pressure bubbles emanated from the cloth as before.

iv) Gas bubbles observed to collapse in unsaturated and saturated solutions were sometimes found to leave a deposit of microscopic debris. Despite the complete collapse of the bubble it was found that in some of these cases reducing the pressure initiated bubble growth from the same point as the original collapse site. In one case the sample was left twenty four hours before the bubble was regenerated.
2.3.1 Analysis of Nucleation Observations

These preliminary experiments are in agreement with the theoretical outline described in Sections 2.1 and 2.2. Prior application of a hydrostatic pressure increases the fracture threshold of the resin which infers that nuclei have been inactivated, i.e. nuclei such as cavities in the container walls can be flooded by increasing the system pressure. It also seems logical that the more inaccessible cavities would require higher hydrostatic pressures to render inactive.

Changing the properties of the resin by increasing the temperature and reducing the viscosity also seems to eliminate nucleation centres although the actual mechanism is more difficult to define. Calculations indicate that the liquid resin should have attained its equilibrium penetration into a cavity (Section 2.2.2), so the increasing temperature probably accelerated the diffusion of entrapped air into the resin as opposed to increasing pore penetration due to reducing the viscosity.

It does seem that in a composite system nuclei will always be present. Even an apparently completely wetted cloth will generate bubbles indicating that nuclei still remain. It also seems that such nuclei are stable and ready to regenerate and that such nuclei are not just a consequence of such obvious substrates as the fibres or the sides of the vessel but also of microscopic debris within the resin.

The difficulty in turning these observations into a quantitative study is relatively apparent. Primarily a knowledge of the nuclei is required and since these are probably contained in submicroscopic cavities, reproducible experiments would be difficult. No two cavities will have exactly the same geometry and since the resin does not have a zero contact angle with the surfaces a wide range of fracture pressures would be observed. These experiments do however, place a lower limit on the size of "bubble" present in a macroscopically (and even microscopically) bubble-free resin. If it is considered that a bubble is entrapped in a crevice of a lyophobic particle then it will remain stable for reasons discussed in Section 2.1.2. For a resin surface tension $\gamma$ of 0.035N/m, if it is assumed that the resin is stored at atmospheric pressure, then the
force balance indicates that stable nuclei will be in the order of 1μm. A reduction in pressure can cause the bubble to grow in accordance with the gas law equations and if the concentration gradient is favourable it can grow to many times its original size within a short period of time due to diffusion, depending on the degree of saturation and the temperature.

2.4 SUMMARY

For a composite system, nucleation of bubbles, homogeneously or heterogeneously at plane or projecting solid surfaces, requires negative pressures (hydrostatic tensions) which are not experienced in the processing route, within the range of observed contact angles. These possibilities can be dismissed from consideration. Well-wetted cavities are also rejected since the work of forming an embryo is of the same order of magnitude as the work of forming a critical nucleus of the same radius of curvature in the bulk phase. If, however, the wetted cavities contain air, or other gas, sufficient time must be allowed for the gas to dissolve completely, otherwise the maximum allowable pressure will be determined by the radius of curvature of the largest remaining air bubble. The rate of diffusion is dependent on the temperature and concentration gradient so pre-pressurisation at slightly elevated temperatures can accelerate this process. If any unwetted cavities exist, nucleation will occur preferentially at these points since it requires only a small amount of work to tear the resin away from the apex of the cavity. After this the cavity will fill rapidly and spontaneously with vapour so the fracture pressure is determined by the radius of curvature of the mouth of the unwetted cavity. If the unwetted cavity has a truly sharp apex, no finite pressure can force the liquid to occupy the cavity completely. Pre-pressurisation will aid the filling of partially wetted cavities. Nucleation will require less work in unwetted cavities than in unwetted grooves, unless only a small part of the groove is unwet.

Such cavities and crevices are present due to lyophobic particles in the resin and the geometry of the fibres. A crevice between two adjacent filaments will
have a sharp apex where air, carried in from the impregnation stage, can remain. These voids could extend along the length of the fibre and if the contact angle is unfavourable, resist diffusion of air into the resin. The interstitial grooves or crevices between fibres are of the correct order of magnitude to harbour gases which can subsequently act as nuclei for growth. Cavities or crevices in the surface of the fibres would have radii that were too small to act a nucleation sites since the radius of the pore must equal or exceed the critical size radius dictated by the Laplace equation (equation 2.1). Such nanoscopic cavities would also be flooded effectively due to the capillary driving pressure for a wide range of contact angles (figure 2.7).

In order to attain minimal porosity it is necessary to remove any retained nuclei and free gas bubbles. Both of these can be eliminated by diffusion processes unless the contact angle between the resin and the substrate is so unfavourable that the nucleus is stabilised by surface tension forces. Such concave meniscuses (viewed from the liquid) are not found between glass fibres and resin.

The problem of porosity in composites can now be viewed from a scientific angle. Bubbles have to be removed either prior to or during production and nuclei have to be inactivated completely or suppressed from growing. Most nuclei can be eliminated by diffusion of the entrapped air into the resin while there are two possibilities for existing bubbles: transporting the bubbles out of the laminate or encouraging them to go into solution. Transportation is not a realistic proposition in that it would require a knowledge of the bubble, pressure gradients within the resin, geometry of the fibre network (the diameter of the narrowest constriction) and resin flow as a function of time and position in the laminate. It is also difficult to envisage how a bubble could be transported through the fibre network which provides an extremely tortuous path, especially in thick laminates. It is concluded that a solution method is a more advantageous and realistic scenario than bubble migration through restrictive geometries since if it is favourable for existing bubbles to collapse, nuclei will also be suppressed from growing. A knowledge of diffusion processes and the ability to model and control them is therefore vital in the production of a void-free composite.
CHAPTER THREE

MASS DIFFUSION

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3. MASS DIFFUSION

Although equilibrium considerations place bounds on the growth and collapse of bubbles, the curing operation also involves changes in temperature and pressure. The time-dependent growth and collapse of bubbles must be considered. During the cure, the radius of an entrapped bubble will change as a consequence of the temperature and pressure in the surrounding resin and due to changes in the mass of gas/vapour inside the bubble as species migrate across the bubble/resin interface. These species could be dissolved air, water or volatile components of the resin/curing agent system.

Since the pioneering work of Raleigh in 1917, the growth and collapse of a stationary, spherical bubble suspended in a stationary infinite medium has been the subject of considerable interest to many researchers [Epstein and Plesset (1950)] [Plesset and Zwick (1954)] [Scriven (1959)]. The classical account of Scriven (1959) accounts for diffusion and convective transport caused by bubble expansion and the moving boundary condition at the gas/liquid interface. Neglecting the hydrodynamic resistance of the liquid to bubble growth, Epstein and Plesset (1950) developed a theory of diffusion-controlled growth (and collapse) of a stationary gas bubble suspended in an inviscid medium. Subramanian and Weinberg (1980) noted that this quasi-stationary approximation, which ignores all motion, is more consistent than the approach which considers only the boundary movement [Tao (1978)].

The exact modelling of bubble kinetics would require the solution of many coupled time-dependent partial differential equations. Exact solutions have been obtained for bubble growth from a zero radius [Scriven (1959)] but no exact solutions exist for growth from a non-zero radius or for bubble collapse. Also, many physical properties are not known with sufficient accuracy to justify the excessive computational time that would be required to deal with the numerical solutions in the literature [Ready and Cooper (1966)] [Duda and Vrentas (1969)]. A number of assumptions and simplifications have been employed in the following and no attempt has been made to include the viscoelasticity of the medium. These are discussed in relation to a
thermosetting matrix composite system and the final model assumptions are listed in Section 3.3.

3.1 DIFFUSION CONTROLLED GROWTH AND COLLAPSE

The theory of diffusion is closely analogous to the theory of heat conduction. A similar problem to bubble growth and collapse is that of the cooling of a perfectly conducting sphere in an infinite isotropic medium [Crank (1956)].

Consider a gas bubble of radius $R$ at the centre of a large volume of resin whose initial gas concentration is $C_\infty$. If the resin at the bubble surface is saturated, then the gas concentration $C$ in the solution should vary with the radial co-ordinate $r$ from $C_s$, the saturated solution concentration at $r=R$, to $C_\infty$ at $r=\infty$. Assuming a constant diffusion coefficient $D$, Fick's second law for this spherically symmetrical geometry is,

$$\frac{1}{D} \frac{\partial C}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} (r \frac{\partial C}{\partial r}) \quad \text{.... (3.1)}$$

The solution of equation 3.1, subject to the boundary conditions at $r = R$ and $r = \infty$, is expressible as an error integral,

$$C-C_\infty = \frac{R}{r} (C_s-C_\infty)[1-2\pi^{-1/2} \int_0^{(r-R)/2(Dt)^{1/2}} e^{-y^2} dy] \quad \text{.... (3.2)}$$

The second term in the square brackets is the probability integral or Gauss error function and its value depends entirely on the value of the upper limit $(r-R)/(2(Dt)^{1/2})$. The rate at which the mass, $m$, of the bubble decreases is determined by the outward flux, $J$, of gas at the bubble surface:
\[ \frac{dm}{dt} = -4\pi R^2 J \quad \ldots \quad (3.3) \]

Now if \( \rho \) is the density of the gas bubble, then \( m = \frac{4}{3}\pi R^3 \rho \) and

\[ \frac{dm}{dt} = 4\pi R^2 \rho \frac{dR}{dt} \quad \ldots \quad (3.4) \]

The rate of decrease of the bubble radius is,

\[ \frac{dR}{dt} = \frac{-J}{\rho} \quad \ldots \quad (3.5) \]

The flux \( J \) can be obtained from Fick's first law,

\[ J = -D \frac{\partial C}{\partial r} \quad \ldots \quad (3.6) \]

The concentration gradient at \( r=R \) is available from equation 3.2,

\[ \frac{\partial C}{\partial r}_{r=R} = \frac{C_0 - C_s}{R} \left[ 1 + \frac{R}{(\pi D t)^{1/2}} \right] \quad \ldots \quad (3.7) \]

From this it is possible to obtain Epstein and Plesset's (1950) differential equation for the bubble radius,
Equation 3.8 shows that a gas/vapour bubble in a liquid-gas/vapour solution will grow or shrink by diffusion according to whether the solution is supersaturated or unsaturated, i.e. the sign of $C_s - C_{\omega}$. Although the analysis does not take into account a transport term due to the motion of the bubble boundary, the physical reasoning behind the approximation seems appropriate for a composite system in that the concentration of dissolved gas in the resin surrounding the bubble will be much smaller than the gas density in the bubble. Thus, the region in the resin around the bubble through which the diffusion process takes place quickly becomes much larger than the bubble itself. Under these circumstances the size of the bubble is of little importance in terms of the diffusional field but is important in so far as it determines the interfacial area across which the mass transfer between phases takes place.

The dissolution velocity of a bubble, as described by equation 3.8, is shown in figure 3.1. It can be seen that the rate of collapse is initially very high as the transient term in equation 3.8 dominates. This is only at short times and reflects the build-up of the diffusional boundary layer adjacent to the bubble surface. The area available for transport increases with radial distance from the centre of the bubble and as the bubble becomes small, the dissolution rate increases as the diffusion area to bubble volume ratio increases markedly, decreasing the size of the solute source with respect to the area of the diffusion zone surrounding it.

Unfortunately the solution to equation 3.8 is highly non-linear and methods for recovering the change in radius with time would require a numerical method. This in itself, although possible, can be seen to be unnecessary in a composite system. For the range of bubble sizes expected in a composite laminate and for the diffusion coefficients of species in a liquid resin, it can be seen that $R/(\pi Dt)^{1/2} << 1$ and the asymptotic solution quickly dominates (figure 3.2). At higher temperatures
Figure 3.1 Quasi-stationary assumption for a collapsing bubble

Figure 3.2 Quasi-stationary assumption for a collapsing bubble with temperature
Figure 3.3 Quasi-stationary assumption for a growing bubble

Figure 3.4 Schematic comparison between bubble growth and collapse showing the differences in the concentration fields
(higher diffusion coefficients) and longer times this becomes increasingly valid and the transient term becomes negligible after a matter of seconds for small bubbles and within the first five minutes of a typical cure cycle for larger bubbles. It may be noted that this would not necessarily be so for the reverse process of bubble growth, where the steady-state and transient solutions would decrease simultaneously (figure 3.3). This observation may be interpreted as an important basic difference between growth and collapse phenomena in bubbles, i.e. during growth the matrix is depleted of solute immediately ahead of the advancing interface, during dissolution the solute concentration in the matrix increases with time at some distance from the bubble but decreases with time at the bubble interface. A schematic comparison of bubble growth and collapse is shown in figure 3.4 and the complexities in the concentration profiles are the reasons why it has not been possible to find a closed-form analytical solution for the problem of diffusion-controlled bubble dissolution or growth from a non-zero radius in an infinite matrix.

For the problem of composite processing, where the cure schedule is sufficiently long to render the transient term negligible, it is assumed that it is possible to neglect the term $R/(\pi Dt)^{1/2}$, which leads to the asymptotic steady-state solution,

$$R^2 = R_o^2 - \frac{2D}{\rho} (C_s - C) t$$

where $R_0$ is the bubble radius at $t=0$. The same solution can be obtained by setting $\partial C/\partial t = 0$ in equation 3.1.

Figures 3.5-3.11 illustrate the steady-state solution in terms of the input variables. The values used to determine these interactions are based on typical values determined from subsequent experiments and so represent at least a qualitative model of how these variables and parameters are expected to influence bubble growth and collapse in a typical composite processing operation.
Figure 3.5 Steady-state - Effect of initial bubble size on collapse

Figure 3.6 Steady-state - Effect of initial bubble size on growth
Figure 3.7 Steady-state - Effect of interfacial concentration (pressure)

Figure 3.8 Steady-state - Effect of diffusion coefficient on collapse (temperature)
Figure 3.9 Steady-state - Effect of diffusion coefficient on growth (temperature)

Figure 3.10 Steady-state - Effect of bulk concentration on bubble collapse
It can be seen that the time for complete solution increases with initial bubble size (figure 3.5) and that growth from an effectively zero radius is rapid (figure 3.6), although it must be remembered that surface tension forces have not been included. The concentration at the bubble/resin interface, which is related to the hydrostatic pressure in the resin (Sections 5.1 and 8.1), is the principal parameter which determines whether a bubble will grow or collapse (figure 3.7), while the rate of growth or collapse is dependent on the diffusion coefficient which increases exponentially with temperature (Sections 5.2, 8.2 and 12.2) (figures 3.8 and 3.9). Thus, manipulation of the process variables can be used to suppress bubble growth and encourage bubble collapse within the practical limitations of the processing window dictated by the other unit models (Section 1.1). A greater concentration of the mobile species in the bulk resin (a parameter that is fundamentally dependent on the history of the resin) can accelerate bubble growth and diminish the bubble collapse rate (figures 3.10 and 3.11). It must also be noted that in a saturated solution, where the dissolved concentration in the bulk equals the concentration at the bubble/resin interface, the bubble is stable indefinitely.
3.2 SURFACE TENSION FORCES

A further modification to the quasi-stationary and the steady-state assumption is the inclusion of surface tension forces which hinder growth but aid collapse of a bubble. Equations 3.8 and 3.9 predict an infinite time for bubble collapse in a saturated solution, indicating that a bubble would be stable against diffusion (figure 3.10). This is obviously not the case since surface tension forces become increasingly important as the bubble size decreases (equation 2.1). These forces are now considered.

If the surface tension constant for the gas/resin system is $\gamma$, then the equation of state for a gas bubble of radius $R$ in resin at a pressure $P$ and temperature $T$ is,

$$ P + \frac{2\gamma}{R} = \left( \frac{R_g}{M} \right) \rho(R)T $$.  

where $\rho(R)$ is the gas density in the bubble, $M$ is the molecular weight of the gas and $R_g$ is the universal gas constant. Thus,

$$ \rho(R) = \frac{M}{R_g T} P + \frac{2M\gamma}{R_g T} \frac{1}{R} $$.  

$$ \rho(R) = \rho(\infty) + \frac{\tau}{R} $$.  

where $\rho(\infty)$ is the density of the gas under the same conditions of pressure and temperature with a gas/liquid interface of zero curvature and

$$ \tau = \frac{2M\gamma}{R_g T} $$.  

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The mass of gas in the bubble is,

\[ m = \frac{4\pi}{3} R^3 \rho(R) = \frac{4\pi}{3} R^3 \rho(\infty) + \frac{4\pi}{3} R^2 \tau \quad \ldots \quad (3.13) \]

and

\[ \frac{dm}{dt} = 4\pi R^2 \frac{dR}{dt} \left[ \rho(\infty) + \frac{2\tau}{3R} \right] \quad \ldots \quad (3.14) \]

so that

\[ \frac{dR}{dt} = -\frac{D(C_s - C_\infty)}{\rho(\infty) + \frac{2\tau}{3} \left( \frac{R}{\pi D t} \right)^{1/2}} \quad \ldots \quad (3.15) \]

The concentration of dissolved gas, \( C_s \), which is in equilibrium with the gas density, \( \rho(R) \), is given by

\[ \frac{C_s}{\rho(R)} = d, \quad C_s = \left[ \rho(\infty) + \frac{\tau}{R} \right] d \quad \ldots \quad (3.16) \]

The initial concentration, \( C_\infty \), is more conveniently expressed in terms of a relative saturation, \( f \), where

\[ f = \frac{C_\infty}{C_s}, \quad \frac{C_\infty}{\rho(\infty)} = fd \quad \ldots \quad (3.17) \]

Equation 3.15 may now be written as,
\[
\frac{dR}{dt} = -Dd \frac{1-f+\tau/(R\rho(\infty))}{1+2\tau/(3R\rho(\infty))} \left[ \frac{1}{R} \left( \frac{1}{\pi D} \right)^{1/2} \right] \quad \cdots (3.18)
\]

The steady-state solution with the inclusion of surface tension forces is,

\[
1 - e^2 - 2\delta \left[ \frac{1}{1-f} - \frac{2}{3} \right] (1-e) +
\frac{2\delta^2}{1-f} \left[ \frac{1}{1-f} - \frac{2}{3} \right] \ln \frac{\delta + (1-f)}{\delta + (1-f)e} = x^2 |1-f| \quad \cdots (3.19)
\]

where \( e = R/R_0 \), \( x^2 = (2Dd/R_0^2)t \) and \( \delta = \tau/[R_0^2 \rho(\infty)] \)

For the special case of \( f=1 \), i.e. a saturated solution, the steady-state assumption including the surface tension forces is,

\[
1 - e^3 + \delta (1-e^2) = \left( \frac{3\delta}{2} \right) x^2 \quad \cdots (3.20)
\]

and the time for complete solution is given by,

\[
x^2 = \left( \frac{2}{3\delta} \right) (1+\delta) \quad \cdots (3.21)
\]

Figure 3.12 shows the effect of including surface tension forces in the steady-state approximation. In contrast to equation 3.9, which predicts indefinite stability, equation 3.20 predicts a finite collapse time.
3.3 MODEL ASSUMPTIONS

The approximations incorporated in these solutions, with the inclusion of surface tension forces, are reasonable for a composite system. Other factors such as the viscous nature of the resin will decrease the rate of growth and collapse since the viscosity effectively increases the resistance to bubble boundary motion. Unfortunately it is not possible to take this into account with the quasi-stationary and steady-state approximations but it can be assumed that for species which have low solubility, the motion of the bubble is predominantly controlled by the mass transfer process and not the fluid rheology, i.e. the rate of change of bubble radius, which is affected by the concentration gradient, is a relatively slow process [Zana and Leal (1975)]. This assumption will not apply once the resin has begun to gel but it must also be remembered that as the viscosity increases dramatically, as a consequence of the crosslinking reaction, it is then virtually impossible to control a bubble by purely manipulating the process variables. This limits the practical problem to that of collapsing existing bubbles before the gel point of the system.
Before the model can be applied directly to a composite system it must be
assumed that;

i) The bubble is stagnant between plies and its centre is not moving with respect
to fixed co-ordinates in the laminate.

ii) The bubble is approximately spherical and its effective size is calculated based
on an equivalent sphere.

iii) There is no interaction between bubbles (no coalescence).

iv) The bubble is considered to be in an infinite isotropic medium (diffusion fields
of other bubbles do not overlap).

v) At any given time, the temperature and concentration of the diffusing species
within the bulk resin are uniform.

vi) At each temperature a pseudo-steady-state is established with respect to the
concentration profile; that is the profile does not change at any particular
temperature.

vii) Viscous and inertial forces are negligible since they are only significant during
the initial stages of bubble expansion or the latter stages of collapse (as the
bubble grows its growth becomes limited by the molecular flux).

These assumptions allow the model described in this chapter to be applied
without further modification. The applicability of the model and the assumptions is
considered with respect to the experimental data in later sections.
CHAPTER FOUR

THE CHEMISTRY OF THE SYSTEM

4.1 EPOXY RESIN TECHNOLOGY

4.2 RESIN-WATER INTERACTIONS
   4.2.1 Equilibrium Considerations for Volatile Species
   4.2.2 Solubility of Species in Resin

4.3 SUMMARY
4. THE CHEMISTRY OF THE SYSTEM

It has been shown that the growth and collapse of bubbles is dependent on the concentration gradient and the diffusion coefficient of the species in the resin. In order to predict the behaviour of bubbles it is therefore necessary to determine which species are present within a composite system and contribute to bubble growth. Concentrations of these species and their respective diffusion coefficients can be subsequently correlated to the process variables. For this reason it is necessary to appreciate the chemistry of the system and the interaction of the resin molecule with the diffusant on a physical and molecular level.

4.1 EPOXY RESIN TECHNOLOGY

Epoxy resins make an excellent matrix material because of their versatility, good handling characteristics, low shrinkage, excellent adhesive properties (especially to glass) and good mechanical properties including toughness. There are numerous epoxy formulations, each of which can be cured by a selection of curing agents. In addition diluents, modifiers and flexibilisers can be blended to change properties such as the viscosity of the uncured resin and the chemical resistance and flexibility of the cured chain [Lee and Neville (1967)].

One of the most important intermediates in epoxy resin technology is the liquid reaction product of excess epichlorohydrin and bisphenol-A, which can be described as the crude diglycidyl ether of bisphenol-A (DGEBA) where the degree of polymerisation $n$ is nearly zero ($n=0.2$):

$$
\begin{align*}
\text{CH}_2\text{CHCH}_2\text{Cl} + \text{HO-} & \text{C} & \text{CH}_3 & \text{C} & \text{OH} + \text{NaOH} \\
\text{epichlorohydrin} & \text{bisphenol A} & \\
\text{CH}_2\text{CHCH}_2 & \left(\text{O-} \text{C} & \text{CH}_3 & \text{CH}_2\text{OH} \text{CHCH}_2 \right) & \text{O-} & \text{C} & \text{CH}_3 & \text{CH}_2\text{OCHCHCH}_2 & \text{CH} & \text{OH} & \text{NaCl} \\
\text{DGEBA} & \text{(1)}
\end{align*}
$$
Epichlorohydrin, which has a boiling point of 115°C (388K), is prepared from propene by chlorination to allyl chloride, followed by treatment with hypochlorous acid forming glycerol dichlorohydrin, which is dehydrochlorinated by sodium hydroxide:

\[
\text{CH}_2\text{CH}==\text{CH}_2 \xrightarrow{\text{Cl}} \text{CH}_2==\text{CHCH}_2\text{Cl} \xrightarrow{\text{HOCl}} \text{ClCH}==\text{CHCH}_2\text{Cl} \xrightarrow{\text{NaOH}} \text{ClCH}==\text{CHCH}_2\text{O}
\]

Bisphenol-A or 2,2-bis(p-hydroxy phenyl)propane, is prepared from 2 moles of phenol and 1 mole of propanone (acetone):

\[
\text{HO} \xrightarrow{\text{C}} \text{OH} \quad \text{HO} \xrightarrow{\text{CH}_3} \text{CH}\_3
\]

In the synthesis of epoxy resins, epichlorohydrin behaves as a difunctional monomer, since it is readily dehydrohalogenated by alkali. For liquid epoxy resin (DGEBA), caustic is used as a catalyst for the nucleophilic ring-opening of the epoxy group on the primary carbon atom of the epichlorohydrin by the phenolic hydroxyl group and as a dehydrohalogenating agent for the conversion of the halohydrin to the epoxide group:

\[
\text{HO} \xrightarrow{\text{C}} \text{OH} \quad \text{HO} \xrightarrow{\text{CH}_3} \text{CH}\_3
\]
In the preparation of commercial DGEBPA, an excess of epichlorohydrin is used in order to minimise polymerisation of the reactants to higher molecular weight species. Nevertheless, the typical viscous final product usually contains \( \approx 80\% \) by weight of the monomeric \((n=0)\) DGEBPA.

The effect of mole ratio of epichlorohydrin to bisphenol-A on the average molecular weight of the liquid resin formula is shown below:

**TABLE 4.1**

<table>
<thead>
<tr>
<th>Epichlorohydrin:Bisphenol-A</th>
<th>Molecular Weight (g/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10:1</td>
<td>370</td>
</tr>
<tr>
<td>2:1</td>
<td>450</td>
</tr>
<tr>
<td>1.4:1</td>
<td>791</td>
</tr>
</tbody>
</table>

The polymerisation of epichlorohydrin with bisphenol-A is a step-growth process. The closer the ratio of the co-reactants to unity, the higher the molecular weight of the products [McAdams and Gannon (1985)].

The typical commercial grade of liquid epoxy resin has a viscosity of 11-15 Pa.s at 25°C and the functionality of the terminal epoxy groups can approach values of 1.9 although this is largely a function of controlling side reactions [McAdams and Gannon (1985)].

The actual commercial preparation of epoxy resins involves vigorous agitation of the reacting epichlorohydrin/ bisphenol-A mixture (an exothermic reaction), washing with water to remove excess NaOH and NaCl and a degassing operation at elevated temperatures to remove any excess water. This can lead to resins that have hydrolysed epoxy groups. The resin precursor can have many volatile components including excess epichlorohydrin and any water that has not been thoroughly removed. Another component that is inevitably present, either from the production of the
precursors or as a consequence of mixing the resin and the curing agent, is dissolved air. Since all production environments are not perfectly dry, air will also have an appreciable water component related to the relative humidity of the environment (section 5.1.2).

Degassing reduces the dissolved air content and the number of suspended bubbles by encouraging air to come out of solution and by expanding existing air bubbles. They can rise to the surface of the vessel through the reduced viscosity resin where the gases are carried away by the vacuum pump. "Nucleation" relieves the gas concentration of the resin until bubbles are no longer formed and the concentration is further reduced by gas diffusion into existing macroscopic bubbles. When no additional gas is available it can be said that the equilibrium or saturated gas concentration of the resin has been reached. The concentration of gas that remains is consequently related to the degree of vacuum of the degassing operation. Volatile components of the resin, such as epichlorohydrin and water, should also be removed as the pressure is reduced, as long as the hydrostatic pressure is below the vapour pressure of the volatile at the degassing temperature. More thorough degassing can be attained by the use of nucleating agents. For the same degree of vacuum an abundance of heterogeneous sites facilitates bubble formation. Both the number and kind of nucleating particles determine the efficiency of the degassing operation [Hansen and Martin (1965)].

An epoxy resin has a long shelf life until the curing agent is added and depending on the type of curing agent, they will cure at room temperature or at elevated temperatures. Curing agents include aliphatic and aromatic amines, amides and anhydrides. The thermoset reaction is by definition a (step-growth) reaction but although the reactions in commercial systems are designed specifically to avoid the formation of a condensate, small quantities of low molecular weight condensate may be formed. By adopting the principles of molecular engineering it is possible to alter the physical properties of the final resin although it is necessary to remain within the bounds of processability, including the uncured resin viscosity, pot life, reaction or cure shrinkage and toxicity. A number of papers deal with the mechanical properties of cured epoxy resins [Kline (1960)] and the effect of structure
of the basic resin and the degree of crosslinking [Kwei (1967)].

Epoxy resins offer considerable variety for formulating prepreg resins. The liquid uncured resin may be reacted with a curing agent to form an intermediate or B-stage resin which is soluble in solvents such as propanone. At this stage, the reaction has been initiated at a number of widely separated points (epoxy groups) in the resinous mass. With additional cure, crosslinking becomes general and the compound assumes its thermoset nature.

The mechanisms of cure are different with each hardener and some are better understood than others. It is pertinent to mention that during the cure the epoxy ring is opened and a crosslinked structure is formed either through the OH group or the terminal epoxy group [Cowie (1973)]. This is accompanied by an increase in viscosity and an increase in the glass transition temperature as the network structure forms [Stevens and Richardson (1983)]. This can be expressed in terms of a time-temperature-transformation (TTT) diagram (figure 4.1) [Enns and Gillham (1983)]. The curing cycle is represented by the resin rheology as a function of time and isothermal temperature. The S-shaped gelation curve and the vitrification curve divide the time-temperature plot into four distinct states of the thermosetting cure process: liquid, gelled rubber, unaged glass and gelled glass. \( T_g \) is the glass transition temperature of the unreacted resin mixture, \( T_{g_{\infty}} \) the glass transition temperature of the fully cured resin and gel. \( T_g \) is the glass transition temperature of the resin at its gel point. Once the system has gelled, even if cure is incomplete, a bubble will be effectively "frozen" within the final composite part.

4.2 RESIN-WATER INTERACTIONS

Composite-water interactions are renowned to affect the mechanical properties of the final composite part [Shen and Springer (1977)][Illinger and Schneider (1980)]. The nature of the interactions can be split into chemical and physical effects. The former results from chemical interactions between the penetrating
Figure 4.1 Time-Temperature-Transformation (TTT) diagram for a typical thermoset water and one of the constituent materials in the composite. Chemical interactions are mainly hydrolyses of polymer bonds and dissolution and leaching out of water soluble species [Brewis et al. (1980)]. Chemical reactions can also occur between the hydrolysed or dissolved products with the resin or curing agent [Marom (1985)]. The physical source of hygrothermal ageing of composite materials is reflected in the plasticisation of the matrix resulting in a reduction of the glass transition temperature [Brewis et al. (1980)] which has been attributed to the breaking of hydrogen bonds by water [Moy and Karasz (1980)] making chain segment rotation possible [Peyser and Bascom (1981)]. Another significant physical phenomenon is the generation of internal stresses due to the accumulation of water molecules within the polymer network [Adamson (1980)].

Glass fibre reinforcement can degrade autocatalytically if the fibres contain alkali ions inducing flaw formation at the fibre surface leading to significant reductions in strength. It is also well known that a fundamental prerequisite for high composite strength is good fibre-matrix bonding. This is achieved by direct chemical bonding or
by the intermediary of a coupling agent [Hull (1981)]. Functional groups are liable to hygrothermal chemical attack leading to interfacial degradation. In addition to chemical bonding, the physical morphologies of the constituents at their interface determine the type of physical bonding which is formed. The strength of such bonds is sensitive to physical processes such as the build-up of destructive internal swelling stresses. The combination of degradation, plasticisation and internal stresses can lead to crazing and cracking which generally leads to failure [Kausch (1978)].

In terms of the processing, water is an unwanted volatile that can diffuse into existing air bubbles causing stabilisation and growth. It can also act as a catalyst, initiating premature curing of the resin/curing agent system and thus reduce its shelf life although, in an amine-cured system, active hydrogen compounds such as water are actually required to initiate cure [Smith (1961)]. Ordered domains of aggregated resin molecules in the unreacted system can also be disrupted by solvents [Stevens et al. (1982)].

Water can enter the resin in several ways; solubility and diffusion of water directly into the resin from humid air during the resin mixing operation, moisture adsorbed onto the surface of the prepreg due to the affinity of the polar epoxy groups for water molecules and humid air entrapment between the plies during the lay-up process. Experiments have shown that laminates made from prepreg which have been exposed to a relative humidity of 35% were "void free" whereas those exposed to 85% exhibited considerable porosity. Also, prepreg that was dried in the presence of phosphorous pentoxide for six days had no porosity when examined ultrasonically. Laminates subjected to hygrothermal soakings resulted in extreme porosity [Browning (1990)].

4.2.1 Equilibrium Considerations for Volatile Species

Whether bubbles are a consequence of mechanical entrapment during the lay-up procedure or due to stable air nuclei, growth and collapse is governed by diffusion of mobile species across the bubble/resin interface. Volatile species such as
water can diffuse into a gas bubble if the concentration gradient is favourable. As water vapour diffuses into these bubbles there will be at any one temperature an equilibrium water vapour pressure (a partial pressure in an gas/water bubble) which, under constant volume conditions, will cause the total pressure in the bubble to rise above that of a pure gas bubble. When the bubble pressure exceeds the surrounding resin pressure, plus the surface tension forces, the bubble will grow. This reasoning can apply equally well for any volatile component in the system.

The equilibrium force balance is given by the Laplace equation (equation 2.1) so when the temperature rises for a constant volume system, the pressure in the bubble will rise faster than the resin pressure in accordance with the perfect gas laws but also due to the exponential temperature effect on the water vapour pressure (figure 4.2) which increases the partial pressure of water within the bubble. Once again this applies to other volatiles within the system although they will have a different temperature dependence on their vapour pressure.

By making some assumptions it is possible to determine how the pressure within the bubble can be affected by temperature. If it is assumed that the air/water vapour mixture behaves as an ideal gas and that Raoult's law is applicable for the partial pressure of water above the water-resin solution at equilibrium, then

\[ p_1 = x_1 P_{ol} \]  

where \( x_1 \) is the water concentration in the resin-water solution, \( P_{ol} \) is the pure component vapour pressure (in this case water) and \( p_1 \) is the partial pressure of water in the gas mixture in the bubble.

The total pressure in the bubble is the sum of the partial pressures of the two components in accordance with Dalton's law for ideal gas mixtures. At constant temperature,
where $p_a$ is the partial pressure of gas.

If $p_a$ is initially atmospheric pressure when the bubble is entrapped and $P_{o1}$ is either taken from steam tables or calculated from the Clausius-Clapeyron equation (Section 5.1.2) for various temperatures, then the pressure within the bubble can be calculated for any initial water/volatile content and throughout the cure cycle.

Figure 4.3 shows that the pressures generated in bubbles due to water vapour are appreciable and that growth is possible unless sufficient pressure is applied to the resin. Consolidating pressures are generally reacted against the solid contact of the reinforcement so resin hydrostatic pressures are considerably lower. By comparing figures 2.1 and 4.3 it can be seen that, for sufficiently high water contents, the pressure inside the bubble can exceed the resin pressure resulting in growth.
Other volatile components of the resin may also cause bubble stabilisation or growth. Diluents that have not been removed or even volatiles emanating from the resin or curing agent will generally be condensible vapours that can migrate to a host bubble.

The fundamental theory described places limits on the state of equilibrium. It assumes that the bubble remains at constant volume and that Raoult's law provides the relationship between the partial pressure of the vapour in the bubble and the vapour dissolved in the resin. This assumption is not drastic with organic solvents, such as excess epichlorohydrin, as they are more likely to be compatible with the resin and deviate less from ideality although, especially in the case of a water-resin solution, it is more likely that Henry's law or some non-ideal rule will apply. This is investigated in Chapter 11.
4.2.2 Solubility of Species in Resin

As a rough guide to solubility it is useful to consider the empirical approach suggested by Hildebrand (1950) which is based on the premise that "like dissolves in like". The treatment involves relating the enthalpy of mixing to the cohesive energy density ($\Delta E/V$) and defines a solubility parameter $\delta = (\Delta E/V)^{1/2}$, where $\Delta E$ is the molar energy of vaporisation and $V$ is the molar volume of the component. The proposed relation for the heat of mixing $\Delta H_m$ of two non-polar components is,

$$\Delta H_m = V_m(\delta_1 - \delta_2)^2\phi_1\phi_2$$  \hspace{1cm} (4.3)

where $V_m$ is the molar volume of the mixture and $\phi_1$ and $\phi_2$ are the volume fractions and $\delta_1$ and $\delta_2$ are the solubility parameters of penetrant and polymer, respectively.

$\Delta H_m$ is small for mixtures with similar solubility parameters which indicates compatibility. This is appreciated by examining the free energy of mixing,

$$\Delta G_m = \Delta H_m - T\Delta S_m$$  \hspace{1cm} (4.4)

where $\Delta G_m$ is the Gibbs free energy change on mixing, $\Delta S_m$ is the entropy change and $T$ is the absolute temperature.

For any solution $\Delta S_m$ will be positive since mixing of different types of species will increase the number of distinguishable arrangements on a molecular or atomic scale and subsequently increase the entropy. The magnitude of $\Delta H_m$ is the deciding factor in determining the sign of $\Delta G_m$. A negative $\Delta G_m$ will cause the components to form a solution. The solubility parameter approach describes the enthalpy of mixing of simple liquids and can predict whether mixing may occur.

Values for the solubility parameter for simple liquids can be calculated readily from the enthalpy of vaporisation. The same method cannot be used for a
polymer and one must resort to comparative techniques. Usually \( \delta \) for a polymer network is established by finding the solvent which will produce the maximum swelling of a network or the largest value of the limiting viscosity, as both indicate compatibility. The polymer is assigned a similar value of \( \delta \). Alternatively, Small (1953) and Hoy [Hansen and Beerbower (1971)] have independently tabulated a series of group molar attraction constants from vapour pressure and heat of vaporisation data which give a good estimate of \( \delta \) for most polymers. In the case of a bisphenol-A resin the value of the solubility parameter will depend on whether the resin is in the cured or uncured state, i.e. the number of repeat units and end groups. For the cured polymer, the solubility parameter can be estimated from the sum of the various molar attraction constants, \( F \), for the groups which make up the repeat unit, hence

\[
\delta = \frac{(\Sigma F)}{V} = \frac{(\Sigma F) \rho_R}{M_o} \quad \text{.... (4.5)}
\]

where \( V \) is the molar volume, \( M_o \) is the molar mass of the repeat unit and \( \rho_R \) is the density of the resin.

**TABLE 4.2**

<table>
<thead>
<tr>
<th>Group</th>
<th>Small</th>
<th>Hoy</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CH(_3)</td>
<td>438</td>
<td>303.4</td>
</tr>
<tr>
<td>-CH(_2)</td>
<td>272</td>
<td>269.0</td>
</tr>
<tr>
<td>-CH</td>
<td>57</td>
<td>176.0</td>
</tr>
<tr>
<td>-C</td>
<td>-190</td>
<td>65.5</td>
</tr>
<tr>
<td>p-phenylene</td>
<td>1346</td>
<td>1442.2</td>
</tr>
<tr>
<td>-O-</td>
<td>143</td>
<td>235.3</td>
</tr>
<tr>
<td>-OH</td>
<td>-</td>
<td>462.0</td>
</tr>
<tr>
<td>-CO-</td>
<td>563</td>
<td>538.1</td>
</tr>
</tbody>
</table>
Table 4.2 shows the group contributions to the solubility parameter. Using Hoy's values for the polyhydroxyether of bisphenol-A with a density of 1.16 g/cm³, these values can be added accordingly:

\[
\begin{align*}
\text{Group} & \quad \text{F (Jcm}^3\text{)}^{1/2} \\
2(\text{p-phenylene}) & \quad 2(1442.2) \\
2(\text{-CH}_3) & \quad 2(303.4) \\
2(\text{-CH}^2) & \quad 2(269) \\
2(\text{ether oxygen}) & \quad 2(235.3) \\
\text{-OH} & \quad 462 \\
\text{-CH} & \quad 176 \\
\text{-C} & \quad 65.5 \\
\hline
\Sigma & \quad 5203 \\
\end{align*}
\]

Hence, \( \delta = \frac{(5203)(1.16)}{284} = 21.25 \text{ (J/cm}^3\text{)}^{1/2} \)

Using Small's constants and assuming that a hydroxyl group is the sum of the ether oxygen and a "variable" hydrogen \( (F_H=204.5(Jcm}^3\text{)}^{1/2}) \) [Wu (1968)], the solubility parameter \( \delta = 18.84 \text{ (J/cm}^3\text{)}^{1/2} \). Small and Hoy's estimates of \( \delta \) have been shown to be within 10% of experimentally determined values [Hansen and Beerbower (1971)].

Table 4.3 shows the solubility parameters for solvents calculated from the respective enthalpies of vaporisation.
TABLE 4.3

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\delta (J/cm^3)^{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propanone</td>
<td>20.3</td>
</tr>
<tr>
<td>Tetrachloromethane</td>
<td>17.6</td>
</tr>
<tr>
<td>Trichloromethane</td>
<td>19.0</td>
</tr>
<tr>
<td>Methanol</td>
<td>29.7</td>
</tr>
<tr>
<td>Water</td>
<td>47.9</td>
</tr>
</tbody>
</table>

Comparing Table 4.3 to the calculated solubility parameter for the cured resin it can be seen that water and bisphenol-A resin are not compatible and will not be very soluble. The first three in Table 4.3 have much similar solubility parameters and it is for this reason that trichloromethane (chloroform) is used as a diluent for the uncured resin in the processing route.

Unfortunately solubility is not a simple process and secondary bonding, e.g. hydrogen bonding, may play an important role in determining component interactions. This qualitative statement is intuitively correct since any specific interaction between the solute and solvent will increase the total solubility. It is also found, in the case of epoxy resin systems, that the polymer characteristics responsible for good composite performance are also responsible for moisture pick-up: -OH, -O- and -N- groups strongly hold $H_2O$ by hydrogen bonding while $N,COO$ and cyclic groups can attract and strongly hold $H_2O$ by $\pi$-bonding [Reinhart (1989)]. It is also possible that a chemical reaction will occur between the resin and the water

$$\text{H}_2\text{O} + \text{CH}_2\text{CHCH}_2\text{O} \xrightarrow{H_2O} \text{CH}_3\text{CHCH}_2\text{OH}$$

This reaction, which yields a glycol (1,2-diol), undergoes nucleophilic attack and is an acid catalysed reaction. The ring opening of an epoxide usually requires hydrolysis at elevated temperatures and in the presence of dilute hydrochloric acid since they do not contain a replaceable proton. The oxygen atom is sufficiently
basic to undergo protonation in an acidic medium by donation of a lone pair of electrons, i.e. it functions as a Lewis base [Murray (1977)]. The protonated species is then susceptible to attack by a nucleophile.

\[
\text{Epoxide undergoes Nucleophilic Attack}
\]

This implies that under ambient conditions sorption of water from humid air is unlikely to form the diol with the pure resin, although it may form with residual water during the cure schedule. This is also reflected in the general low solubility of ethers in water since there are no available hydrogen atoms to form hydrogen bonds. The effect is more pronounced as the hydrocarbon content is increased. Water interactions with a bisphenol-A resin would therefore appear primarily to be a consequence of hydrogen bond formation with the pendant OH group.

This can be more clearly appreciated by examining the hydrogen bonding component of the solubility parameter. This is not known for most resin systems but it can be calculated by the summation of attraction constants developed by Hansen (1969). In this case the solubility parameter is divided into contributions from dispersion forces, polar forces and hydrogen bonding forces. Table 4.4 shows some attraction constants of interest for a composite system. The molar attraction constants of Small (1953) are considered purely to be that of dispersion forces, as these constants were based on data from classes of compounds with negligible dipole interaction energy and no hydrogen bonding. It has also been considered that the contributions to \( F \) for dispersion and polar forces would be additive (\( \Sigma V \delta \)) while hydrogen bonding is added on an energy basis (\( \Sigma V \delta^2 \)) [Hansen and Beerbower (1971)]. It must be emphasised that the hydrogen bonding contribution is slightly misleading in that it contains all association bonds, including \( \pi \)-bonds and any other forces that are not included in the polar or dispersion contributions.
The contributions can be summed accordingly using,

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_H^2$$

which for the uncured resin system where \(n=0.2\) (using Small's constants for the dispersion forces and Hansen's parameters for the other contributions) gives \(\delta_d=17.74\), \(\delta_p=5.56\), \(\delta_H=8.51\) and \(\delta=20.45\) (J/cm³)¹/².

The polar force is the smallest contributor to the solubility parameter which is in agreement with other observations in polymeric systems [Small (1953)][Hansen (1969)]. The contributions to water are \(\delta_d=15.55\), \(\delta_p=15.95\), \(\delta_H=42.34\) and hence \(\delta=47.9\) (J/cm³)¹/². These theoretical calculations indicate that the hydrogen bonding component for water will strongly influence its solubility in the resin forming bonds mainly with the pendant OH group on the resin as this is has a higher hydrogen bond propensity than the ether oxygen.

### 4.3 SUMMARY

The physical and chemical processes behind epoxy resin technology indicate that dissolved air, water and excess epichlorohydrin can be present in the epoxy resin pre-cursor. The mixing operations and the composite production procedure can entrap air that has a finite water concentration unless the production environment is perfectly dry. Such volatile species and any that emanate as a result of the
thermosetting reaction, can stabilise existing air bubbles which may subsequently grow. Solubility parameter theory indicates that water and resin are not compatible and that the solubility will be determined predominantly by the hydrogen bonding components. By comparing the behaviour of water with pure ethers it seems that resin-water interactions, under ambient conditions, will be predominantly with the OH group on the resin backbone, since the nucleophilic attack of the epoxide groups is an acid catalysed reaction that occurs more readily at elevated temperatures.
CHAPTER FIVE

SORPTION

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5. SORPTION

Sorption is a generalised term used to describe the penetration and dispersal of penetrant molecules to form a mixture. In a polymeric system the sorption process can include adsorption, absorption, incorporation into micro-voids, cluster formation and solution. Since water generally gets into the resin system from humid air at some stage along the processing route the resin will therefore have some finite air and water content before being committed to the cure cycle unless stringent measures are taken to remove these components. It is therefore advantageous to consider the process of sorption since it can provide information about diffusion coefficients and modes of mixing.

It is important to note that penetrant molecules may participate in more than one concurrent or sequential mode of sorption in a polymeric material. Furthermore, the distribution of penetrant between different modes of sorption may change with changes in sorbed concentration, temperature, swelling, time of sorption to equilibrium and other factors. The equilibrium amount of penetrant sorbed and its sorption mode in a polymer under given conditions are governed by the thermodynamics of the system.

5.1 SORPTION ISOTHERMS

The simplest case is that of ideal solution behaviour with sorbed species randomly dispersed within the polymer such that Henry's law is obeyed. The solubility is then a constant, independent of sorbed concentration, at a given temperature and the sorption isotherm is a linear relation of concentration vs. pressure (partial pressure) (Type I in figure 5.1). Ideal solution behaviour is observed in practice when most permanent gases are sorbed by polymers [Michaels et al. (1963)]. This behaviour is readily understood since the solubility of permanent gases is very small due to lack of polymer-penetrant interactions [Van Amerongen (1946)]. Specific gas-gas interactions are also negligible and ideal dilute solution behaviour is observed.

83
Figure 5.1 Isotherm plots of sorbed concentration vs. ambient vapour pressure (I) Henry's law, (II) Langmuir-type, (III) Solution/Clustering, (IV) Site saturation at point B

Other types of sorption behaviour are illustrated in figure 5.1. The figures on these isotherms also allude to the BET classification of isotherms [Rogers (1985)]. In terms of the molecular pair distribution approach, type II represents a preference for polymer-penetrant pairs to be formed at relatively small pressures with a smaller amount of sorption of nearly ideal behaviour at higher pressures. In physical terms this represents initial sorption on some kind of specific sites in the polymer [Jacobs and Jones (1990)]. When the sites are nearly occupied, a small amount of penetrant dissolves in the polymer with a more or less random distribution. This situation is exemplified by polymers that contain polar groups.

Type III isotherms represent a preference for penetrant-penetrant pairs to be formed such that the solubility coefficient increases continuously with pressure. There are two principal interpretations of this behaviour. One is that the first molecules sorbed tend to loosen the polymer structure locally and make it easier for subsequent molecules to enter in the neighbourhood of the first than go elsewhere. This
interpretation implies that the sorbed penetrant effectively plasticises the polymer [Moy and Karasz (1980)] and type III isotherms are observed when a liquid or vapour penetrant is a strong solvent or swelling agent for the polymer. Although polymer-penetrant interactions are relatively strong, they are not specific in the sense of site-penetrant interactions. Another physical interpretation of type III behaviour is reserved for systems in which penetrant-penetrant interactions are inherently stronger than the corresponding polymer-penetrant interactions. Water is associated through hydrogen bonding in the liquid state [Searcy (1949)] which distinguishes it from the majority of organic penetrants. Association or clustering of water molecules inside a polymer is an important consideration. It might be anticipated that stable clusters or aggregates of sorbed penetrant molecules would be relatively less mobile in comparison with isolated molecules [Rouse (1947)]. Hence, if the proportion of clustered molecules increases with increasing sorbed concentration, as implied by a type III isotherm, then it would be expected that the diffusion coefficient of the penetrant in the polymer-penetrant system would decrease with increasing penetrant concentration [Barrer and Barrie (1958)]. This contrasts the behaviour of sorbed solvents or swelling agents when the diffusion coefficient increases with the concentration of sorbed penetrant [Barrie (1968)].

Type IV isotherms may be considered as a combination of type II at low pressures and type III at higher pressures. This type of behaviour is exemplified by water in hydrophillic polymers where initially, water molecules are strongly sorbed on sites corresponding to the polar groups while at higher relative pressures solution or a clustering process predominate.

Low pressure (low vapour activity) regions will approach ideal solution behaviour for all penetrants, although this may not always be easy to detect due to sequential sorption processes [Glasstone (1948)]. At the higher pressures, isotherms either tend to increase continuously with increasing pressure or level out to some finite value at unit activity. The former can be associated with plasticisation of the sorbent while the latter can be interpreted as a hole-filling exercise as in the case of a specific site sorption process. In the case of the type IV isotherm, where chemical site
saturation has already occurred at lower pressures, another point of inflection in the
curve at higher pressures can only be explained in terms of geometric limitations [Barrer
et al. (1958)]. Clustering occurs and the size of the cluster is limited by pore size of the
adsorbent (as in the case of water sorption by charcoal) which is directly relatable to
the volume of the pores, i.e. clustering and solution (with the possibility of increased
solution due to plasticisation) are occurring with clustering becoming dominant as the
water concentration is increased [Goosey (1985)].

5.1.1 Temperature Dependence of Sorption

In the case of adsorption, the effect of a rise in temperature is always to
reduce the adsorption at a given pressure for a given adsorbate-adsorbent pair. By
elementary thermodynamics this implies that adsorption is an exothermic process
[Atkins (1990)]. The extent of the reduction in adsorption for a given rise in
temperature may be calculated from the heat of adsorption, if known. The nature of
the gas or vapour is of prime importance in terms of its condensibility. Generally, the
more easily the gas or vapour is condensed, the greater the adsorption. This explains
the reason for the low solubility of permanent gases in polymeric materials compared
to vapours such as water with the heat of condensation being small for permanent gases
(under ambient conditions) and very negative (exothermic) for the more condensible
vapours.

In terms of penetrant solubility it is necessary to examine the heat of
mixing $\Delta H_m$ as well as the heat of condensation. This was introduced earlier in terms
of the solubility parameter (Section 4.2.2) and occurs due to deviations from ideality
embodied in the need to break solvent-solvent and solute-solute contacts to form
polymer-penetrant contacts. For unlike molecules with different cohesive energies this
usually leads to a positive $\Delta H_m$ (endothermic), i.e. an increase in temperature increases
the solubility [Young and Lovell (1991)].

The heat of sorption is a combination of both the condensation process
and the solubility [Hildebrand and Scott (1950)]. For gases above their critical point
(nitrogen, oxygen etc. at room temperature), the hypothetical value of the heat of condensation is small and the sorption process is governed by the positive heat of mixing. The heat of sorption is subsequently endothermic and the solubility of permanent gases increases with temperature. For more condensible gases and vapours the heat of condensation will be very negative and the solubility will decrease with increasing temperature.

5.1.2 Relative Humidity

When resin, either cured or uncured, homogeneous or composite, is exposed to a moist environment, it will either undergo sorption or desorption depending on the environmental conditions and the condition of the resin [Shen and Springer (1975)]. The isotherms in the Section 5.1 indicate the equilibrium uptake for the ambient vapour pressure. In a practical sense the water vapour pressure of an environment is measured in terms of relative humidity which is a more useful parameter since the mass of water vapour in the air is strongly dependent on temperature [Spalding and Cole (1973)].

The relative humidity, RH, is defined as the ratio of the actual vapour pressure, $p_{H2O}$, to the saturated vapour pressure, $p^{*}_{H2O}$, over a plane liquid surface at the same temperature. It can be measured by a wet-and-dry-bulb hygrometer.

The relative humidity (expressed as a percentage) is,

$$ RH = \frac{p_{H2O}}{p^{*}_{H2O}} \times 100 \quad \text{(5.1)} $$

Equation 5.1 shows that the relative humidity will decrease with an increase in temperature because of the exponential temperature dependence of the saturated water vapour pressure (figure 4.2).
As the temperature of the air is reduced the water vapour concentration is increased until the air becomes saturated (figure 5.2). $a$ is the water vapour activity defined as the relative humidity/100.

Prior to processing the water concentration in the bulk resin is a function of the initial relative humidity exposure under which the resin was equilibrated, i.e. the humidity of the production environment during resin fabrication, the mixing operation, storage or the lay-up. If this relative humidity is known the water concentration of the bulk resin can be determined directly from the sorption isotherm.

In the case of an entrapped water vapour bubble the resin, adjacent to the bubble, will also sorb or desorb water depending on the environment within the bubble.
and the condition of the resin. The effective relative humidity (activity) within the bubble will change throughout the cure cycle since it will undergo changes in pressure and temperature.

The vapour pressure of water is dependent on temperature according to the Clausius-Clapeyron equation [Atkins(1990)],

\[
\frac{dp_{H_2O}}{dT} = \frac{\Delta H_v}{T(v_g - v_l)} 
\]

...(5.2)

where \(v_l\) and \(v_g\) are the volumes in the liquid and gaseous state.

For the range of temperatures in the composite processing route it can be assumed that the heat of vaporisation, \(\Delta H_v\), is constant and the vapour phase behaves like an ideal gas. These assumptions allow the following dependence of the vapour pressure on temperature,

\[
p_{H_2O} = \left(p_{H_2O_0} \exp \frac{\Delta H_v}{R_g T_0} \right) \exp \left(-\frac{\Delta H_v}{R_g T} \right) 
\]

...(5.3)

where \(T_0\) (K) is the boiling point of water at atmospheric pressure, \(p_{H_2O_0}\) is the vapour pressure of water, \(p_{H_2O_0}\) is the water vapour pressure at boiling at atmospheric pressure, \(R_g\) is the universal gas constant and \(T\) is the absolute temperature.

The isotherm can provide the equilibrium uptake of water in the resin at a particular temperature. Using the relative humidity instead of the partial pressure on the ordinate axis encompasses the heat of condensation (from the Clausius-Clapeyron equation) for the sorption process but it does not provide information on the heat of mixing which is governed by component interactions. It does place a set of limits on the temperature dependence of sorption, although component interactions may be influence the solubility at different temperatures.
5.2 DIFFUSION OF SPECIES IN RESIN

Several authors have investigated the diffusion characteristics of epoxy resins in the cured state [Shen and Springer (1976)] since generally the effect of moisture on the mechanical performance of the final composite is the critical concern. In terms of processing, the parameters of primary interest are the rate of moisture sorption and the equilibrium uptake of the uncured resin since these parameters dictate the rate at which a bubble will grow or collapse due to the transport of water molecules. This reasoning applies to any volatile including permanent gases (such as the main components of air) as the concentration gradient and diffusion coefficient are critical in determining the growth and collapse of bubbles due to molecular migration. As the rate of growth or collapse is strongly dependent on the diffusion coefficient, the relationship between the process variables, material parameters and the diffusion coefficient is of paramount importance.

5.2.1 Temperature/Concentration Dependence of Diffusion Coefficient

Two major factors which affect the segmental motion of a polymeric material are the temperature and the concentration of the sorbed penetrant. An increase in temperature provides energy for a general increase in segmental mobility, which may be expressed in terms of the increase in free volume and directly related to the bulk expansion of the polymer [Fujita et al.(1960)]. The presence of sorbed penetrant can also increase the free volume of the system. In the absence of specific component interactions a penetrant can increase the segmental motion to the same extent that it would by a corresponding temperature increase leading to the same free volume increase [Peterlin (1975)].

Concentration dependence does, or may, differ from the temperature dependence due to the possibility of specific component interactions which affect the mobilities and the relative free volume contribution to the mixture by components involved in different modes of sorption. Even if the free volume change is negligible
plasticisation by the penetrant can be the consequence of the solvation or rupture of intermolecular bonds [Peyser and Bascom (1981)]. This will result in a reduction of $T_g$, even if the free volume is unaffected due to efficient packing of the molecules within the free volume [Starkweather (1969)].

The unit diffusion or jump involves a cooperative rearrangement of the penetrant molecule and the surrounding medium. It is not necessary that a "hole" be formed in the medium between two successive penetrant positions since it is equally feasible that the penetrant and matrix may share some common volume before and after the diffusion jump. However, a certain number of van der Waals type or other interactions of the medium must be broken to allow rearrangement of the local structure. This process requires a localisation of energy to be available to the diffusing molecule and the polymer, to provide the energy needed for rearrangement against the cohesive forces of the medium and the effective movement of the penetrant, for a successful jump [Meares (1954)]. In a polymer above its glass transition temperature, as in simple liquids, fluctuations in density (holes) are constantly disappearing and reforming as a result of thermal fluctuations [Frenkel (1946)]. Diffusive motion will subsequently depend on the relative mobilities of penetrant molecules and polymeric chain segments as they are affected by changes in size, shape, concentration, component interactions, temperature and other factors which affect polymeric segmental mobility.

Since diffusion requires rearrangement of the relative molecular conformations within a mixture, the behaviour is closely related to the rheological properties of the medium. However, it must be emphasised 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 coordination of segmental motions are involved. In viscous flow processes, there is an actual displacement of the matrix molecules requiring more coordination of these segmental motions [Bueche (1952)]. Hence, there will be closer relationship for low penetrant concentrations and large-size penetrants between the diffusion coefficient and the bulk viscosity. This will be discussed in more detail in Section 8.2.
The mode of sorption which relates to the position, manner and strength by which a sorbed molecule is held is a primary factor affecting mobility. When penetrant molecules are held by sites of varying energies the driving force for diffusion contains energy factors which depend on concentration and the number and distribution of sites within the system. As sorbed concentration changes with time, external concentration or temperature, the relative number of component contacts may change greatly. The resultant change in the mode of sorption is often reflected by a marked change in the overall diffusion coefficient.

Depending on the magnitude and nature of the interaction forces, a given penetrant molecule may be localised at a site or within a volume element for periods of time greater than that required for a unit diffusion step. Such molecules are essentially immobilised and do not contribute to the overall flux [Crank (1956)].

Mechanisms for penetrant immobilisation include chemical or physical interactions with polymer groups or chemical reactions. When the cohesive forces are greater than the attractive forces between penetrant and polymer, the penetrant tends to cluster within the system. A molecule within a cluster will generally be less mobile than an isolated molecule owing to the additional energy required to break free from the cluster. The energy required for hole formation for the migration of clusters will exceed that of a single molecule and may exceed the energy of evaporation of single molecules from the cluster.

The concentration of free molecules depends on the equilibrium distribution of molecules between the bound and free sorption modes and on the rate of exchange between the two states. When the exchange rate is equal to or greater than the diffusion rate, the presence of clusters will have little effect on the transport rate. When the exchange rate is less than the diffusion rate of free molecules the observed diffusion coefficient will be concentration dependent. The concept of penetrant immobilisation due to clustering is discussed in Chapter Twelve.
The temperature dependence of the diffusion coefficient can be expressed in terms of an Arrhenius relation,

\[
D = D_0 \exp\left(-\frac{E_a}{R_g T}\right)
\] .... (5.4)

where \(E_a\) is the activation energy for the diffusion process and \(D_0\) is the pre-exponential (entropy related) term.

When diffusion coefficients are measured over a range of temperatures plots of \(\ln D\) vs. \(1/T\) often exhibit non-linearities concave to the temperature axis. This type of temperature dependence is common with rates of reaction. It has been suggested that for the case of diffusion, \(E_a\) can be considered as the energy required to loosen the molecular chain for a given distance [Van Amerogen (1950)]. This involves the cohesive energy of the chain element which, like the heat of vaporisation, must depend on temperature, i.e. an increase in temperature provides energy to increase segmental mobility which increases the penetrant diffusion rate. A comparable loosening or increase in segmental mobility is brought about by the plasticising action of sorbed penetrant which serves to lower the apparent activation energy for diffusion.

5.2.2 Free Volume Theory

Various aspects of the free volume concept have already been mentioned. The free volume is the unoccupied space which arises as a result of inefficient packing of molecules. Flory and Fox (1951) have suggested that above the \(T_g\) a decrease in temperature of a polymer will be accompanied by a decrease in 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.
In terms of migration of molecules (whether solute or solvent), transport is affected by the free volume and the viscosity of a liquid can be related to the number of "holes" or more realistically 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 free volume facilitates molecular motions and that most of the thermal expansion at constant pressure goes into providing extra free volume [Meares (1965)]. This temperature dependence can be expressed in a linear form,

\[ f(T) = f(T_g) + \alpha(T - T_g) \]  

where \( f(T_g) \) is the free volume fraction at the glass transition and is considered to have the universal value of 0.025 for all polymers [Williams et al. (1955)]. \( \alpha \) is the difference in the respective thermal expansion coefficients above and below the glass transition temperature and is also deemed to have a universal value of \( 4.8 \times 10^{-4} K^{-1} \) or at least provides a first estimate.

The free volume theory has been 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 is found to be almost constant for a large number of liquids. At higher temperatures \( (> > T_g) \), a simple activation energy approach should prevail while as the temperature is decreased towards the \( T_g \) this is no longer valid as 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. At lower temperatures, free volume theory should describe the temperature dependence of the viscosity as the chemical structure of the resin is of secondary importance.
Penetrant diffusion can also be described in terms of a free volume approach as both viscous flow and diffusion are controlled by the same frictional constant, i.e. at higher temperatures an Arrhenius relationship should prevail as with the viscosity. Complications come with the penetrant disturbing the free volume of the matrix although ideally this should be a predictable effect. Peterlin (1975) invoked the Hildebrand concept of fractional free volume,

\[ f = \phi_1 f_1 + \phi_2 f_2 \]  

where, \( f_1 \) and \( f_2 \) are the fractional free volumes of the penetrant and polymer and \( f \) is the resultant free volume fraction in the mixture.

Unfortunately this method, although successful in several cases [Fujita et al.(1960)] is difficult to use with penetrants such as water which have anomalous behaviour. Starkweather (1969) has shown paradoxically that water in amides can cause a decrease in the glass transition temperature as well as a decrease in the specific volume, presumably as a result of breaking polymer-polymer bonds and forming water-polymer bridges. This suggests that although the viscosity should be predictable using a free volume approach, penetrant diffusion can only be predicted if the penetrant does not affect the free volume or obeys equation 5.6.

5.3 SUMMARY

Sorption is a temperature and pressure dependent process which is influenced by the condensability of the vapour and component interactions. The mode of sorption will therefore be different for each penetrant-polymer system which can affect the mobility of the penetrant within the polymer. It becomes clear that non-condensible gases, such as the main components of air and condensible vapours, such as water vapour, will behave very differently in a resin system.
CHAPTER SIX

EXPERIMENTAL I

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6. EXPERIMENTAL I

The experimental work has been split into two sections. The first deals with bubbles containing a permanent non-condensible gas and the second investigates the sorption of water. The latter can be found in Chapter Eleven. The materials used in this study and their preparation have been discussed as have the techniques used to evaluate the various input parameters. The resin was selected because it was a typical unmodified commercial formulation and the rationale behind the experimental methods was to use simple, time-efficient techniques that could be realistically used in a normal production environment.

6.1 MATERIALS AND CHARACTERISATION

The resin used in the study was an unmodified liquid bisphenol-A/epichlorohydrin resin (Shell Epikote 828) with an epoxy group content of 5.128 moles/kg [Shell (1987)]. Using the relation \( M_n = \frac{2000}{\text{epoxide content}} \) [Batzer and Zahir (1975)] [Ravindranath and Gandhi (1979)], this corresponds to an average molecular weight of 390 g/mole. This indicates that the ratio of epichlorohydrin to bisphenol-A of the resin used was approximately 10:1 (Table 4.1, Section 4.1).

The diepoxide prepolymer has the following chemical structure,

\[
\text{CH}_2\text{CHCH}_2\left(\text{O}\begin{array}{c}
\text{C} & \text{C} & \text{OCH}_2\text{CHCH}_2
\end{array}\right)_n\text{O}\begin{array}{c}
\text{CH}_3 & \text{CH}_3 & \text{OCH}_2\text{CHCH}_2
\end{array}\]

and therefore, the average value of \( n \) is 0.176 for the resin used in this study.
The density of the resin was measured by placing a known mass of resin into a graduated capillary tube. The tube was placed in an oven and the volume of the resin was measured over a range of temperatures (293K-373K). The measured density agreed with the manufacturer's specifications (1.16 g/cm³) and was not found to change significantly over the temperature range studied.

The viscosity of the resin was measured using a simple falling sphere method and was found to be extremely temperature dependent having a room temperature value (293K) of between 23-26 Pa.s (figure 6.1). This method was limited to a temperature of 353K at which point the sphere velocity was too high to attain consistent readings. A capillary tube method was used for the higher temperature (low viscosity) data [Flory (1940)]. The tube was calibrated against glycerol which had a known viscosity (1.499 Pa.s at 293K). 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 broken and the flow time for the resin to pass through the tube under gravity was measured and correlated to the viscosity. Corrections for the thermal expansivity of the borosilicate glass tube were found to be negligible over the temperature range with respect to other experimental errors. All measurements were within ±10% of the mean value.

The surface tension of the resin was measured using a capillary rise method. A capillary tube of known dimensions was placed in a comparatively wide glass vessel filled with resin. This ensured a planar surface. The rise was measured at different temperatures using a travelling microscope and a correction was made for the radius of curvature of the meniscus [Glasstone (1948)]. The correction assumes a zero contact angle but was considered justifiable as the heat-sealed clinically clean capillary tubes used were not opened prior to testing. Experiments were performed over the temperature range 293K-373K. The room temperature value of 0.035 N/m in air is in agreement with most gas/polymer systems [Wu (1970)]. This decreased slightly with increasing temperature although not significantly with respect to the calculated experimental errors (±10%).
VISCOSITY/TEMPERATURE DATA FOR RESIN

![Graph](image_url)

Figure 6.1 Temperature dependence of the resin viscosity

Volatile was measured in terms of weight loss at elevated temperature. A thermo-gravimetric method was used. Systematic weight losses were not directly relatable to temperature and it was considered that removal of volatiles was strongly dependent on the history of the resin, i.e. temperature and degree of degassing, relative humidity exposure, etc. Subsequent experimentation, where weight gains and losses were important criteria, was performed on resin for which the history was known and where volatile components had already been removed. The resin preparation is discussed in the next section.

Pure dry nitrogen gas was used in the gas bubble experiments. This was used instead of air as it was readily available and the use of a single gas facilitated subsequent modelling.
6.1.1 Resin Preparation

All resin was thoroughly degassed in a vacuum oven at 333K until all suspended bubbles were removed. The dissolved gas concentration could also be reduced by encouraging bubble formation. Silica anti-bumping granules were introduced to succour bubble formation because they were inert and could be separated easily after the degassing operation. Volatile weight losses, measured using a thermal balance with an accuracy of $1 \times 10^{-4} \text{g}$, were found to be minimal ($\leq 0.1\%$) after degassing under the above conditions. Long times at high temperatures ($>120^\circ\text{C}$) did show weight losses although this was attributed to resin degradation since there were noticeable colour changes. The resin, after this procedure, was considered as the base for the subsequent experiments. The resin was stored in a desiccator containing silica gel which maintained a relative humidity of less than 10%.

6.2 MONITORING THE BEHAVIOUR OF GAS BUBBLES

The objective behind the experimental work was to determine and measure the rate of bubble collapse or growth due to the mass diffusion of species within the resin. A non-curing system was used since it was necessary to reduce the number of variables by knowing what species were diffusing. Since the resin was thoroughly degassed it was possible to monitor the growth and collapse of bubbles containing a non-condensable gas due the diffusion of a non-condensable gas.

6.2.1 Bubble Size

In order to assess the behaviour of bubbles quantitatively it was necessary to introduce bubbles into the resin and monitor the rate of growth or collapse before any predictive modelling could be done. The models used are based on a spherical geometry (Chapter Three) and so it was necessary to deal with bubbles that were approximately spherical. Since it is difficult to suspend a bubble in a liquid medium without it floating, the bubbles were restrained against a surface. Preliminary
experiments dealt with deviations from the spherical shape with increasing bubble size (figure 6.2). This was measured by injecting bubbles of different sizes into the resin with a hypodermic syringe and retaining them against a flat transparent glass slide. The width and depth dimensions were measured using a travelling microscope.

Figure 6.2 shows that gas bubbles approximate to the spherical shape at low bubble radii while at higher radii the shape is spheroidal. The deviation from the spherical line dictated the upper limit of the bubble size measurements.

The size of the bubble is also important in terms of the rate at which the bubble wall moves. The bubble diameter was the measured parameter. If the bubble was too large, the bubble wall velocity was found to be too slow, especially in a saturated resin where the driving force for diffusion was solely the surface tension forces. Times for complete solution were in the order of days at ambient temperatures. If the bubble size was too small then the rate of collapse or growth was too rapid for accurate measurements to be taken. The limit of optical microscopy is \( \approx 1 \mu m \) so all initial bubble sizes were in excess of this value and a bubble was considered to have collapsed below this value. Most bubble size measurements fell into the region 1\( \mu m \) to 100\( \mu m \), which are reasonable limits for spherical bubbles in a composite system.

6.2.2 Optical Microscopy

Gas bubbles are relatively poor objects for optical microscopy and reasonable definition is required to measure their diameters accurately. Transmission microscopy was used and photographic measurements were made throughout the experiments.

The resin was contained in a glass cuvette with flat transparent sides. A thermocouple was placed in the cuvette so that the temperature of the resin was known at all times. A heating stage was designed that applied both heat and back lighting (figure 6.3). The source was a halogen bulb which was found to be more controllable than other heat sources. Experiments at elevated temperatures were done isothermally
Figure 6.2 Deviation from spherical shape for gas bubbles in resin

Figure 6.3 Monitoring bubbles using an optical microscope with heating stage
so it was necessary to raise the temperature quickly and maintain the temperature accurately (±2°C) for the duration of the experiment. With all experiments it was imperative that the sample was level to prevent bubble movement, especially at elevated temperatures when the viscosity of the resin was very low (≈0.1 Pa.s at 80°C (353K)). It was also found that to attain sufficient illumination for photographic measurement it was always necessary to back light the sample. As a consequence of this back lighting from the microscope, the sample temperature (even in the absence of the heat from the halogen bulb) was 40°C (313K). Temperatures were always allowed to stabilise.

6.3 MEASURING THE INPUT VARIABLES

The process of mass diffusion depends on the concentration gradient and the diffusion coefficient of the diffusing molecule through the matrix. These parameters are critical for any predictive model of the diffusion process.

This section describes how the input parameters were measured. The rationale behind many of the techniques used is that a predictive model is only as useful as the accuracy and availability of the input data. It is often necessary to have a quick and convenient method of determining these parameters without having to resort to some expensive or difficult or, for all intents and purposes, "academic" technique. These are major criteria for a production environment.

6.3.1 Gas Concentrations and Solubility

The molecules of gases are small and relatively insoluble in polymers and organic liquids which makes direct determination of the solubility quite difficult. The volume fraction of gas sorbed at any reasonable pressure is quite negligible and does not affect the free volume and segmental motions in a polymer [Meares\(^a\)(1965)]. This negates weight measurements as a method of determining gas concentrations in the resin.
The saturated gas concentration and its dependence on temperature and pressure is required to determine the driving force for the diffusion process. The gas concentration in the bulk resin is also needed which will primarily be a function of the resin's history. In other words, resin that has been exposed to gas at room temperature and pressure will have an equilibrium or saturated gas concentration for those conditions assuming that the resin has had sufficient time in the environment to attain the equilibrium gas content.

The technique used to measure the concentration of gas in the resin was similar to the Van Slyke blood analyser [Orcutt and Seevers (1937)] which outgasses the sample by simple agitation and measures the volume of gas liberated. For the viscous resin system this concept was adapted with the measured parameter being the instantaneous foaming level of resin in a capillary tube when suddenly placed under reduced pressure (figure 6.4).

The apparatus was designed so that the pressure on the resin could be reduced (virtually) instantaneously. Resin foams under vacuum as dissolved gases come out of solution. The rate of formation and growth is strongly dependent on the degree of supersaturation. In a typical degassing operation resin is placed in a vacuum chamber at a slightly elevated temperature to reduce the viscosity. The resin foams as the pressure is reduced and the emitted gas is carried away by the vacuum pump. Application of an "instantaneous vacuum" causes the resin to foam spontaneously. If the resin has sufficient sites for the dissolved gas to come out of solution then it can be assumed that the subsequent change in volume is a consequence of the expansion of the gas phase (figure 6.5).

In a normal degassing operation there are an abundance of sites where dissolved gas can come out of solution and diffuse into existing gas bubbles remaining from the resin mixing operation. The efficiency of the degassing operation is partially dependent on bubbles being present as well as nucleation from cavities in the container walls. This reasoning suggests that the total gas content of the resin can be split into two parts; the dissolved gas concentration and the free gas content, the latter in the
Figure 6.4 Instantaneous Vacuum Technique

Figure 6.5 Determination of gas concentrations from foaming levels
form of suspended bubbles. To determine the dissolved gas concentration of the resin it was imperative that no suspended bubbles could contribute to the volume change on reducing the pressure. Although this was done optically (the resin was allowed to stand until no suspended bubbles were observed with a travelling microscope) it is reasonable to assume that any bubbles smaller that the lower limit of the magnification (= 1 \( \mu \text{m} \)) would dissolve in a very short time solely due to surface tension forces. The resin was considered to have no suspended gas bubbles after this procedure.

The resin was sucked into a graduated glass capillary tube of known dimensions and one end was sealed using a rapid cure epoxy adhesive and silicone rubber compound. The capillary tube was placed within a glass boiling tube that was connected to a reservoir of larger dimensions than the boiling tube and connecting pipes. The reservoir was attached to a rotary vacuum pump. Manipulation of a series of valves enabled a vacuum to be held within the reservoir before being applied to the sample. The reduced pressure was measured by a manometer, heat was applied by placing the boiling tube inside a furnace and the temperature was measured by a thermocouple within the boiling tube.

Reducing the pressure caused the resin to foam and the change in height of the resin in the capillary was recorded. Stable foaming allowed accurate determination of the level of the foam. A stable foam was attained by heating the resin to 60°C (333K) which reduced the viscosity significantly. The optimum capillary radius was found to be \( \approx 1 \text{mm} \). It was considered that larger diameter tubes would underestimate the gas concentration since nucleation may only occur at the walls and not in the bulk. With smaller diameter tubes it was much more difficult to suck the viscous resin, even when heated, into the capillary and the change in height was often too large for the experimental apparatus.
The change in height of the resin was attributed to the dissolved gas. The foam level quickly decreased with time as the gas was carried away by the vacuum. The initial (and maximum) height of the foam was used to determine the gas content of the resin. Simple manipulation of the ideal gas laws enabled determination of the gas concentration of the resin.

6.3.1.1 Temperature Dependence of the Saturated Gas Concentration

A series of experiments were performed at different equilibrium temperatures to determine whether the saturated gas concentration was temperature dependent over the temperature range under consideration.

Pure dry nitrogen was bubbled through resin at different temperatures and allowed to equilibrate over a number of days. Equilibrium was generally attained within a few hours using this method. Normal exposure to the gaseous environment would take considerably longer since the gas would have to diffuse through the resin, i.e. the depth of penetration of a diffusate is related to \((Dt)^{1/2}\) [Cottrell (1975)], where \(D\) is the diffusion coefficient of the gas in the medium and \(t\) is time. Bubbling the gas through the medium accelerates the diffusion process due to the increased interfacial area for diffusion and the translatory motion of the gas bubble due to buoyancy effects.

Resin was equilibrated at atmospheric pressure for a range of temperatures between 313K and 373K. The bubble injection pressure was just above atmospheric pressure. The lower limit of the temperature was dictated by the viscosity of the resin below which bubbling was difficult without using larger injection pressures. The time for bubbles to separate from the resin due to buoyancy effects was also considerable (vacuum could not be used since there is also a pressure dependence on the saturated gas concentration). Higher temperatures were not used in case the resin degraded during the equilibration time.

The gas concentration of the resin samples were then measured using the instantaneous vacuum technique. The temperature of the furnace was the same for all
the samples 333K (60°C), which were tested immediately after removing from the equilibrium environment. No significant differences were found between the foaming levels for all of the equilibrated temperatures indicating that the gas concentration of the resin at saturation was independent of temperature for the measured conditions. The maximum difference in readings was ±20% of the mean value for all the temperatures tested. Repeat tests at each temperature gave much similar readings (±5%).

6.3.1.2 Pressure Dependence of the Saturated Gas Concentration

The pressure dependence of the saturated gas concentration was determined by equilibrating resin at different pressures but at a constant temperature of 313K. For pressures below atmospheric pressure the resin was placed in a vacuum oven and pure dry nitrogen was bubbled through the resin from a gas bottle outside the oven. Once again, the resin was allowed to equilibrate over a number of days. The resin was allowed to stand at the reduced pressures to remove suspended bubbles from the resin. The vacuum was then released and the gas concentration was measured directly using the instantaneous vacuum technique. Experiments were performed at several pressures ranging from 1 atmosphere (1.01x10^5 Pa) to 0.2 atmospheres (0.202x10^5 Pa) which were measured using the bourdon gauge on the vacuum oven. The deviation from the mean concentration, for each pressure level, was no more than ±8%.

For pressures in excess of atmospheric pressure the resin was equilibrated in a resin injection unit (figure 6.6). The unit injects bubbles into the resin and maintains the desired overpressure. This positive pressure was held until suspended bubbles had been removed. Problems were encountered once the pressure was released in that bubbles spontaneously came out of solution. These bubbles, although suspended in the resin, were in solution at the equilibrium pressure and thus would contribute to the overall dissolved gas concentration. Unfortunately it was not possible to prevent these bubbles escaping before the dissolved gas concentration could be measured. Although cooling the resin significantly reduced the motion of these nucleated gas
Figure 6.6 Resin Injection Unit

bubbles, difficulties were found in sucking the resin up into the capillary tube. It was also necessary to perform the instantaneous vacuum technique at low temperatures which made measurement of the change in height inaccurate due to unstable foaming. The higher the initial pressurisation the more quickly the gas came out of solution and subsequently the more inaccurate the measurement. Although a method could have been developed to apply an overpressure within the vacuum unit, this was found not to be necessary due to the linearity of the pressure/concentration plot for the reduced pressures. Extrapolation to higher positive pressures does not seem unjustified and has proved to be successful (Section 8.1).

6.3.2 Gas Diffusion Coefficient

A novel method was used to measure the gas diffusion coefficient over the range of temperatures under investigation. The fundamental theory behind the experimentation is that the rate of solution of a stationary gas bubble in a liquid is governed by both the solubility and the diffusion coefficient of the gas in the liquid.
The liquid at the bubble surface maintains a gas concentration equal to the saturated solution concentration at the local pressure. If the surrounding fluid has a lower concentration, then gas molecules diffuse outward, thereby depleting the solution at the bubble surface and permitting more gas to dissolve. By applying the steady-state solution to Fick's law as described in Chapter Three, an equation is obtained giving the bubble radius as a function of time (equation 3.9). The parameters of this equation are the solubility and the diffusion coefficient; if the solubility is known then the diffusion coefficient may be determined by fitting the equation to experimental radius vs. time data.

The experimental procedure took the form of monitoring small gas bubbles in a saturated resin. A saturated resin was used since it was possible to make up reproducible solutions thus eliminating the variable of the dissolved gas concentration in the bulk resin from the theoretical analysis. This reduced a possible source of error in the calculations. The surface tension forces are solely responsible for the collapse of gas bubbles in a saturated system since they increase the gas pressure in the bubble and thus lead to the increase in the dissolved gas concentration in the resin at the surface of the bubble. Equations 3.20 and 3.21 were used although, since the theory is applicable only to small gas bubbles where a spherical shape can be assumed, it is imperative that surface tension forces are taken into account even if an unsaturated resin is used.

A possible source of experimental error is that a bubble that is retained by a surface has a finite contact angle and therefore a finite area of contact, thus reducing the area for diffusion. Another consequence of a surface is to reduce the rate of mass transfer by causing a concentration build-up between the bubble and the surface. Both of these effects were considered negligible as the bubbles monitored were small and the effect of contact on the rate of solution was considered to be much less than the overall precision of the experimental procedure.

The resin was saturated with pure dry nitrogen at atmospheric pressure and 313K and allowed to equilibrate as before. Discrete bubbles were then injected into
the resin at a pressure just above atmospheric pressure using the resin injection unit (figure 6.6). The resin was poured carefully into a glass cuvette and placed on the optical microscope. A bubble was selected that was in the centre of the cell and away from other bubbles. This limited interference from gas diffusing from other bubbles in the vicinity and effects from having more than one solid surface contact. A stopwatch was started as soon as a suitable bubble was located. The bubble diameter was measured photographically at various time intervals. An optical scale was photographed in order to calibrate bubble photographs. All observations were made at constant temperature which was measured by a thermocouple inserted in the glass cuvette (figure 6.3). All bubbles were monitored until complete collapse. Experiments were performed at different temperatures and times for complete solution ranged from a few minutes to several hours.

The main advantage of this technique is that it offers a convenient means to determine diffusion coefficients of gases in transparent liquids. The input parameters required to determine the diffusion coefficient are also easily measured, i.e. the gas concentration and the surface tension forces. The accuracy was determined as a percentage deviation from the mean value, which was found to be ±20%. This is as accurate as other methods of determining the diffusion coefficient, e.g. diffusion coefficients for oxygen in water, using a volumetric uptake method, range from $1.9 \times 10^{-9}$ to $2.6 \times 10^{-9}$ m$^2$/s at 298K which is ±15% from the mean value [Himmelblau (1964)].

Deviations from run to run were attributed to convection currents in the liquid caused by temperature and concentration gradients. Convection is not an easily measured quantity but intuitively it will increase the rate of solution. This will become increasingly important at higher temperatures as the viscosity of the fluid is reduced. Although all measured bubbles were stationary (apart from movement of the bubble wall) and all bubbles collapsed in a similar fashion to that dictated by the steady-state theory, it is feasible that rates of solution were accelerated due to convection thus producing higher values for the diffusion coefficient. Since this effect is more pronounced with increasing temperature this could yield an inflated activation energy for diffusion. It must also be considered that in a real system this is actually what is
happening. It can therefore be concluded that in terms of a realistic diffusion coefficient which is required to predict bubble growth/collapse rates it is as good if not superior to other methods of measuring the diffusion coefficient of gases in a liquid resin. In fact since convection of the medium or the movement of the bubble through the medium is difficult to take into account from a theoretical point of view or measure practically, especially in a composite system, one could argue that other methods of deducing a realistic diffusion coefficient for purpose of predicting the behaviour of gas bubbles are extremely limited.
CHAPTER SEVEN

ANALYSIS OF MATERIAL PARAMETERS

7.1 VISCOSITY OF RESIN

7.1.1 Viscosity - High Temperature Regime

7.1.2 Viscosity - Low Temperature Regime

7.2 SURFACE TENSION OF RESIN
7. ANALYSIS OF MATERIAL PARAMETERS

Any model requires a number of input parameters which may be interactive with other material parameters or external variables. The utility of a model is improved by reducing the number of experimentally determined data or by placing limits on this data. For a model to be useful in an industrial environment, where characterisation of materials is expensive and time consuming, predictive techniques need to be employed that can be applied to many systems. This section investigates the viscosity of the resin and the surface tension from a theoretical and semi-empirical angle using the data obtained from the experiments described in Section 6.1.

7.1 VISCOSITY OF RESIN

The viscosity of the resin is of critical importance in the processing of a composite in terms of the infiltration of reinforcement and determining the optimum time to apply pressure to consolidate the laminate. It is also important as it is related to the resistance of the medium to molecular motion. For a resin system the viscosity is also extremely temperature dependent, decreasing as the temperature is raised.

An Arrhenius type 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, $E_\eta$, in order to pass to another position. This energy is regarded as consisting mainly of that required for the formation of a "hole" into which the molecule can pass in its motion from one equilibrium position to the next [Eyring (1936)].

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 vaporise a single molecule would require an energy $U/2$, since each bond is shared between two other molecules, provided the rest join up as to leave no hole in the liquid. If a hole is left, the vaporisation 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 energy 
U/2 and therefore the energy required to make a hole of molecular size in the liquid 
without vaporisation 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 to 
evaporate a molecule without leaving a hole. The latter quantity is related to the latent 
heat of vaporisation, 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 
vaporisation.

In reality the activation energy for viscous flow is much smaller than this 
[Frenkel a (1946)]. 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 for asymmetric molecules 
the ratio is approximately 4. For the range of temperatures in the composite processing 
route H_v, the enthalpy of vaporisation, is approximately equal to the energy of 
vaporisation, ΔE.

The resin molecule is a long molecule even before the polymerisation 
reaction and will not have a spherical ﬁeld of force. The space required for it to ﬂow 
is only a fraction of that occupied by a single molecule. Using the various molar 
attraction constants F for the resin precursor (n=0.2) it is possible to calculate the 
notional molar heat of vaporisation for a resin molecule using the relationship 
δ=(ΔE/V) 1/2 (Section 4.2.2). The molar volume can be calculated from the density 
and the molar mass to give ΔE≈140kJ/mole. Using the empirical ratio ΔE/E_η = 4 gives 
an activation energy for viscous flow E_η ≈35kJ/mole.
Figure 7.1 Arrhenius plot of viscosity data

Figure 7.1 shows the temperature dependence of the resin used in this study. The figure clearly shows that an Arrhenius relationship of the type,

\[ \eta = A \exp\left(\frac{E_\eta}{R \cdot T}\right) \]  \hspace{1cm} \ldots \text{(7.1)}

is not a good representation of the data in that \( E_\eta \) decreases as the temperature is increased. Figure 7.1 does not imply a discrete change in mechanism but merely indicates the extreme differences in the energy of activation as the temperature is raised.

These observations indicate that viscous flow is not a simple thermally activated process in the resin system. The observations may be explained by the fact that the viscosity is sensitive to the extra free volume made available by thermal expansion as well as the extra violence of kinetic agitation [Glasstone (1948)]. The Arrhenius relation may apply at higher temperatures. This would be in agreement with
observations in many polymer systems where the activation energy now represents a potential energy barrier rather than the availability of a suitable hole. Empirically it has been noted that polymers that are still stable at temperatures in excess of 100K above their glass transition temperature obey an Arrhenius relationship [Cowie (1973a)].

Two literature values were found for the glass transition temperature, $T_g$, of epoxy prepolymermers. For the resin used in this study, glass transition temperatures of 253K [Stevens and Richardson (1983)] and 223K [Aleman (1980)] were calculated from their respective semi-empirical formulae based on the molecular mass dependence of the $T_g$ [Fox and Flory (1950)] (Section 7.1.2). This implies that free volume theory will apply over some, if not all, of the temperature range before gelation in this system. At higher temperatures the Arrhenius relation may be appropriate while at the glass transition temperature, the activation energy for viscous flow is dominated by the available free volume. $E_\eta$ will therefore range from the asymptotic value dictated by free volume theory at the glass transition temperature (the point at which there is not enough free volume to allow molecular rotation or translation to take place), to the empirical value $E_\eta/4$ [Frenkel (1946)] where thermal agitation plays the dominant role. These limits were investigated for the resin system in this study.

7.1.1 Viscosity - High Temperature Regime

As a polymer is cooled towards its glass transition temperature there is a very large increase in viscosity such that the chemical structure is of secondary importance to the non-specific vitrification phenomenon. At higher temperatures energy activated processes become increasingly important and differences in chemistry become a significant consideration.

Liquids that are held together by hydrogen bonds show an activation energy for viscous flow that changes markedly with temperature, e.g. glycol, glycerol and water [Glasstone (1948)]. The energy of activation of such substances consists not only of the fraction of the enthalpy of vaporisation 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 probably diminishes because of the thermal movements of the molecules and the energy of activation will therefore decrease, i.e. the larger number of hydroxyl groups, the more complex the number of hydrogen bonds and the greater resistance to flow.

The resin molecule has a hydroxyl group on the backbone which can interact with other hydroxyl groups on other resin molecules. Such interactions are thermally labile and this partly explains the changing $E_\eta$ with 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 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 35kJ/mole to 29kJ/mole. In order to apply this to the viscosity data it is also necessary to know the pre-exponential constant in the Arrhenius relationship.

The absolute rate theory [Kingery et al. (1976)] states that at small stresses the viscosity, $\eta$, is independent of stress and that the flow process is dependent on the height of the energy barrier, $\Delta E_\eta$, the number of times the barrier is attempted $v$ and the flow volume, $V_o$. Hence,

$$
\eta = \frac{kT}{vV_o} \exp \left( \frac{\Delta E_\eta}{R_g T} \right)
$$

\[ \text{(7.2)} \]

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

These pre-exponential parameters are not known but one can make order-of-magnitude estimates. 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 $v$ is appropriate for this temperature range in a
simple liquid [Frenkel (1946)]. The flow volume can be considered simply as a spherical volume dictated by the mean jump distance. The jump distances that are believed to occur in liquids are between 0.2-0.5 nanometres (2-5 angstroms), or about an eighth of the volume of a polymer molecule [Meares (1965)]. If a value of 0.3nm is taken then the pre-exponential is $3.6 \times 10^{-6}$ Pa.s. at 293K. This value will not change much over the temperature range under consideration. This Arrhenius relationship, using this value for the pre-exponential constant and 29kJ/mole for the activation energy for viscous flow, is compared with the free volume theory and the experimental data in the next section.

### 7.1.2 Viscosity-Low Temperature Regime

Utilising equation 5.5 (Section 5.2.2) it is possible to calculate the free volume fraction of the resin over the temperature of the experimental data using the universal values of the thermal expansion coefficient $\alpha$ and the fractional free volume at the $T_g$. A relationship has been proposed by Doolittle (1951)(1952) between the free volume fraction and the viscosity,

\[
\eta = C \exp \left( \frac{B_\eta}{f(T)} \right) \quad \ldots \quad (7.3)
\]

where $C$ and $B_\eta$ are constants and $f$ is the free volume fraction.

Therefore incorporating equation 5.5 gives,

\[
\eta = C \exp \left( \frac{B_\eta}{f(T_g + (T - T_g))} \right) \quad \ldots \quad (7.4)
\]

and substituting the universal values,
Williams, Landel and Ferry (WLF) [Williams (1958)] proposed that the log viscosity varies linearly with $1/f$ above the $T_g$.

\[
\eta = C \exp \left( \frac{B_\eta}{0.025 + 4.8 \times 10^{-4} (T - T_g)} \right) \quad \ldots \quad (7.5)
\]

\[
\ln \left( \frac{\eta}{\eta_{T_g}} \right) = \frac{1}{f} - \frac{1}{f_{T_g}} \quad \ldots \quad (7.6)
\]

Therefore substituting equation 5.5 gives,

\[
\log \left( \frac{\eta}{\eta_{T_g}} \right) = \frac{-17.44(T - T_g)}{51.6 + T_g} \quad \ldots \quad (7.7)
\]

where the numerical coefficients are the consequence of the universal constants.

If the viscosity at one temperature is known then the viscosity can be calculated at other temperatures by determining the viscosity at the glass transition temperature. The two literature values of the glass transition temperature applicable to this system have been investigated.

The resin viscosity at 293K is $\approx 25\text{Pa.s}$ (figure 6.1)(Section 6.1) and therefore, from equation 7.7, the viscosity $\eta_{T_g} = 1 \times 10^9\text{Pa.s}$, for $T_g = 253\text{K}$ [Stevens and Richardson (1983)]. Figure 7.2 shows that the theoretical and the experimental data are not in good agreement especially at higher temperatures, although the interaction is clearly of a similar form.

The limitations of the WLF modification are clearly related to temperature, in that at higher temperatures it can no longer be assumed that the viscosity is only temperature dependent due to free volume considerations. It has been shown that such a treatment should be appropriate to $T_g + 100\text{K}$ [Williams et al.(1955)]. This is clearly not the case as deviations occur well below 353K. This can possibly be due to
inaccuracies in specifying the $T_g$ which is markedly influenced by small amounts of residual solvent, method of measurement and interpreting the data, as well as thermal history. The equation also forces coincidence at a reference temperature which in the case of $T_g$ is near the limit of the equation's applicability, i.e. any small error can severely affect the predicted viscosity over the entire temperature range. It also assumes that the constant $B_\eta$ in equation 7.4 is unity, which is true for many systems [Williams (1958)] [Doolittle (1951)] and is often a common assumption, although it should also presumably be partly dependent on polymer species. Also, the universal values are only a first estimate and may vary between systems [Cowiea (1973)].

Improvements to the model predictions can be made by using a reference temperature above the $T_g$ with a set of empirical constants in place of the universal constants. Machin and Rogers (1972) in trying to predict $T_g$ from these empirical constants found that the predicted $T_g$ was extremely sensitive to small changes in these values. To examine the relationship in more detail it is necessary therefore to determine what constants fit the data to ascertain if the WLF equation is appropriate.
The basic form of the WLF equation is expressed in the form of a shift factor \( a_T \), which is simply the ratio of the viscosity at \( T \) relative to that at \( T_\text{g} \). This shift factor, \( a_T \), has also been applied successfully to relaxation and creep behaviour. The expression states,

\[
\log a_T = \frac{-C_1(T-T_\text{g})}{C_2+T-T_\text{g}} 
\]

where \( T_\text{g} \) is a reference temperature and \( C_1 \) and \( C_2 \) are constants characteristic of \( T_\text{g} \) and, to a lesser extent, the polymer. This equation is exactly the same as equation 7.7 if the reference temperature is the \( T_\text{g} \) and the universal constants are used.

Hence a plot of \((T-T_\text{g})/\log a_T\) versus \( T-T_\text{g} \) should be linear with a slope \( 1/C_1 \) and an ordinate intercept of \( C_1/C_2 \). Figure 7.3 shows a plot of this type reduced to 293K for the experimental data. This was chosen as the reference temperature as it was the lowest temperature measured and had 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 are well in excess of the applicability of free volume theory.

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 the constants at the $T_g$ using the interrelations,

\[
C_{1T_g} = \frac{C_1C_2}{C_2+T_g-T_o} \quad \ldots (7.9)
\]

\[
C_{2T_g} = C_2+T_g-T_o
\]

These equations can now be used in two ways. Firstly substituting in the values of the empirical constants gives the values of the constants for $T_g=253K$. The viscosity at the $T_g$ can then be calculated by using the WLF equation with these constants and the viscosity at 293K. This is shown in figure 7.4 which shows that the data is represented remarkably well by this albeit semi-empirical relationship. The viscosity at the $T_g$ using these constants was found to be $98\times 10^3 \text{Pa.s}$. The higher temperatures are not represented by the model for the reasons discussed earlier. Equating these constants yields $T_g=0.038$ and $a=4.5\times 10^{-4} \text{K}^{-1}$. This free volume fraction at the $T_g$ is higher than the universal WLF value of 0.025 although it is not unreasonably high considering the number of chain ends with respect to most polymers. The difference in thermal expansion coefficients above and below the $T_g$ is well within the range of scatter found in individual polymers [Williams et al. (1955)]. The data representation is also consistent with the observation that free volume theory is only applicable to the point where the temperature dependence is so great that it is independent of molecular structure, i.e. $T_g$ to $T_g+100K$. Deviation from the equation occurs at approximately the reciprocal temperature 0.0028K$^{-1}$ which corresponds to 357K, about 100K above the proposed $T_g$ of the resin.
The second interpretation of the data is made by considering that the universal constants are correct thus allowing calculation of the $T_g$ from equations 7.9. This concept is more consistent with the view that the glass transition point is an iso-free volume state [Fox and Flory (1950)].

Substituting the empirical constants and the universal constants into both equations yields values for $T_g$ of 223K and 219K, respectively. The similarity of these values indicates that the resin used in this study may have had a lower $T_g$ than the published data value of Stevens and Richardson (1983). Their relationship, originally proposed by Fox and Flory (1950), shows that the $T_g$ for epoxy prepolymer is inversely related to the molecular mass according to the relation,

$$T_g = 333.4 - \frac{3.12 \times 10^4}{M_n} \quad \text{... (7.10)}$$

where $M_n$ is the molecular mass, which for the resin used in this study is 390g/mole.
Aleman's (1980) relation for epoxy prepolymer takes exactly the same form as the above but has different coefficients,

$$T_g = 377.5 - \frac{6 \times 10^4}{M_n}$$ .... (7.11)

This relation gives a value of 223K as the glass transition temperature of the resin. This is exactly what the WLF equation requires to predict the viscosity data using the universal constants. This is shown in figure 7.5 where the universal constants were used with $T_g=223K$. This relationship gives a viscosity at the $T_g$ of $2.74 \times 10^{11}$ Pa.s.

![Figure 7.5 Viscosity data - WLF equation with universal constants ($T_g=223K$)](image-url)
The difference between published data exemplifies the difficulty in specifying the glass transition temperature. It must also be noted that the method of interpreting the \( T_g \) data from calorimetric measurements was effectively the only difference between the two cited literature values (thermal histories were not stated). Examination of the calculated viscosity at the \( T_g \) does provide an insight into the correct \( T_g \) value for the resin since for many substances the viscosity at the glass transition temperature is in the region of \( 10^{12} \text{Pa.s} \) [Billmeyer (1962)]. The WLF equation using the universal constants and a \( T_g \) of 223K is the only representation of the data that begins to approach this value and is well within an order of magnitude. Supplementary evidence is also provided by examining Doolittle's original equation. If this is fitted to the viscosity data using the universal constants and a \( T_g \) of 253K then \( B_\eta = 0.62 \), while if the universal constants are used with a \( T_g \) of 223K then \( B_\eta = 0.98 \). This value is much closer to the accepted value of unity.

The reciprocal relationship of molecular weight to the glass transition temperature is known to show the greatest deviation at low molecular masses. It therefore does not seem unreasonable to suggest that Aleman's relation for epoxy prepolymer (1980) is possibly more representative of the resin used in this study (Shell 828 has a high epoxide group content compared to many resin systems). Aleman (1980) also used a more conventional method of interpreting the calorimetric data than Stevens and Richardson (1983).

If this is the case it implies that the temperature dependence of the resin viscosity can be determined by an independent physical measurement (the glass transition temperature), where free volume theory is applicable. This allows the viscosity to be predicted for many resin systems; all that is required is the \( T_g \) (which can be calculated from the semi-empirical molecular mass dependence) and the viscosity at any one temperature, i.e. the temperature dependence of the viscosity can be predicted.

In terms of processing, where a knowledge of the viscosity is critical, such a predictive technique is probably not sufficiently reliable in that the \( T_g \) of an uncured
resin is not generally a readily available parameter and is also influenced by the method of measurement, thermal history and other factors. Naturally, in any kind of model, the behaviour of the system has to be represented mathematically, either empirically or theoretically, and it has been shown that the Doolittle equation and the WLF modification can represent the viscosity behaviour of the resin over a large temperature range. In fact if the Arrhenius relationship, predicted by the absolute rate theory (Section 7.1.1), is also applied it can be seen that it starts to represent the data where the free volume theory begins to fail (figure 7.6). However, the pre-exponential constant is too freely adjustable to give a reliable quantitative value of the point at which it is the dominant mechanism. This may not be too severe a problem for most composite systems as the resin will have started to gel before the free volume theory breaks down completely, remembering that it is the gel point which places limits not only on the process of eliminating bubbles but also consolidating the laminate.

![Viscosity/Temperature Data for Resin](image)

Figure 7.6 Viscosity data - Doolittle equation ($B_\eta=0.98, C=1.36\times10^{-6}\text{Pa.s}$)

Absolute rate equation ($E_\eta=29\text{kJ/mol}, \eta_0=3.58\times10^{-6}\text{Pa.s}$)
7.2 SURFACE TENSION OF RESIN

The surface tension has already been shown to play a significant role in the nucleation, stabilisation and growth and collapse kinetics of bubbles (Chapters Two and Three). The interfacial surface tension is related to the cohesive energy density of the resin, in that dispersion and polar forces between molecules will lead to a drawing together of liquid molecules [Wu (1968)]. It is generally considered that hydrogen bonding does not contribute greatly to the liquid-vapour interfacial energy as these interactions do not involve the breaking of bonds. This is in qualitative agreement with experiments on the resin since the surface tension of the resin was not found to be a temperature dependent parameter (Section 6.1), i.e. if hydrogen bonds were playing an active role, their thermal instability would cause the surface tension to decrease with increasing temperature.

Many workers have attempted to correlate the surface tension forces from molecular constitution [Hansen and Beerbower (1971)]. Most of these are semi-empirical but work with a good degree of accuracy. Wu (1968) correlated the critical surface tension with Small’s molar attraction constants (section 4.1.2) with coefficients based on data from 36 polymer systems. His preferred equation is dimensionally unbalanced but he also offers a second balanced equation which gives approximately the same results,

\[
\gamma_c = 5.5 \times 10^{-3} \left( \Sigma F \right)^2 \frac{\rho_R^{5/3}}{n^{1/3} M^{5/3}} \]

where \( \gamma_c \) is the critical surface tension, \( \Sigma F \) is the sum of the molar attraction constants, \( n \) is the number of atoms in the molecule, \( M \) is the molar mass of the molecule and \( \rho_R \) is the density of the polymer.
Therefore, for the resin molecule
\[ \Sigma F = 5963.8 \text{ (Jcm}^3\text{)}^{1/2} \text{ (from Small's attraction constants)} \]
\[ n \approx 55 \]
\[ M \approx 390 \text{g} \]
\[ \rho = 1.16 \text{g/cm}^3 \]

This gives a value for the critical surface tension of 0.032N/m for the resin system compared to the experimental value of 0.035N/m. This concordance between theory and experiment is encouraging as it allows prediction of the surface tension forces solely from the chemistry of the system. Although the surface tension is a relatively easily measured parameter, it is not a parameter that is generally measured for the processing of composite materials. In the case of solid precursors it is also difficult to measure what the effective surface tension force will be prior to liquification.
CHAPTER EIGHT

ANALYSIS OF INPUT VARIABLES

8.1 GAS SOLUBILITY DATA

8.1.1 Thermodynamic Correlation of Gas Solubility

8.2 GAS DIFFUSION DATA
8. **ANALYSIS OF INPUT VARIABLES**

This chapter analyses the gas solubility and diffusion data obtained from the experimental work discussed in Section 6.3. The data is compared to theory introduced in earlier sections and the gas diffusion coefficient is compared to the viscosity data that was discussed in Section 7.1.2.

### 8.1 GAS SOLUBILITY DATA

The saturation concentration within a resin should theoretically be a function of both temperature and pressure. The key is given by Henry's law which establishes the connection between the partial pressure of a gas acting on a liquid surface and the equilibrium or saturation concentration.

\[
p = \frac{x_g}{K_H} \quad \text{.... (8.1)}
\]

where \( p \) is the partial pressure of the gas, \( x_g \) is the mole fraction of the gas and \( K_H \) is Henry's law constant for the system and is a function of temperature.

It is therefore possible to determine the solubility of a gas in the resin at a particular temperature if the partial pressure of the gas acting on the resin and Henry's law constant are known.

Sorption of a gas may be considered as two processes; condensation of the gas, followed by mixing. The enthalpy change, \( \Delta H_s \), can be summed in two parts; the heat of condensation, \( \Delta H_{\text{cond}} \), and the partial molar heat of mixing, \( \Delta H_{\text{mix}} \) [Rogers (1985)].
The heat of condensation is purely a consequence of the gaseous solute and does not depend on the solvent while the heat of mixing is the enthalpy change which accompanies the dissolution of the solute in the solvent. The heat of solution may be endothermic or exothermic depending on the temperature, nature of the gas and the solvent. The temperature dependence of the solubility is often expressed in terms of an Arrhenius-type equation [Michaels et al. (1964)],

\[
S = S_0 \exp\left(-\frac{\Delta H_s}{R_g T}\right)
\]  

(8.3)

where \( S \) is the solubility, \( S_0 \) is a pre-exponential constant, \( R_g \) is the universal gas constant and \( T \) is the absolute temperature.

For permanent gases such as the main components of air (nitrogen and oxygen), the heat of condensation is small and the heat of solution is determined primarily by the heat of mixing. The sorption process can be pictured as making a hole of molecular size in the fluid (an endothermic process), and transferring a molecule from the gas phase into the hole (an exothermic process). The energy absorbed in the first stage depends on the molecular volume of the gas and the cohesive energy density of the matrix. The energy involved in the second stage is governed by the strength of the van der Waals bonds formed between the sorbed gas molecules and the surrounding resin. This increases with the complexity and polarizability of the penetrant molecule and is relatively insensitive to the structure and morphology of the solvent. Holes would have to be created in this system as no pre-existing frozen holes are available as in the case of glassy polymers. This would make the solution of a gas much less exothermic and the solubility will be commensurate with the solubility parameter of the polymer, i.e. \( \delta = (\text{cohesive energy density})^{1/2} \) (Section 4.2.2). This balance of endothermic mixing and exothermic condensation is a potential reason for the temperature independence of the gas solubility data (Section 6.3.1.1).
For the pure dry nitrogen system used in the experiments Henry's law was obeyed up to a pressure of $1.01\times10^5$Pa (1 atmosphere) (figure 8.1). A linear regression through the experimental points yielded a gas concentration at atmospheric pressure of 0.0207kg/m$^3$. This was also the mean value of the experimental data at atmospheric pressure for all the temperatures tested. A linear relationship was assumed for higher pressures since other polymeric systems have exhibited a virtual linear dependence with nitrogen up to 10 atmospheres [Durrill and Griskey (1966)]. This ideal dilute solution behaviour is readily understood since the solubility of permanent gases in polymeric materials is small due to the lack of strong polymer-penetrant interactions. It is possible that deviations from ideal dilute solution behaviour would be exhibited by carbon dioxide since it is inherently more polar than either oxygen or nitrogen in the gaseous form. Since carbon dioxide is only a small component of air, the main constituent of an entrapped bubble, it has been considered that this can be neglected which would allow Henry's law to be assumed for dry air as well as individual permanent gas penetrants. Also, the processing of polymer matrix composites generally involves pressures of no greater than 10 atmospheres.
Henry's law constant was calculated from equation 8.1 and it was found to be similar to that of nitrogen in aromatic liquids (Table 8.1).

**TABLE 8.1**

<table>
<thead>
<tr>
<th>Henry's Law Constants for Nitrogen at 298K, $K_H (1/Pa)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
</tr>
<tr>
<td>Benzene</td>
</tr>
<tr>
<td>Epoxy Resin (313K)</td>
</tr>
</tbody>
</table>

The temperature and pressure dependence of the gas solubility enables the saturated gas concentration to be directly related to the processing variables, i.e a two-fold increase in applied pressure will increase the equilibrium gas concentration by a corresponding amount due to the linearity of the isotherm while an increase in temperature has a negligible effect on the overall solubility. The relative saturation of the resin $f$ (the ratio of the dissolved gas concentration in the bulk to the saturation concentration) can now be determined throughout the processing route as the process variables are changed. This is of major importance since the relative saturation fundamentally determines whether an entrapped gas bubble will grow or collapse in the resin medium; if $f<1$ then the resin is unsaturated with gas and the bubble will collapse, while if $f>1$ the solution is supersaturated and the bubble will grow.

### 8.1.1 Thermodynamic Correlation of Gas Solubility

The Henry's law constant will be different for each system and it is fundamentally an empirical parameter. In terms of a process model it would be useful to be able to predict the solubility of gases in any resin system from theory because characterisation of each resin system restricts the utility of a predictive model.

In the case of permanent gases such as the main components of air it is not a straightforward procedure to calculate theoretical solubilities as these gases are above their critical temperature (it is possible to determine the ideal solubility of a gas
below its critical temperature simply by using Raoult’s law if the vapour pressure is known (section 4.2.1)). A similar method can be employed for permanent gases by estimating the hypothetical vapour pressure of the liquid by suitable extrapolation. This is done by using the Clausius-Clapeyron equation (section 5.1.2). In the case of nitrogen, which has a critical temperature of 126K, the hypothetical vapour pressure is $120 \times 10^6 \text{Pa} (\approx 1200 \text{ atmospheres})$ at 298K. This calculation assumes that the molar heat of vaporisation is constant over the temperature range (figure 8.2). The ideal solubility is determined as in the case of condensible vapours i.e. $p_1 = x_1 P_{o1}$ where $P_{o1}$ is the hypothetical vapour pressure of the pure liquified gas, $p_1$ is the pressure of the system and $x_1$ is the mole fraction of gas in the liquid. This implies that under room temperature and pressure the mole fraction of nitrogen in any solvent will be $8.4 \times 10^{-4}$, which approximately corresponds to a concentration of $0.07 \text{kg/m}^3$ in the resin system under investigation. This is over three times higher than the experimental value for these conditions, so it can be concluded that nitrogen and the resin are not an ideal
solution as dictated by Raoult's law. It does corroborate that gases with high vapour pressures (low boiling points) liquify with difficulty and will have low solubilities under ambient conditions.

Although the solubility of a gas should ideally be independent of the nature of the solvent this will not be the case due to component interactions, e.g. nitrogen in water is about 1% of the theoretical value whereas nitrogen in ethanol is 33% [Glasstone\(^a\) (1948)]. The nature of the solvent is therefore critical in determining the solubility, i.e. in the case of water the degree of association and the polarity seriously affect the solubility of nitrogen. In order to take the solvent into account the problem has to be addressed in terms of the solubility parameter before a rigorous theoretical procedure can be used to predict gas solubilities in the resin system.

Hildebrand and Scott (1962) gave a chart which is reasonably accurate at predicting solubilities of a number of gases with respect to the solubility parameter of the liquid. This empirical work was extended by Prausnitz (1969) who introduced the concept of condensing a gas to a hypothetical state having a liquid-like volume. This hypothetical fluid is then mixed with the solvent, essentially on the basis of liquid miscibility.

The key information is the molar volume and the solubility parameter of the gas as "condensed" at the required temperature. By considering a gaseous component at fugacity \( f^G \) dissolved isothermally in a liquid not close to its critical temperature, the solution process is accompanied by a change in enthalpy and entropy just as occurs when two liquids are mixed. In the case of a gas the solution process is also accompanied by a large decrease in volume since the partial molar volume of the condensed phase is much smaller than that of the gas. In order to apply regular solution theory (which assumes no volume change) it is necessary first to "condense" the gas to the partial molar volume which it has as a solute in the liquid solvent. The isothermal solution process is then considered in two steps;
i) The gas "condenses" isothermally to a hypothetical state having a liquid-like volume, 

\[ \Delta G_i = R_g T \ln \frac{f^L_{\text{pure1}}}{f^G_1} \]  

\[ \text{.... (8.4)} \]

ii) The hypothetical liquid-like fluid dissolves in the solvent,

\[ \Delta G_u = R_g T \ln \gamma_1 x_1 \]  

\[ \text{.... (8.5)} \]

where \( f^L_{\text{pure1}} \) is the fugacity of (hypothetical) pure liquid solute and \( \gamma_1 \) is the activity coefficient of the solute referred to the (hypothetical) pure liquid, \( x_1 \) is the mole fraction of the gas in solution and \( \Delta G_i \) and \( \Delta G_{ii} \) are the respective changes in free energy for each step.

The solute in the liquid is in equilibrium with the gas which is at the fugacity \( f^G_1 \), therefore

\[ \Delta G = \Delta G_i + \Delta G_u = 0 \]  

\[ \text{.... (8.6)} \]

If it is assumed that the regular solution equation gives the activity coefficient for the gaseous solute, then

\[ R_g T \ln \gamma_1 = \nu^L_1 (\delta_1 - \delta_2)^2 \phi_2^2 \]  

\[ \text{.... (8.8)} \]

where \( \delta_1 \) is the solubility parameter of the solute, \( \delta_2 \) is the solubility parameter of solvent, \( \nu^L_1 \) is the molar "liquid" volume of the solute and \( \phi_2 \) is the volume fraction of the solvent.
Combining equations 8.4-8.8 gives the solubility in terms of mole fraction,

\[
\frac{1}{x_1} = \frac{f_{\text{pure}}^L}{f_1^G} \exp \frac{v_1^L(\delta_1 - \delta_2)^2 \phi_2^2}{R \delta T} \quad \text{.... (8.9)}
\]

Equation 8.9 involves three parameters for the gaseous component as a hypothetical liquid; the pure liquid fugacity, the liquid volume and the solubility parameter. Although these parameters are all temperature dependent the theory of regular solutions assumes that at a constant composition \(\ln \gamma \propto 1/T\), and therefore the quantity \(v_1^L(\delta_1 - \delta_2)^2 \phi_2^2\) is not temperature dependent (the individual solubility parameters may be temperature dependent but \((\delta_1 - \delta_2)\) is approximately temperature independent [Prausnitz (1969)]). This allows any convenient temperature to be used for \(v_1^L\) and \(\delta_1\) provided that the same temperature is used for \(\delta_2\) and \(v_2^L\). The fugacity of the hypothetical liquid, however, must be treated as a function of temperature. Equation 8.9 also contains \(\phi_2\), the volume fraction of the solvent. This means that in order to recover \(x_1\) it is strictly necessary to use an iterative method. However, it has been shown from experiments and the ideal mixing calculation that the solubility of nitrogen in resin is not high and that even if it were to behave ideally the volume fraction, \(\phi_2 = (v_2/v_1 + v_2)\), is essentially unity for pressures well in excess of those experienced in the composite processing route.

The molar volume, \(v_1^L\), and the solubility parameter, \(\delta_1\), both at 25°C (298K), have been taken from Prausnitz and Shair's paper (1961) for gases that may affect a composite system.
Although the table gives "liquid" volumes and solubility parameters for gaseous solutes at 298K it is relevant for any temperature from the argument described above.

The fugacity of the hypothetical pure liquid is determined from the graph taken from the same paper (figure 8.3) where the axes are the fugacity of the solute divided by its critical pressure ($f^L_{\text{pure}}/P_c$) as a function of the ratio of the solution temperature to the solute's critical temperature ($T/T_c$). The fugacity of the gaseous component is equivalent to the absolute pressure for pressures well in excess of those encountered in the composite processing route.

Therefore, for nitrogen in resin at 298K and atmospheric pressure, where $T_c=126K$ and $P_c=33.9\times10^5 Pa$

\[ \frac{T}{T_c} = 2.37 \]
\[ f^L_{\text{pure}}/P_c = 6.5 \] (from figure 8.3)
\[ f_1^G = 1.01\times10^5 Pa \]
\[ \delta_1 = 5.28 (J/cm^3)^{1/2} \] (from Table 8.2)
\[ \delta_2 = 20.45 (J/cm^3)^{1/2} \] (calculated from the molar attraction constants for the resin for 298K)
\[ \nu_2^L = 32.4 cm^3/mole \] (from Table 8.2)
\[ \phi_1 \approx 1 \]

and, from equation 8.9, the mole fraction of nitrogen in the resin at room temperature and pressure is $2.257\times10^{-4}$, which corresponds to a gas concentration of 0.0188kg/m$^3$.  

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The experimental work was performed over a range of temperatures, the minimum was 313K. For this temperature the treatment gives a mole fraction of 2.608x10^{-4} and a concentration of 0.0217kg/m^3. This compares admirably with the experimental value of 0.0207kg/m^3 determined at 313K.

The experiments in Section 6.3.1.1 indicated that the solubility was independent of temperature between 313-373K. This is not in agreement with the theoretical analysis which implies an increase in solubility with temperature by about 1.5 for this temperature range, i.e. the theoretical gas solubility at 373K is 0.0344kg/m^3. Although the experiments did not show such a temperature dependence, since solubility data in the literature is not plentiful for pure liquids (and often varies depending on the source) and very scarce for resin systems, such a theoretical procedure is a remarkably good estimate for gas solubilities with minimal experimentation. The whole analysis requires only the molecular chemistry of the resin precursor and its density to provide the dissolved gas concentration for the resin pressures in the processing cycle.
Subsequent experiments tend to agree qualitatively with the model predictions in that resin saturated with dry nitrogen at 313K and stored at 283K contained microscopic bubbles after a few days. This phenomenon can only be explained in terms of the temperature effect on the gas solubility giving rise to a concentration gradient causing stable nuclei to grow. This area needs further investigation as composites are generally stored at low temperatures. In terms of the model it is feasible that the solution of gases such as nitrogen and oxygen are exothermic at low temperatures and endothermic at higher temperatures which can be seen by considering the Arrenhius equation (equation 8.3), where

\[ \Delta H_{\text{cond}} = \frac{R_g T_c d\ln f^L / P_c}{d1/T} \]

\[ \Delta H_{\text{mix}} = v_2(\delta_1 - \delta_2)^2 \]

In the first equation the heat effect does not depend on the solvent, it is determined by the slope of the graph in figure 8.3 and is exothermic. The heat of mixing depends on the solvent but will generally be endothermic for a mixture of unlike molecules with different cohesive energies. It is therefore probable that the conditions for growth and collapse of gas bubbles are temperature dependent although further work is required to define these thermodynamic boundaries.
The changing gas solubility with temperature has not been taken into account in the subsequent sections as the pressure effect on the solubility is much more significant in terms of composite processing. The theoretical analysis produces a linear isotherm for composite processing pressures in agreement with the experimental data (figure 8.4) providing a Henry’s law constant within 10% of that determined using the instantaneous vacuum technique.
One of the most valuable sources of information on the mechanism of diffusion is the variation of diffusion coefficient with temperature. Usually it is found that for the diffusion of gases ln D is a linear function of 1/T over a wide temperature range above the glass transition temperature (T_g) in solid polymers. This has lead to the conclusion that diffusion may be regarded as a thermally-activated process with the relation between D and T expressed by an equation of the Arrhenius type (equation 5.4) (Section 5.2.1).

The graph of ln D vs. 1/T for this system does not exhibit this linear dependence over the measured temperature range as the graph becomes concave towards the 1/T axis with increasing temperature (figure 8.5). Such an interaction indicates that free volume effects play an increasingly important role with decreasing temperature, as in the case of viscosity. The diffusion coefficient was found to increase by approximately three orders of magnitude with increasing temperature over the temperature range investigated.

Theories and models to represent or estimate diffusion coefficients and/or their dependence on temperature are based on the fundamental premise that the diffusing molecule makes a successful jump of a particular length in a random direction in a particular time. These parameters are either in terms of energy required for a critical volume disturbance or conversely the availability of a favourable distribution of localised excess volume (free volume) to allow a diffusive jump. The approach can be in terms of models of specific molecular motions using statistical mechanics to calculate the thermodynamic parameters or to consider the system not on a molecular level but as a statistical thermodynamic region characterised by system parameters, such as energy distributions or free volume fractions.

Although expressions based on molecular models of the diffusion process rather than free volume or related approaches would seem to offer the advantage that the necessary parameters should be predictable from the inherent properties of the
penetrant and resin components, all models to date have one or more "adjustable" parameters except for certain systems in certain temperature ranges [Meares (1954)][Brandt (1959)]. Molecular models are also more complex thus requiring considerable parameter input.

Models based on free volume have a definite advantage in that they can relate other measurable parameters such as the viscosity to the diffusion coefficient. According to the free volume theory it is usually postulated that the free volume fraction $f(T)$ in the medium at a temperature $T$, above $T_g$, can be expressed in the linear form as dictated by equation 5.5 (Section 5.2.2).

From the viscosity data (Section 7.1.2) it has been assumed that the resin used in the experimentation has a glass transition temperature of 223K in the uncured state [Aleman (1980)]. The free volume fraction can be calculated from equation 5.5 using this glass transition temperature value and the "universal values" for $f(T_g)$ and $\alpha$. It is possible to relate the viscosity to the free volume through a semi-empirical equation.
developed by Doolittle (Section 7.1.2), which shows that a liquid of viscosity $\eta$ is related to the fractional free volume by equation 7.3.

One can modify the Doolittle equation by noting that the diffusion coefficient is inversely proportional to the frictional resistance in accordance with molecular friction theory [Bueche (1952)]. In a very crude approximation one can say that this is proportional to the viscosity of the medium so that,

$$D = D_0 \exp\left(\frac{-B_d}{\ell(T)}\right)$$  \hspace{1cm} \text{... (8.11)}

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 [Peterlin (1975)(1979)].

It is interesting to compare the ln viscosity and diffusion coefficient vs. $1/T$ graphs. Figure 8.6 shows that the diffusion coefficient for nitrogen in resin has a very similar interaction to the viscosity. To compare this quantitatively the temperature dependence is often expressed in terms of an activation energy. If the WLF equation (equation 7.8) is used it can be seen that the activation energy for viscous flow, $\Delta E_\eta$, can be represented by,

$$\Delta E_\eta = \frac{R_g d(\ln a_T)}{d(1/T)}$$  \hspace{1cm} \text{... (8.12)}

where $a_T$ is the shift factor, $R_g$ is the universal gas constant and $T$ is the absolute temperature.
Figure 8.6 Temperature dependence of viscosity and diffusion data

Figure 8.7 Free volume theory applied to viscosity and diffusion data
Therefore, differentiating the generalised form of the WLF equation gives,

\[
\Delta E_{\eta} = \frac{2.303 R \gamma C_1 C_2 T^2}{(C_2 + T - T_0)^2}
\].... (8.13)

where \(C_1\) and \(C_2\) are constants and \(T_0\) is the reference temperature.

It is apparent that the activation energy for viscous flow is not a function of \((T - T_0)\) alone and thus it can be concluded that although there is a universal \(a_T\) function there is no universal \(\Delta E_\eta\), i.e. at a constant \(T - T_0\), \(\Delta E_\eta\) is proportional to \(T^2\) and therefore at 293K \(\Delta E_\eta = 100\,\text{kJ/mole}\) while at 353K \(\Delta E_\eta = 65\,\text{kJ/mole}\).

Since one can not compare activation energies apart from at a specified 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 7.3 and 8.11) for the viscous flow and the diffusion process, directly. Figure 8.7 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 \(B_\eta\) are unity within experimental error. The ratio of the Doolittle coefficients \(B_d\) and \(B_\eta\) 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 resin than the diffusion of a resin molecule required for viscous flow. It implies that the temperature dependence of the diffusion process is characterised by the mutual action between molecules of the resin and not of that between the dissolved nitrogen and the resin.

This interesting result is examined in terms of molecular considerations. If the solute is larger than the solvent then the motion of the solute can not be described in terms of vibrations about an equilibrium position and displacements of the latter but 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 also 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 is not implying that a nitrogen molecule is of comparable molecular size to a resin molecule. A semi-quantitative argument says that polymers do not flow as single rigid units [Meares (1965)]. 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, i.e. the effective activation energy for diffusion must refer to the whole complex of particles participating in the transition which, for dilute solutions, can not markedly differ from that governing viscous flow.

The apparent relationship between the diffusion of nitrogen and the viscosity of the medium is extremely fortuitous since the gas diffusion coefficient in the resin is a required, but not readily available, parameter. 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. This relationship between the viscosity and the diffusion coefficient should even hold for higher temperatures where the viscosity is governed by a thermally activated process, i.e. in a dilute solution the diffusion coefficient of the solute in the solvent is a characteristic of the solvent, whether the viscosity is governed by free volume or energy barrier considerations. If this is the case then 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 crosslinking reaction. It will then be possible to determine the point at which the bubble is effectively "frozen" into the laminate and so place limits on the time required to eliminate bubbles for any cure cycle. The temperature dependence of the diffusion coefficient can be calculated from the viscosity using either the Doolittle equation or the WLF equation described in Section 7.1.2. However, it must be remembered that the diffusion coefficient can only be as accurate as the model that predicts the viscosity, i.e. 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.
CHAPTER NINE

EVALUATION OF MODEL

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9. EVALUATION OF MODEL.

The input parameters for the steady-state approximation of the diffusion equation can now be determined in terms of the processing variables, i.e. the temperature and the pressure. The dissolved gas concentration in the bulk needs to be measured as it is a function of the resin's history although the equilibrium value can be determined if the storage conditions are known. In the following, the dissolved gas concentration has always been measured and it is this value that has been used in the subsequent modelling. The saturated gas concentration is primarily a function of pressure and can be calculated for different pressures using Henry's law. The diffusion coefficient of a permanent non-condensible gas has been found to obey a relationship similar to the viscosity over a wide temperature range and has also been assumed to be independent of gas concentration due to the linearity of the plot of gas concentration vs. equilibrium pressure.

The steady-state diffusion model, described in Chapter Three, can now be evaluated to determine whether the growth and collapse of gas bubbles can be predicted for different processing situations. The following describes the procedures and the analyses for the different conditions that may be experienced in a typical composite processing operation. The growth and collapse of gas bubbles is shown for the saturated, unsaturated and supersaturated resin. This has been achieved by varying the dissolved gas concentration in the bulk prior to testing and by changing the equilibrium gas concentration with pressure during the testing. The effects of initial bubble size and temperature have also been investigated.

Examples of the effects of these conditions are summarised below and modelled using the theory described in Chapter Three and the material parameters and input variables from Chapters Seven and Eight.
Nitrogen was bubbled through the base resin (Section 6.1.1) at atmospheric pressure and 313K and was allowed to stand under these conditions until all suspended bubbles had risen to the surface of the vessel. Samples were removed to measure the dissolved gas concentrations using the instantaneous vacuum technique (figure 6.4)(Section 6.3.1). Pure dry nitrogen bubbles were then injected using the resin injection unit (figure 6.6)(Section 6.3.1.2) and the resin was carefully poured into a glass cuvette. The samples were monitored using an optical microscope and bubble diameters were monitored with respect to time by taking photographs at various intervals (figure 6.3)(Section 6.2).

In all cases where gas bubbles were monitored in a saturated resin, collapse occurred. The only bubbles present were those that had been injected and no nucleation events were observed. Figure 9.1 shows two bubbles of the same initial radius collapsing in a saturated resin at different temperatures. The difference in the times for complete solution clearly indicates the large temperature dependence of the diffusion coefficient. The theoretical predictions were calculated using the steady-state approximation including surface tension forces which for a saturated solution simplifies to equations 3.20 and 3.21 (Section 3.2). It was necessary to use the steady-state approximation that included surface tension forces in order to predict a finite collapse time.

The surface tension forces were assumed to be independent of temperature and the experimental value of 0.035N/m at 293K was used in all subsequent modelling calculations (Section 6.1). The diffusion coefficients were taken from figure 8.7 for the appropriate temperatures using the free volume theory semi-empirical line (Section 8.2); at 333K, \( D = 3 \times 10^{-10} \text{m}^2/\text{s} \) and at 361K, \( D = 1.8 \times 10^{-9} \text{m}^2/\text{s} \). The dissolved gas concentrations (which in this case equals the saturated gas concentration) were measured using the instantaneous vacuum technique and were found to agree with the isotherm and with the thermodynamic correlation within experimental error (figure 8.4)(Section 8.1). The mean value of 0.0207kg/m³ for the gas concentration at
atmospheric pressure was used. This was also assumed to be independent of
temperature (Section 6.3.1.1).

Figure 9.1 shows that the experimental data is represented by the model
with a good degree of accuracy. In the example shown here, an increase in temperature
of 28K reduces the time for complete solution by an order of magnitude.

Figure 9.2 shows the difference in collapse time for two bubbles of
fractionally different initial radii at the same temperature. In both cases the rate of
change of radii increases as the bubble collapses with larger bubbles exhibiting greater
times to complete solution.

9.2 GAS BUBBLES IN AN UNSATURATED RESIN

Nitrogen was bubbled through resin at 313K under reduced
pressure (in this case 0.808x10^5Pa) and was allowed to stand until all suspended
bubbles had been removed. Samples were removed to measure the dissolved gas
concentration using the instantaneous vacuum technique. Pure dry nitrogen bubbles
were introduced using the resin injection unit and the resin was carefully poured into
a glass cuvette. Samples were placed on the optical microscope and bubbles were
selected that were isolated from other bubbles and the sides of the vessel. The
temperature was held constant (in this case 313K) and the external pressure was
atmospheric. The bubbles were monitored throughout the experiments.

As expected from the theory, gas bubbles collapse in unsaturated solutions
(figure 9.3). The dissolved gas concentration in the bulk was equilibrated at a reduced
pressure and therefore had a gas concentration associated with that pressure, while the
resin immediately adjacent to the bubble had a dissolved gas concentration associated
with the external pressure and the surface tension forces.
Figure 9.1 Temperature dependence of bubble collapse rate

Figure 9.2 Collapse rate for bubbles with different initial radii
The theoretical line was deduced from the steady-state approximation with and without surface tension forces. The diffusion coefficient was taken from figure 8.7 at 313K ($D=4.5 \times 10^{-11} \text{ m}^2/\text{s}$) using the free volume semi-empirical line. The relative saturation, $f$, was simply the ratio of the dissolved gas concentration to the saturated gas concentration. The saturated gas concentration at the external pressure was taken from figure 8.4 ($0.0207 \text{ kg/m}^3$ at atmospheric pressure). The dissolved gas concentration was measured using the instantaneous vacuum technique and was found to agree with the experimental isotherm and the theoretical correlation within experimental error. The measured dissolved gas concentration yielded a relative saturation, $f$, of 0.812. This value was used in the subsequent analysis.

It is interesting to note that if surface tension forces had not been taken into account the time for complete solution, as predicted by equation 3.9 (Section 3.1), would have been longer. The extended model that includes surface tension forces represents the data remarkably well although it can be seen that the radius deviates from the line at lower times, convex to the time axis. This initial decrease in radius was
not possible to measure since it occurred between the point of injection and the location and measurement of the bubble. Theoretically it can be assumed that it is a consequence of the build up of the diffusion boundary layer immediately adjacent to the bubble. The rate of solution will initially decrease with time before it increases with time due to two competing effects (figures 3.1 and 3.2). In the first place the concentration gradient at the interface decreases with time due to the increased gas concentration in the solution near the interface. This influence is most important at short times when the gradient is decreasing sharply from its initially infinite value. At these times the rate of solution is theoretically proportional to $t^{-1/2}$.

As the bubble becomes smaller the dissolution rate again increases as now the interfacial area of the bubble becomes markedly less than the volume through which diffusion is taking place. Since the total flux at the bubble surface is affected by the area available for diffusion throughout the diffusion zone, this effect will predominate over the influence of the increased gas concentration and the rate of bubble shrinkage will tend to increase as the bubble size decreases.

Although the time derivative in the quasi-stationary assumption potentially takes this effect into account, it is difficult to determine experimentally since it occurs at short times. Generally it can be assumed that this will only be a problem with freshly nucleated bubbles since the gas concentration at the interface of mechanically entrapped bubbles will have had time to attain the equilibrium value. The neglect of the time derivative on the rate of collapse in the theoretical analysis will marginally overestimate the time for complete solution, a situation which is favourable to the converse when the ultimate aim is to remove bubbles during the processing cycle.

9.3 GAS BUBBLES IN A SUPERSATURATED RESIN

Resin was equilibrated under positive pressure by injecting gas bubbles into the resin using the resin injection unit, which also maintained the desired over pressure. The resin was left under pressure at 313K until all suspended bubbles had
been removed. The pressure was released and the resin was poured into a glass cuvette and placed on the optical microscope. Bubbles were monitored photographically with time at atmospheric pressure and constant temperature.

As soon as the overpressure had been released nucleation occurred and bubbles began to grow. It was not possible to witness nucleation due to limitations of magnification and the inability to predict the point of the next nucleation event. Isolated bubbles were selected and growth was monitored with time.

Growth occurred due to the dissolved gas concentration in the bulk being greater than the gas concentration at the bubble surface, i.e. the dissolved gas concentration is a consequence of the equilibrated pressure while the interfacial concentration is related to the ambient pressure. The diffusion coefficient was determined from figure 8.7 for the experimental temperature and the relative saturation from the ratio of the equilibrium pressure (in this case $4.04 \times 10^5$ Pa) to the experimental external pressure. The dissolved gas concentration in the bulk was not measured independently due to difficulties in using the instantaneous vacuum technique for solutions that had been equilibrated at pressures greater than atmospheric pressure. Henry's law was assumed to have been obeyed and the dissolved gas concentration was calculated by extrapolating the linear relationship to the equilibrated pressure in figure 8.4, i.e. the relative saturation was 4 as the equilibrated pressure was 4 times higher than the ambient pressure.

Figure 9.4 shows that the steady-state approximation initially represents the data very well. It was also found that the steady-state approximation with and without the inclusion of surface tension forces were almost identical for a growing bubble (the difference is not distinguishable in figure 9.4). This can be explained by the fact that surface tension forces only become significant at small bubble sizes, i.e. during the latter stages of collapse (figure 9.3) or growth from an effectively zero radius.
Figure 9.4 Gas bubble growing in a supersaturated resin - Differences between steady-state models, with and without surface tension forces, are not distinguishable

At longer times there was a significant deviation from the model predictions. This was attributed to the decreasing dissolved gas concentration in the bulk as a consequence of nucleation and growth of gas bubbles. As more bubbles are nucleated and as existing bubbles grow the dissolved gas concentration of the resin is depleted. The model assumes a constant and uniform dissolved gas concentration (section 3.3). It is apparent that this will not be the case especially in areas of high bubble density. The higher the bubble density the more the resin is depleted of gas, thus reducing the concentration gradient and the rate of growth. Unfortunately, without a knowledge of the bubble densities in every situation this is an unpredictable parameter but consolation can be found in that the model overestimates the extent of bubble growth which is preferable from a processing point of view. On the negative side one can also postulate that, in regions of high bubble density, coalescence between gas bubbles is more likely. This emphasizes the importance of suppressing bubble growth completely by on-line manipulation of the processing variables within the limits dictated by the other unit processes.
Deviations from the model of this type were not seen with saturated or unsaturated resins which provoked the question to whether there is a fundamental difference between a growing and collapsing gas bubble. The effects of surface tension forces have already been taken into consideration and it can has seen that in the case of a growing bubble their effects become increasingly negligible. Another difference can be seen by examining the quasi-stationary solution to the diffusion equation. In the case of a collapsing bubble the transient term is becoming more insignificant with increasing time whereas the steady-state solution becomes progressively more dominant as the bubble radius decreases (figure 3.1). In the case of a growing bubble the steady state and the transient solutions decrease simultaneously (figure 3.3).

Neither of these differences explain the deviations from the model in figure 9.4 since the steady-state solution overestimates the growth rate at long times and neglect of surface tension forces or inclusion of the transient term would amplify the difference between the model and the experimental data. It has been concluded that the difference lies in the experimentation. In the case of supersaturated solutions the nucleation and growth of bubbles caused difficulties in isolating a gas bubble, while saturated and unsaturated solutions not only allowed an isolated bubble to be selected but also guaranteed that no bubbles would infringe unpredictably on its diffusion field for the duration of the experiment.

Although theory exists for interacting diffusion fields [Avrami (1940)] further input is required, namely a knowledge of bubble densities and exact initiation times. These parameters will not be known in a composite system so growth times will be underestimated and conversely times for collapse will be overestimated by the model.

9.4 EFFECTS OF PRESSURE ON GAS BUBBLES

It has already been shown that different equilibrium pressures affect the behaviour of gas bubbles. Generally, unless one is trying to produce a foamed material, the resin will not be supersaturated with gas under ambient conditions. The dissolved
gas concentration in the bulk will approach or equal the saturated or equilibrium gas concentration for the resin processing or storage environment. In a typical processing cycle the resin will be subjected to different temperatures and pressures (positive and vacuum). This will change the saturated gas concentration at the bubble/resin interface which can ultimately determine whether a gas bubble will grow or collapse.

Resin was saturated using nitrogen at atmospheric pressure using the method described earlier and the dissolved gas concentration was measured using the instantaneous vacuum technique. The measured gas concentration agreed with previous measurements for atmospheric pressure. Gas bubbles were injected into the resin as before. These bubbles were monitored and were found to collapse in accordance with theory due to surface tension forces, as with those in figures 9.1 and 9.2.

Resin from the same solution was injected with gas bubbles under the same conditions then carefully poured into a glass phial that was attached to a vacuum pump. Bubbles were selected and photographed at atmospheric pressure and constant temperature (323K). The pressure was then reduced to 0.505x10^5 Pa using the vacuum pump and measured using a bourdon gauge. Photographs were taken before and after the pressure change and throughout the experiment. The pressure was then increased by releasing the vacuum.

The diffusion coefficient was calculated from the semi-empirical correlation in figure 8.7 and the relative saturation was determined from the isotherm (figure 8.4). In this case it was necessary to assume that Henry's law was obeyed in that it was not possible to determine the gas concentration at the bubble/resin interface. The reduction in pressure therefore increased the relative saturation from 1 to 2, a condition which caused the initially collapsing bubble to grow due to gas expansion and diffusion. The difference between the steady-state assumptions (with and without surface tension forces) was negligible, emphasising that surface tension forces are significant only in the early stages of growth of a nucleated bubble, during the latter stages of collapse of a collapsing bubble or in a saturated system.
The immediate increase in size of the gas bubbles was attributed solely to the reduction of pressure (figure 9.5). This was verified by the fact that the initial change in radius could be predicted from the change in pressure in accordance with the ideal gas laws (the temperature was maintained at 323K so Boyle's law could be applied). Lower pressures were not used since spontaneous nucleation and rapid growth of existing bubbles caused problems in isolating a bubble and preventing coalescence. The interesting consequence of reducing the pressure was that bubbles that were initially collapsing under surface tension forces not only grew due to the immediate pressure effects but also continued to grow as a consequence of reversing the concentration gradient, i.e. the saturated concentration decreases as the pressure is reduced but the dissolved gas concentration is a parameter dependent on the resin’s history.

Once again model predictions represented the data well but deviations were found at longer times. This, as before, was attributed to the decreasing dissolved gas concentration in the bulk due to nucleation and diffusion of gas into existing bubbles. The photographs, corresponding to the graph in figure 9.5, show the successive increases in bubble size and the decreasing inter-bubble distances. Figure 9.6 shows a plot of radius$^2$ vs. time (for the diffusion controlled growth) showing a deviation from the expected linear relationship at the same time for the different sized in the same solution indicating that the deviation is a system parameter and not directly a consequence of bubble size (figure 9.6). Figures 9.5 and 9.6 and the photo-history imply that the bubbles are depleting the surrounding resin of gas, thus reducing the diffusion driving force and subsequently decreasing the growth rate.

The bubble size, on increasing the pressure to atmospheric pressure, directly shows the contribution due to the diffusion of gas into the host bubble. It shows that gas diffusion is an equally if not more important consideration than the initial gas expansion, due to the pressure reduction, when considering a typical composite processing route that maintains a vacuum throughout the cure cycle. The vacuum drawn in the experiments was also not as severe as that used in a typical cure cycle (figure 1.8)(Section 1.4)
Figure 9.5 Pressure dependence of bubble behaviour and respective photo-history
Figure 9.6 Deviation from linear relationship for growing bubbles
CHAPTER TEN

CONCLUDING REMARKS : GAS BUBBLES

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10. GAS BUBBLES: CONCLUDING REMARKS

The investigation has so far shown that the presence of a non-condensable gas in the resin can affect the growth or collapse of gas bubbles depending on the process variables. Free gas in the form of suspended bubbles can grow as the pressure is reduced in accordance with the perfect gas laws and as a consequence of diffusion. The rate of growth is determined by the diffusion coefficient of the gas molecules in the resin which is affected by the temperature and the viscosity of the resin. The driving force for the mass diffusion process is the concentration gradient which will be affected by the pressure of the system and by the dissolved gas concentration in the bulk resin. Changing the pressure can ultimately determine whether a gas bubble will grow or collapse.

The behaviour of gas bubbles can be predicted relatively well for a wide range of processing conditions. The input variables necessary for the predictive modelling have been determined from simple experiments as have their dependencies on the processing variables. Novel methods have been used to measure the gas diffusion coefficient and the dissolved gas concentrations and these parameters have been compared to theory. This chapter draws together the earlier work and outlines the main parameters that are required for a production model.

10.1 IMPLEMENTATION OF MODELS

Utilising the scientific principles and the easily measured materials data discussed in previous chapters it is possible to develop a systematic method of determining the growth and collapse of gas bubbles in a resin system. This has now be converted into a simple computer routine that predicts the behaviour of such bubbles throughout the cure cycle. The input parameters required include the processing schedule and those associated with the mass diffusion equations.
10.1.1 System Parameters

1) Cure Temperature as a Function of Time

If the temperature cycle is known then the diffusion coefficient can be calculated for each temperature incrementally using the free volume theory. It is also postulated that the relationship between the viscosity and the diffusion coefficient would hold even as cure commences. The temperature is also required to determine the density of the gas bubble and possibly the equilibrium gas concentration, although the latter was not found to be significantly affected by temperature in this system. These parameters can be substituted into the steady-state diffusion equations to predict the change in radius with time. This relies on accurate information regarding the temperature distribution in the composite, i.e. an accurate heat transfer model.

2) Cure Pressure as a Function of Time

The pressure cycle is needed to determine the driving force for diffusion. The saturated gas concentration can be calculated from Henry's law for each pressure realised by the resin which can be determined empirically or by using the thermodynamic correlation. The density of gas in the bubble is also pressure dependent. It must be remembered that the pressure used in these calculations is the resin pressure, so a distinction must be made between the applied pressure and the actual hydrostatic pressure with consolidating pressures being largely reacted against the solid-to-solid contact of the reinforcement.

From these processing variables (the changing temperature-pressure/time profiles) the growth and collapse kinetics of a gas bubble can be predicted. The generalised model can be applied theoretically to any system where the input parameters are known. These input parameters are summarised below.
10.1.2 Model Parameters

Manufacturers supply limited information on their resin products. Material parameters usually include the density and viscosity at one temperature, the epoxide group content and empirical information on cure schedules and cured resin properties. Although this information is limited, it has been shown that it is possible to determine many of the parameters used in this study purely from these values and a knowledge of the resin chemistry. The required parameters are:

1) Initial Void Size

This information is generally unavailable but one can place limits on the initial size of a gas bubble. In the case of negligible mechanical entrapment during the lay-up procedure it can be assumed that the largest size of gas bubble will be governed by equilibrium considerations, i.e. although surface tension forces increase the internal pressure of a bubble, on a lyophobic surface the effect of surface tension can reverse. Whenever these opposing forces are equal the bubble will remain indefinitely with surface tension forces acting opposite to the hydrostatic pressure.

It is reasonable to assume that prior to processing, the hydrostatic pressure in the resin will be atmospheric, i.e. manufacture of the prepreg and storage is at normal pressures. The surface tension force for the resin system under investigation was 0.035 N/m and therefore bubbles of dimensions of \( \approx 1\mu\text{m} \) would be expected to remain stable.

It is possible that larger bubbles exist due to the inability of the resin to penetrate cavities or crevices in a reasonable time. This could occur when the resin is applied to the reinforcement in the form of a viscous paste. In most systems, however, the reinforcement is infiltrated by a low viscosity liquid resin, either as a solution or by heating the resin to reduce its viscosity. The viscosity in this case is sufficiently low that the rate of penetration into microscopic cavities of either wetted or unwetted cavities will occur very rapidly due solely to capillary forces. This will either totally
inactivate the cavity or it will attain equilibrium penetration.

The size of a gas bubble due to mechanical entrapment during lay-up is a more difficult parameter to predict as it is strongly dependent on the individual or technique used to stack the laminae. Careful lay-up techniques can significantly reduce porosity although one can say there will be an upper limit to the size of an entrapped bubble realised by an observer. Glass fibre laminae prior to processing are generally translucent thus making it very difficult to spot bubbles without resorting to elaborate techniques while carbon fibre systems are totally opaque.

The solid-to-solid contact of the reinforcement of each layer is effectively the closest that the laminae can come to each other during lay-up. Intuitively this implies that there will be small air pockets, the size of which are dependent on the mismatch between the tows. This is more readily appreciated when lamina of different orientations are stacked. Air can easily nestle in the interstices and will have dimensions dictated by the geometry of weave. Since the resin within each lamina is effectively solid during the lay-up process these interstitial voids will remain until the pack is committed to the processing cycle. Once subjected to the processing cycle, these air pockets will act as suspended bubbles in the resin in the inter-ply regions.

2) Saturated Gas Concentration of the Resin System

An expression is required that relates the dissolved gas concentration to the pressure. Whether it obeys Henry's law or not, such a relationship can be used directly to determine the driving force for diffusion with respect to the hydrostatic pressure. It is considered that the gas concentration in most systems will obey Henry's law and will not be significantly temperature dependent for the temperatures experienced in a typical composite processing route. If Henry's law constant is known for the gas/resin system the saturated gas concentration can be calculated directly from Henry's law for each pressure experienced by the resin prior to or during the cure cycle. If Henry's law constant is not known for the resin system it can be measured using the
3) Dissolved Gas Concentration of the Bulk Resin

This should be measured for each processing operation as it is primarily a function of the resin's history. The degassing of resin under vacuum, prior to the impregnation of the reinforcement, will reduce the dissolved gas concentration although air will inevitably diffuse into the resin subsequent to degassing during the infiltration stage, especially if the resin is hot. The depth of penetrant diffusion over a plane surface is related to \((Dt)^{1/2}\). Sorption of air into a resin will occur rapidly due to the high mobility of gas in a liquid resin. Even in the case of prepreg layers containing solid resin it can be assumed that equilibrium is achieved rapidly as the layers are thin (≈1/8mm). Hence, as a first approximation and worst case scenario in terms of eliminating bubbles, it can be said that the dissolved gas concentration will equal the saturated gas concentration for the ambient conditions before processing. This can be calculated directly from the relationship between the gas concentration and the pressure.

4) Surface Tension at Bubble/Resin Interface

This can be measured directly using a number of techniques or it can be calculated from the cohesive energy density of the resin. The cohesive energy density of the resin can be calculated from the solubility parameter which can be determined from the molar attraction constants. Although the relationship between the solubility parameter and the surface tension is semi-empirical it seems to be applicable to a resin system, as it is to other polymeric systems. It was also found that the surface tension was not significantly temperature-dependent over the temperature range investigated for this system.
5) Gas Diffusion Coefficient

An expression is needed to relate temperature to the diffusion coefficient of gas in the resin. The temperature range of the relationship need only be up to the point at which the resin gels. Beyond this point any bubble will effectively become "frozen" within the laminate. The gel point is a material and time-temperature dependent parameter so it is necessary to ensure that the diffusion coefficient is represented over a wide temperature range to take different cure schedules into account.

A method has been described to measure the diffusion coefficient from bubble dissolution rates. The method has proven to be satisfactory showing a relationship between the diffusion coefficient and the temperature that can be predicted by free volume theory. For this system it was also noted that there was a direct relationship between the gas diffusion coefficient and the viscosity. The temperature dependence of the diffusion coefficient can subsequently be calculated from the viscosity/temperature data. The latter can be directly measured or determined from free volume theory if the glass transition temperature is known. If the glass transition temperature is not known then it can be measured using differential scanning calorimetry or by using the semi-empirical relationship between $T_g$ and the molecular mass of the resin precursor. The advantage of using the viscosity to determine the diffusion coefficient is that in a curing system, where the relationships between cure kinetics and the process variables are still in their infancy, the diffusion coefficient can be determined from an industrially accessible parameter. This is of considerable use since although the diffusion coefficient is the more easily interpreted physical quantity, the viscosity is far easier to measure and viscosity/temperature data is more readily available.
10.1.3 Model Predictions

Using the input information described above, the behaviour of a gas bubble can now be described for the typical cure cycle in figure 1.8, where it is assumed that the initial dissolved gas concentration is that for a resin degassed at 0.5 atmospheres. The initial bubble size was assumed to be 5x10^{-5} m.

Figure 10.1 was taken from a simple computer routine which shows the temperature and pressure cycle and the changing bubble radius with time. The stages are the same as those in figure 1.8. During stage one, under constant pressure (vacuum) but increasing temperature, the diffusivity increases dramatically with temperature, the viscosity decreases with temperature and the density of the gas in the bubble decreases with temperature. All these factors favour bubble growth and a rapid increase in bubble radius is predicted during this stage. During stage two, the temperature and pressure are constant so therefore the driving force for diffusion is constant (neglecting surface tension forces) and growth is a function of $t^{1/2}$ from the steady-state approximation. During stage three, the pressure is increased and the volume of the bubble will decrease in accordance with the ideal gas laws. In this case it was assumed that the pressure realised by the resin was atmospheric pressure, although it would probably be lower despite the consolidating pressure. Stage four is similar to stage two except that now there is a negative driving force for diffusion and bubble collapse occurs. Similarly stage five mimics stage one except that bubble collapse is encouraged. In reality stage five will probably not affect the bubble in that the viscosity will rise due to the crosslinking reaction in stage four. If the resin gelled before the consolidating pressure was applied the remaining void would have had an effective radius of over sixty times its original dimensions, i.e. a diameter of about 6.5mm.
Figure 10.1 Computer routine to predict the growth and collapse of gas bubbles from the system and model input parameters.
CHAPTER ELEVEN

EXPERIMENTAL II

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11.2 WATER DROPLET AND HUMID AIR BUBBLE EXPERIMENTS 177
11. EXPERIMENTAL II

Up to this point the effects of a dry non-condensible gas have been considered. In a real system any entrapped air will have a finite water concentration and water will be also present in the resin, primarily as a result of sorption due to resin exposure to humid air. For these reasons it is necessary to take water into consideration but it is also of interest to examine the effects of water as it is a condensible volatile and will behave differently to a permanent gas.

The initial relative humidity exposure dictates the water concentration in the resin which may influence whether a bubble will grow or collapse due to the diffusion of water molecules. Maintaining low humidities in a production environment can be prohibitively expensive depending on the climate of the production facility. A knowledge of how the relative humidity is related to the water concentration is vital in tailoring the temperature and pressure profile of the cure cycle to suppress bubble growth. The following experiments investigated the sorption of water by the resin and its effects on bubble behaviour.

11.1 GRAVIMETRIC EXPERIMENTS

As in the gas-resin system, the diffusion coefficient and concentrations were required. It was necessary to determine the diffusion coefficient and equilibrium sorption of water in the resin. A gravimetric method was used to determine the water uptake of the resin because the uptake of condensible vapours is significantly greater than permanent gases. Thoroughly dried resin (0.2ml) was injected into a glass cuvette of dimensions 10mm x 10mm and placed in a thermal balance with an accuracy of $10^{-4}$g. All samples had been degassed under vacuum and at 333K. The geometry was constant for all samples. The initial weight was recorded independently on a microbalance and the specimens were then conditioned by exposure to a humid environment.
The relative humidities were created by means of saturated salt solutions. The reason for using salt solutions is that they can liberate or release large quantities of water without changing the equilibrium humidity. Several lists of relative humidities over saturated solutions have been compiled [Young (1967)] and a number were selected to monitor the moisture pick-up over the full relative humidity range. The list of solutions used is given below.

**TABLE 11.1**

<table>
<thead>
<tr>
<th>Saturated Salt Solution</th>
<th>Relative Humidity(%) (293K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium Chloride</td>
<td>12</td>
</tr>
<tr>
<td>Potassium Acetate</td>
<td>22</td>
</tr>
<tr>
<td>Magnesium Chloride</td>
<td>33</td>
</tr>
<tr>
<td>Sodium Dichromate</td>
<td>55</td>
</tr>
<tr>
<td>Sodium Nitrite</td>
<td>65</td>
</tr>
<tr>
<td>Sodium Chloride</td>
<td>75</td>
</tr>
<tr>
<td>Potassium Chloride</td>
<td>85</td>
</tr>
<tr>
<td>Potassium Sulphate</td>
<td>97</td>
</tr>
</tbody>
</table>

The specimens were placed on the balance which was housed in a tubular oven. Air was passed through the salt solutions using a small pump and the resulting humid air was passed over the sample at a constant rate (figure 11.1). The relative humidity of the air passing out of the furnace was monitored intermittently using a wet-and-dry-bulb hygrometer. The temperature of the furnace and salt solutions were constant throughout all experiments. The change in weight with time was plotted simultaneously and sorption and desorption were monitored in most cases. The system was considered to be at equilibrium when there was no detectable weight change over a time period equivalent to the attain the weight change. Desorption was attained by passing air through a column containing calcium chloride before being passed over the sample. Although zero relative humidity was not attained in the chamber using this method, all samples were desorbed to the same humidity (=12%).
Care had to be taken to ensure that no liquid water was transferred into the chamber so a trap was placed in the piping between the salt solution and the balance. A diffuser was also used to prevent the humid air flow from disturbing the balance. The diffuser was simply a cone in which the air entered at the apex allowing the air to flow in a circulatory fashion in the chamber. Blank samples were used to assess the degree of moisture pick-up by the glass cuvette that held the resin. It was found that small weight gains occurred even at low humidities although this did not increase appreciably at the higher humidities. Nearly 50% of the weight gain occurred within the first minute and the remainder within the first five minutes. This small correction was remedied by exposing the cuvette to the humid atmosphere before the resin was injected. The weight increase was noted and taken into account for the desorption experiments.

Temperature effects due to the high heat of condensation of water vapour can lead to temperature changes during sorption and desorption. If these are considerable then a decrease in relative humidity will occur locally at the surface (in the
case of sorption) which would result in a decrease in the amount sorbed. Such effects are only significant at high humidities where the equilibrium uptake is high but even this can be avoided by tailoring the geometry of the sample [Yashuda and Stannet (1969)]. The samples used were sufficiently thick that the moisture uptake was slow enough to allow the heat to be dissipated. In these experiments it is conceivable that the flow of humid air across the sample would further reduce any temperature effects.

Gravimetric experiments were also carried out at higher temperatures in order to determine the temperature dependence of the water diffusion coefficient. Resin was equilibrated with different water contents and desorption was monitored, as before, for a range of temperatures.

11.2 WATER DROPLET AND HUMID AIR BUBBLE EXPERIMENTS

Water droplets were injected into resin using a hypodermic syringe and retained by means of a metal gauze. A glass retainer could not be used as water has a low contact angle with glass and a spherical shape could not be maintained. The resin was thoroughly dried by degassing at 333K until the water content of the resin, measured thermo-gravimetrically, was considered negligible (<0.1wt%). Some experiments dealt with changing the water concentration in the bulk resin. The dried resin was exposed to the controlled humid environments and samples were taken to determine the water content using the thermo-gravimetric method previously outlined.

The experiments aimed to monitor the size of droplet with time for different water concentrations in the bulk resin and at different temperatures. Preliminary experiments dealt with deviation from spherical shape as with the gas bubbles in Section 6.2.1. The droplet size was monitored with time at several temperatures using a similar method to the bubble experiments in Section 6.2.2. The droplets were not monitored to complete solution due to limitations of the gauze. Room temperature experiments required a settling time to allow the injected droplet to stabilise against the gauze. This was due to the high resin viscosity and the small
density difference between the resin and water. Droplets with larger initial radii had to be used than in the corresponding gas bubble experiments and subsequently observation times ranged from minutes, in the case of elevated temperature experiments, to several days for room temperature experiments.

The behaviour of humid air bubbles were also monitored in a prepared resin. Humid air (55%RH at 293K) was bubbled through resin at 313K for 24hours and the resulting concentration was measured thermo-gravimetrically. The resin, for all samples, had a water concentration in the bulk of 1wt% ±0.1. The air concentration in the resin could not be measured using the instantaneous vacuum method as water would also contribute to the foaming level. It was assumed that as the resin was equilibrated at atmospheric pressure and as the partial pressure of water is small compared to the partial pressure of air at this humidity and temperature, the resin attained the equilibrium air concentration for atmospheric pressure. Humid air bubbles were injected into the resin using a hypodermic syringe and their behaviour was monitored with time for different temperatures.

For all water droplet and humid air bubble experiments, the initial radii used were large enough to render surface tension forces negligible. In the case of humid air bubbles, growth could be subsequently directly related to the transport of water molecules into the bubble and the transport of air out of the bubble could be considered negligible, i.e. the driving force for air out of the bubble were the surface tension forces in this air-saturated system.
12. ANALYSIS OF WATER INVESTIGATION

The following chapter primarily deals with water in the resin in relation to bubble dynamics although the investigation is also of interest in terms of characterising an uncured resin which has been exposed to humid environments. A thermodynamic analysis is performed to determine the prerequisite input parameters for the diffusion equations in Chapter Three.

12.1 GRAVIMETRIC EXPERIMENTS AT 293K

The microbalance chart records of weight against time were sampled at appropriate intervals and plots of fractional uptake against the square root of time were constructed (figure 12.1). The mass uptake ($M_t$) at any time $t$ is the mass increase per initial mass of the dry resin. The fractional uptake ($M_t/M_\infty$) is the fraction sorbed at a time $t$ with respect to the uptake at equilibrium.

For the lower humidity tests plots of $M_t/M_\infty$ versus $t^{1/2}$ were typically linear out of the origin up to 50% of the total concentration change. Above the linear portions, the curves were concave to the time axis and there were no inflections in the curve, which indicates that sorption was truly Fickian [Crank$^b$(1956)]. Difficulties were encountered with very low humidity exposures where the uptake was so small that consistent readings were not attained. The minimum relative humidity exposure used was 22%. Sorption and desorption data were not coincidental with sorption generally being faster than desorption for the lower relative humidity exposure tests, i.e. $<$ 65% (figure 12.2). The desorption curves also showed deviations from linearity at lower concentrations than the sorption curves. At higher relative humidity exposures the sorption and desorption curves became increasingly sigmoidal indicating a deviation from Fickian kinetics (figure 12.3). Such a time-dependent diffusion coefficient indicates that water is entering by normal solution with some kind of immobilisation of a proportion of the penetrating molecules [Crank$^a$ (1956)]. In these cases desorption was equivalent or faster than sorption.
Figure 12.1 Fractional moisture uptake of resin with relative humidity exposure

Figure 12.2 Sorption and desorption at 54% relative humidity exposure
The diffusion coefficient was determined from the slope of the linear regions of the fractional plots and was based on Fickian kinetics for all samples. The one dimensional case of Fick's second law could be applied and no corrections for edge effects were required as the cuvette was impermeable to moisture. The diffusion coefficient was calculated from the initial slope and half time measurements. The diffusion coefficient from the initial slope measurement was calculated from,

\[
\frac{M_t}{M_\infty} = \frac{4}{l} \left( \frac{Dt}{\pi} \right)^{1/2}
\]

\[\text{.... (12.1)}\]

where \(l\) is related to the thickness of the specimen.
When the process is Fickian, the value of t/1^2 for which M_t/M_\infty = 0.5 is given as,

$$ (t/1^2)_{1/2} = -(1/\pi^2 D)\ln[(\pi^2/16) - (1/9)(\pi^2/16)^9] \tag{12.2} $$

The error in equation 12.2 is about 0.001% [Crank^c (1956)]. Hence,

$$ D = 0.04939/(t/1^2)_{1/2} \tag{12.3} $$

Exposure was only from one side for all experiments and so l was twice the sample thickness [Shen and Springer (1976)].

The plot of diffusion coefficient vs. equilibrium concentration was found to be concentration dependent (figure 12.4). The diffusion coefficient was found to decrease by approximately an order of magnitude for a 1% uptake and level out over the rest of the concentration range. This was based on half time measurements which was in agreement with gradient measurements for the lower relative humidity data. At higher exposures (>65%RH) the initial slope was found to be considerably lower with corresponding diffusion coefficients of $3.7 \times 10^{-11}$m^2/s at 75%RH and $3 \times 10^{-11}$m^2/s for 85%RH while, at 97%RH, the initial slope method yielded a diffusion coefficient of $1.38 \times 10^{-10}$m^2/s.

The equilibrium sorption was plotted against relative humidity exposure (figure 12.5) and was found to exhibit an anomalous isotherm with a point of inflection between 55% and 65% relative humidity exposure. The equilibrium sorption levelled out to a finite value of 4.68wt% at unit activity (100%RH). Middle range humidity exposures exhibited a possible plateau with downward curvature at progressively lower humidities.

The isotherm indicates that more than one mode of sorption is occurring and that the resin contains between 0.6wt% and 1wt% water in a typical laboratory environment (30-60%RH).
Figure 12.4 Concentration dependence of diffusion coefficient at 293K

Figure 12.5 Water sorption isotherm for resin at 293K
12.1.1 The Sorption Isotherm

The isotherm represents the concentration of water that the resin will pick up when exposed to a humid environment at this temperature. The isotherm is a useful empirical tool for determining the water concentration of the resin with respect to its storage or production conditions, showing that low humidity environments can reduce the water concentration in the resin. If the data is replotted in terms of activity vs. mole fraction of water it can be seen that there is a definite positive deviation from Raoult's law and ideal solution behaviour (figure 12.6). Most mixtures exhibit positive deviations of this type as they generally occur when the components have differences in polarity, molecular size and if one of the components is associated in the liquid state. It can be seen after the initial deviation from ideal behaviour that the curve begins to flatten out at approximately 0.2 mole fraction. This flattened portion indicates that the mixture will separate out into two layers as the temperature is lowered, i.e. water and resin are only partially miscible although a distinct phase separation was not expected in a viscous resin. Conversely, an activity vs. mole fraction graph of this type also indicates that as the temperature is increased the mixture will behave more ideally. The apparent point of inflection at 0.5 mole fraction is not considered to be a consequence of the thermodynamics of mixing and is discussed in Section 12.1.1.1.

At very low concentrations the graph also shows a point of inflection at about 0.05 mole fraction. This can only be a consequence of a mixture of sorption modes. If there is a tendency for water and resin to interact the number of molecules of both resin and water will be less than if there was no interaction. Since the resin is less volatile than water then this interaction will cause the vapour pressure of water in the resin to be lower than the theoretical ideal value, i.e. a negative deviation from Raoult’s law. The fact that the graph does not exhibit a negative deviation from Raoult’s law corroborates the extreme differences in the chemical and physical nature of the water and resin that produce the strong positive deviation from Raoult’s law.
In terms of the isotherm at least two distinct regions can be seen (figure 12.5). At middle range humidities the water concentration tends to a plateau with a downward curvature at the lower humidities. This indicates that polymer-water contacts are strongly preferred which can be represented by the dual mode theory, i.e. the total solubility can be split into contributions from Henry's law mode and a Langmuir-type mode [Michaels et al. (1963)]. The model assumes that the penetrant dissolves by ordinary solution and by interacting with specific sites in the polymer.

\[ C = C_H + C_L = K_H p + \frac{C_L'}{1 + bp} \]  

... (12.4)

where C is the total concentration, \( C_H \) is the contribution from Henry's law mode, \( C_L \) is the contribution from the Langmuir type mode, \( K_H \) is Henry's law constant, b is the affinity constant (the ratio of the rate constants for the sorption and desorption process), \( C_L' \) is the site saturation constant and p is the partial pressure.
This theory can not describe the whole isotherm which can be seen by differentiating C with respect to p twice,

\[
\frac{\delta^2 C}{\delta p^2} = \frac{2C_L b^2}{(1+bp)^3} \quad \text{.... (12.5)}
\]

which implies that there is no point of inflection in a sorption plot since b and C_L' are always positive.

This point of inflection (55-65%RH) in the isotherm indicates that another mode of sorption is dominant. If normal solution was the dominant mechanism then it could be represented by a solution model such as that described by the Flory-Huggins theory [Florya(1953)].

The isotherm from the Flory-Huggins model is described by,

\[
\frac{p_1}{p_{o1}} = \phi_1 \exp(\phi_2 + \chi \phi_2^2) \quad \text{.... (12.6)}
\]

where \(\phi_1\) and \(\phi_2\) are the volume fractions of the penetrant and polymer respectively and \(\chi\) is the Flory-Huggins interaction parameter for the system. The Flory-Huggins model produces an isotherm of the BET III type (figure 5.1)(Section 5.1) and also predicts Henry’s law as \(\phi_1\) approaches zero. \(p_1/p_{o1}\) is the vapour activity which, in the case of water, is usually related to RH/100. This relationship has a similar interaction to the experimental isotherm with the equilibrium uptake increasing with increasing relative humidity exposure.

The interaction parameter \(\chi\) is a dimensionless quantity which is related to the energy of formation of a polymer-penetrant contact and the lattice co-ordination number (solution is treated as placing a penetrant in a simple lattice of polymer segments). The quantity can be estimated by using the solubility parameter approach [Young and Lovell (1991)] which also describes the temperature dependence of \(\chi\),

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\[
\chi = \frac{V_1(\delta_1 - \delta_2)^2}{R_g T} \quad \text{.... (12.7)}
\]

where \(V_1\) is the molar volume of the penetrant, \(\delta_{1,2}\) are the solubility parameters of the penetrant and polymer respectively, \(R_g\) is the universal gas constant and \(T\) is the absolute temperature. This relationship considers \(\chi\) as an enthalpy parameter.

From Flory-Huggins theory \(\chi\) has to be less than 0.5 for complete miscibility over the entire composition range, i.e. the solubility parameters have to be similar. This is not the case for the water resin system with \(\chi\) having a value of 5.57 at 293K using the solubility parameters in Section 4.2.2. This indicates that the uncured resin is not very hydrophillic. It also shows that over the temperature range in the composite processing route \(\chi\) does not decrease enough to make water soluble in the resin over the entire composition range. Using this value of the interaction parameter in the isotherm equation shows that the amount sorbed would be considerably less than the experimental sorption data (\(\approx 0.12\)wt% at unit activity). It can therefore be concluded that random solution of water is not the dominant mechanism or at least it can not be directly described in terms of the Flory-Huggins model.

One of the main limitations of the Flory-Huggins model applied to penetrant-polymer systems is that it implies random mixing of penetrant in the polymer, i.e. it assumes no specific component interactions. This random mixing includes polymer-polymer contacts, polymer-penetrant contacts and penetrant-penetrant contacts. If the experimental values of equilibrium sorption (in terms of volume fraction, \(\rho_R=1.16\)g/cm\(^3\) (Section 6.1)) are substituted into equation 12.6 with their corresponding activities (RH/100) it can be seen that \(\chi\) is a decreasing function of concentration (figure 12.7). If the solution was completely random then the Flory-Huggins parameter would be constant over the activity range. It can be concluded that the changing \(\chi\) reflects deviations from ideal (random) mixing.
Experimental data on water sorption by polymers is usually presented based on some form of Henry's law, i.e. a measure of the quantity of water sorbed per unit quantity of polymer is plotted against the activity of water in the surrounding vapour. For a large number of polymers, a plot of the reciprocal of water sorption against the reciprocal of the partial pressure of water exhibits near linear behaviour [Brown (1980)]. With the expectation that the volume fraction of water will be the expression of water concentration relevant to basic polymer solution thermodynamics, this measure has been used. This has been considered to be a better parameter than mole fraction when dealing with molecules that have significantly different molecular volumes, although a variety of expressions of concentration can be used which will alter the slope and the intercept but not the linearity of the plot. It can be seen that the data is reasonably represented by a linear function (figure 12.8) and the limiting or infinite dilution isotherm, as the activity approaches zero, is given by the inverse Henry's law expression,
where $p_{H2O}$ is the partial pressure of water, $P^{*}_{H2O}$ is the saturated water vapour pressure at the corresponding temperature and the quotient equates to the water vapour activity or $RH/100$. $k_1$ is the proportionality constant and $\phi_H$ is the volume fraction of water in the Henry's law mode.

Using the value of 91.75 for $k_1$ (determined by a linear regression though the experimental points), this equation is plotted as the upper line in figure 12.8. Graphically this is done by drawing a line parallel to the experimental data passing through the origin. The inverse of this relationship is the notional Henry's law isotherm which has been plotted on the original isotherm (figure 12.9). This is clearly an approximation as the experimental points deviate from linearity at low pressures (low
activity) in figure 12.8. The deviation seems to occur between a reciprocal activity of 2 and 3 which corresponds to between 33% and 50% relative humidity exposure, i.e. the plateau on the original isotherm. It is assumed that a linear relationship prevails in the following analyses although this deviation is investigated in Section 12.3.1.

It is assumed that at infinite dilution the behaviour of water is normal, representing the true interaction of water and polymer molecules. If water sorption occurs on two types of site, a polymer site and a polymer-water site, the influence of the former will predominate as $p_{H2O}$ and the amount of sorbed water simultaneously approach zero. Hence using the limiting (Henry’s law) approximation of the Flory-Huggins theory (equation 12.6)[Florya(1953)] the interaction parameter can be found,

$$\frac{p_{H2O}}{p_{H2O}} = \phi_1 e^{(1+\chi)} = k_1 \phi_1$$

$$\chi = \ln k_1 - 1$$

This can now be directly compared to the previous graph of $\chi$ against activity showing that extrapolation of the $\chi$ values from each experimental point coincides with the limiting value at zero activity (figure 12.10). This limiting value is not that dictated by the solubility parameter approach which is possibly due to limitations of the solubility parameter theory in dealing with penetrants that have a large hydrogen bond component or possible errors incurred in the linear extrapolation of the inverse isotherm. The interaction clearly reflects deviations from ideal mixing with increasing water activity.
Figure 12.9 Sorption isotherm with Henry's law isotherm

Figure 12.10 χ vs. activity with infinite dilution value
To determine the deviation from ideality is to compare the isotherm to that predicted by the Henry's law isotherm. The ratio of relationship between the reciprocal of the volume fraction of penetrant against the reciprocal of the activity in figure 12.9 to the Henry's law relationship from equation 12.8 gives a measure of the extent to which the sorption of water is increased by the abnormalities of the sorption process which result from non-random mixing. Hence this enhancement can be described by,

\[
N_e = \frac{\phi_1}{\phi_H} = \frac{k_1}{k_1 - k_2 \frac{p_{H_2O}}{p_{H_2O}^*}} = 1 + k_2 \phi_1
\]

Equation 12.10 indicates that the degree of deviation from Henry's law continually decreases with lower water contents and approaches Henry's law as the water concentration approaches zero, i.e. \(N_e = 1\). The enhancement number is quantitatively assessed in Section 12.1.1.1.

The diffusion data also indicate deviations from ideal mixing in that such transport processes would be invariant with concentration if the mobile water was molecularly dispersed in the resin. The decrease in diffusion coefficient (figure 12.4) can be explained in terms of immobilisation of species, i.e. if the proportion of immobilised water increases with concentration then the diffusion coefficient will decrease as the concentration of mobile molecules per total concentration decreases. It can therefore be supposed that water enters the resin and forms clusters. This is not only evidenced by the decreasing diffusion coefficient but also by the upward curvature of the isotherm and the positive deviation from Raoult's law, the differences in the individual component solubility parameters and the strong associative nature of water in the liquid state.
12.1.1.1 Cluster Analysis

Another index that represents deviations from random mixing is based on the cluster integral determined by Zimm and Lundberg (1956). The clustering function can be calculated from the activity-concentration behaviour of the system and gives a measure for the tendency of like molecules to cluster or alternatively to segregate from each other. The theory was originally developed to determine the degree of non-mixing in two-component gas systems and it is based on statistical mechanics.

Clustering of water in polymers has been noticed in a number of systems where initiation has occurred completely randomly or at polar centres within the polymer. It is a mechanism that explains positive deviations from ideal solution behaviour and has been used successfully to explain positive deviations from dual mode theory [Jacobs and Jones (1990)].

The clustering function can be determined from the analysis of the equilibrium sorption isotherm, and is described quantitatively by the equation proposed by Zimm (1953),

\[
\frac{G_{11}}{v_1} = \frac{kT\beta}{v_1} - (1 - \phi_1) \left[ -\frac{\partial \phi_1}{\partial a_1} \right] - 1 \quad \text{.... (12.11)}
\]

where \(G_{11}/v_1\) is the clustering function, \(\phi_1\) is the volume function of penetrant, \(a_1\) is the water activity equated to \((RH/100)\), \(v_1\) is the partial molar volume of component 1, \(k\) is the Boltzmann constant, \(\beta\) is the isothermal compressibility of the system and \(T\) is the absolute temperature. The volume fraction of penetrant was calculated from the density of the resin (1.16g/cm\(^3\) at 293K).

For a random solution the volume fraction is proportional to the activity and therefore,
In this ideal case each penetrant molecule excludes its own volume to other molecules but does not otherwise affect their distribution. The extent to which $G_{11}/v_1 > -1$ indicates the extent of clustering in the solution.

In order to perform the differentiation as required in equation 12.11, $a/\phi_1$ was plotted against $a$ (figure 12.11). A straight line represents the data adequately especially at higher activities and the function was differentiated accordingly. It should be noted that the small term involving compressibility for the penetrant in a binary mixture has been considered negligible which is a reasonable assumption for a binary system far from the gas-liquid critical region, i.e. a condensed system [Brewis et al. (1980)]. The cluster function, based on the linear regression from figure 12.11, is clearly greater than -1 which indicates clustering of the water molecules in the resin (figure 12.12). It must be remembered that this function was calculated from a linear line and so the resulting function is also linear. If non-linear regression had been used it is clear that the cluster function would also show non-linearities. Figure 12.12 shows the general interaction which was considered acceptable for the subsequent analysis.

Zimm and Lundberg (1956) have provided a more useful index in the quantity $\phi_1 G_{11}/v_1$. This quantity is the number of type 1 molecules in excess of the mean concentration of type 1 molecules in the vicinity of a given type 1 molecule. This definition of $\phi_1 G_{11}/v_1$ specifies the excess penetrant molecules in the vicinity of the central penetrant molecule but does not include the central penetrant molecule. Using this definition Starkweather (1980) has suggested that the average number of penetrant molecules in a cluster $N_c$ (cluster number), can be calculated from the equation,
Figure 12.11 Determination of cluster function for water-resin system

Figure 12.12 Cluster function vs. volume fraction of water
For a random solution the activity coefficient, $a/\phi_1$, is invariant with concentration and from a combination of equations 12.11 and 12.13 this would give,

$$N_c = \frac{\phi_1 G_{11}}{\nu_1} + 1 \quad \text{.... (12.13)}$$

for such a solution. As Brown (1980) points out there should be no clustering in this case and the cluster number should be 1.

If the central penetrant molecule is included then the cluster number should be given by the equation,

$$N_c = 1 - \phi_1 \quad \text{.... (12.14)}$$

Values of $N_c$ calculated from equation 12.15 exceed those calculated from equation 12.13 by the quantity $\phi_1$. These corrected equations provide a cluster number of 1 for an ideal (randomly distributed) solution.

It can now be seen that both the enhancement number (Section 12.1.1) and the cluster number represent deviations from ideal mixing the former being a direct measure of the peculiarities of the isotherm. The derivative within the brackets of equation 12.15 is equal to $-k_2$ and therefore the cluster number is,
and comparing this to the enhancement number from equation 12.10 gives,

\[ N_c = 1 + k_2 \phi_1 - k_2 \phi_1^2 \quad \ldots \quad (12.16) \]

\[ N_c = N_e - k_2 \phi^2 \quad \ldots \quad (12.17) \]

Figure 12.13 compares the cluster number with the enhancement number and clearly shows clustering is an important consideration in the water-resin system although the comparison also indicates that clustering is not the only phenomenon causing the enhancement from ideal mixing.

With a knowledge of the number of water molecules per epoxy group (from the isotherm data) and the size of a cluster (from the cluster number), the number of clusters can be calculated. Figure 12.14 relates the corresponding number and size of clusters to the resin. The sloping lines correspond to various average numbers of water molecules per cluster. Water begins to cluster at low concentrations although it seems to be unclustered up to approximately 0.2 water molecules per resin molecule. As the concentration of water is increased the number of clusters remains within a narrow range levelling off at about 0.225 clusters per resin molecule. This implies that water clusters are initiated at particular sites and grow with increasing water concentration around these sites. These sites are probably the OH group on the resin backbone which can form hydrogen bonds with the water molecules. This is intuitively correct and also is substantiated by the fact that there is approximately 0.2 OH groups per resin molecule, i.e. the number of resin molecules that have an OH group (which is equivalent to the number of repeat units per molecule) is approximately 0.2 for this uncured system. This approximate 1:1 ratio between the number of sites and water molecules implies that all sites are easily accessible to water molecules. This would indicate that any inter-resin bonds are disrupted by water, i.e. water has a higher hydrogen bond propensity for the OH group on the resin backbone than the resin molecule itself. Near saturation the apparent average cluster size is between four and five molecules.
Figure 12.13 Comparison of cluster number $N_c$ and enhancement number $N_e$

Figure 12.14 Clustering related to resin structure
It is interesting to note that the equilibrium sorption value as unit activity is approached (figure 12.5) is consistent with clustering if it is assumed that water cluster growth is limited by steric considerations. The resin molecules will provide resistance to cluster growth since movement of the surrounding molecules requires energy. If the cluster totally occupies the free volume of the resin then the equilibrium sorption (in terms of volume of water/volume of resin) represents the free volume fraction. The free volume fraction, calculated from equation 5.5 (Section 5.2.2), is 0.0586 at 293K compared to the volume of water uptake of 0.0543. The similarity between these values could indicate that the free volume, that aids the mobility of a penetrating molecule, may also restrict the size of a cluster.

The qualitative mechanism suggested by the data and its interpretation is that at low concentrations water is distributed throughout the resin but probably preferentially where hydrogen bonding is possible. At higher concentrations water molecules begin to cluster together, predominantly at these hydrogen bonding centres.

It is also anticipated that aggregates or clusters of molecules will be less mobile in comparison with isolated molecules. The diffusion coefficient was determined from the total sorbed concentration (the overall solubility is a measure of all water molecules) which implies that as the sorbed concentration increases the diffusion coefficient will decrease. In the simplest case it can be assumed that all clustered water is effectively immobilised. If the concentration of free-to-diffuse molecules is denoted by \( c' \) and the total concentration by \( c \), then

\[
D = D'(\frac{\partial c'}{\partial c}) \quad \ldots \ (12.18)
\]

where \( D \) is the measured diffusion coefficient and \( D' \) is the diffusion coefficient of mobile molecules.
Figure 12.15 Concentration dependence of diffusion coefficient using cluster theory

\[ D = D' \left[ -\phi(1-\phi) \left( \frac{\alpha(\phi)}{\phi} \right) \frac{1}{\partial a_1/\partial a_1} \right]^{-1} \] .... (12.19)

Figure 12.15 shows the interaction of the diffusion coefficient with concentration, with a limiting diffusion coefficient of \(7 \times 10^{-10} \text{m}^2/\text{s}\) at \(c=0\) (extrapolated from the low activity data). Although the concentration dependence of the diffusion coefficient is consistent with the concept of clustering the data is only adequately represented. The large decrease in experimental diffusion coefficient compared with that from cluster theory (equation 12.19) implies that clustering is not the only immobilisation mechanism affecting the diffusion coefficient. Application of the
enhancement number in equation 12.18 yields an improved interaction although the difference is small. It is therefore concluded that a linear extrapolation of the inverse isotherm is an oversimplification of the sorption in the water-resin system.

It can be concluded that the clustering of the water is indicated in terms of deviations from ideal mixing and changes in the diffusion coefficient. The Flory-Huggins interaction parameter $\chi$ also decreases with concentration although this will be a less sensitive indicator to clustering. Their model for polymer-penetrant systems implies random mixing of the penetrant in the polymer matrix. This random mixing includes penetrant-penetrant interactions which may be reasonably termed clusters. Deviations in $\chi$ will therefore reflect deviations from Flory-Huggins behaviour which infers deviations from random mixing. The concordance between the enhancement number and the independent cluster number provides strong support for the postulate that associated water accounts for a substantial proportion of the sorption isotherm.

12.1.2 Polycondensation Model

The cluster function is a useful parameter to analyse sorption data by equating a geometric probability to two thermodynamic measurements without recourse to a geometric model. It does provide a mathematical representation of the concentration dependence of the diffusion coefficient and the sorption isotherm although this is insufficiently accurate to predict the behaviour of bubbles where an accurate diffusion coefficient and driving force are prerequisite to the success of mass diffusion theory. Another weakness of the cluster function is that it is non-predictive.

If it is considered that water is a tetra-functional monomer then clustering can be treated in a similar way to a polymerisation process in which hydrogen bond formation occurs in a purely random fashion [Gordon et al. (1960)] and to which standard polycondensation distribution formulae can be applied [Flory (1953)]. This assumes that the resin is an inert continuum and that polymer-penetrant interactions are weak. Although this is not the case, as interactions are occurring between the resin and water, it is also considered that any interactions between the resin and water will
be hydrogen bonds. Such interactions will be energetically similar to those between associating water molecules. The significance of this statement is discussed in section 12.2.1.

The "gel point" of this polymerisation process can be identified with the saturation point of the system [Barrie and Platt (1963)] and the weight fraction of polymeric species composed of n water molecules is given by,

\[ W_n = \frac{f q^{n-1} (1-q)^{n-2} (f_n - n)!}{(n-1)! (f_n - 2n + 2)!} \quad \ldots (12.20) \]

where \( f = 4 \) is the functionality of the water molecules and \( q \) is the fraction of the hydrogen bonds actually formed; the saturation point of the system is defined by,

\[ q_c = \frac{1}{(f-1)} \quad \ldots (12.21) \]

and the law of mass action for the breaking of a hydrogen bond, i.e. the equilibrium constant governing the equilibrium between broken and unbroken hydrogen bonds, may be written as,

\[ K = C(1-q)^2 q \quad \ldots (12.22) \]

If \( C_s \) is the saturation concentration of water it follows that,

\[ K = \frac{4}{3} C_s \quad \ldots (12.23) \]

Since \( W_n = C_n/C \) and substituting the root of the quadratic in equation 12.22 into equation 12.20,
where \( k = (K^2 + 4KC)^{1/2} \). The positive root was discarded in equation 12.22 since it gives \( q > 1 \). Therefore, the concentration of monomeric water is,

\[
C_n = \frac{(3n)!}{(n-1)!(2n+2)!} \frac{(2C+K-k)^{n-1}(k-K)^{2n+2}}{2^{3n-1}C^{3n}} \quad \ldots (12.24)
\]

The polycondensation theory can now be applied to predict the isotherm. If it is assumed that only monomeric water exists in the vapour phase (pressure \( p_{H2O} \)) and that \( C_1 \) is related to \( p_{H2O} \) by Henry's law, then the sorption isotherm follows

\[
C_1 = \frac{(k-K)^4}{16C^3} \quad \ldots (12.25)
\]

i.e. the concentration of monomeric water, \( C_1 \), is a function of the total concentration \( C \) from equilibrium considerations.

The polycondensation theory can now be applied to predict the isotherm. If it is assumed that only monomeric water exists in the vapour phase (pressure \( p_{H2O} \)) and that \( C_1 \) is related to \( p_{H2O} \) by Henry's law, then the sorption isotherm follows

\[
p_{H,O} = \frac{(k-K)^4}{16C^3K_H} \quad \ldots (12.26)
\]

where \( K_H \) is Henry's law constant for the water-resin system.

From figure 12.8 and equation 12.8 the value of Henry's law constant can be used from the infinite dilution isotherm. From equation 12.23 the value of \( C_s \) can be determined for the saturation pressure \( p_{H2O}^* \).

\[
p_{H,O}^* = \frac{16}{81} \frac{C_s}{K_H} = \frac{4}{27} \frac{K}{K_H} \quad \ldots (12.27)
\]

The saturation concentration using the infinite dilution value of Henry's law is 5wt% compared to the experimental value of 4.68wt%. The sorption isotherm in terms of relative pressure (activity or relative humidity/100) is then,
Figure 12.16 shows the isotherm predicted from equation 12.28 to the experimental data. Although there is deviation of the model from the experimental isotherm the data is reasonably represented especially when it is remembered that the only adjustable parameter is Henry's law constant for the water/resin system. Inaccuracies are inevitably incurred with the linear extrapolation to infinite dilution and by assuming that the Henry's law isotherm is a composite parameter, i.e. the extrapolated Henry's law isotherm is a combination of a Langmuir-type isotherm and the true Henry's law isotherm.

Higher humidities are represented less well than lower humidities and the levelling of the isotherm as unit activity is approached is not represented. The reason

\[
\frac{p_{H_2O}}{p_{H_2O}^*} = \frac{27(k-K)^4}{64KC^3}
\]

... (12.28)
for this change in gradient at high humidity exposures can not be explained in terms of the polycondensation model which assumes saturation at $\frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2\text{O}^*}} = 1$.

The polycondensation theory can also be used to determine the concentration dependence of the diffusion coefficient by noting that,

$$D = \Sigma D_n^* \frac{dC_n^*}{dC}$$ .... (12.29)

The quantity $\frac{dC_n^*}{dC}$ can be determined from polycondensation theory which for a water monomer is found by differentiating equation 12.25,

$$\frac{dC_1}{dC} = \frac{(k-K)^3}{16C^3} \left\{ \frac{8K}{k} \frac{(k-K)}{C} \right\}$$ .... (12.30)

As $C$ approaches zero, $\frac{dC_1}{dC}$ approaches 1 and $(D_1)_{C=0}$ can be identified with the experimental diffusion coefficient $D_{c=0}$, which at 293K has already been shown to be $7 \times 10^{-10}$ m$^2$/s. This can be regarded as a constant throughout the concentration range if it is considered that no plasticisation of the resin occurs (or has already occurred). An estimate of the diffusion coefficients of water dimers and trimers is made by the analogy with the results of Barrer and Skirrow (1948) for the diffusion of methane, ethane and propane in natural rubber. The ratios of the diffusion coefficient for these hydrocarbons applied to the water/resin system gives 7:2.4:1.4 for $D_1:D_2:D_3$ at 293K. Polymer species of four molecules or more are considered to have an average, although somewhat arbitrary diffusion coefficient of $1 \times 10^{-10}$ m$^2$/s. Equation 12.29 can now be written as,

$$D = D_1 \frac{dC_1}{dC} + D_2 \frac{dC_2}{dC} + D_3 \frac{dC_3}{dC} + D_{av} \left[ 1 - \left( \frac{dC_1}{dC} + \frac{dC_2}{dC} + \frac{dC_3}{dC} \right) \right]$$ .... (12.31)

since
It can be seen in figure 12.17 that for most of the concentration range the diffusion coefficient can be represented reasonably purely by considering the monomeric water as the sole diffusing species. At higher concentrations it seems necessary to take polymeric water into account since it would be an over simplification to consider polymerised water as totally immobile, although it must also be remembered that at high concentrations a deviation from Fickian kinetics was observed, which leads to difficulties in specifying the diffusion coefficient from the sorption data. In terms of the utility of the model, the assumption that monomeric water is the sole diffusing species over most of the concentration range does allow extension of the model to take into account the temperature dependence of the diffusion coefficient without resorting to numerical methods. This seems to be the natural progression as the temperature dependence of the diffusion coefficient is required for predicting bubble behaviour.

Figure 12.17 Concentration dependence of diffusion coefficient from polycondensation theory
12.2 GRAVIMETRIC DATA AT ELEVATED TEMPERATURES

Gravimetric experiments were performed on resin with a known moisture content to determine the temperature dependence of the diffusion coefficient for different concentrations. Resin was equilibrated with a very low moisture level (0.3-0.5wt%) to determine the activation energy for water diffusion. Desorption experiments were made over a range of temperatures (293-384K) and the diffusion coefficient was determined from plots of the fractional loss vs. time$^{1/2}$ as before. Although there was scatter in the data at lower temperatures, a linear regression provided an activation energy of 29kJ/mole (figure 12.18). This gave a value of the diffusion coefficient at 293K of $3\times10^{-10}\text{m}^2/\text{s}$ which is slightly lower value than the earlier experiments ($5.5\times10^{-10}\text{m}^2/\text{s}$).

Desorption experiments with a higher water concentration (1.8wt% ± 0.1) exhibited a changing activation energy for diffusion and a significantly lower diffusion coefficient than the lower concentration data over the temperature range (figure 12.18). The diffusion coefficient for the higher concentration was approximately an order of magnitude lower than the lower concentration data at 313K in agreement with the concentration dependence exhibited at 293K. At higher temperatures, the low and high concentration diffusion coefficient data begin to converge, with the high concentration data being approximately 2-3 times lower at 345K. Once again the diffusion coefficient at 293K, determined by linear extrapolation, was lower than the earlier experimental data.

The discrepancy between the higher temperature data and that at 293K can be explained in terms of the inevitable plasticisation that will occur when water enters the resin. At lower temperatures water will disrupt bonds between resin molecules which are thermally labile. At higher temperatures such plasticisation will not be so apparent in that the probability of any site interaction will be diminished by increasing the average energy of the system. This is discussed in Section 12.4.
The converging diffusion coefficients of the high concentration and low concentration data with increasing temperature can be explained in terms of the polycondensation model.

### 12.2.1 Polycondensation Model - Temperature Dependence

K is the equilibrium constant for breaking a hydrogen bond and will obey Le Chatelier's principle. Breaking a hydrogen bond will be an endothermic process (cluster formation is exothermic) and therefore as the temperature is raised the products of the reaction will be favoured, i.e. the cluster will break up. If it is assumed that the standard enthalpy change on breaking a hydrogen bond ($\Delta H_{\text{H}}$) does not vary appreciably with temperature over the temperature range of interest then the Van't Hoff equation can be used to predict the value of K at different temperatures. Hence,
where \( K_0 \) is the equilibrium constant at a reference temperature \( T_0 \).

If a reduced concentration \( C_r \) is defined by

\[
C_r = \frac{4C}{3K_0}
\]  

(12.34)

then

\[
k = K \left( 1 + \frac{3K_0C_r}{K} \right)^{1/2}
\]  

(12.35)

As \( T_0 \) is the lowest temperature of the working range then \( C_r \) goes from 0 to 1. Equation 12.35 can now be written as \( k = kX \), where

\[
X = \left( 1 + 3C_r \exp \left[ \frac{\Delta H_H}{R_T} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right] \right)^{1/2}
\]  

(12.36)

The value of the standard enthalpy change for breaking a hydrogen bond is between 14.4 and 27.6kJ/mole [Pimentel and McClellan (1960)] [Searcy (1949)]. A simple mean value (21kJ/mole) was taken for the subsequent analysis. The reference temperature used was the lowest experimental temperature (293K).

Since \( D = D_{c=0} (dC_1/dC) \), then from equation 12.30,

\[
E_D = (E_D)_{c=0} - 3R_T \left( \frac{\partial \ln(k-K)}{\partial (1/T)} \right)_c - R_T \left( \frac{\partial \ln \left[ \frac{8K}{k} \frac{3(k-K)}{C} \right]}{\partial (1/T)} \right)_c
\]  

(12.37)

where \( (E_D)_{c=0} \) is the limiting value of the activation energy at \( C=0 \). Therefore,
The diffusion coefficient can be subsequently calculated for any temperature above the reference temperature and any water concentration. The value used for \((E_D)_{c=0}\) was taken as the activation energy for the low concentration data (29kJ/mole). Figure 12.19 shows the concentration of monomeric water with increasing total concentration at different temperatures as calculated from equation 12.25 using the respective values of \(k\) and \(K\) for each temperature, i.e. at higher temperatures more "free" water is available in agreement with equilibrium considerations. Figure 12.20 shows the theoretical curves for the changing diffusion coefficient with temperature and water concentration. It indicates that at low temperatures and concentrations approaching saturation the diffusion coefficient will decrease dramatically.

Although the model underestimates the diffusion coefficient by not taking into account polymeric water, the relative mobilities of polymeric species are not known and it is difficult to determine what contribution each n-mer will make to the overall diffusion coefficient. This partially explains why the diffusion coefficient for a saturated resin at 293K tends to a constant value (from half-time measurements). It is also possible that near saturation bulk plasticisation occurs and that water is now acting as an internal lubricant to penetrant mobility which would introduce a competing mechanism for diffusion, i.e. bulk plasticisation will tend to increase the diffusion coefficient. The experimental work at 293K showed that as the concentration increases the diffusion coefficient decreases. However, at 97%RH it was noted, from half time and especially initial slope methods of determining the diffusion coefficient, the diffusion coefficient increased which is indicative of a plasticisation phenomenon.
CONCENTRATION OF MONOMERIC WATER VS. TOTAL CONCENTRATION AT DIFFERENT TEMP.

H-BOND ENTHALPY = 21kJ/mole

293K
313K
333K
353K
373K
393K

Figure 12.19 Temperature dependence of monomer concentration with total concentration

TEMPERATURE/CONCENTRATION DEPENDENCE OF WATER IN RESIN

H-BOND ENTHALPY = 21kJ/mole

ACTIVATION ENERGY (C=O) = 29kJ/mole

0% SAT.
20% SAT.
40% SAT.
60% SAT.
80% SAT.
100% SAT.

Figure 12.20 Concentration dependence of activation energy for diffusion
If the model is fundamentally correct and only monomeric water is mobile then it could provide another explanation for the levelling off of the equilibrium sorption isotherm at unit activity in that the uptake experiments were stopped when there was no weight gain over a time equivalent for the weight gain to be attained. If the diffusion coefficient at high humidities is significantly reduced as the model predicts, then it is possible that the saturation concentration was never reached. Since calculation of the diffusion coefficient requires the equilibrium sorption value (equations 12.1-12.3), then the diffusion coefficient would have been overestimated. It is probable that the difference is a combination of all possibilities which is further complicated by an increasing deviation from Fickian kinetics with increasing concentration.

Figure 12.21 shows the theoretical line for a water concentration of 1.8wt%. It can be seen that the model represents the data reasonably well qualitatively over the temperature range. Quantitatively, the model produces a slightly inflated diffusion coefficient over the temperature range implying that more water is available for diffusion than is actually the case. This deviation is more noticeable at progressively lower temperatures and is probably a consequence of resin-water contacts further reducing the amount of mobile water. Such contacts which will be destroyed, or at least weakened, with increasing temperature as in the case of the associated water molecules. It is therefore not inconsistent that the model should better represent the data as the temperature is increased.

It can be concluded that the activation energy for the diffusion of water increases with concentration as more molecules become clustered. The activation energy decreases with temperature as a direct consequence of more monomeric water being available due to the thermal lability of the hydrogen bond.
The qualitative success of the polycondensation model at predicting the temperature and concentration dependence of water in the resin is probably a direct consequence of the similar dissociation energies of water interacting with the resin and with other water molecules. The model, although overestimating the amount of mobile water available for diffusion, represents the change in diffusion coefficient with temperature and concentration reasonably well. The error can subsequently be considered to be systematic allowing the temperature and concentration dependence of the diffusion coefficient to be predicted from a semi-empirical angle. More importantly, the data is consistent with the concept of mobile and immobile water in the water-resin system, the former having an activation energy for diffusion of 29kJ/mole (figure 12.21). This mobile component is a critical parameter in the mass diffusion problem of bubble dynamics.
12.3 ANALYSIS OF WATER DROPLET/HUMID AIR BUBBLE DATA

It has been shown that considering monomeric water as the sole diffusing species represents the isotherm and the temperature and concentration dependence of the diffusion coefficient reasonably well for the range of variables within a composite processing route. Although these interactions are useful it was also considered that the actual mobile concentration needed to be determined independently.

The analysis so far has been based on a notional Henry's law constant from the extrapolated inverse isotherm, which although simplifying the analysis overestimates the mobile concentration if the resin can not be treated as an inert continuum. As the concentration of mobile water is needed, to determine the concentration gradient for the growth and collapse of bubbles, this was investigated further. This analysis is based on the experimental work described in Section 11.2.

12.3.1 Water Droplet Data

Water droplet experiments allowed a direct measure of the mobile concentration by effectively measuring the flux of molecules.

If the flux, \( J \), is considered it can be shown that,

\[
J = -D(C) \frac{\partial C}{\partial p} \frac{\partial p}{\partial x}
\]

.... (12.39)

where \( p \) is the equilibrium isotherm pressure corresponding to the concentration \( C \) at a distance \( x \).

For isotherms of type III (figure 5.1)(Section 5.1) \( \partial C/\partial p \) will increase with concentration and tend to cancel any decrease in \( D(C) \) with concentration. This rather fortuitous cancellation of opposing terms is useful in terms of analysing the clustering of sorbed water in the resin. According to equation 12.18 the concentration
dependence of D(C) will be determined solely by the term $\partial C_1/\partial C$ if $D_1(C)$ is assumed constant and it is assumed that two forms of water exist, namely mobile and immobile.

If the mobile water is associated with monomeric water then one may identify $D_1(C)$ with $D_{c=0}$, which to a first approximation can be assumed to obey Henry's law, i.e. $C = K_H P$. The term in the brackets will therefore be constant and the flux will vary linearly with the driving force.

Figure 12.22 shows the normalised radius $^2$ vs. time for a number of water droplets in resin with different bulk concentrations at 293K. The droplets were of similar initial radii. The slope is related to the product of the diffusion coefficient $D$ and the concentration gradient, i.e. $2D(C_s - C_\infty)/(R_o^2 C_0)$ from the steady-state approximation (equation 3.9) (Section 3.1), where $D$ is the mobile diffusion coefficient, $C_s$ is the mobile water concentration at the droplet surface, $C_\infty$ is the mobile water concentration in the bulk and $C_0$ is the concentration in the droplet. This is equivalent to the driving force for the diffusion of gas bubbles where for this case the density term has been replaced by concentration. If the concentrations are specified in g/cm$^3$ then $C_0$, the concentration of water in the droplet, will be unity.

The gradients of the plots decrease as the water concentration in the bulk becomes finite. Using the diffusion coefficient for monomeric water at this temperature (figure 12.19) it is possible to calculate the concentration at the interface of the droplet using the zero bulk concentration data for a droplet of initial size, $R_o$, since $C_\infty=0$ and $C_0=1$. The concentration within in the droplet is assumed constant. At 293K, it was found that the concentration at the interface was 0.24wt% +/-0.05. The errors incurred are predominantly those in determining the diffusion coefficient at this temperature.

The change in droplet size is a direct measure of the mobile concentration. It is also substantially lower than that from the inverse isotherm which gave a mobile concentration at saturation of approximately 1wt% (figure 12.9)(Section 12.1.1), i.e. even less water is mobile at this temperature.

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Figure 12.22 shows that at higher concentrations the gradient does not increase which is in agreement with the cluster theory, i.e. water is immobilised. The exact bulk concentration at which the water droplets became stable is difficult to measure as it was at the limits of accuracy of the thermo-gravimetric method used. The concentration was below 0.4wt% and so it does not seem unreasonable that stable droplets occur once the mobile water in the bulk exceeds the mobile concentration at the interface (>0.24wt%). It seems that only small water concentrations are required to render a droplet stable to diffusion and any additional water is immobilised either by interacting with the resin molecules or by association. It is proposed therefore, that it is only in the case of a thoroughly dried resin that a water droplet will collapse at room temperature, i.e. the isotherm indicates that there is a water concentration in the resin greater than that required to stabilise water droplets over most of the relative humidity range (figure 12.5).

Water droplet experiments were also performed at elevated temperatures on thoroughly dried resin (figure 12.23), i.e. the water concentration in the bulk was effectively zero. A plot of the product of concentration gradient and the diffusion coefficient vs. 1/temperature is shown in figure 12.24 using the gradients from figures 12.23 and 12.22 and applying the steady-state approximation (equation 3.9) (Section 3.1). The data clearly shows a good linear relationship when plotted in this way. The slope of the plot can be directly interpreted as the sum of the heat of solution $\Delta H_s$ and the activation energy for diffusion $\Delta E_d$ over the universal gas constant $R_g$ (equations 5.4)(Section 5.2.1)(equation 8.3)(Section 8.1). The activation energy for diffusion of monomeric water has been identified already as 29kJ/mole so therefore the heat of solution is 23kJ/mole, which agrees admirably with the standard enthalpy change on breaking a hydrogen bond (14.4-27.6kJ/mole). It is therefore suggested that the concentration of mobile water at the droplet/resin interface increases with temperature as dictated by the energy required to break a hydrogen bond. This is in qualitative agreement with the solubility parameter theory in Section 4.2.2 which clearly indicated that the solubility of water in the resin would be predominantly influenced by the differences in their hydrogen bonding components.
Figure 12.22 Steady-state interactions for finite concentrations

Figure 12.23 Steady-state interaction for different temperatures in dry resin
Therefore, applying an Arrhenius relation for the concentration of mobile water $C_{mob}$, gives

$$C_{mob} = C_{mob0} \exp\left(\frac{-\Delta H_H}{R_g T}\right) \quad \text{.... (12.40)}$$

where $\Delta H_H$ is the enthalpy change to break a hydrogen bond and $C_{mob0}$ is the pre-exponential constant.

At 293K the concentration of mobile water is 0.24wt% and from equation 12.40 the concentration at 358K is therefore 1.33wt%, using 23kJ/mole as the standard enthalpy change on breaking a hydrogen bond. Droplets monitored at elevated temperatures for different bulk concentrations verified this temperature dependence in that, for a bulk water concentration of 1wt%, a water droplet was found to be stable at 313K for over a week, while at 358K a water droplet in the same solution and of similar size decreased in radius by 40% in a matter of hours (figure 12.25).
indicates that at 313K the mobile water concentration at the interface of the droplet equals the mobile concentration in the bulk causing the droplet to be stable (at 313K the concentration of mobile water is 0.44wt% from equation 12.40). At 358K all the available water in the bulk is mobile but the interfacial concentration has also increased accordingly exceeding the bulk concentration by 0.33wt%. This is the driving force for diffusion showing that the overall concentration at the interface increases with temperature and more importantly that when the mobile concentration at the interface exceeds the mobile concentration in the bulk a water droplet will diffuse into the resin.

The discrepancy between the mobile concentration determined from inverse isotherm (section 12.1.1) (figure 12.8) and from the droplet experiments is due to the fact that the inverse isotherm produces a composite parameter that combines the Henry's law and Langmuir components. Such a parameter does not have any simple meaning in dual mode terminology but if it is assumed that the concentration gradient is comprised of monomeric and completely unattached water molecules then the water concentration from the droplet experiments can be identified with the true Henry's law.
mode. If it is also assumed that the site saturation constant is determined by the hydroxyl group concentration of the resin (Section 12.1.1.1), then the total concentration at 293K will be a combination of the Henry's law mode and the Langmuir type mode from equation 12.4, i.e. \( C = C_H + C_L \). The value of \( b \) used is a literature value for water uptake on a cured epoxy resin [Jacobs and Jones (1990)]. Although this value is for a cured system it is proposed that the site affinity constant will not be appreciably different for an uncured resin if it is considered that similar groups are responsible for water molecule immobilisation. The interaction using these values is shown in figure 12.26 showing the Henry's law and Langmuir components. The dual mode theory represents the lower humidity range plateau although the downward curvature at progressively lower activities is not well represented. Figure 12.27 shows the dual mode theory and the inverse isotherm representation of the data, the latter using the regression values in figure 12.8 (Section 12.1.1). It shows that the inverse isotherm, which is predominantly a consequence of the clustering phenomenon (figure 12.13), begins to represent the data at the point where the dual mode theory stops. It is therefore concluded that the low humidity range is adequately represented by dual mode theory while with higher humidities a clustering approach is more appropriate.

Dual mode theory does not fully explain the water droplet experimental data since a water droplet should always collapse in a resin that has not been exposed to 100%RH. If one considers the steady-state equation it can be seen that the rate of growth and collapse of any bubble (or droplet) is dictated by the driving force and the diffusion coefficient. In the case of nitrogen bubbles the saturation concentration and the interfacial concentration of a gas bubble are synonymous, neglecting surface tension forces. In the case of water droplets, the driving force is also the concentration gradient, although in this case the saturation concentration of water in the resin and the interfacial concentration for diffusion are not equivalent as not all of the water in the resin is mobile. This also applies to the bulk concentration in that if the resin has been exposed to, say, 55%RH then the water concentration in the resin, determined by weight measurements, will be approximately 1wt%. Of this, about 0.1wt% will actually contribute to the concentration gradient, if Henry's law is obeyed (figure 12.26).
Figure 12.26 Application of dual mode theory to isotherm data

Figure 12.27 Application of dual mode and cluster theory to isotherm data
It can therefore be said that if a water droplet is placed in a perfectly dry resin it will collapse because the interfacial concentration exceeds the bulk concentration. Resin with a 1wt% bulk concentration, at 293K, will have a mobile concentration of about 0.1wt% from the true Henry's law isotherm and the mobile concentration at the interface of a water droplet will be 0.24wt%. There would also seem to be a driving force for collapse of the droplet which was not found to be the case (figure 12.22 and figure 12.25).

It is proposed that Henry's law is not obeyed and that adding water to the water-resin system does not significantly increase the mobile concentration. An analogous situation is that of micelle formation in soap solutions, where once the initial micelle concentration has been exceeded the concentration of molecularly dispersed soap molecules remains constant. Only a small amount of water is molecularly dispersed (true solution), i.e. a point is attained where adding water to the bulk only assists in the growth of clusters and does not significantly contribute to increasing the mobile concentration. Figure 12.14 (Section 12.1.1.1) provides evidence for this hypothesis showing that once a certain concentration has been exceeded any additional water predominantly increases the size of existing clusters and not the number of clusters. In terms of the mobile concentration of water, the resin is effectively saturated once clustering has initiated and will be virtually constant over most of the range of activity.

At higher temperatures the amount of mobile water increases at the interface of a droplet but it must exceed the bulk concentration of mobile water if its stability is to be perturbed, i.e. the mobile concentration of the bulk will also increase with temperature. Hence, depending on the bulk water concentration, a water droplet can be stable with increasing temperature as the mobile concentration in the bulk and at the interface increase proportionally.
12.3.2 Humid Air Bubble Data

Humid air bubbles were also examined at different temperatures. Bubbles were injected into a prepared resin which had a total bulk concentration of 1wt%. These bubbles were monitored with time. The air injected was at ambient humidity (55%RH). Figure 12.28 and 12.29 show the growth of these bubbles. The initial radius of these examples were similar and so the plots compare the difference in growth rate with increasing temperature. The growth rate for all bubbles tested was much lower than expected remembering that for a 1wt% water concentration in the bulk resin there is approximately one molecule of water for every five resin molecules (figure 12.14)(Section 12.1.1.1). The growth rates should be very rapid considering that resin saturated with nitrogen will have a 1:3000 ratio of nitrogen to resin molecules at room temperature and pressure.

Linear regressions allowed the determination of growth rates which were substituted into the steady-state approximation. The temperature dependence is shown in figure 12.30 where an Arrhenius interaction represents the product of the diffusion coefficient and concentration gradient vs. reciprocal temperature remarkably well. The gradient can be directly interpreted as the sum of the activation energy for diffusion and the temperature dependence of the driving force over the universal gas constant. The activation energy for diffusion has already been identified as 29kJ/mole so therefore the temperature dependence of the driving force is 42kJ/mole. This value is similar to the heat of vaporisation of water which is 44kJ/mole at 293K and 40kJ/mole at 373K. This result provoked the following model which is based on the water droplet and humid air bubble data and its interpretation.
Figure 12.28 Steady-state interaction for humid air bubble at 293K

Figure 12.29 Steady-state interaction for humid air bubble at 363K
A humid air bubble in the resin will have a water activity which will decrease as the temperature is increased in accordance with the Clausius-Clapeyron equation (equation 5.3) (Section 5.1.2). Initially a humid air bubble will have a finite water concentration which will exert a partial pressure $p_{H_2O}$. The bubble will have a water activity defined in a similar way to the relative humidity, i.e. $p_{H_2O}/p_{H_2O}^*$. As the temperature increases the vapour pressure $p_{H_2O}^*$ increases exponentially and the activity inside the bubble will decrease in a similar fashion (figure 4.2) (Section 4.2.1). This would in turn reduce the interfacial concentration providing a driving force for growth.

If it is assumed that the equilibrium amount of mobile water varies linearly with relative humidity exposure then,

\[
M_{mob} = \Omega(RH) = \Omega \frac{p_{H_2O}}{p_{H_2O}^*} \quad \text{.... (12.41)}
\]

where $M_{mob}$ is the weight fraction of mobile water in the resin and $\Omega$ is a constant of proportionality.
The mobile water concentration in the resin is a function of the mobile water solubility and therefore,

\[ C_{\text{mob}} = \frac{M_{\text{mob}}}{100} \rho_R \]  

\((12.42)\)

where \(\rho_R\) is the density of the resin.

The mobile concentration in the bulk resin, \(C_{\infty}\), is only dependent on the initial relative humidity under which the resin was equilibrated. It must be remembered that this is not equivalent to the total concentration of water in the resin. Therefore,

\[ C_{\infty} = \frac{\Omega \rho_R (R\text{H})}{100} \]  

\((12.43)\)

The mobile water concentration at the bubble surface, \(C_s\), is a function of both temperature and partial pressure of water within the bubble,

\[ C_s = \Omega \rho_R \left( \frac{p_{H_2O}}{p_{H_2O}} \right) \]  

\((12.44)\)

Using the Clausius-Clapeyron equation for the temperature dependence of the vapour pressure (equation 5.3)(Section 5.1.2),

\[ p_{H_2O} = 7.74 \times 10^{10} \exp \left( \frac{-\Delta H_v}{R_s T} \right) \]  

\((12.45)\)

where the pre-exponential constant was determined from the vapour pressure of water at the boiling point under atmospheric conditions. A representative value for the heat of vaporisation of 42kJ/mole was taken for the temperature range of a typical
composite processing route. This relationship can be substituted directly into the equation 12.44 to give,

\[
C_s = 1.29 \times 10^{-11} \Omega \rho_R^k \exp\left(\frac{42000}{R_g T}\right) p
\] ...

(12.46)

This clearly shows that the concentration at the interface, \(C_s\), will decrease exponentially with temperature and that the temperature dependence is directly related to the heat of vaporisation of water. This indicates that there is a linear relationship between the mobile concentration at the surface of the bubble and the activity within the bubble as inferred by figure 12.30.

The steady-state approximation states that the growth of a bubble is dependent on the diffusion coefficient, the driving force (which is the difference between the mobile concentration in the bulk and at the surface of the bubble) and the density of the bubble. The density can be defined as,

\[
\rho_g = (1-x)M_{H_2O} \frac{P}{R_g T} + x M_{air} \frac{P}{R_g T}
\] ...

(12.47)

where \(P\) is the hydrostatic pressure in the resin, \(x\) is the mole fraction of air and \(M_{H_2O}\) and \(M_{air}\) are the molecular masses of water and air respectively. The mole fraction of air can be determined directly from the initial activity of the bubble if it is assumed that the total pressure within the bubble obeys Dalton's law, i.e. \(p=(1-x)P\).

It can therefore be said that at constant temperature and pressure the growth of humid air bubbles is dependent primarily on the diffusion coefficient and the concentration gradient since the density will only change fractionally due to diffusion of water molecules, i.e. a pure water vapour bubble will have a density of 0.75 kg/m\(^3\) at 293K and atmospheric pressure, while the density of a pure air bubble is 1.2 kg/m\(^3\) under the same conditions.
Although the concentration of mobile water is temperature dependent, with more mobile water present at higher temperatures (equation 12.40)(figure 12.23)(Section 12.3.1), the mobile concentration in the bulk and at the interface will increase proportionally so the driving force will not increase due to this effect. The growth of humid air bubbles at different temperatures will be predominantly dependent on the temperature dependence of the diffusion coefficient and the temperature dependence of the activity within the bubble which are functions of the activation energy for the diffusion of mobile water and the heat of vaporisation respectively. This is in agreement with experiment (figure 12.30).

It can also be implied from equation 12.46 that decreasing the partial pressure of water within the bubble (by reducing the system pressure) will increase the driving force for diffusion of water molecules by decreasing the concentration at the interface and increasing the system pressure will not only increase $C_s$ but also increase the density of the bubble which will lower the driving force for diffusion.

All parameters in the steady state approximation (equation 3.9)(Section 3.1) are now identified as well as their respective dependence on the pressure and temperature. As the temperature is increased the diffusion coefficient will increase exponentially and the concentration at the interface will decrease exponentially both of which favour the growth of a humid air bubble due to the diffusion of water. At constant temperature and pressure, the concentration at the interface and the density within the bubble are virtually constant.

The only parameter that has to be inferred from experiment is the relationship between the mobile concentration and the water vapour activity. At 293K, if Henry's law is obeyed, then the mobile concentration will decrease linearly from 0.24wt% at unit activity (determined from water droplet experiments) to zero at zero activity, i.e. the proportionality constant $\Omega$ can be directly related to Henry's law constant. This relationship for the concentration gradient for the humid air bubbles provided a significantly larger growth rate than that measured, e.g. the growth of the bubble in figures 12.28 and 12.29 would occur in a matter of seconds. This indicates
three possibilities;

i) The concentration of mobile water in the resin is significantly lower than determined from the water droplet experiments.

ii) The mobile concentration is virtually constant over the entire activity range

iii) The diffusion of water molecules is not the rate determining phenomenon.

(i) seems to be unlikely as a water droplet is at unit activity and should thus provide the mobile concentration associated with unit activity unless the zeroth law of thermodynamics is contravened. The second, (ii), is feasible if it is assumed that the water concentration increases rapidly with increasing water activity and levels off over the rest of the humidity range. This is the analogy with micelle formation which was mentioned in the previous section. In this case the mobile concentration must increase with activity with a virtually linear relationship (after the initial rapid increase from zero activity) although the rate of increase would be significantly less than that dictated by Henry's law. If it were not linear then the Arrhenius relationship in figure 12.30 would not be directly related to the heat of vaporisation from equation 12.46.

The third (iii) possibility is that the rate of growth is influenced by interfacial kinetics as well as diffusion. At first sight it may seem that interface control would be unlikely since diffusion requires many successful molecular jumps while an interface reaction requires only one. Then again, if the interface of a humid air bubble is mainly clustered or attached water then a phase change is required for such molecules to enter the bubble before growth can occur, i.e. if there is insufficient energy to vaporise a molecule or if the molecule is not accommodated in the bubble environment it will recondense increasing the concentration at the interface thus reducing the concentration gradient for diffusion. In this interfacial situation the limiting cases are total diffusion control, where the growth of humid air bubbles is determined totally by the large concentration gradient provided by Henry's law, and zero growth where zero mobility at the interface increases the interfacial concentration (figure 12.31). As such an interfacial reaction will be related to the reaction enthalpy then it would be expected that the temperature dependence of the growth rate would also be related to the
activation energy for diffusion and the heat of vaporisation as in figure 12.30, i.e. molecules diffuse to the interface and subsequently vaporise.

It is therefore concluded that the surprisingly low growth rates of humid air bubbles in a resin with an appreciable water concentration is due to most of the water being immobile due to resin-water interactions and clustering. Growth is also limited by a low concentration gradient for diffusion, which may possibly be a consequence of the mobile concentration being virtually constant over the activity range or low reaction kinetics at the interface which increase the concentration of water at the surface of the bubble. Both cases render $\Omega$ an empirical constant in equation 12.46 although this is not a significant drawback to the model since if one knows the growth rate of a humid air bubble at one temperature the growth rate can be predicted at other temperatures, i.e. growth is a function of the diffusion coefficient of the mobile species and the heat of vaporisation of that species. Further work is required to identify the mechanism.
In terms of eliminating humid air bubbles the lower than predicted driving force for growth is fortuitous and it has been found that in the case of small bubbles, where surface tension forces play a significant role, bubbles collapsed in the 1 wt% solution corroborating the small concentration gradient for the diffusion of water into the bubbles, i.e. the diffusion of air out of the bubble was presumably greater than the water diffusing into the bubble resulting in collapse. This tends to imply that although growth will occur due to the diffusion of water, the rate of growth will be slow at the temperatures experienced in a typical cure cycle, although it will increase if the pressure is reduced in accordance with equation 12.46. It is therefore postulated that any humid air bubble can be eliminated in a similar way to that required to encourage the collapse of nitrogen bubbles, i.e. by encouraging the air to diffuse out of the bubble.

12.4 COMPARISON OF WATER AND GAS DIFFUSION DATA

At 313K the diffusion coefficient for nitrogen in resin is \(4.5 \times 10^{-11} \text{m}^2/\text{s}\) while the corresponding diffusion coefficient for unclustered water is \(6 \times 10^{-10} \text{m}^2/\text{s}\). The apparent activation energy at this temperature is also higher for nitrogen (figure 12.32). As both molecules have similar molecular radii \((\text{N}_2=0.188\text{nm}, \text{H}_2\text{O}=0.193\text{nm})\) it has been concluded that even small quantities of water plasticise the resin thus enhancing penetrant mobility. Such plasticisation is probably a result of the scission of bonds between the resin molecules by water molecules.

This rather qualitative explanation is evidenced by examining the activation energy for diffusion of nitrogen at higher temperatures. The diffusion coefficient begins to level as the temperature is increased, i.e. the activation energy for diffusion decreases at the point where free volume theory breaks down and the thermal barrier theory takes over. If the glass transition temperature is lowered by some kind of plasticisation phenomenon then this transition will occur at lower temperatures.

If the activation energy for unclustered water is extrapolated to higher temperatures it can be seen that the nitrogen data and the water data converge. Such
similar activation energies for water and nitrogen is explained in terms of the energy required to loosen the polymer structure. At high temperatures the structure is loosened by thermal agitation of the resin molecules and the activation energy for any penetrating molecule will be similar (unless the molecule is large with respect to molecules of the medium) and for low penetrant concentrations will be similar to the activation energy for viscous flow. At lower temperatures the presence of water plasticises the resin and the activation energy is lower compared to the unplasticised resin.

If free volume theory is still applicable to the water resin system at 313K then the depression of $T_g$ can be calculated assuming that a water molecule has the same efficiency in utilising the free volume of the resin as the similar sized nitrogen molecule. Using the adapted Doolittle theory for diffusion (Section 8.2) with $B_d$ as unity and the same pre-exponential constant as for nitrogen, the decrease in the resin's $T_g$ by water is 30K. This seems to be a perfectly reasonable value as reductions in $T_g$ of 50K are common by water in cured resins [Peyser and Bascom (1981)]. This type
of reasoning is not strictly appropriate as the free volume is not necessarily increased by the presence of water molecules. In polyamides abnormally large decreases in the glass transition temperature occur on small additions of water [Starkweather (1969)]. These polymers are held together by interchain hydrogen bonds and the presence of water is believed to disrupt the bonding network, i.e. the hydrogen bonds act as crosslinks in increasing the $T_g$. It is therefore considered that the rather vaguely defined plasticisation phenomenon may be considered as a disruption of intermolecular bonding in the resin predominantly comprised of thermally labile hydrogen bonds. It is known that ordered domains are present in the uncured resin which are destroyed by an increase in temperature or by solvents [Stevens et al. (1982)], so it is not inconceivable that the presence of water molecules either break these intermolecular bonds thus plasticising the resin, or form bridges between the resin molecules. In the latter case one would expect such bridges to be weaker than direct contacts between the bulkier resin molecules and thus dissociate at lower temperatures due to differences in the thermal mobility of a water molecule and the resin molecule. The glass transition temperature will subsequently be lower for a resin where intermolecular bonds are weaker or broken. If this is the case then it seems reasonable to infer that once these bonds are broken, plasticisation of the resin by this mechanism will be stopped with additional water forming clusters.

It is therefore postulated that there may be effectively only two conditions for the resin in a normal environment; a dry resin where bonds are destroyed by thermal agitation and "wet" where such bonds have already been destroyed or weakened by the penetrating water molecules. Naturally, at significantly higher concentrations water will act as a low molecular weight plasticiser and it is such cases that plasticisation can be represented by some kind of rule of mixtures equation, i.e. plasticisation could be based on the additivity of some property such as the respective fractional free volumes of penetrant and polymer to determine the increasing free volume of the system.

The coinciding diffusion coefficients of nitrogen and water in resin at high temperatures allows the activation energy for unclustered water to be predicted. At
higher temperatures intermolecular bonds will be broken by thermal agitation and so in terms of penetrant mobility the presence of water, which can plasticise the resin at lower temperatures, will have an increasingly negligible affect as the temperature is raised. The activation energy for low concentration water data has been extrapolated to higher temperatures and represents the nitrogen data quite well. This implies that the activation energy for the diffusion of air will be reduced if small quantities of water are present that disrupt intermolecular bonding in the resin. This is extremely useful since it has already been shown that there is concurrency between the temperature dependence of the viscosity and the gas diffusion coefficient. The activation energy for unclustered water can be determined subsequently from the more readily available viscosity/temperature data.

12.5 SUMMARY - WATER INVESTIGATION

It has been shown that water can easily enter the resin under normal conditions and will have a finite water concentration dictated by the relative humidity of the environment. The water-resin system exhibited strong positive deviations from ideal solution behaviour and a thermodynamic analysis indicated that this deviation was predominantly due to the clustering of water in the resin potentially around hydrogen bonding centres. Experiments on diffusing water droplets identified that only a fraction of the total water concentration in the resin was mobile which was evidenced by a diffusion coefficient that decreased with increasing water concentration.

The sorption isotherm and the concentration dependence of the diffusion coefficient were investigated and could be represented adequately using cluster analysis and dual mode theory. The temperature and concentration dependence of the diffusion coefficient were qualitatively represented by treating water sorption and cluster formation in a similar way to condensation polymerisation. Deviations from the theory were considered to be due to treating the resin as an inert continuum, which overestimated the monomeric water component.
In agreement with solubility parameter theory, the concentration of molecularly mobile molecules was mainly a consequence of differences in the hydrogen bond propensity of water and the resin. The temperature dependence of the mobile concentration was found to be related to the standard enthalpy change on breaking a hydrogen bond and the success of the polycondensation theory was attributed to similar dissociation energies between associated water molecules and water molecules attached to the hydroxyl group on the resin backbone.

Humid air bubbles were found to grow in resin with a finite water concentration. The growth rate was related to the heat of vaporisation of water and the diffusion coefficient of the mobile component, although it was significantly lower than predicted. This was considered to be a consequence of a slow interfacial reaction at the bubble surface or due to a mobile concentration that was virtually invariant with activity over most of the humidity range. Small humid air bubbles collapsed in a water-resin system, corroborating this low driving force, as air diffused out of the bubbles due to surface tension forces. The diffusion coefficients of water and nitrogen were found to converge with increasing temperature which was considered to be due to water disturbing thermally labile bonds between the resin molecules.

It is considered that humid air bubbles can be eliminated utilising the same procedures as for gas bubbles with the expectation that the gas and mobile water diffusion coefficients will not only be similar at high temperatures but also at lower temperatures in a resin with a finite water concentration. As the growth of bubbles due to water diffusion is related to the heat of vaporisation then reducing the system pressure (by using a vacuum bag) would potentially affect a water-resin system more severely than a permanent gas-resin system, due to the effects of pressure on condensible vapours.
CHAPTER THIRTEEN

CONCLUDING REMARKS AND FURTHER WORK

13.1 CONCLUDING REMARKS

13.2 FURTHER WORK

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13.1 CONCLUDING REMARKS

It is apparent that process modelling of composite materials requires a multidisciplinary approach to characterise the operation from the formulation of the materials through to the manufacture of the component. Each unit model has to work interactively with the others to characterise the whole process operation. The rationale behind this investigation was that such models should preferably be based on fundamental scientific principles and easily measured materials data and translate to different materials and geometries with minimal experimentation. The utility of any model is reduced significantly with the need for empirical relationships.

The concepts behind the formation, growth and collapse of bubbles have been investigated using nucleation and mass diffusion theory. A thorough analysis has been performed on the applicability of these theories for the materials and conditions found in the processing of polymer matrix composite materials. The input parameters required for the models have been measured using quick and simple methods that could easily be incorporated into a production schedule. The dependence of these parameters on the processing variables has been investigated and in many cases relationships were found that could be extended to other systems.

The problem of voids in the final composite part has been addressed and their origin has been discussed. A theoretical and qualitative experimental investigation of the ill-defined nucleation phenomenon has shown that macroscopic mechanical entrapment of air and microscopic nuclei are the main cause of voids in the final composite. Entrapped air can be eliminated by utilising mass diffusion while nuclei, entrapped in crevices or cavities of the fibres or foreign materials, can only be eliminated by such methods if the contact angle is favourable. The problem of eliminating porosity from the final composite is therefore limited to suppressing the growth of nuclei and causing existing bubbles to collapse within the processing window dictated by the other unit processes.

It has been shown that the growth and collapse of bubbles can be
predicted successfully using mass diffusion theory. The input parameters for the
diffusion equations are the diffusion coefficient of the mobile species in the resin and
the concentration gradient. These parameters were found to be influenced by the
materials and the processing variables. Experimental methods have been outlined to
determine these parameters and their interactions with temperature and pressure.

The material parameters of the resin were measured using conventional

techniques. The temperature dependence of the viscosity of the resin could be predicted
from the semi-empirical free volume theory and the WLF equation over a large
temperature range, i.e. the temperature dependence of the resin viscosity can be
predicted from the glass transition temperature and the viscosity at any one
temperature. The surface tension could be predicted from the cohesive energy density
of the resin which could be determined from molar attraction constants, which are
known quantities, i.e. the surface tension can be calculated from the structure of the
resin molecule and the density.

A simple method was designed to measure dissolved gas concentrations
in the resin. It was found that the concentration of nitrogen in the resin with pressure
obeyed Henry's law and was not found to be significantly temperature dependent over
the temperature range investigated. The pressure dependence could also be predicted
successfully using a solubility parameter approach in conjunction with regular solution
theory. This allows determination of the driving force for gas diffusion solely from a
knowledge of the resin chemistry and the density.

A novel method was used to measure the gas diffusion coefficient using
bubble dynamics. The temperature dependence of the diffusion coefficient could be
represented by free volume theory and a correlation was found between the
temperature dependence of the gas diffusion coefficient and the viscosity. The
temperature dependence of the gas diffusion coefficient can thus be determined from
the diffusion coefficient at any one temperature and the relationship between the
viscosity and temperature, i.e. there is a correlation between mass transport and
momentum transfer.
The growth and collapse of gas bubbles could be predicted from mass diffusion theory at different temperatures, equilibrated pressures and processing pressures. Deviations from the model predictions were exhibited with growing bubbles which is believed to be a consequence of a decreasing gas concentration in regions of high bubble density. It was found that surface tension forces were only significant in the latter stages of collapse of a diffusing bubble and for bubbles in saturated solutions.

Resin exposed to humid environments was found to pick up water readily. A thermo-gravimetric method showed that resin will have a finite water concentration over most of the humidity range and the resulting sorption isotherm exhibited strong deviations from ideal behaviour. A thermodynamic analysis indicated that water was present in monomeric, bound and associated forms.

The diffusion coefficient of water in resin was measured using the thermo-gravimetric method. It was found to decrease with increasing concentration and increase with increasing temperature. The concentration dependence of the diffusion coefficient and the sorption isotherm could be represented by considering that sorbed water was either mobile or immobile. It is believed that water is attached to the resin molecule on the pendant OH group which acts as a nucleation centre for the association or clustering of water molecules.

The temperature and concentration dependence of the diffusion coefficient of water in the resin can be predicted from polycondensation theory although the actual concentration of monomeric (mobile) water is overestimated with the need to assume that the resin is an inert continuum.

Water droplet experiments qualitatively agreed with the thermodynamic analyses and the polycondensation theory showing that the solubility of water in the resin was determined predominantly by the need to break hydrogen bonds. It was concluded that water-resin interactions, although reducing the concentration of mobile water, must have similar dissociation energies to associating water molecules.
Humid air bubbles were found to grow in resin that had been exposed to a humid environment although the concentration gradient was significantly lower than that predicted from the inverse isotherm and the true Henry's law determined from water droplet experiments. The temperature dependence of bubble growth was found to be related to the heat of vaporisation of water and its activation energy for diffusion. It was concluded that the mobile water concentration in the bulk resin and at the interface of a humid air bubble increased proportionally with temperature. A semi-empirical relationship was found that identified the parameters that effected the growth of humid air bubbles. Small humid air bubbles were also found to collapse in resin with a finite water concentration, corroborating the low concentration gradient for growth due to water molecule diffusion. This low concentration gradient is a consequence either of a slow interfacial reaction or a mobile concentration that increases only slightly with increasing activity.

A correlation was found at high temperatures between the diffusion coefficient of nitrogen and monomeric water. It is considered that small amounts of water plasticise the resin by rupturing inter-resin bonds or by forming water bridges between the resin molecules. It is proposed that the diffusion coefficient of permanent gases and mobile water in resin will be similar for a system that has been exposed to normal environmental conditions, enabling the temperature dependence of the diffusion coefficient of mobile water to be determined from the gas diffusion coefficient and the viscosity-temperature data.

In conclusion it has been shown that bubbles can be eliminated by manipulating the processing variables. Positive pressure can encourage the collapse of bubbles and a reduction in pressure can cause bubble growth. Vacuum can prevent infiltration of the reinforcement by the resin, cause existing bubbles to grow in accordance with the ideal gas laws, reverse a concentration gradient encouraging bubble growth due to diffusion, and activate sub-microscopic nuclei. It is therefore concluded that extreme care must be taken if a vacuum bag system is to be used. If the pressure is reduced purely to extract entrapped air bubbles from the laminate then it is proposed
that forcing bubbles into solution is a significantly better method in that it is unlikely that all expanded air bubbles will be transported out of the laminate.

Prior application of positive hydrostatic pressures to the precursors will eliminate nuclei and the use of positive hydrostatic pressures during the cure cycle can also accelerate the diffusion of gases and vapours into solution. Even if the application of positive pressure is not a realistic proposition for some process methods, manipulation of the temperature profile can encourage small bubbles to go into solution before the resin gels. If it is favourable for existing bubbles to collapse, the growth of microscopic nuclei will also be suppressed.

13.2 FURTHER WORK

The proposed direction for further work is direct application of this study to actual composite systems. This would primarily require a fusion with the other unit models which describe the heat transfer, cure and consolidation processes. As these are still in their infancy, requiring considerable parameter input, it is considered that the models that describe bubble kinetics are applied initially using measured instead of predicted temperature-pressure-viscosity/time profiles.

Direct extension of mass diffusion theory is required to take into account bubbles that have non-spherical geometries. Cylindrical geometries would be the natural progression since bubbles have been observed along the length of fibres. If it is assumed that elongated bubbles are surrounded by fibres then the interfacial area for diffusion would be the hemispherical ends of the cylindrical bubble. This can easily be represented mathematically and simple experiments could measure the change in cylinder length with time.

Multi-component systems need to be investigated since resin is mixed with a curing agent and often accelerators and modifiers. Rule-of-mixture type equations should be appropriate to predict such parameters as the initial viscosity of the system.
from the viscosities of the individual components or from their respective glass transition temperatures, i.e. the fractional free volume of a mixture can be based on the additivity of each component. This would enable direct relationships to be found for the gas diffusion coefficients in the matrix precursor from the diffusion coefficients in each component. Similarly, it is of interest to determine the solubility parameter of such mixtures, which would allow the surface tension and gas solubility to be predicted without the need to characterise each resin formulation.

Compatible volatile components of the system need to be studied as these may play a significant role in bubble dynamics. Diluents and volatile components emanating from the resin or curing agent will generally have similar solubility parameters to the resin system and will thus behave more ideally than water. Mass diffusion theory should still apply although the concentration of mobile volatiles may be temperature-dependent with different species becoming dominant throughout the cure cycle. The physical significance of $\Omega$ in equation 12.41 could be ascertained by monitoring the growth of air bubbles due to organic vapours, as each will have different heats of vaporisation.
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