Moisture solubility and diffusion in epoxy and epoxy-glass composites

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The solubility and kinetics of moisture transport mechanisms in epoxy-type resin and resin-glass composites have been investigated over a range of partial pressure and temperature. Moisture absorption-desorption in these systems is a quasi-reversible process, the kinetics of which are non-Fickian (Type II) and dependent on prior history. The multistaged sorption and transport behavior are interpreted in terms of multiphase models.

Introduction

The diffusion and/or solubility characteristics of H_2O and other molecular species in polymer materials have been discussed in numerous papers, mostly on studies conducted in the last fifteen years [1–10]. These investigations have highlighted the limited understanding of the actual solution and transport processes in resins and resin-glass composites, particularly the role of chain chemistry and sinks, i.e., chain sites or cavities, in affecting the sorption-desorption process.

The process by which permeation occurs when these materials are pore-free is activated diffusion. The molecules dissolve in the surface of a polymer, equilibrating with the atmosphere, establish a chemical potential, and diffuse in the direction of the gradient. Thus two fundamental properties are of interest which lead to an understanding of the phenomena. The first of these is solubility (c), which is related to the partial pressure (P) through Henry's law ($c = \gamma P$), where γ is an activity coefficient. The second property is the diffusion constant (D), which is the ratio of the molecular flux (Q) divided by the gradient of the concentration (dc/dx) of the diffusing species, i.e., Fick's law, $Q = Ddc/dx$. These parameters can be evaluated as functions of concentration and temperature, and reversibility can also be determined.

In the case of highly sorbed penetrants [11, 12] the diffusion coefficient normally increases with concentration. This has been discussed as a plasticizing effect and is often accompanied by a decrease in glass transition temperature T_g. Although this behavior is exhibited by H_2O in some polymers, a more common behavior appears to be a decrease in the diffusion coefficient with increasing concentration. In this case an appropriate model involves the clustering of the penetrant so as to render immobile an increasing fraction of it. An alternative model might be devised by considering the polymer chains to include reacting sites or trapping sites. This type of behavior is exhibited by polyurethane elastomers and is described as a clustering phenomenon by Barrie et al. [13].

The network of epoxies can be easily modified by varying the appropriate components. In dicyanamide (DICY) epoxies, for example, the functionality is affected by the

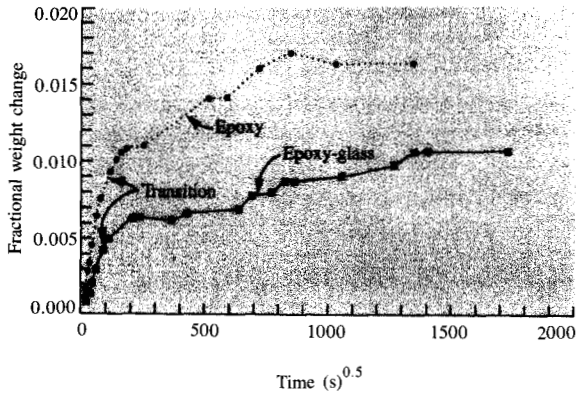

Figure 1

Typical moisture absorption in epoxy-glass composites vs time compared to the same event for epoxy alone. Fractional increase in weight: Epoxy and epoxy-glass exposed to 75°C/100% relative humidity.

DICY content. One may therefore expect the solubility and diffusion to vary from system to system, and even within a system depending on chemistry, degree of cure, and other factors. However, the effects observed by Diamant et al. [9] are not dramatic in epoxy even though the experiments covered a range of densities of 10% and T_g varied from 113°C to 150°C for the cured epoxy system. Surprisingly enough, the highest solubility occurred with the highest-density material, which also had the highest T_g. A most interesting effect is that shown by Apicella et al. [10], wherein there is a humidity history dependency which is progressively lost as the test temperature is decreased.

E. R. Lange [14] and E. L. McKange et al. [15] have shown that pure resins and composites have approximately the same D and saturation moisture contents when corrections are made for fiber content. Apparently there is no degradation of the fiberglass interface in this experiment. Nevertheless at very long exposures (e.g., 25 days) at 98% relative humidity, an incremental increase of 0.2% (0.66% of bulk resin) occurs in absorbed moisture. This effect was not shown in any of the base polymer absorption experiments.

In the case of Kevlar epoxy [16] composites, neither diffusion nor absorption is well-behaved. Diffusion occurs two orders of magnitude more rapidly in the composite (compared to the base epoxy) and the solubility is increased by a factor of three to four over that accommodated by the base resin. It has been speculated [16] that the rapid diffusion is due to preferential diffusion of moisture in the Kevlar filaments along their length.

Rapid diffusion has also been shown by Judd [17] and correlated to void content in carbon fiber composites. Again it is speculated that moisture can permeate into a composite by diffusion through the resin and then flow along defects such as porosity and voids.

The studies previously noted for epoxy-glass were not conducted on dicyanamide hardened material, the system which we report on in this paper. When this DICY system is used as discussed by Bonniau et al. [18], we find almost all of the very interesting anomalous behavior described earlier for other polymers, which requires sophisticated two-phase-diffusion analytical treatment to model the experimental results. Since our results are substantially more copious than those of Bonniau et al. [18] and the other papers on epoxy, we now proceed to discuss our experimental results.

Experimental apparatus and [illegible]

Prior to each test the samples were dried in desiccators kept at 50°C. The desiccators consisted of four-inch-diameter Pyrex tubes 16 inches long [19], each supplied with a commercial desiccant. Each tube was surrounded by a resistance heater and insulation. The temperature of the vapor, and hence the relative humidity, was controlled to within 0.5°C. Sample weight was measured with a Mettler analytical balance having a precision of ±10 μg. Exposures to humid air environments were obtained by placing samples inside three-inch-diameter Pyrex tubes, 16 inches long, mounted on top of a Braun Thermomix controller. The temperature of the Thermomix was maintained to within 0.05°C of the desired temperature for a specific vapor pressure.

Materials

Cast epoxy resin films and epoxy-glass composite samples laminated from 3, 5, and 10 plies of impregnated glass cloth were used in this study. The sample size was 5.1 cm × 5.1 cm (2 in. × 2 in.). There were three samples per exposure. The specific epoxy system was a blend of a brominated bis-phenol A and Cresol Novolac, with dicyanamide as the curing agent and TMBDA as the catalyst.

The glass is E-type with a yarn diameter of 122 μm (0.0048 in.) in both the warp and fill directions. Each strand of the yarn contains approximately 204 filaments; each filament diameter is approximately 5.3 μm (210 μin.). The nominal weight percent resin in the composite is 60%.

No special attention was given to the laminate other than making it to manufacturing specifications; thus there is a possible range of behavior to be expected if the chemical concentrations noted above fluctuate due to mixing or the cure state. The range of behavior will in itself be interesting because the specifications are most closely tied to rheological functional factors.

Analytical procedure

- *Diffusion*

Gravimetric–time data measuring the sample absorption-desorption response to an external environment have been

analyzed (see Appendix) by conventional approximations [19, 20] to Fick's second law. Non-Fickian diffusion of moisture in resin composites has been examined in terms of absorption into mobile and bound phases (Carter and Kibler [21]). The evidence for anomalous absorption stems largely from the multistaged shape of weight gain–time data graphs. Such plots are characterized by plateaus or inflections preceding the actual saturation absorption. Experimental conditions are shown in the matrix in **Table 1**.

Following the analysis by Carter–Kibler [21] and Gurtin–Yatomi [22], the kinetic approach to moisture saturation at specific temperatures and partial pressures of moisture has been analyzed on the basis of the following equation:

$$[M = M_m\{(b/a + b)\exp(-at)y(t) + (b/a + b)[\exp(-bt) - \exp(-at) + [1 - \exp(-bt)]\},$$

$$y(t) = (1 - 8/\pi^2) \sum_{\text{add}}^{\infty} (2n + 1)^2 \exp[-(2n + 1)^2 Dt]. \quad (1)$$

In these equations a is the probability per unit time with which absorbed moisture molecules become "bound," b is the corresponding probability with which "bound" molecules become mobile. If n and N are the concentrations per unit volume of mobile and bound molecules, respectively, an equivalent statement of equilibrium is the constancy of the n/N with temperature and partial pressure of moisture.

Further study of this model raises a number of questions. For example, what is the magnitude of the ratio n/N; i.e., does the number of mobile sites exceed the quantity of bound sites? From an absorption/solubility viewpoint, at what fraction of saturation does the occupation of bound sites cause non-Fickian deviations? Does the appearance of the plateau (i.e., the second stage of absorption) signal the onset of clustering or trapping? If so, the ratio $N/n + N_n$ should then correspond to an inflection point (M_t) in the absorption with time and in the plot of log D vs concentration, i.e., a point of macro-deviation from Fickian diffusion.

Another issue of interest in clarifying moisture absorption is the issue of history-dependent saturation concentration. If (n, N) are dependent on relative humidity, reducing humidity after an absorption will bring about a saturation that differs from when the sample is equilibrated from an initially lower saturation condition. That is, the bound water does not get a chance to redistribute during the experiment.

Information collected in this study attempts to shed some light on the above questions.

Results and discussion

• *Solubility*

The saturation solubility of moisture in epoxy and epoxy-glass composites was determined at various conditions of temperature and humidity, i.e., partial pressure (see the Appendix). **Figure 1** illustrates typical moisture absorption in epoxy-glass composites versus time compared to the same event for epoxy itself. It is evident that the absorption process is a multistage process. The first stage occurs very rapidly (at a rate approximately proportional to $\sqrt{t}$) with completion at a temporary saturation. Then the second stage of absorption begins and very slowly proceeds. (On desorption the process appears predominately single-staged.) The total absorption of moisture in the composite and that in the epoxy itself are about the same if one takes into account the fact that the composite contains about 40% less resin. The second absorption, i.e., following a desorption, occurs very rapidly (see **Figure 2**). **Figure 3** demonstrates

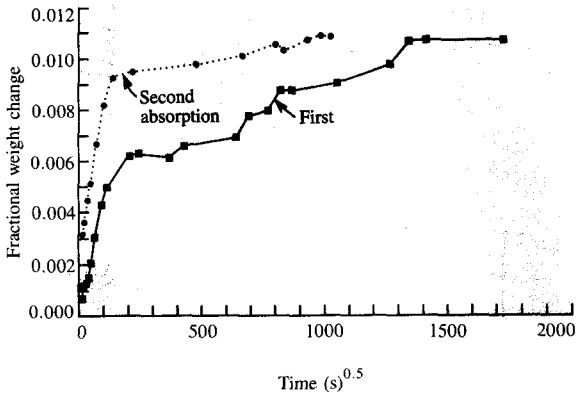

Figure 2

Fractional increase in weight: epoxy-glass first and second absorptions. Exposed to 75°C/100% relative humidity.

Table 1 Test matrix of experimental conditions.

Temperature (°C)	*Layers*	*Pressure* (mm Hg)					*Immersion*
		760	*355*	*285*	*220*	*92*	
50	3						×
	5					×	×
	10						×
	Epoxy						×
75	3			×			
	5			×	×	×	
	10			×			×
	Epoxy			×			
85	3			×		×	×
	5		×	×		×	×
	10		×	×		×	×
	Epoxy			×		×	×
100	3	×		×			×
	5	×	×	×	×		×
	10	×		×			×
	Epoxy	×		×			×

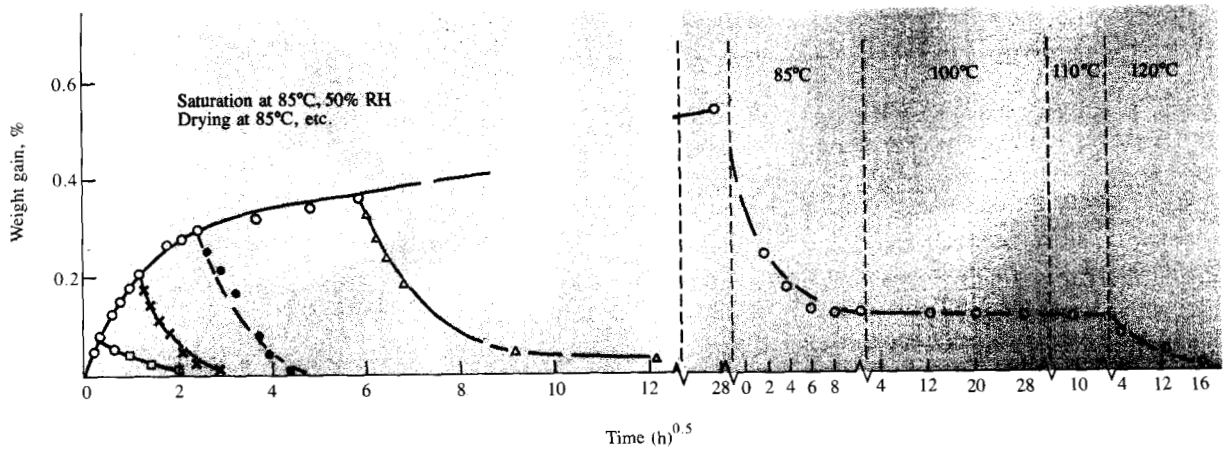

Figure 3

The onset of residual moisture at the transition to second stage and stability to temperatures greater than 120°C.

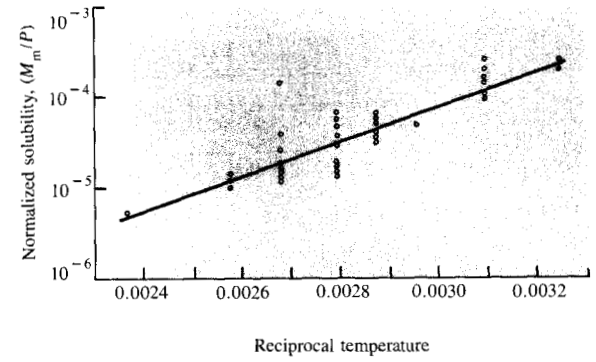

Figure 4

Temperature dependence of normalized solubility for epoxy-glass composites.

that the onset of residual moisture occurs roughly at the transition region, the end of the first stage, where there appears to be a temporary saturation. Samples experiencing absorption to values less than M_t lost the gained moisture on desorption; weight gain in excess of M_t resulted in the retention of residual moisture, as shown in the last desorption in Fig. 3. It is clear that temperatures in excess of the glass transition temperature (>120°C) are required to remove the residual moisture.

The dependence of the saturation solubility, M_m, on temperature and moisture partial pressure was obtained from data reflecting the sample weight gain/loss equilibrium with the test environment. The thermodynamics are expressed by the reaction

$$P_{vapor} \leftrightarrows (H_2O)ad \leftrightarrows (H_2O)$$

in epoxy solution, expressing the equilibria between the vapor-adsorbed film at the surface and the dissolved H_2O in the epoxy. From the equilibrium constant, and assuming Henry's law to be valid,

$$M_m = Ap \exp(-H/RT), \quad (2)$$

where H is the heat of solution and p is the vapor pressure. The value of A is 1.34×10^{-10}, and 2.05×10^{-10} for epoxy-glass and epoxy, respectively. The quantity M_m is expressed in percent.

The heat of solution derived from our total data set, given in **Figure 4**, is 8.8 kcal per mole as shown by regression analysis, with fit better than 95% confidence. "Bound" and "residual" moistures are included. The solubility decrease with increasing temperatures means that the reaction is endothermic.

An additional facet of the sorption behavior of moisture into epoxy and epoxy composites is shown in **Figure 5**. In these experiments we saturated at 65°C to 30% and at 85°C to 80%; then we equilibrated at reversed humidities and temperatures. From Eq. (2) and the thermodynamic argument behind it one would expect sorption reversibility: an equation of state behavior. This is clearly not the case for the second stage of absorption. These data reveal that the final moisture content, which includes the second-phase absorption, is strongly dependent on prior history. It is expected that this behavior is attributable to the multistage nature of the sorption process and the existence of internal sites or regions containing trapped moisture. The reader may wonder whether the true equilibrium would be established if the samples were left long enough. Clearly this question needs to be addressed in future studies.

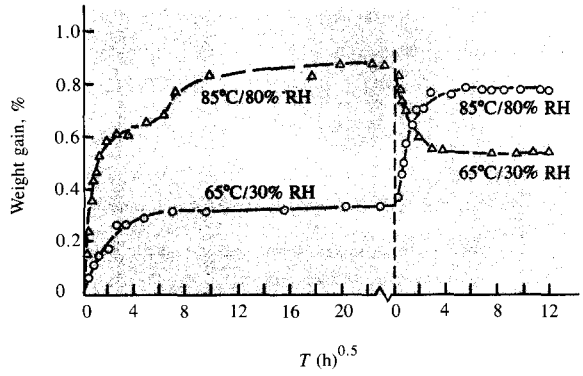

Figure 5

Weight gain data showing lack of reversibility or history dependence to prior exposure for epoxy-glass.

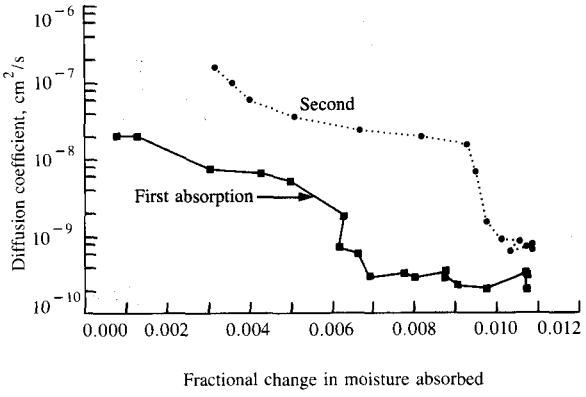

Figure 6

Variation of moisture diffusion coefficient with absorbed moisture at 75°C/100% relative humidity. The material is an epoxy-glass. Data for first and second absorption.

• *Moisture diffusion in resin and resin-glass*

The non-Fickian behavior of the absorption-desorption process is best shown by a plot of D vs M, where the transition between stages is indicated by the change in the slope in **Figure 6**. The value of the initial slope is consistently less than the 0.5, with a range of 0.3 to 0.5. As a consequence of this nonlinearity, the procedure for estimating the diffusion coefficient is chosen as follows: 1) obtain the variation of D with the amount of sorbed moisture from Eq. (A2). 2) Obtain a mean value of D for M less the M_i by regression analysis of Eq. (A3). A reference is needed, however, so $D(M = 0.001 + M_i)$ was taken to be the standard and was obtained from a linear regression analysis of Eq. (A2). **Figure 7** is a typical example of this variation of D with quantity of moisture absorbed/desorbed in epoxy-glass. Here it is apparent that D decreases by an order of magnitude with increasing H_2O concentration. Initially, we might explain the strong decrease in D with concentration as a decrease in the number of transport sites or paths available. This would decrease the configurational part D_0 of the diffusion constant. However, the data in the next section for the temperature dependence of D would not support sufficient analysis to establish relevant contributions for D_0 or activation energy as a function of concentration. The Arrhenius plot in Fig. 7 illustrates the temperature dependence of moisture diffusivity for epoxy-glass. The activation energies, 9500 cal/mol and 9940 cal/mol epoxy-glass and epoxy, respectively, are essentially the same and the values of D_0 are also consistent (i.e., 0.023 and 0.28 for the composite and resin, respectively). The great scatter in individual results, a contribution from an inconsistency in the basic material, is overcome by the large number of data points and computer-aided regression analysis. We can also look at previous references on epoxy for activation energy

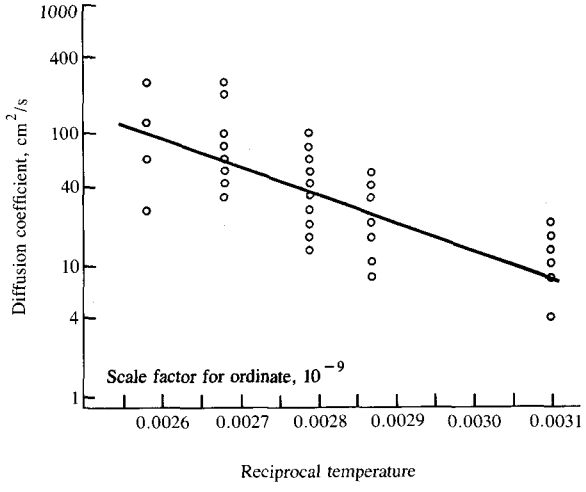

Figure 7

Variation of moisture diffusion coefficient with temperature for an epoxy-glass composite.

(10 ± 1.5 kcal/mol) and find that the results are about the same. It would appear that diffusion is dominated by bulk transport and the resin-glass interface contributes little to the process.

Application of the non-Fickian, Type II analysis described earlier was investigated. Standard regression techniques determined the optimum set of values for each set of environmental conditions. The question of the partial pressure and temperature dependence of a and b was determined. Analysis yielded the following relations:

$a = (251.3/p) \times \exp(-4817/T)$,

$b = (314.7/p) \times \exp(-5198/T)$.

From the equilibrium condition $an = bN$, constancy of the ratio n/N would be expected and was found.

Summary

This study of the moisture absorption and diffusion into epoxy and epoxy-glass composites has demonstrated that the solubility follows Henry's law over the range of pressures and temperatures covered. The reaction is endothermic. The diffusion is best described as non-Fickian, having a strong decrease in D with the amount absorbed, and can clearly be described by a model embracing Type II diffusion involving a mobile component and a component trapped at unspecified sites but whose number is fixed. In addition, the absorption is dependent on prior exposure history, indicating that the complexity of the solution process relative to the base laminate chemistry requires additional study. The scatter of our results may be due a) to initial chemical conditions in the base laminate which depend on manufacturing processes or b) to the incomplete removal of "bound" moisture in the stabilizing treatment.

One of the most interesting observations of this work is that the very small concentration of H_2O molecules absorbed has an anomalously large effect on those yet to be absorbed. This leads us to consider that the distribution of occupied bond sites set initially at the lamination is a significant factor in the absorption process. In fact, we have shown that the stabilizing treatments above T_g are important in desorbing all of the water.

Appendix

Shen and Springer [19] approximated Jost's [21] solution with

$$M = M_i + \{(M_m - M_i) \times [1 - \exp(-7.3)(Dt/S^2)]\}^{3/4}, \quad \text{(A1)}$$

which, on re-arranging, gives

$$D - (s^2/t) \times [(1/7.3) \times \ln (M_m - M_i)/(M_m - M)]^{4/3}, \quad \text{(A2)}$$

where

M = fractional (or percent) weight gain,
M_i = initial content of diffusing species,
M_m = maximum content (equilibrium) of species.

For a given temperature and partial pressure,

s = diffusion path: sample thickness,
D = diffusion coefficient,
t = time.

For the case of Fickian diffusion, D can be satisfactorily estimated by (A1):

$$D = \pi(s/4M_m)^2 \times [(M - M_i)/\sqrt{t} - \sqrt{ti}]^2. \quad \text{(A3)}$$

In this analysis both Eqs. (A2) and (A3) have been employed to obtain values for the diffusion coefficient.

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