

Effects of the Aluminum Filler Content on Moisture Diffusion into Epoxy Adhesives in Distilled Water and Sea Water

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Received 7 July 2004; accepted 20 January 2005

DOI 10.1002/app.22122

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Epoxies are the most common of high-performance structural adhesives, especially in automotive and aircraft manufacturing. In a variety of industrial applications, epoxy adhesives are required to have enhanced thermal conductivity. The normal method of changing this property is to add to the epoxy a filler of higher conductivity than the continuous phase. Although the improvement in the thermal properties of adhesives by the addition of metal fillers is obvious, their influence on water sorption characteristics of adhesives is not clear. It was the objective of this study to shed light on these aspects, which are lacking in the literature. The emphasis was placed on determining the moisture sorption behavior of aluminum-powder-filled epoxy adhesives under complete immersion in distilled water

and sea water. Moisture diffusion tests show that the addition of aluminum filler into epoxy decreases the total amount of water intake at saturation in both fluids. However, there appears to be no significant effect of the aluminum filler content on the moisture diffusivity in epoxy adhesive specimens in either distilled water or seawater. It has also been determined that the adhesives adsorb a larger amount of water upon exposure to distilled water than when exposed to seawater, whereas the moisture diffusion rate in the adhesive immersed in seawater is higher than that in distilled water. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1165–1171, 2005

Key words: adhesives; diffusion; fillers

INTRODUCTION

There is a growth of interest in the application of adhesive bonding for the production of structural joints. Some advantages of adhesive bonding over common mechanical joining techniques such as riveting and welding are lightness, neatness, simpler design, increased fatigue and corrosion resistance, and reduced costs.^{1–3}

The perfect adhesive that 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 high-performance structural adhesives, especially in automotive and aircraft manufacturing, are epoxies.^{1,4–6} Many spot-welded automotive parts are being replaced by adhesive-bonded components because of the difficulties encountered in welding galvanized or coated steels.⁴ Adhesives also help to isolate dissimilar metals or galvanized steel from ungalvanized steel. In this way, they help reduce the danger of galvanic corrosion;⁷ this is an increasingly important function as specialty metals and coatings become more com-

mon in automobile bodies. Epoxies are able to bond well to a variety of treated or untreated metal surfaces.⁸ In aircraft manufacturing, 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.⁵

Epoxy resins are attractive for metal-bonding adhesive systems because of their ability to cure without producing volatile byproducts and their low shrinkage upon curing (<0.5%).⁴ Epoxies are two-component systems that begin curing when mixed and generally require elevated temperatures to speed up the reaction to useful production times.⁵

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.^{4,9–17} By the incorporation of fillers into the adhesive, the resin content (and thus the cost) is also reduced.

Achieving improved thermal conductivity is dependent on the filler selection and loading level. The filler type, size, shape, and volume fraction determine the adhesive thermal conductance. The factor increases with an increasing volume fraction of the filler, and high-aspect-ratio particles increase thermal conductivity more effectively than spherical particles. Theoretically,

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Contract grant sponsor: King Fahd University of Petroleum and Minerals; contract grant number: SAB-2001/08.

cally, the thermal conductivity of the filler is not an important variable, except when it is within a factor of 10 of the thermal conductivity of the polymeric matrix (adhesive). Most metal fillers have thermal conductivities greater than 10 times the matrix thermal conductivity.⁹

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.^{9,18,19} The filler level must be sufficiently high to achieve point-to-point contact before electrical conductivity is attained.⁹ However, too high a filler content might cause a degradation in the mechanical properties of the adhesive.¹⁷ There are also several commercially available epoxy adhesives reinforced with other metal fillers such as aluminum powder.

Upon deleterious environmental exposure, the durability of adhesive-bonded structural joints can be seriously influenced. In particular, moisture and aggressive ion ingress into the bonded joint are the primary causes of adhesive bond degradation.^{4,20–31} 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, degrading the chemical bond between the adhesive and the metal, and/or inducing stresses in joints by nonuniform swelling of the adhesive.^{27,29,30,32}

Although the improvement in the thermal properties of adhesives by the addition of metal fillers is obvious,^{9–13} their influence on water sorption characteristics of adhesives is not clear. It was the objective of this study to shed light on these aspects, which are lacking in the literature. The emphasis was placed on determining the moisture sorption behavior of aluminum-powder-filled epoxy adhesives under complete immersion in distilled water and seawater.

MATHEMATICAL FORMULATION

If diffusion is restricted to one dimension, such as is the case presented by a thin film of thickness l adsorbing a fluid according to Fick's law, where diffusion into the edges of the film can be ignored, the amount of diffusant taken up by the sheet in time t (M_t) can be obtained by³³

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

The uptake is considered to be a diffusion process controlled by a constant diffusion coefficient (D), and

M_∞ is the equilibrium sorption attained theoretically after infinite time. Equation (1), with a suitable interpretation of M_t and M_∞ , also describes desorption from the same sheet, initially conditioned to a uniform concentration, whose surface concentrations are instantaneously brought to some lower value or zero at $t = 0$. 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 constant D , the graph for a sorption experiment is a straight line, within the normal limits of experimental error, for M_t/M_∞ as high as about 50%. That is, at short times, at which M_t/M_∞ is less than 0.5, eq. (1) can be approximated by the following:³³

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

Although analytical methods for obtaining expressions for the sorption rate from Fick's equations are not possible when D is a function of the concentration, eq. (2) can be used as an initial sorption law but with D substituted by \bar{D} , where \bar{D} represents some kind of average diffusion coefficient. It turns out, however, that eq. (2) holds up to higher values of M_t/M_∞ when D increases with the concentration, whereas for D decreasing with increasing concentration, M_t/M_∞ is only proportional to $t^{1/2}$ over the very initial region of the sorption.³³

EXPERIMENTAL

Materials

The epoxy adhesive used in this investigation was a general-purpose, two-part epoxy (Fusor 309) obtained from Lord Corp., Erie, PA. The adhesive was prepared by the mixing of equal volumes of the resin and hardener parts. The mixed adhesive cured 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 Ltd., Leamington Spa, UK. The Al particles were spherical and roundish and smaller than 50 μm in diameter.

Diffusion tests

The adhesive sheets ($30 \times 30 \times 1 \text{ mm}^3$) for the moisture diffusion tests were molded between wax-covered metal sheets. Four different aluminum filler contents (0, 10, 25, and 50 wt %) were studied. Three pieces of each particular adhesive were immersed in distilled water and seawater for several months at room temperature.

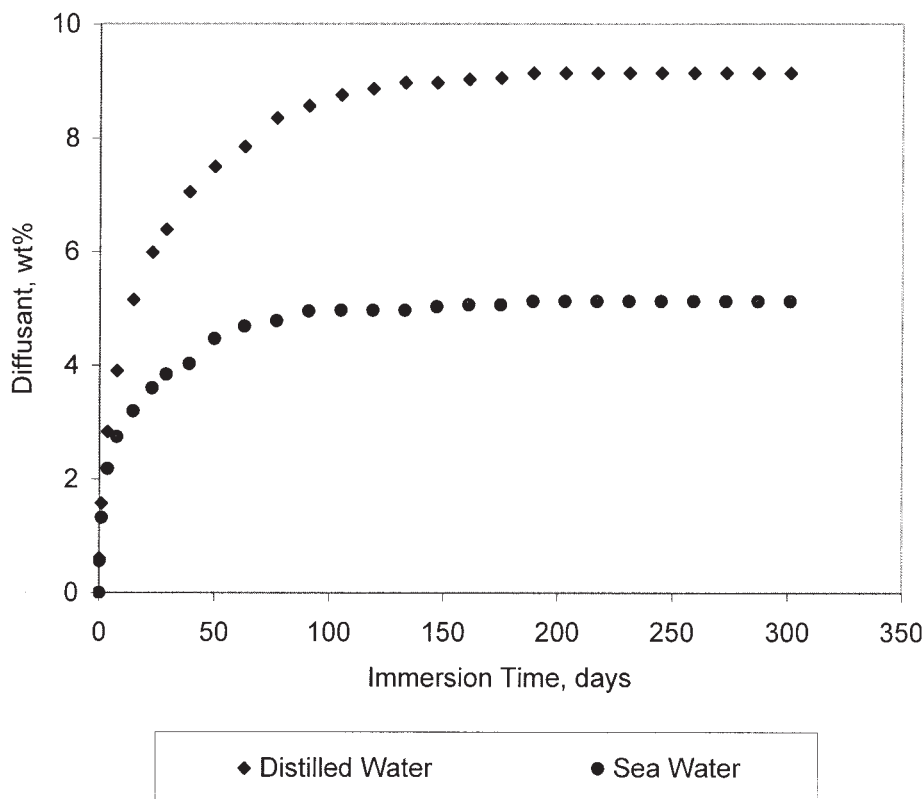


Figure 1 Diffusant intake (with respect to the original weight of the specimen) versus the immersion time in distilled water and seawater for an epoxy adhesive with no filler content.

All test specimens were suspended/immersed in the test fluids without 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, dried with clean tissue, and weighed with an analytical balance with precision to 0.0001 g.

RESULTS AND DISCUSSION

The moisture diffusion experiments lasted about 10 months, during which the diffusion in almost all the test specimens reached equilibrium. Plots of the moisture uptake versus the immersion time in distilled water and seawater for epoxy adhesive specimens with four different aluminum filler contents (0, 10, 25, and 50 wt %) are presented in Figures 1–4. The diffusion curves in these figures show that the adhesives adsorb a larger amount of water upon exposure to distilled water than when exposed to seawater. This situation may be explained by the reverse osmosis mechanism.⁴ When water is adsorbed by the adhesive from the bulk solution, an electrolyte is produced upon the dissolution of the internal water-soluble substances (inorganic fillers). Because of osmosis, water from the bulk solution is driven into the adhesive matrix to dilute the electrolyte. However, when the bulk sodium chloride solution is more concentrated

than the electrolyte produced inside the adhesive matrix, reverse osmosis occurs. The adsorbed water is driven out of the adhesive matrix during reverse osmosis; this balances the concentration difference between the internal electrolyte and the bulk NaCl solution. As a result, the amount of water adsorbed in the adhesive decreases with the concentration of the bulk NaCl solution (seawater in this case).

Figures 5 and 6 present plots of the moisture intake versus the immersion time in distilled water and sea water, respectively, for epoxy adhesives with four different aluminum filler contents. In general, the diffusant uptake decreases as the aluminum filler content increases. This is reasonable because aluminum filler incorporation in the adhesive is expected to reduce the available volume for water uptake.

The diffusivities of moisture in epoxy adhesive specimens with different filler contents in five different test solutions were determined with eq. (2). As discussed earlier, 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 diffusivity is determined from the initial slope of the plot (the slope is $D^{1/2}$). The apparent diffusivities are presented in Figure 7. The results do not show a significant trend for the effect of the aluminum filler content on the apparent moisture diffusivity in epoxy adhesive specimens, with some scattering in the data. On the other hand, the rate of diffusion

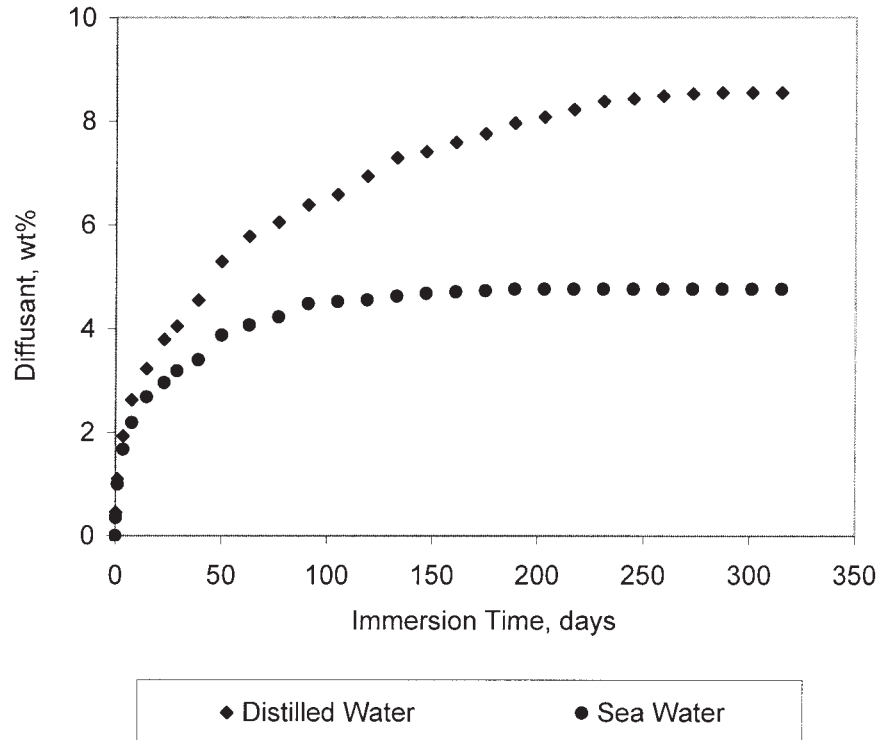


Figure 2 Diffusant intake (with respect to the original weight of the specimen) versus the immersion time in distilled water and seawater for an epoxy adhesive with 10 wt % Al filler.

was higher in sea water than in distilled water. The diffusivity values ranged from about $3 \times 10^{-10} \text{ cm}^2/\text{s}$ in distilled water to about $8 \times 10^{-10} \text{ cm}^2/\text{s}$ in sea water. It

is believed that salt in sea water somehow enhances the formation of microcavities in adhesive materials,²³ thereby increasing the rate of moisture diffusion.

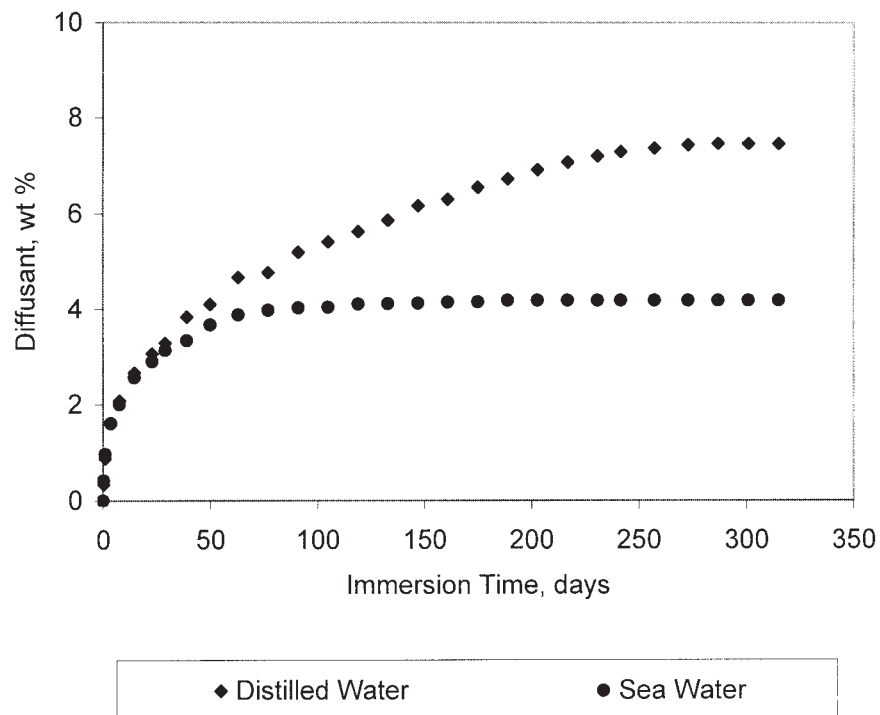


Figure 3 Moisture intake (with respect to the original weight of the specimen) versus the immersion time in distilled water and seawater for an epoxy adhesive with 25 wt % Al filler.

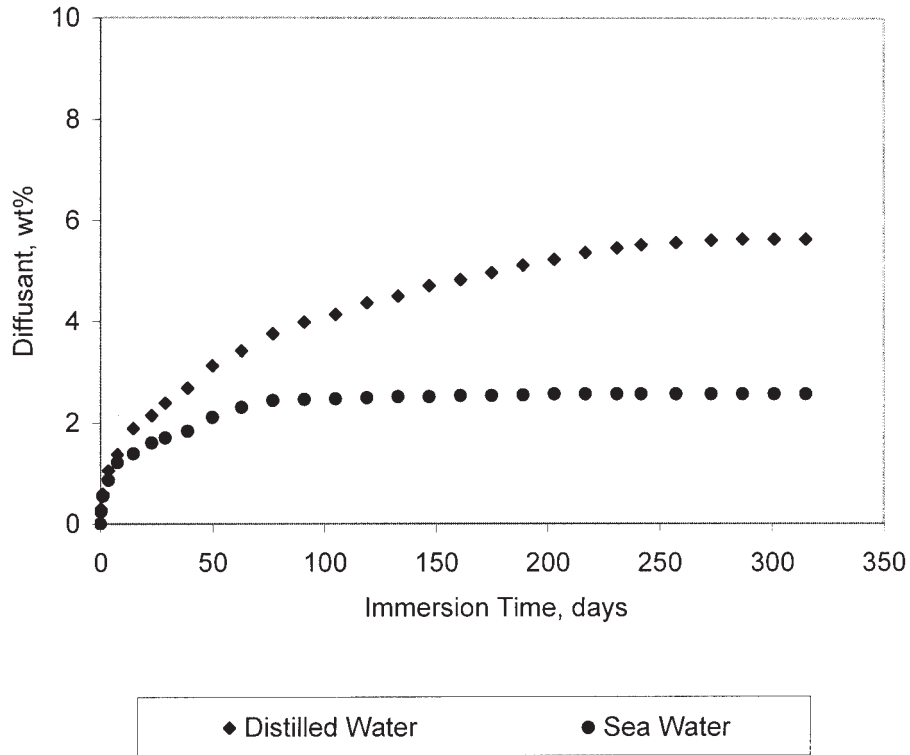


Figure 4 Diffusant intake (with respect to the original weight of the specimen) versus the immersion time in distilled water and seawater for an epoxy adhesive with 50 wt % Al filler.

These results indicate that incorporating as much as 50 wt % aluminum filler into the epoxy adhesive does not enhance moisture diffusion into the adhesive. This

is a promising result for the use of aluminum powder in an epoxy adhesive without an adverse affect on the moisture sorption characteristics of the adhesive. In

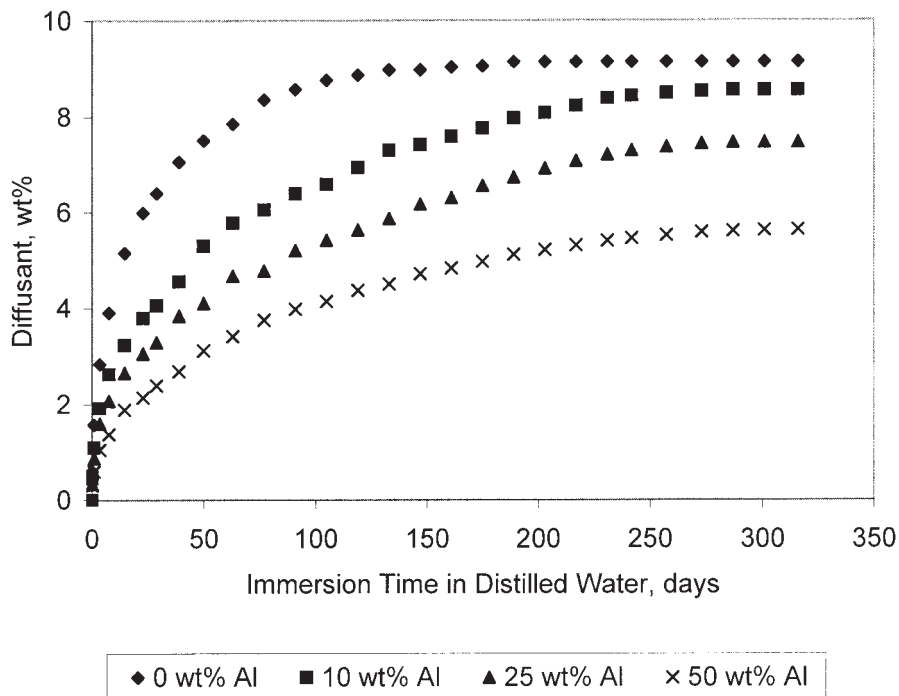


Figure 5 Diffusant intake (with respect to the original weight of the specimen) versus the immersion time in distilled water for an epoxy adhesive with four different aluminum filler contents.

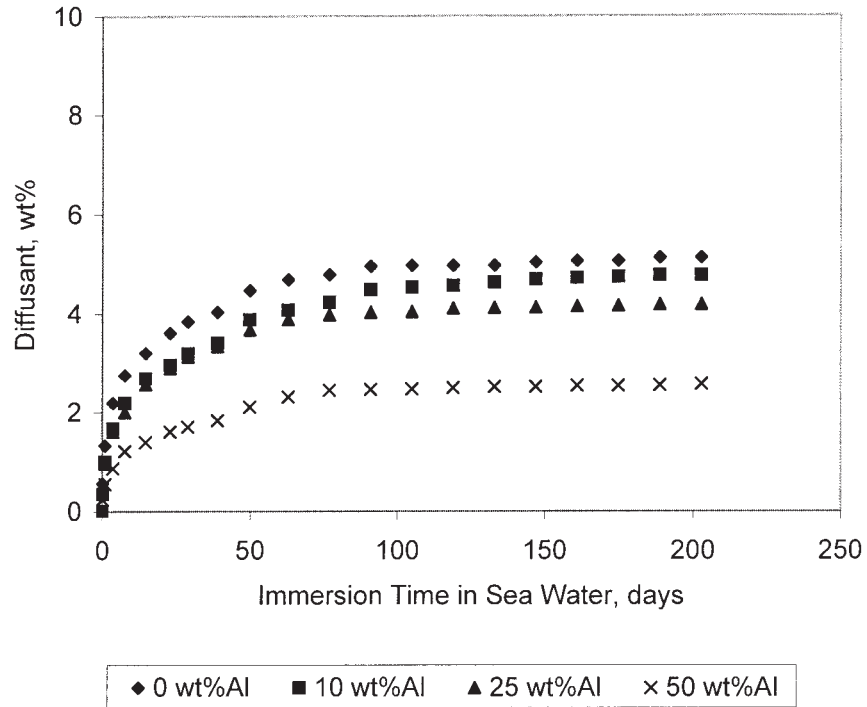


Figure 6 Diffusant intake (with respect to the original weight of the specimen) versus the immersion time in seawater for an epoxy adhesive with four different aluminum filler contents.

most applications, the epoxy-based components have the potential of being exposed to moist conditions or a humid environment, and adsorbed moisture has deleterious effects on the physical properties of epoxies and can, therefore, greatly compromise the performance of an epoxy-based component.

CONCLUSIONS

The followings can be concluded from the findings of this study.

In general, the moisture intake decreases as the aluminum filler content increases. This is reasonable

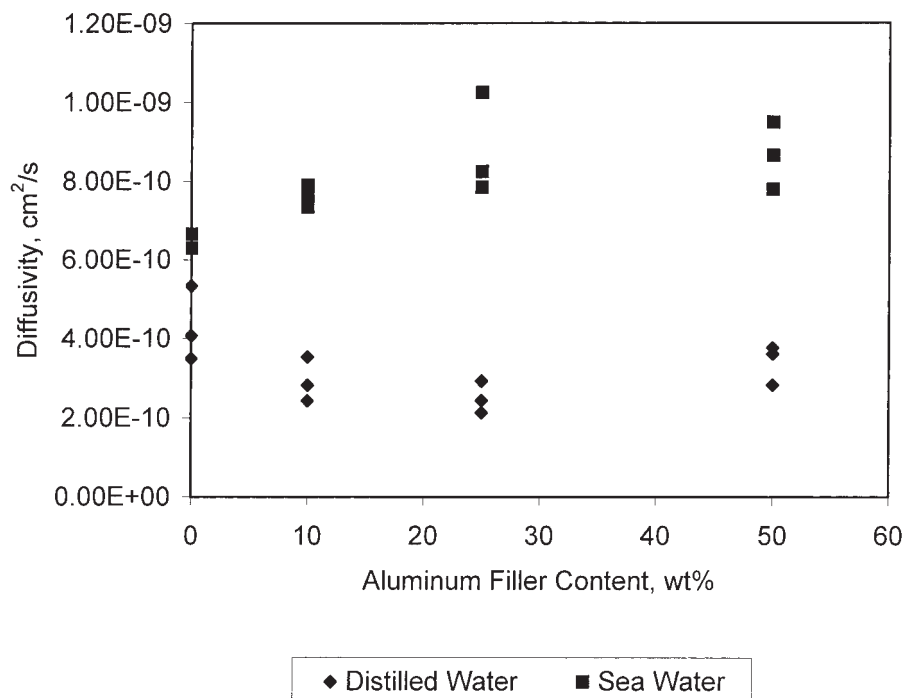


Figure 7 Diffusivity of moisture in epoxy in distilled water and sea water versus the aluminum filler content in the adhesive.

because aluminum filler incorporation in the adhesive decreases the available volume for water diffusion.

The adhesives adsorb a larger amount of water upon exposure to distilled water than when exposed to sea water with a high salt content.

The aluminum filler content does not affect the moisture diffusion rate in an epoxy adhesive significantly, but the effect of the salt content is significant. The rate of diffusion is higher in sea water than in distilled water. The diffusivity values were determined to be about 3×10^{-10} cm²/s in distilled water and about 8×10^{-10} cm²/s in sea water.

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