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# Moisture diffusion into epoxy adhesive: testing and modeling

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**Abstract** Moisture diffusion into epoxy adhesive is investigated through utilizing complete fluid immersion tests in distilled water. Apparent diffusivity for each specimen is determined by two methods, one using the diffusion data at early times (at low loading) and the other using the data at large times (close to the saturation point). The results of the two methods are quite different, indicating that diffusivity is concentration dependent. The apparent diffusivity values obtained through the method using the early data points are about twice those obtained through the method utilizing the data points at large diffusion times. Variance of diffusivity with concentration is also considered as the third method of analysis to determine the concentration dependency. A good agreement is observed between the resultant Fickian model solved numerically and the experimental data. The latter result appears to indicate a change in the excess volume of mixing during the sorption process.

**Keywords** Adhesive · Epoxy · Diffusion · Diffusivity · Distilled water · Concentration · Model · Test

## 1 Introduction

There is a growing interest in the application of adhesive bonding for the manufacture of structural joints. Some advantages of adhesive bonding over the common mechanical joining techniques such as riveting and welding are lightness, neatness, design simplicity, improved fatigue and corrosion resistance, and reduced costs (Kozma and Olefjord 1987; Eagland 1990; Watson 1987).

The perfect adhesive which will do all things in all industries does not yet exist. Different materials, applications and production needs, all call for different adhesives. However, the most common of the high-performance structural adhesives, especially in automotive and aircraft manufacture, are epoxies (Kozma and Olefjord 1987; Tai and Szklarska-Smialowska 1993a; Chasser et al. 1993; Dixon et al. 1998). Many spot-welded automotive parts are being replaced by adhesive-bonded components because of the difficulties encountered in welding of galvanized or coated steels (Tai and Szklarska-Smialowska 1993a). Adhesives also help to isolate dissimilar metals, or galvanized from ungalvanized steel. In this way they help reduce the danger of galvanic corrosion (Brewis 1985)—an increasingly important function as specialty metals and coatings become more common in automobile bodies. Epoxies are able to bond well to a variety of treated or untreated metal surfaces (Mohan 1990). In aircraft manufacture, there is a great need for evenly stressed, smooth bonding of thin aluminum sheet and honeycomb materials. Epoxy adhesives have a good affinity for aluminum alloy surfaces, and the oxide layers produced during surface preparation (Chasser et al. 1993).

Epoxy resins are attractive for metal-bonding adhesive systems because of their ability to cure without producing volatile by-products and their low shrinkage upon curing (less than 0.5%) (Tai and Szklarska-Smialowska 1993a). Epoxies are two component systems that begin curing when mixed and generally require elevated temperatures to speed up the reaction to useful production times (Chasser et al. 1993).

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Environmental exposures can have deleterious effects seriously compromising the durability of adhesive-bonded structural joints. Especially moisture and aggressive ion ingress into the bonded joint are primary causes of adhesive bond degradation (Tai and Szklarska-Smialowska 1993a, 1993b; Kinloch 1983; Shaffer et al. 1992; Brewer 1988; Prakash et al. 1987; Stevenson and Priest 1991; Kim and Ajersch 1994; Comyn 1983; Xiao and Shanahan 1997; Srivastava and Hogg 1998; Moidu et al. 1998; Lindberg 1992). Water may enter a joint by diffusion through the adhesive, by transport along the adhesive-adherend interface and by capillary action through cracks in the adhesive. Once inside a joint, it may cause strength degradation by inducing changes in the physical properties of the adhesive and/or degrading the chemical bond between the adhesive and the metal and/or inducing stresses in joints by nonuniform swelling of the adhesive (Comyn 1983; Srivastava and Hogg 1998; Moidu et al. 1998; Srivastava 1999).

The objective of this study is to determine the moisture sorption behavior of epoxy adhesive under complete immersion in distilled water.

## 2 Mathematical formulation

If diffusion is restricted to one dimension, such as is the case represented by a thin film of thickness, $l$, adsorbing a fluid according to Fick's law with constant surface boundary conditions, where diffusion into the edges of the film can be ignored, the amount of diffusant, $M_t$, taken up by the sheet in a time, $t$, is given by (Crank and Park 1968)

$$\frac{M_t}{M_\infty} = 4\left(\frac{Dt}{l^2}\right)^{\frac{1}{2}}\left(\frac{1}{\pi^{\frac{1}{2}}} + 2\sum_{n=0}^{\infty}(-1)^n \operatorname{ierfc}\frac{nl}{2\,(Dt)^{\frac{1}{2}}}\right). \quad (1)$$

The uptake is considered to be a diffusion process controlled by a constant diffusion coefficient, $D$, and $M_\infty$ is the equilibrium sorption attained theoretically after infinite time. The value of $D$ can be deduced from an observation of the initial gradient of a graph of $M_t/M_\infty$ as a function of $(t/l^2)^{1/2}$. This observation is made easier by the fact that, for a constant diffusion coefficient, the graph for a sorption experiment is a straight line, to within the normal limits of experimental error, for $M_t/M_\infty$ as much as about 50 percent. That is, at short times, where $M_t/M_\infty$ is less than 0.5, (1) can be approximated by the following (Crank and Park 1968).

$$\frac{M_t}{M_\infty} = 4\left(\frac{Dt}{\pi l^2}\right)^{\frac{1}{2}}. \quad (2)$$

Another form of equation describing sorption and desorption (for the same boundary conditions) is (Crank and Park 1968)

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{m=0}^{\infty}\frac{1}{(2m+1)^2}\exp\left[-\frac{D\,(2m+1)^2\pi^2 t}{l^2}\right]. \quad (3)$$

This equation is more suitable for moderate and large times and can be approximated by the following long time solution

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}e^{-\frac{D\pi^2 t}{l^2}} \quad (4)$$

that is, at large times, a plot of $\ln(1 - M_t/M_\infty)$ vs. $(t/l^2)$ gives a straight line with a slope of $-D\pi^2$ from which $D$, assumed constant, can be determined.

## 3 Experimental

The epoxy adhesive used in this investigation is a general-purpose, two-part epoxy (Fusor 309) obtained from Lord Corporation. The adhesive is prepared by mixing equal volumes of the resin and hardener parts. The mixed adhesive cures fully in 24-48 hours at room temperature with handling strength in about 8 hours.

Three adhesive sheets ($30 \times 30 \times 1$ mm$^3$) were molded between wax covered metal sheets. Subsequently they were immersed in distilled water for several months at room temperature. The test specimens were suspended/immersed in distilled water without making contact with each other. The containers were covered with aluminum foil to prevent moisture evaporation. At various time intervals, test specimens were removed from the test fluid, extra water on the surface was dried with clean tissue and the specimen was weighed by an analytical balance with precision to 0.0001 g.

## 4 Results and discussion

Plots of moisture uptake vs. immersion time for the epoxy adhesive specimens in distilled water are presented in Fig. 1. As the figure shows, moisture diffusion experiments lasted over 7 months in which the diffusion in all three test specimens reached equilibrium. The moisture sorption behaviors of the three specimens were quite similar.

Diffusivities of moisture in epoxy adhesive specimens in distilled water were first determined by use of (2). As discussed earlier, $M_t/M_\infty$ (where $M_t$ and $M_\infty$ are the amounts of moisture intake in time, $t$, and at saturation, respectively) is plotted against $4(t/\pi l^2)^{1/2}$ (as in Fig. 2) and the diffusivity is determined from the initial slope of the plot (slope is $D^{1/2}$). Diffusivity values ranged from about $3.50 \times 10^{-10}$ cm$^2$/s to about $5.34 \times 10^{-10}$ cm$^2$/s as presented in

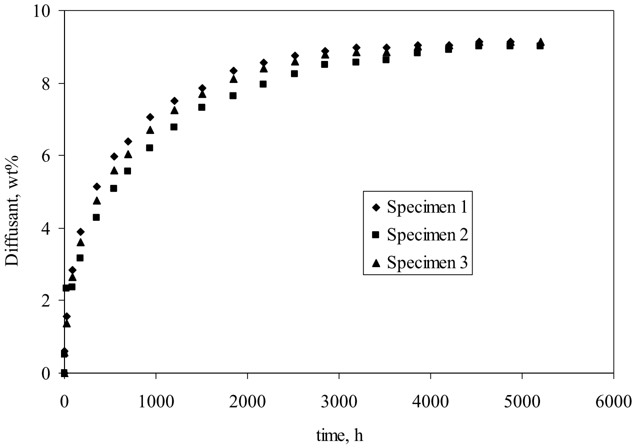

**Fig. 1** Diffusant intake (relative to the original weight of the specimen) vs. immersion time for epoxy adhesive in distilled water

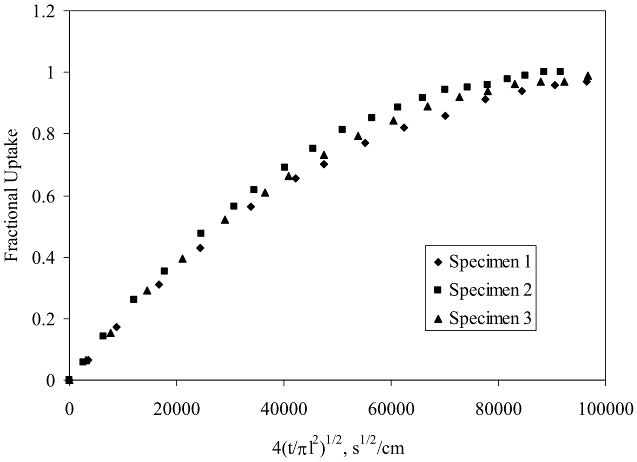

**Fig. 2** Fractional uptake ($M_t/M_\infty$) vs. $4(t/\pi l^2)^{1/2}$ for epoxy adhesive in distilled water

**Table 1** Apparent diffusivities of distilled water in epoxy adhesive specimens as determined by two different methods (by use of (2) and (4))

| Specimen number | Apparent diffusivity, $cm^2/s$ | |
|---|---|---|
| | From (2) | From (4) |
| 1 | $3.4969 \times 10^{-10}$ | $1.62 \times 10^{-10}$ |
| 2 | $5.3361 \times 10^{-10}$ | $2.43 \times 10^{-10}$ |
| 3 | $4.0808 \times 10^{-10}$ | $1.97 \times 10^{-10}$ |

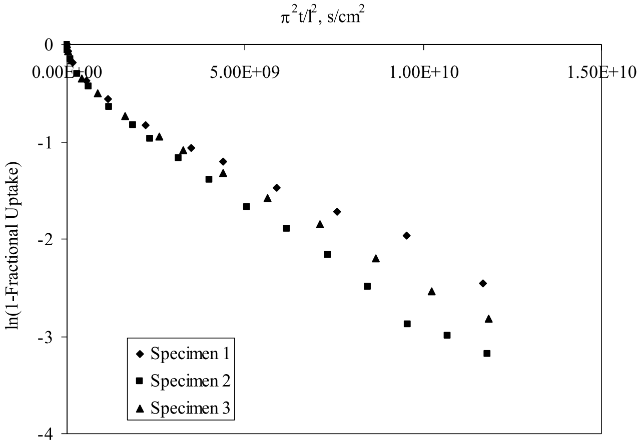

**Fig. 3** Plot of $\ln(1 - M_t/M_\infty)$ vs. $\pi^2 t/l^2$ for epoxy adhesive in distilled water

Table 1. Higher and lower values are reported in literature. De Neve and Shanahan (1993) studied the diffusion of water into an epoxy resin. The epoxy resin studied was based on the diglycidyl ether of bisphenol A (DGEBA), crosslinked with dicyandiamide (DDA), and contained fillers (Ciba-Geigy X B3131). The diffusion coefficient at 40 °C is $2.6 \times 10^{-9}$ $cm^2/s$. Martin and Marta (2000) studied the diffusion of water into an epoxy based adhesive supplied by 3M company (3M 5042). The diffusion coefficient at 30 °C is $2.18 \times 10^{-13}$ $cm^2/s$. Barron et al. (2000) studied the diffusion of water into polyurethane adhesive. The diffusion coefficient is recorded for the polyurethane stored in distilled water at 37 °C with value $5.22 \times 10^{-8}$ $cm^2/s$.

Apparent diffusivities were also determined by the second method (by use of (4)) in which $\ln(1 - M_t/M_\infty)$ is plotted against $\pi^2 t/l^2$ (as in Fig. 3) and the diffusivity is determined from the slope of the straight line at large times (ranges between $-1$ and $-4$ in the y-axis) (slope is $-D$). The resulting apparent diffusivities are also included in Table 1. Diffusivity values determined by this second method ranged from about $1.62 \times 10^{-10}$ $cm^2/s$ to about $2.43 \times 10^{-10}$ $cm^2/s$. As can be deduced by comparing the diffusivity values presented for both methods in the table, the results of the two methods are significantly different, the apparent diffusivity values obtained through Method 1 (at early times) are about twice those obtained through Method 2 (at large times). It is clear that diffusivity is concentration dependent.

Concentration dependency of the diffusivity was also considered as the third method of analysis. Fick's Law contains the implicit assumption that the driving force for diffusion is the concentration gradient. However, since diffusion is simply an inherent characteristic of systems to move to equilibrium, it is clear that the true driving force for diffusion is the gradient of chemical potential. This seems to have been first recognized by Einstein (1906). The flux of diffusant A, $J_A$, diffusing through B in the axial direction, $x$, derived starting from the chemical potential, is in general given by (Karger and Ruthven 1992)

$$J_A = -D_{AB}\left(\frac{d\ln p_A}{d\ln c_A}\right)\frac{dc_A}{dx} \tag{5}$$

where $D$ is diffusivity, $p$ is pressure and $c$ is concentration. An alternative and equivalent form may be obtained by introducing the activity correction (defined by $p_A = \gamma_A c_A$) as (Karger and Ruthven 1992)

$$J_A = -D_{AB}\left(\frac{d\ln\gamma_A}{d\ln c_A}\right)\frac{dc_A}{dx}. \tag{6}$$

This concept can be applied to represent diffusion of a single component (A) in a porous material (B). In this situation, $D_{AB}$, is the diffusivity for component A relative to the fixed coordinates of the pore system. Furthermore in a microporous material, there is no clear distinction between materials on the surface and molecules in the central porous region. For small pores (<20 Å), molecules in the interior will always be subject to the surface potential forces of the solid, such as attraction, repulsion, polar and quadropolar energies. It is therefore convenient to consider only the total "interior" concentration ($q$). The transport equation may then be written in this form

$$J = -D\frac{dq}{dx}, \quad D = D_o\frac{d\ln\gamma}{d\ln q}. \tag{7}$$

$D_o$, defined in the this way, is generally referred to as the "corrected diffusivity". If the system is thermodynamically ideal ($\gamma \propto q$), $d\ln\gamma/d\ln q \to 1$ and the Fickian and corrected diffusivities become identical. However, in the more general case of thermodynamically non ideal systems, the Fickian diffusion coefficient is seen to be a product of a mobility ($D_o$) and the thermodynamic correction factor $d\ln\gamma/d\ln q$ which arises from the non-linearity of the relationship between activity and concentration. Thermodynamic ideality is generally only approached in dilute systems (gases or dilute liquid or solid solutions). For instance in the Henry Law region $d\ln\gamma/d\ln q \to 1$. For the present system, this arises when the sample is exposed to a fixed low relative humidity of vapor. Except of dilute systems, the Fickian diffusivity is generally found to be concentration dependent. Equation (7) indicates that this concentration dependence may arise from the concentration dependencies of either $D_o$ or $d\ln\gamma/d\ln q$. In liquid phase systems, both these effects are often of comparable magnitude (Ghai et al. 1973) and the advantage of using the "corrected diffusivity" over the Fickian transport diffusivity ($D$) is minor. The situation is different in adsorption systems where at low loadings (Henry's Law) $d\ln\gamma/d\ln q \to 1$ and at high loadings (at saturation) $d\ln\gamma/d\ln q$ varies substantially.

The Fickian diffusivity model for the present concentration dependent diffusivity system becomes

$$\frac{\partial q}{\partial t} = \frac{\partial}{\partial x}\left(D(c)\frac{\partial q}{\partial x}\right) \tag{8}$$

where

$$D(c) = D_0\frac{d\ln\gamma}{d\ln q}. \tag{9}$$

Substituting gives

$$\frac{\partial q}{\partial t} = \frac{\partial}{\partial x}\left(D_0\frac{d\ln\gamma}{d\ln q}\frac{\partial q}{\partial x}\right). \tag{10}$$

To solve this problem, an expression for $d\ln\gamma/d\ln q$ is needed. Initially, we assumed

$$\frac{d\ln\gamma}{d\ln q} = \frac{1}{1-\gamma\,(q/q_s)} \tag{11}$$

analogous to a Langmuirian system but this did not give the correct concentration dependence behavior. After, some trial and error, the following expression was found to fit satisfactorily

$$\frac{d\ln\gamma}{d\ln q} = \frac{1}{1+\gamma\,(q/q_s)}. \tag{12}$$

The revised concentration dependent diffusivity model is

$$\begin{aligned}&\frac{\partial q}{\partial t} = \frac{\partial}{\partial x}\left(\frac{D_0}{1+\gamma\,(q/q_s)}\frac{\partial q}{\partial x}\right)\\ &q\,(\pm l, t) = q_s\\ &q\,(x, 0) = 0.\end{aligned} \tag{13}$$

Assuming $D_o$ is concentration independent, Fick's Second Law was normalized as follows

$$\begin{aligned}&\frac{\partial Q}{\partial \tau} = \frac{\partial}{\partial \eta}\left(\frac{1}{1+\lambda Q}\frac{\partial Q}{\partial \eta}\right)\\ &Q\,(1,\tau) = 1\\ &\frac{\partial Q}{\partial \eta}(0,\tau) = 0\\ &Q\,(\eta, 0) = 0\end{aligned} \tag{14}$$

where $Q = \frac{q}{q_o}$, $\tau = \frac{D_o t}{l^2}$, $\eta = \frac{x}{l}$, $q$ is the concentration inside the solid and $q_o$ is the concentration at the surface of the solid.

The fractional uptake is given by

$$\bar{Q} = \frac{M_t}{M_\infty} = \int_0^1 Q\,d\eta. \tag{15}$$

The orthogonal collocation method (8 orthogonal collocation points) was used to solve (14).

The model was applied for the diffusion tests in distilled water. The results of the model were compared with the experimental data in Fig. 4 for one of the epoxy adhesive specimens. As seen in the figure, a good agreement was observed between the Fickian model solved numerically and the experimental data. The corrected diffusivity ($D_o$) and the activity parameter $\gamma$ were calculated to be about $8.0 \times 10^{-10}$

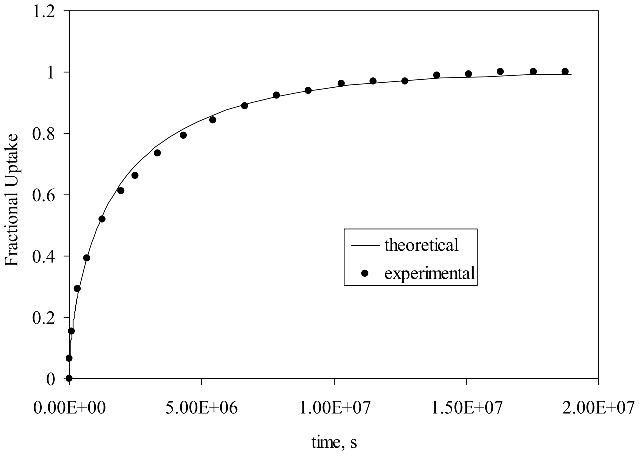

**Fig. 4** Theoretical and experimental plots of the fractional diffusant uptake ($M_t/M_\infty$) vs. time for epoxy adhesive in distilled water

$cm^2/s$ and 0.8, respectively. It should be noted that the corrected diffusivity is concentration independent. The same value of $D_o$ also fitted well the experimental data for the other two specimens.

The activity parameter value of 0.8 represents an average value for this system. When $Q \rightarrow 0$ the diffusivity is high ($\approx 8.0 \times 10^{-10}$ $cm^2/s$) but as the system saturates the diffusivity decreases till at close to saturation ($Q \rightarrow 1$), $D \approx 4.44 \times 10^{-10}$ $cm^2/s$ which is quite similar to that measured by (2). This implies that the diffusivity decreases as the loading increases. A similar observation has been observed by Karger et al. (1983) for the diffusion of n-dodecane in NaX zeolite (Karger and Ruthven 1992).

The physical meaning of the activity parameter in (7) is not clear. It obviously represents the value of the activity in a mixture of moisture and epoxy adhesive and is thus an average value. This is because the diffusivity measured is for an integral step measurement from zero loading to saturation. To get the true activity coefficient variation with loading requires execution of a vapor phase study at varying relative humidities (RH) using differential step measurements, e.g. for a surface step change from 7 to 10% RH. As the experiments take 7 months, this may not be practical, due to the difficulty of maintaining the moisture relative humidity constant in the atmosphere.

Thermodynamics tells us (Smith et al. 2001)

$$\left(\frac{\partial \ln \gamma_i}{\partial p}\right)_{T,x} = \frac{\bar{V}_i^E}{RT} \tag{16}$$

implying that there appears to be a change in the excess volume of mixing of the moisture on entry into the adhesive. This is not an unreasonable result.

One factor not discussed is macropore diffusion due to steric hindrance (Karger and Ruthven 1992). The system was not considered to be a macropore controlled system due to the length of time of the experiments take.

## 5 Conclusions

Apparent diffusivity for epoxy adhesive was determined by two methods, one using the diffusion data at early times (at low loading) and the other using the data at large times (close to the saturation point). The apparent diffusivity values obtained through the method using the early data points are about twice those obtained through the method utilizing the data points at large diffusion times. Concentration dependency of the diffusivity was then considered as the third method of analysis by assuming a relation for concentration dependency. Good agreement was observed between the proposed Fickian model solved numerically and the experimental data.

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