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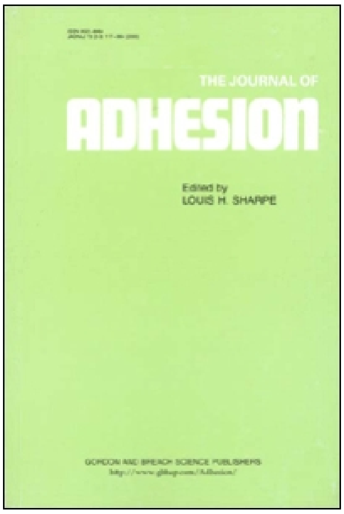

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Concentration Dependence of Moisture Diffusivity in Aluminum Particle Filled Epoxy Adhesive in Salt Solutions

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Moisture and aggressive ion ingress into bonded joints are primary causes of adhesive degradation. In this study, moisture diffusion behavior of aluminum-powder-filled epoxy adhesive was investigated through utilizing fluid immersion tests under complete immersion in salt solutions with varying NaCl concentrations. Aluminum powder is used in the adhesive for the purpose of improvement of its thermal properties, as demanded in a variety of industrial applications. Mass diffusivity for each specimen was determined by two methods, one using the diffusion data at early times (away from the saturation point) and the other using the data at large times (close to the saturation point). The results of the two methods were quite different, indicating that diffusivity is concentration dependent and a constant diffusivity assumption might lead to error in determining moisture diffusivity values in epoxy systems. Qualitatively, however, both methods indicated similar diffusion behavior. According to the results of both methods, the aluminum filler content did not affect the moisture diffusivity in the epoxy adhesive significantly but the effect of salt concentration was significant; the higher the salt content in the test solution, the higher the moisture diffusivity in the adhesive.

Keywords: Adhesive; Aluminum; Diffusion; Diffusivity; Epoxy; Filler; NaCl; Salt

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1. INTRODUCTION

The most common of the high-performance structural adhesives, especially in automotive and aircraft manufacture, are epoxies [1–4]. Epoxies are able to bond well to a variety of treated or untreated metal surfaces [5]. 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 [3].

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 (typically less than 0.5%) [2]. Epoxies are two-component systems that begin curing when mixed and generally require elevated temperatures to speed up the reaction to useful production times [3].

In a variety of industrial applications, epoxy adhesives are required to have enhanced thermal conductivity. The normal method for changing this physical property is to add to the epoxy a filler of higher conductivity than the continuous phase [2,6–14]. Alumina powder is a commonly used filler for improving the thermal conductivity of adhesives used as dielectrics (electrically insulative adhesives). Silver powder or flakes are commonly used to improve the thermal conductivity and attain electrical conductivity for adhesives intended to be an electrical path [6,15,16]. There are also several commercially available epoxy adhesives reinforced with other metal fillers such as aluminum powder.

Upon deleterious environmental exposures, durability of adhesive-bonded structural joints can be seriously influenced. Especially moisture and aggressive ion ingress into the bonded joint are primary causes of adhesive degradation by inducing changes in the physical properties of the adhesive, degrading the chemical bond between the adhesive and the metal, and/or inducing stresses in joints by nonuniform swelling of the adhesive [2,17–29]. The objectives of this project were to investigate the moisture diffusion behavior of aluminum-powder-filled epoxy adhesive under complete immersion in salt solutions with varying NaCl concentrations and also to investigate the validity of the constant diffusivity assumption (which is often used for moisture diffusion in epoxy systems) by determining the mass diffusivity by two methods, one using the diffusion data at short times (at low concentration of diffusant) and the other using the data at long times (close to the saturation point).

2. MATHEMATICAL FORMULATION

If diffusion is restricted to one dimension, such as is the case presented by a thin film of thickness l, where diffusion into the edges of the film can be ignored, application of the Fick's law with the assumptions of constant diffusivity and no swelling results in the following analytical equation for the amount of diffusant M_t taken up by the sheet in time, t[30]:

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

The uptake is considered to be a diffusion process controlled by a constant diffusion coefficient, D, and M_∞ is the equilibrium sorption attained theoretically after an infinite time. The value of D can be deduced from an observation of the initial gradient of a graph of M_t/M_∞ 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_∞ as much as about 50%. That is, at short times, where M_t/M_∞ is less than 0.5, Equation (1) can be approximated by the following [30]:

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

Another form of equation describing sorption and desorption (for the same boundary conditions) is [30]

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

This equation is more suitable for moderate and long times at which it can be approximated by the following:

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

that is, at long 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 (Erie, PA, USA). The adhesive is prepared by mixing equal volumes of the resin and hardener parts as specified by the manufacturer. The mixed

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adhesive cures fully in 24–48 h at room temperature with handling strength in about 8 h.

The aluminum powder used for filling the epoxy adhesive was obtained from Allied Britannia Limited (Leamington Spa, UK). The Al particles were spherical/roundish with sizes smaller than 50 μm in diameter.

Four different aluminum filler contents (0, 10, 25 and 50 wt%) were studied. The adhesive sheets ($30 \times 30 \times 1\,mm^3$) for the moisture diffusion tests were molded between waxed-paper-covered metal sheets. The following procedure was used.

1. Aluminum metal sheets of 3 cm by 8 cm and aluminum metal strips of 0.7 cm by 4 cm with a thickness of 1 mm were prepared.
2. The metal sheets were covered with waxed paper.
3. Epoxy adhesive was mixed with 0, 10, 25, and 50 wt% aluminum powder.
4. Two metal strips were placed at the edges of a waxed-paper-covered metal and the adhesive was spread on the surface to a thickness of about 1 mm.
5. Another waxed-paper-covered metal sheet was placed on the top to mold the adhesive specimen, and the metal sheets were clamped.
6. Excess amount of adhesive at the sides of the metal sheets was removed.
7. After 24 h the clamp was removed, and the sample was cut into 3 cm by 3 cm pieces using a sharp knife.

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Three pieces of each particular adhesive were immersed in a solution for several months at room temperature (23 ± 2°C). Five test solutions were used in the investigation: distilled water and sodium chloride solutions at 100 ppm, 1000 ppm, 0.5 M, and 1.0 M concentrations. The test specimens were suspended/immersed in the test fluids 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 fluid, surface water was dried with clean tissue, and the specimens were weighed using an analytical balance.

4. RESULTS AND DISCUSSION

Figures 1–5 present plots of diffusant intake vs. immersion time in each of the five test solutions for epoxy adhesive with four different aluminum-filler contents. The diffusion tests lasted almost a year, in which the diffusion in all the test specimens reached equilibrium. In

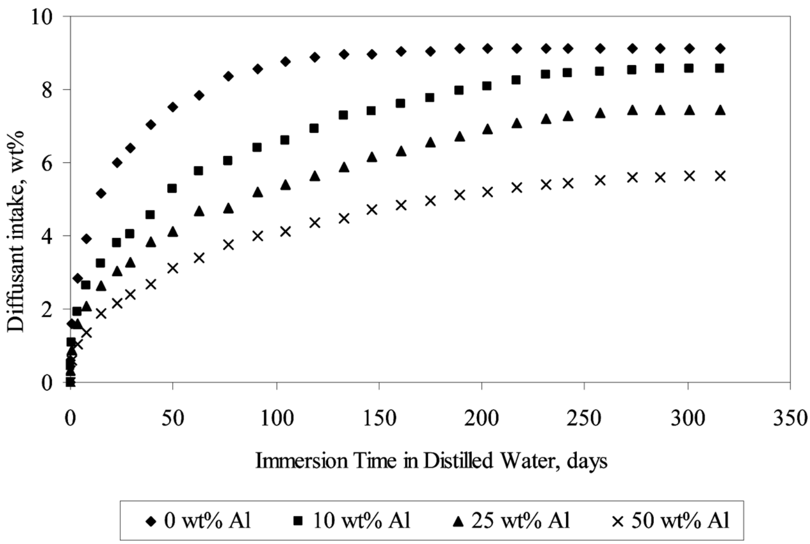

FIGURE 1 Diffusant intake (relative to the original weight of the specimen) *vs.* immersion time in distilled water for epoxy adhesive with four different aluminum-filler contents.

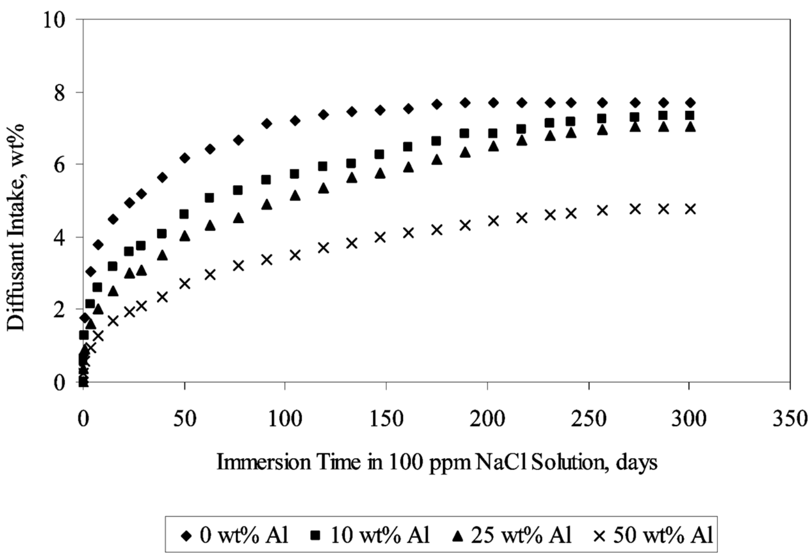

FIGURE 2 Diffusant intake (relative to the original weight of the specimen) *vs.* immersion time in 100 ppm sodium chloride solution for epoxy adhesive with four different aluminum-filler contents.

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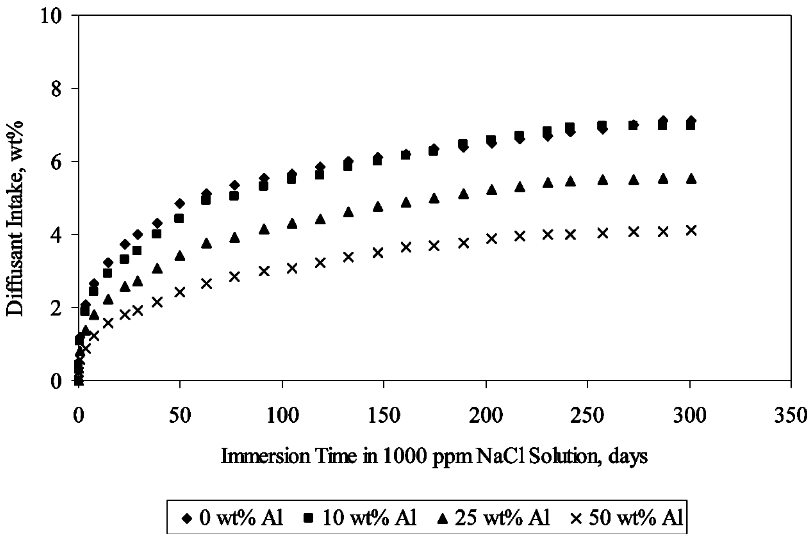

FIGURE 3 Diffusant intake (relative to the original weight of the specimen) *vs.* immersion time in 1000 ppm sodium chloride solution for epoxy adhesive with four different aluminum-filler contents.

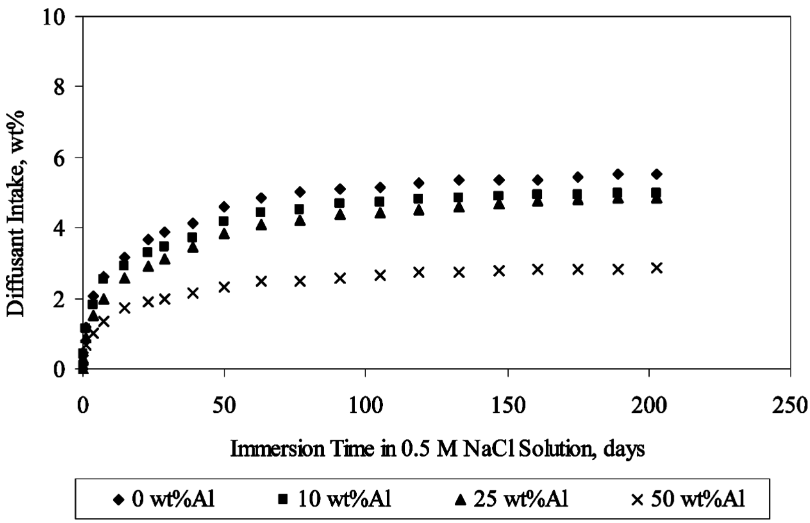

FIGURE 4 Diffusant intake (relative to the original weight of the specimen) *vs.* immersion time in 0.5 M sodium chloride solution for epoxy adhesive with four different aluminum-filler contents.

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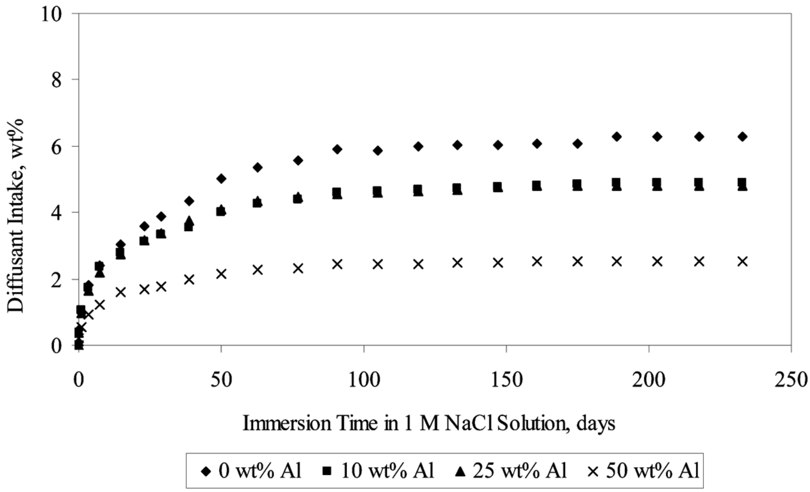

FIGURE 5 Diffusant intake (relative to the original weight of the specimen) *vs.* immersion time in 1 M sodium chloride solution for epoxy adhesive with four different aluminum filler contents.

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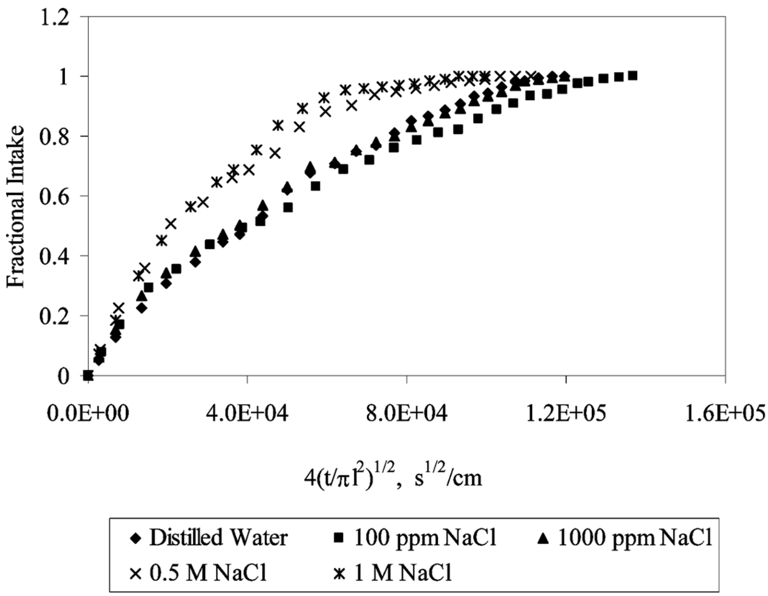

FIGURE 6 Representative plots of fractional uptake (M_t/M_∞) *vs.* $4(t/\pi l^2)^{1/2}$ for epoxy adhesive with 10 wt% aluminum-filler content in five different test solutions.

general, diffusant intake decreases as the aluminum-filler content increases, which is reasonable because aluminum filler incorporation in the adhesive decreases the available volume for moisture sorption. Comparison of the diffusion curves in these figures also shows that the adhesives adsorb a larger amount of water upon exposure to distilled water than when exposed to different sodium chloride solutions. The higher the concentration of the NaCl solution, the less water adsorbed by the adhesives. This situation is explained by the reverse osmosis mechanism [2].

Diffusivities of moisture in epoxy adhesive specimens with different filler contents in five different test solutions were determined by these two methods. In Method 1 (by use of Equation 2), M_t/M_∞ (where M_t and M_∞ are the amounts of moisture intake in time t and at saturation, respectively) is plotted against $4(t/\pi l^2)^{1/2}$, and the apparent diffusivity is determined from the initial slope of the plot (first four points) (slope is $D^{1/2}$). Representative plots are presented in Figure 6.

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TABLE 1 Apparent Diffusivities of Moisture in Aluminum-Powder-Filled Epoxy Adhesive Specimens in NaCl Solutions as Determined by Two Different Methods (by Use of Equations 2 and 4)

		Diffusivity (10^{-10} cm^2/s)	
Test solution	Aluminum filler content (wt%)	From Equation 2	From Equation 4
Distilled water	0	4.3 ± 0.7	2.0 ± 0.3
	10	2.9 ± 0.5	1.2 ± 0.1
	25	2.5 ± 0.3	0.9 ± 0.1
	50	3.4 ± 0.4	1.4 ± 0.2
100 ppm NaCl solution	0	4.0 ± 0.8	1.0 ± 0.2
	10	3.0 ± 0.7	1.0 ± 0.2
	25	2.0 ± 0.5	1.0 ± 0.1
	50	2.6 ± 0.9	1.5 ± 0.2
1000 ppm NaCl solution	0	4.8 ± 0.9	1.5 ± 0.1
	10	2.9 ± 0.8	1.4 ± 0.4
	25	1.8 ± 0.4	0.9 ± 0.1
	50	3.0 ± 1.1	1.2 ± 0.3
0.5 M NaCl solution	0	6.4 ± 0.5	2.1 ± 0.2
	10	6.6 ± 0.1	2.1 ± 0.2
	25	6.8 ± 0.1	2.2 ± 0.2
	50	8.4 ± 1.6	2.7 ± 0.1
1 M NaCl solution	0	6.0 ± 0.4	2.3 ± 0.6
	10	7.1 ± 0.2	2.6 ± 0.3
	25	7.8 ± 0.4	3.0 ± 0.1
	50	10.2 ± 0.5	3.3 ± 0.1

The apparent diffusivities are given in Table 1 for three specimens in each case (for four different aluminum-filler contents in five test solutions).

Apparent diffusivities were also determined by the second method (by use of Equation 4) in which $\ln(1 - M_t/M_\infty)$ is plotted against $\pi^2 t/l^2$ and the diffusivity is determined from the slope of the straight line at long times (ranges between -1 and -4 in the y-axis) (slope is $-D$). Representative plots are presented in Figure 7. The resulting apparent diffusivities are also included in Table 1.

Qualitatively, similar results were obtained in both methods. The diffusivity values presented in Table 1 do not show a significant trend for the effect of aluminum-filler content on the apparent moisture diffusivity in epoxy adhesive specimens, with some scatter in the data. On the other hand, the effect on apparent moisture diffusivity by the salt concentration of the test solution is significant. The rate of diffusion was faster in the test solutions with high salt content (0.5 M and 1 M salt solutions) than in those with low or no salt content (distilled water, 100 ppm and 1000 ppm salt solutions). Apparent diffusivity values ranged from about $3 \times 10^{-10}\,cm^2/s$ in distilled water to about $1 \times 10^{-9}\,cm^2/s$ in 1 M NaCl solution. It is believed that concentrated salt

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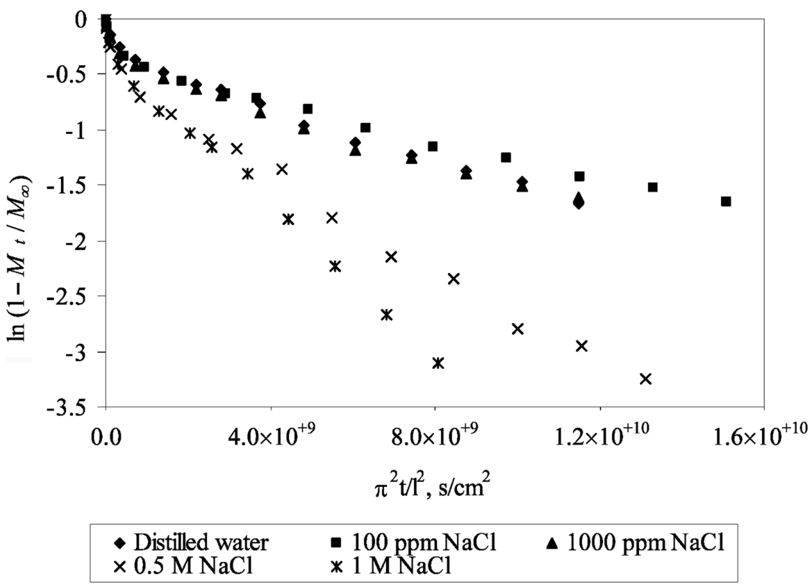

FIGURE 7 Representative plots of $\ln(1 - M_t/M_\infty)$ *vs.* $\pi^2 t/l^2$ for epoxy adhesive with 10 wt% aluminum-filler content in five different test solutions.

solutions somehow enhance the formation of microcavities in adhesive materials [20], thereby increasing the rate of moisture diffusion.

Quantitatively, however, the results of the two methods were different. The apparent diffusivity values obtained through Method 1 (at short times) were about twice those obtained through Method 2 (at long times). It is clear that diffusivity is concentration dependent and that it decreases with diffusant concentration as the diffusion progresses to saturation. The future plan on this work is to model moisture diffusion into aluminum-powder-filled epoxy adhesive considering concentration dependency of diffusivity in Fick's law.

5. CONCLUSIONS

Mass diffusivity for aluminum-powder-filled epoxy adhesive immersed in salt solutions with varying concentrations was determined by two methods, one using the diffusion data at short times (away from the saturation point) and the other using the data at long times (close to the saturation point). It took about a year for the 1-mm-thick diffusion specimens to reach saturation. Significant difference between the results of the two methods indicated that diffusivity is concentration dependent. The method using the data at long times resulted in lower diffusivity values, meaning that the diffusivity is a decreasing function of concentration. Hence, it can be stated that constant diffusivity assumption might lead to error in quantifying moisture diffusion in epoxy systems using Fick's law. Qualitatively, however, both methods indicated similar diffusion behavior. Mass diffusivity was determined to be proportional to NaCl concentration but independent of aluminum-filler content by both methods.

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