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# Modelling the behaviour of gas bubbles in an epoxy resin: evaluating the input parameters for a diffusion model using a solubility parameter approach

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Models based on mass diffusion theory successfully represent the growth and collapse of gas bubbles in an epoxy resin. Solution of the steady-state diffusion equations requires measurement of the diffusion coefficient and solubility of the mobile species within the resin pre-cursor. These parameters are affected by changes in temperature and/or pressure and are generally not measured as part of a processing schedule. Models have been evaluated that predict the prerequisite driving force in terms of a concentration gradient and the interaction with the processing variables from the chemistry of the resin molecule. A solubility parameter approach has been used to estimate the solubility of gas in the resin in conjunction with regular solution theory. The surface tension forces, which also play an active role in bubble stability and dynamics, have been estimated from molar attraction constants.

## 1. Introduction

The objective behind the processing of thermosetting matrix composite materials is to produce void-free laminates of the specified dimensions with the optimum degree of cure of the resin. Porosity can occur due to inappropriate changes in the fabrication procedure and will have a detrimental effect on the mechanical properties of the final part [1]. In order to process high-performance structural laminates consistently, it is necessary to identify the material and processing inter-relationships which are critical to the production of void-free laminates and to formulate models that can be used to optimize the processing variables.

Bubbles present within the resin will grow or collapse according to the temperature and hydrostatic pressure in the resin during the cure cycle. Bubble behaviour is influenced by such changes in accordance with the ideal gas law equations and due to the diffusion of mobile species across the bubble/resin interface, i.e. gaseous species in the bubble diffuse into the resin or dissolved gases in the resin diffuse into the bubble. An increase in temperature or decrease in pressure will cause the gas within the bubble to expand resulting in bubble growth. Changes in pressure and temperature can also have a pronounced effect on the solubility of mobile species in the resin which may influence not only the magnitude of the driving force for diffusion but also the direction of the concentration gradient. As an increase in temperature also causes an increase in the diffusion coefficient, the rate of mass transfer of molecularly mobile species will also increase, resulting in more rapid bubble growth or collapse depending on the direction of the diffusion gradient relative to the host bubble. [2].

Models based on mass diffusion theory have been investigated [2,3] and it is considered that entrapped bubbles can be collapsed or suppressed from growing by manipulating the process variables during the curing operation, i.e. it is possible to influence bubble behaviour by changing the processing temperature and pressure. To implement these models successfully, a number of input parameters and their respective interactions with the process variables need to be evaluated before it is possible to predict the growth or collapse rate of gas bubbles in the resin pre-cursor. The material parameters include the diffusion coefficient and the solubility of the mobile species in the liquid resin, both of which are functions of temperature and/or pressure. As a model is only as successful as the accuracy and *availability* of the input data, it is beneficial to have relationships that can predict these input parameters and/or their interaction with the changing process variables from fundamental materials data or from more accessible physical quantities. The rationale behind the investigation is that the relationships and the input parameters required for a void model can be translated to other systems with minimal materials characterization and to different composite processing options. By minimizing empiricism it is also easier to confront the problem that there is no universal cure cycle but that it is necessary to deter-

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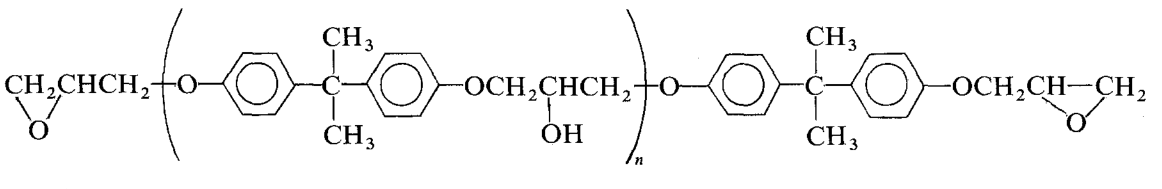
mine an optimum schedule within a processing window dictated by the heat transfer, cure and consolidation processes.

## 2. Materials characterization

The resin investigated in this study was a commercial unmodified bisphenol-A/epichlorohydrin resin (Shell 828) that had an epoxide group content of 5.128 mol/kg$^{-1}$ [4]. Using the relation $M_n = 2000/$ epoxide content [5, 6], this corresponds to an average molecular weight of 390 g mol$^{-1}$. The diepoxide prepolymer has the following chemical structure



and therefore using the relation $M_n = 340 + 284n$, the average value of $n$ is 0.176.

The density of the resin was measured and was found to agree with the manufacturers specifications (1160 kg m$^{-3}$ at 298 K) and was not found to change significantly over the temperature range of interest (293–373 K). The surface tension of the resin was measured using a capillary rise technique [7] to give a value of 0.035 N m$^{-1}$. It was observed to decrease slightly with increasing temperature. The gas used in the investigation was pure dry nitrogen.

The solubility of nitrogen gas in the resin, determined using a vacuum degassing technique [8], was found to obey Henry's law and was independent of temperature over the temperature range 313–373 K (Fig. 1). The constant of proportionality in the relationship between the pressure and the gas concentration was $2.46 \times 10^{-9}$ Pa$^{-1}$ ($\pm$ 20%) and the saturated gas concentration in the resin at atmospheric pressure and 313 K was 0.0207 kg m$^{-3}$.

The temperature and pressure dependence of the gas solubility in the resin 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 changes in temperature over the range of practical interest 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 resin to the saturation concentration), can now be determined throughout the processing route as the process variables are changed. This is of major importance because 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 undersaturated with gas and the bubble will tend to collapse, while if $f > 1$ the solution is oversaturated and the bubble will grow. If resin is equilibrated at atmospheric pressure it will have a gas concentration associated with this pressure. If a vacuum is drawn subsequently during the processing, the gas concentration at the bubble surface will correspond to the local pressure. The difference in concentration in the bulk resin and at the surface of the bubble will lead to a concentration gradient into the bubble resulting in bubble growth. Collapse will occur if the resin has been degassed so that the gas concentration in the bulk is lower than the concentration associated with the local hydrostatic pressure. It becomes clear that the concentration gradient can be influenced by the conditions under which the resin was equilibrated and by changing the pressure on the resin, e.g. vacuum reduces the saturated gas concentration at the bubble surface which will reduce the driving force for collapse or even initiate growth, depending on the gas concentration in the bulk.

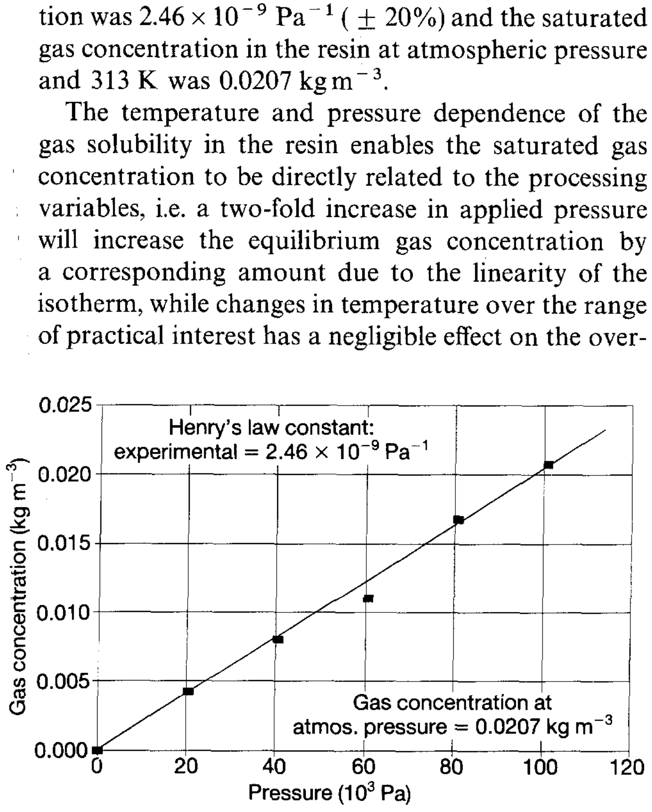


*Figure 1* Pressure dependence of gas concentration in a nitrogen/resin system at 313 K.

## 3. Solubility parameter theory

As a rough guide to solubility it is useful to consider the empirical approach suggested by Hildebrand [9] 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 vaporization and $V$ is the molar volume of the component. The enthalpy of mixing is small for mixtures that have similar solubility parameters which indicates compatibility. Values for the solubility parameter for simple liquids can be readily calculated from the enthalpy of vaporization. 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 [10] tabulated a series of group molar attraction constants from vapour pressure and heat of vaporization data which give a good estimate of $\delta$ for most polymers. The solubility parameter can be estimated from the sum of the various molar attraction constants,

TABLE I Group contributions to $F$

| Group | $F((\mathrm{J\ cm^3})^{1/2})$ |
|---|---|
| $-CH_3$ | 438 |
| $-CH_2$ | 272 |
| $-CH$ | 57 |
| $-C$ | − 190 |
| *p*-phenylene | 1346 |
| –O– | 143 |
| –OH | – |
| –CO– | 563 |

$F$ (Table I) for the groups which make up the polymer

$$\delta = \frac{(\Sigma F)}{V} = \frac{(\Sigma F)\rho_R}{M_n} \qquad (1)$$

where $V$ is the molar volume, $M_n$ is the molar mass and $\rho_R$ is the density of the polymer.

Using Small's constants [10] and assuming that a hydroxyl group is the sum of the ether oxygen and a "variable" hydrogen ($F_H = 204.5(\mathrm{J\ cm^3})^{1/2}$) [11], the constants for the bisphenol-A resin ($n = 0.176$) used in this study are given in Table II. Hence, $\delta = (5963.8)(1.16)/390 = 17.74\ (\mathrm{J\ cm^{-3}})^{1/2}$.

Small's estimates of $\delta$ have been shown to be within 10% of experimentally determined values [12]. Table III shows some solubility parameters for some typical solvents calculated from their respective enthalpies of vaporization [13]. In terms of the differences in solubility parameter it is clear that water and bisphenol-A resin are not compatible and will not be very soluble while the first three in the table have much closer solubility parameters. It is for this reason that trichloromethane (chloroform) is used as a diluent for the uncured resin in the processing route and that both tetrachloromethane and propanone are good solvents for the resin system. Water and methanol are virtually immiscible under ambient conditions.

TABLE II Constants for bisphenol-A resin

| Group | $F(\mathrm{J\ cm^3})^{1/2}$ | |
|---|---|---|
| 2(*p*-phenylene) | 2(1346) | |
| $2(-CH_3)$ | 2(438) | |
| $2(-CH_2)$ | 2(272) | |
| 2(ether oxygen) | 2(143) | |
| –OH | 347.5 | |
| –CH | 57 | |
| –C | − 190 | |
| | $\Sigma 4612.5 \times n =$ | 811.8 |
| 2(*p*-phenylene) | | 2(1346) |
| $2(-CH_3)$ | | 2(438) |
| $4(-CH_2)$ | | 4(272) |
| 4(ether oxygen) | | 4(143) |
| 2(–CH) | | 2(57) |
| –C | | − 190 |
| | | $\Sigma 5963.8$ |

TABLE III Solubility parameters for solvents

| Solvent | $\delta((\mathrm{J\ cm^{-3}})^{1/2})$ |
|---|---|
| Propanone | 20.3 |
| Tetrachloromethane | 17.6 |
| Trichloromethane | 19.0 |
| Methanol | 29.7 |
| Water | 47.9 |

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, because any specific interaction between the solute and solvent will increase the total solubility. 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 (Table IV) [14]. In this case the solubility parameter is divided into contributions from dispersion forces, polar forces and hydrogen bonding forces. The table shows some attraction constants of interest for a composite system. The molar attraction constants of Small are considered to be purely 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 ($\Sigma V\delta^2$) [12]. It must be emphasized that the hydrogen bonding contribution is slightly misleading in that it contains all association bonds including π-bonds and any other forces that are not included in the polar or dispersion contributions.

The contributions can be summed accordingly using

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_H^2 \qquad (2)$$

which, for the uncured resin system where $n \approx 0.176$ (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 $\delta = 20.45$ $(\mathrm{J\ cm^{-3}})^{1/2}$. The polar force is the smallest contributor to the solubility parameter which is in agreement with other observations in polymeric systems [10, 14]. As solubility parameter theory is most successful and considerably less empirical with non-polar systems, it is necessary to determine whether the approach is applicable for the commerical resin system and thus evaluate some of the parameters required for the diffusion model [2, 8].

### 3.1. Surface tension

The surface tension plays a significant role in the nucleation, stabilization and growth and collapse kinetics of bubbles. The interfacial surface tension is related to the cohesive energy density of the resin as

TABLE IV Hansen parameters for polar and hydrogen bond components

| Group | Polar parameter, $V\delta_p$ | H-bond parameter, $V\delta_H^2$ |
|---|---|---|
| –O– | 409 | 4812 |
| –OH | 511 | 19456 |

forces between molecules will lead to a drawing together of liquid molecules [11]. It is generally considered that hydrogen bonding and polar forces do not greatly contribute 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 in that the surface tension of the resin was found not to be a temperature-dependent parameter. If hydrogen bonds were playing an active role, their thermal instability would cause the surface tension to decrease rapidly with increasing temperature, although the hydrogen bonding component for this system is half of the dispersion force contribution.

Many workers have attempted to correlate the surface tension forces from molecular constitution of which most are semi-empirical. Wu [11] correlated the critical suface tension with Small's molar attraction constants using coefficients based on data from 36 polymer systems. His preferred equation is dimensionally unbalanced, but he also offers a second balanced equation which gives about the same results,

$$\gamma_c = 5.5 \times 10^{-5} \frac{(\Sigma F)^2 \rho_R^{5/3}}{q^{1/3} M^{5/3}} \tag{3}$$

where $\gamma_c$ is the critical surface tension, $\Sigma F$ is the sum of the molar attraction constants, $q$ 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 epoxy resin molecule $\Sigma F = 5963.8\ (\text{J cm}^3)^{1/2}$ (neglecting the H-bond and polar components), $q \approx 55$, $M = 390$ g, $\rho = 1.16\ \text{g cm}^{-3}$. This gives a value for the critical surface tension of $0.032\ \text{N m}^{-1}$ for the resin system compared to an experimental value of $0.035\ \text{N m}^{-1}$. 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.

### 3.2. Gas solubility

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.

$$p = \frac{x}{K_H} \tag{4}$$

where $p$ is the partial pressure of the gas, $x$ 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 is 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 and the partial molar heat of mixing [15].

$$\Delta H_s = \Delta H_{cond} + \overline{\Delta H_{mix}} \tag{5}$$

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 depndence of the solubility, $S$, is often expressed in terms of an Arrhenius-type equation [16]

$$S = S_0 \exp\left(\frac{-\Delta H_s}{R_g T}\right) \tag{6}$$

where $S_0$ is the pre-exponential constant, $R_g$ is the universal gas constant, and $T$ is the absolute temperature.

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 increases with the complexity and polarizability of the penetrant molecule and is relatively insensitive to the structure and morphology of the solvent. 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 primarily determined by the positive (endothermic) heat of mixing, i.e. the gas solubility increases with increasing temperature. This implies that the temperature dependence of the gas solubility will be commensurate with the solubility parameter of the polymer, although this balance of endothermic mixing and exothermic condensation is a potential reason for the temperature independence of the gas solubility data.

For the pure dry nitrogen system used in the experiments, Henry's law was obeyed up to a pressure of 1 atm (Fig. 1). This ideal dilute solution behaviour is readily understood because the solubility of permanent gases in polymeric materials is small due to the lack of strong polymer–penetrant interactions [17]. 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 characterization of each resin system restricts the utility of a predictive model.

In the case of permanent gases 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 by simply using Raoult's law if the vapour pressure is known). 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 which relates the vapour pressure of a liquid to the absolute temperature [18]. In the case of nitrogen, which has a critical temperature of 126 K [13], the hypothetical vapour pressure is $120 \times 10^6$ Pa ($\approx$ 1200) atm) at 298 K. This calculation assumes that the molar heat of vaporization is constant over the temperature range (Fig. 2). The ideal solubility is determined as in the case of condensible vapours, i.e. $p_l = x_l P_{0l}$ where $P_{0l}$ is the hypothetical vapour pressure of the pure liquified gas, $p_l$ is the pressure of the system and $x_l$ 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 corresponds approximately to a concentration of $0.07\,\mathrm{kg\,m^{-3}}$ 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, however, 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 component interactions, e.g. nitrogen in water is about 1% of the theoretical value, whereas nitrogen in ethanol is 33% [19]. 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 [20] 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 [21] 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 on essentially a liquid miscibility basis.

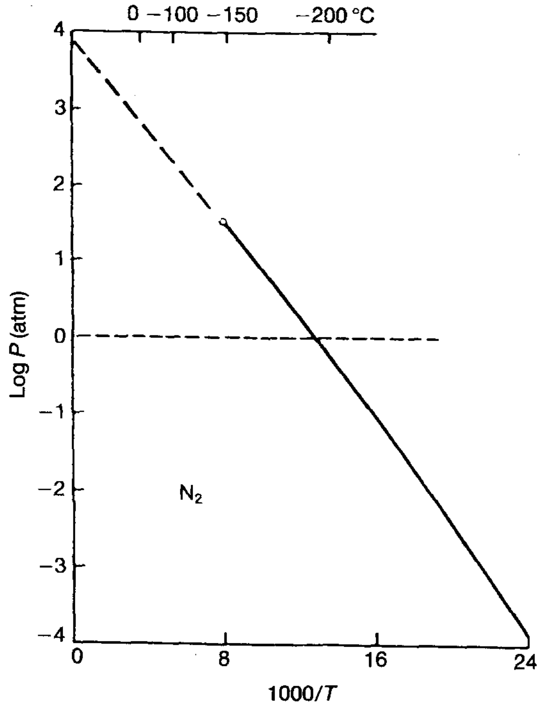


*Figure 2* Linear extrapolation of vapour pressure of nitrogen gas above its critical temperature.

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, $f_1^G$, dissolved isothermally in a liquid not near 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 also is accompanied by a large decrease in volume because 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 isothermally "condenses" to a hypothetical state having a liquid-like volume

$$\Delta G_{\mathrm{i}} = R_g T \ln \frac{f^{\mathrm{L}}_{\mathrm{pure}1}}{f_1^{\mathrm{G}}} \qquad (7)$$

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

$$\Delta G_{\mathrm{ii}} = R_g T \ln \gamma_1 x_1 \qquad (8)$$

where $f^{\mathrm{L}}_{\mathrm{pure}1}$ is the fugacity of (hypothetical) pure liquid solute and $\gamma_1$ is the activity coefficient of the solute referred tot he (hypothetical) pure liquid and $x_1$ is the mole fraction of the gas in solution and $\Delta G_{\mathrm{i}}$ and $\Delta G_{\mathrm{ii}}$ 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, $f_1^{\mathrm{G}}$, therefore

$$\Delta G = \Delta G_{\mathrm{i}} + \Delta G_{\mathrm{ii}} = 0 \qquad (9)$$

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

$$R_g T \ln \gamma_1 = v_1^{\mathrm{L}} (\delta_1 - \delta_2)^2 \phi_2^2 \qquad (10)$$

where $\delta_1$ is the solubility parameter of the solute, $\delta_2$ is the solubility parameter of solvent, $v_1^{\mathrm{L}}$ is the molar "liquid" volume of the solute and $\phi_2$ is the volume fraction of solvent.

Combining these equations gives the solubility in terms of mole fraction,

$$\frac{1}{x_1} = \frac{f^{\mathrm{L}}_{\mathrm{pure}1}}{f_1^{\mathrm{G}}} \exp \frac{v_1^{\mathrm{L}} (\delta_1 - \delta_2)^2 \phi_2^2}{R_g T} \qquad (11)$$

Equation 11 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 [22] 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 [21]). 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 11 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 although it has been shown from experimentation 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, $\phi_2 = (v_2/v_1 + v_2)$, essentially equals 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 (298 K), have been taken from Prausnitz and Shair's paper (Table V) [23] for permanent gases that may affect a composite system.

Although the table gives "liquid" volumes and solubility parameters for gaseous solutes at 298 K 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 [23] (Fig. 3) where the axes are the fugacity of the solute divided by its critical pressure $(f^L_{\text{pure}\,1}/P_c)$ as a function of the ratio of the solution temperature to the solute's critical temperature $(T/T_c)$. The fugacities are for a total pressure of 1 atm $(1.01 \times 10^5$ Pa) although 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.

TABLE V Liquid volumes and solubility parameters for gaseous solutes

| Gas | $v^L$ (cm$^3$ mol$^{-1}$) | $\delta$(J cm$^{-3}$) |
|---|---|---|
| $N_2$ | 32.4 | 5.28 |
| $O_2$ | 33.0 | 8.18 |
| $CO_2$ | 55.0 | 12.27 |

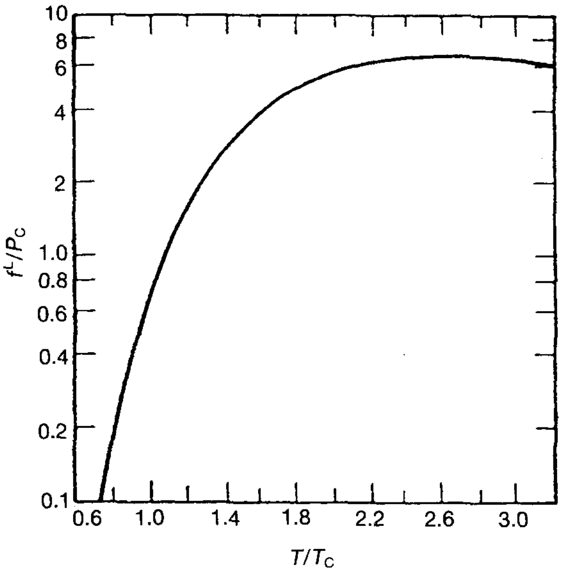


*Figure 3* Fugacity of a hypothetical liquid at atmospheric pressure.

Therefore, for nitrogen in resin at 298 K and atmospheric pressure, where $(T_c = 126$ K), $(P_c = 33.9 \times 10^5$ Pa), $T/T_c = 2.37$, $f^L_{\text{pure}\,1}/P_c = 6.5$ (from Fig. 3), $f_1^G = 1.01 \times 10^5$ Pa, $\delta_1 = 5.28$ (J cm$^{-3})^{1/2}$ (from Table V), $\delta_2 = 20.45$ (J cm$^{-3})^{1/2}$ (calculated from the molar attraction constants), $v_2^L = 32.4$ cm$^3$ mol$^{-1}$ (from Table IV), $\phi_1 \approx 1$, and, from Equation 11, the mole fraction of nitrogen in the resin at room temperature and pressure is $2.257 \times 10^{-4}$, which corresponds to a gas concentration of 0.0188 kg m$^{-3}$.

The experimental work was performed over a range of temperatures; the minimum was 313 K. For this temperature the treatment gives a mole fraction of $2.608 \times 10^{-4}$ and a concentration of 0.0217 kg m$^{-3}$. This compares admirably with the experimental value of 0.0207 kg m$^{-3}$ determined at 313 K.

The experiments indicated that the solubility was temperature independent in the measured range (313–373 K). This is not in agreement with the theoretical analysis which implies an increase in solubility with temperature by about 1.5 for these temperatures, i.e. the theoretical gas solubility at 373 K is 0.0344 kg m$^{-3}$. It is uncertain whether this is a consequence of the experimentation or the inadequacy of the model although it is feasible that the solution of gases such as nitrogen and oxygen are exothermic at low temperatures and endothermic at higher temperatures. This can be seen by considering the Van't Hoff equation

$$\Delta H_{\text{cond}} = \frac{R_g T_c \, \mathrm{d}\ln f^L/P_c}{\mathrm{d}1/T} \qquad (12a)$$

$$\overline{\Delta H_{\text{mix}}} = v_2(\delta_1 - \delta_2)^2 \qquad (12b)$$

In Equation 12a the heat effect does not depend on the solvent, it is determined by the slope of the graph in Fig. 3. 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 possible that the increase in gas solubility in the resin with increasing temperature is negligible in this system.

Nevertheless, because solubility data in the literature are 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 only requires the molecular chemistry of the resin precursor and its density to provide the dissolved gas concentration for the resin pressures in the processing cycle. The theoretical analysis produces a linear isotherm for composite processing pressures in agreement with the experimental data (Fig. 4) providing a Henry's law constant within 10% of that determined using the instantaneous vacuum technique [8].

## 4. Discussion

The solubility parameter of a resin precursor has been determined from molar attraction constants and

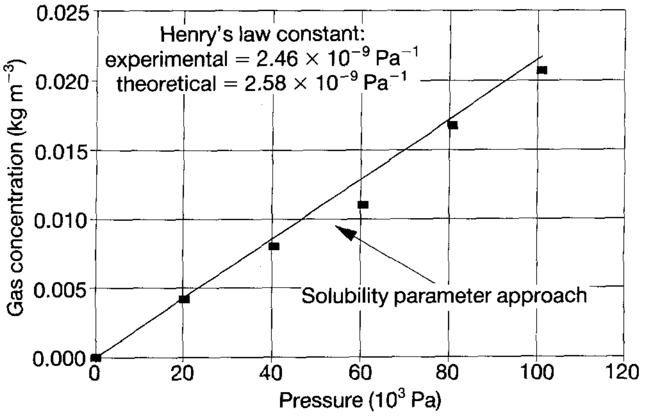


*Figure 4* Pressure dependence of gas concentration compared to thermodynamic correlation at 313 K.

found to be comparable with liquids that are known solvents. The molar attraction constants were used to determine the surface tension of the resin using a semi-empirical approach. This compared favourably with experiment. The solubility of nitrogen in the resin and its dependence on pressure and temperature were compared to ideal solution theory using extrapolated vapour pressure data. Raoult's law was not obeyed due to component interactions. A thermodynamic correlation enabled the nitrogen gas to be condensed to a hypothetical liquid-like volume which could then be mixed with the resin essentially on the basis of liquid miscibility. The gas solubility and its interaction with temperature were well within the errors of the experimental data.

The solubility of gases in the resin system and the surface tension of the resin can be determined from an independent physical quantity, namely the solubility parameter of the polymer. This, in turn, can be calculated from tabulated molar attraction constants. The concentration gradient for the growth and collapse of gas bubbles and its relationship with the process variables can subsequently be estimated from the chemistry of the system and the density of the resin. Although solubility parameter theory is most successful with non-polar systems it is evident that it is appropriate for the resin system in this study. It is apparent though, that a procedure based on the solubility parameter can only be as successful as the theory itself and so care must be taken if specific chemical interactions are involved which may affect the solubility, e.g. polar, hydrogen bonds or chemical reactions. This will become more probable in resin systems where the hydrogen bonding or polar components of the solubility parameter play a more significant role in contributing to the overall solubility parameter and for more complex penetrants such as condensible vapours, e.g. water.

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