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Moisture diffusion into aluminum powder-filled epoxy adhesive in sodium chloride solutions

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Abstract

The objective of this study was to shed light on the influence of metal fillers on water/moisture sorption characteristics of adhesives. For that purpose, epoxy adhesive was filled by aluminum powder at four different contents (0, 10, 25 and 50 wt%). Water and fluid immersion tests were utilized to determine the moisture sorption behavior of aluminum powder-filled epoxy adhesive under complete immersion in distilled water and NaCl solutions. It was observed that the adhesives adsorb a larger amount of water upon exposure to distilled water than when exposed to different sodium chloride solutions. The moisture diffusion rate in the adhesive immersed in a test solution is, however, proportional to the salt concentration of the solution. It was also determined that there is no significant effect of aluminum filler content on moisture diffusivity in epoxy adhesive specimens while the addition of aluminum filler into epoxy decreases the total amount of water intake at saturation.

Keywords: Adhesive; Epoxy; Metal filler; Aluminum powder; Diffusion; Diffusivity; Sodium chloride

1. 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 the common mechanical joining techniques such as riveting and welding are lightness, neatness, simpler design, increased fatigue and corrosion resistance, and reduced costs [1–3].

One of the important points to consider when bonding metals is that adhesives are active only on the top molecular layer. In most cases, the base metal is very reactive and forms various oxides, sulfides and hydrates when exposed to the atmosphere. As a result, it is necessary to consider the ability of the adhesive to bond not only the metal itself but also its oxide, as well as the inherent nature of the adhesive force between the base metal and its oxide [4].

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 [1,5–7]. Many spot-welded automotive parts are being replaced by adhesive-bonded components because of the difficulties encountered in welding of galvanized or coated steels [5]. Adhesives also help to isolate dissimilar metals, or galvanized from ungalvanized steel. In this way they help to reduce the danger of galvanic corrosion [8]—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 [9]. 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 [6].

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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%) [5]. Epoxies are two component systems that begin curing when mixed and generally require elevated temperatures to speed up the reaction to useful production times [6].

In a variety of industrial applications epoxy adhesives are required to have an 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 [5,10–18]. 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 filler selection and loading level. Filler type, size, shape and volume fraction determine the adhesive thermal conductance. The factor increases with increasing volume fraction of filler and high aspect-ratio particles increase thermal conductivity more effectively than spherical particles. Theoretically, 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 [10].

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 [10,19,20]. The filler level must be sufficiently high to achieve point-to-point contact before electrical conductivity is attained [10]. However, too high filler content might cause a degradation in mechanical properties of the adhesive [18]. 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 bond degradation [5,21–32]. 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 [28,30,31,33].

While the improvement on thermal properties of adhesives by addition of metal fillers is obvious [10–14], 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 upon determining the moisture sorption behavior of aluminum powder filled epoxy adhesive under complete immersion in distilled water and in NaCl solutions.

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, M_t, taken up by the sheet in a time, t, can be given by [34]

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

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 infinite time. Eq. (1), with 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 deducted 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 percent. That is, at short times, where M_t/M_∞ is less than 0.5, Eq. (1) can be approximated by the following [34]:

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

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 $\overline{D}$ where $\overline{D}$ represents some kind of average diffusion coefficient. It turns out, however, that Eq. (2) holds up to higher values of M_t/M_∞ when the diffusion coefficient increases with concentration, while for D decreasing with increasing concentration, M_t/M_∞ is only proportional to $t^{1/2}$ over the very initial region of the sorption [34].

2. Experimental

2.1. Materials

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 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. The Al particles were spherical/roundish with size smaller than 50 μm in diameter.

2.2. *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 a solution for several months at room temperature.

Five test solutions were used in the investigation: (1) distilled water; (2) 100 ppm sodium chloride solution; (3) 1000 ppm sodium chloride solution; (4) 0.5 M sodium chloride solution; (5) 1.0 M sodium chloride solution.

All test specimens were suspended/immersed in the test solutions without making contact with each other. The test solutions were covered with aluminum foil to prevent moisture evaporation. At various time intervals, test specimens were removed from the solution, dried with clean tissue and weighed by an analytical balance with precision to 0.0001 g.

3. Results and discussion

Moisture diffusion experiments lasted about 10 months in which almost the diffusion in all the test specimens reached equilibrium. Plots of moisture uptake vs. immersion time in various solutions for epoxy adhesive specimens with four different aluminum filler contents (0, 10, 25 and 50 wt%) are presented in Figs. 1–4. Diffusion curves in these figures show 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 may be explained by the reverse osmosis mechanism [5]. When water is adsorbed by the adhesive from the bulk solution, an electrolyte is produced upon 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, in the cases where 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, therefore balancing 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.

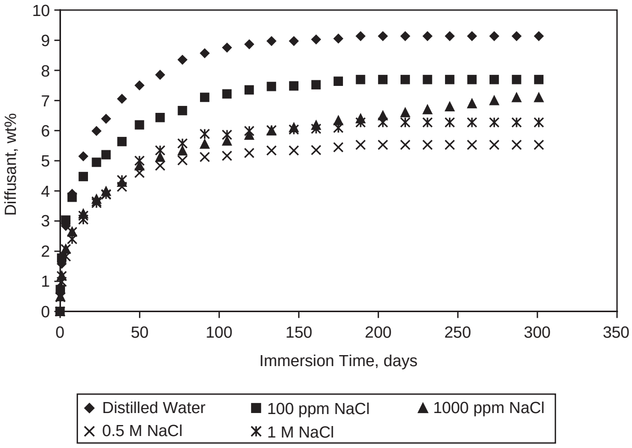

Fig. 1. Diffusant intake (relative to the original weight of the specimen) vs. immersion time in various test solutions for epoxy adhesive with no filler content.

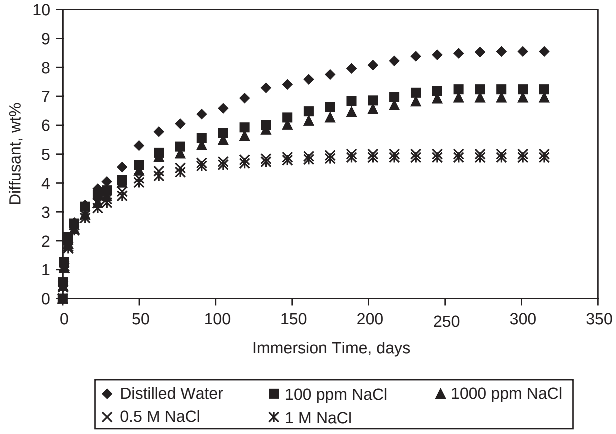

Fig. 2. Diffusant intake (relative to the original weight of the specimen) vs. immersion time in various test solutions for epoxy adhesive with 10 wt% Al filler content.

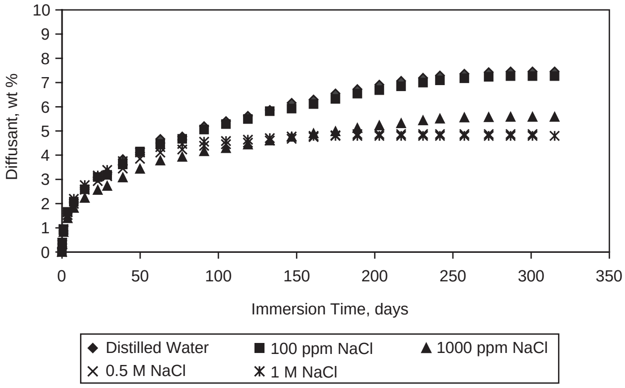

Fig. 3. Moisture intake (relative to the original weight of the specimen) vs. immersion time in various test solutions for epoxy adhesive with 25 wt% Al filler content.

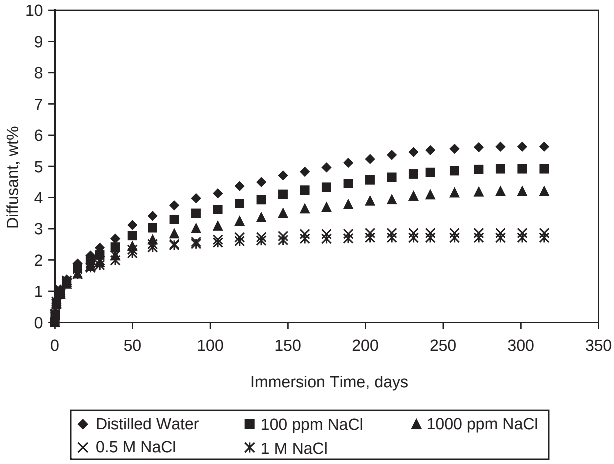

Fig. 4. Diffusant intake (relative to the original weight of the specimen) vs. immersion time in various test solutions for epoxy adhesive with 50 wt% Al filler content.

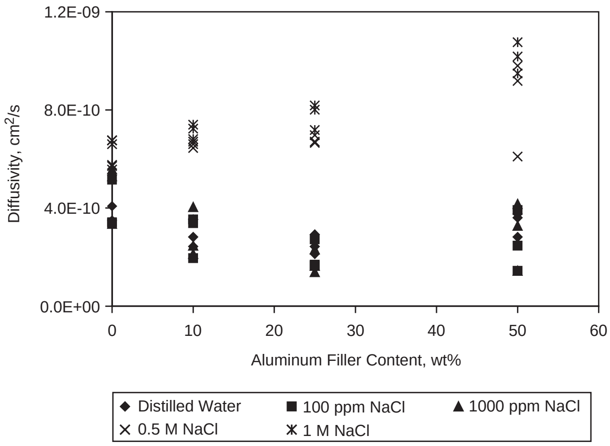

Fig. 5. Diffusivity of moisture in epoxy adhesive vs. aluminum filler content in the adhesive in various test solutions.

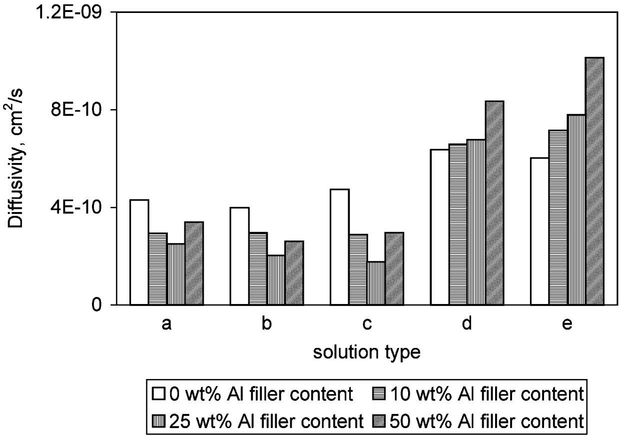

Fig. 6. Diffusivity of moisture in epoxy adhesive with various aluminum filler contents in different test solutions: (a) distilled water, (b) 100 ppm NaCl solution, (c) 1000 ppm NaCl solution, (d) 0.5 M NaCl solution and (e) 1 M NaCl solution.

If Figs. 1–4 are compared, it is also seen that in general diffusant uptake decreases as the aluminum filler content increases. This is reasonable because aluminum filler incorporation in the adhesive decreases the available volume for water uptake.

Diffusivities of moisture in epoxy adhesive specimen with different filler contents in five different test solutions were determined by use of 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 (slope is $D^{1/2}$). The apparent diffusivities are presented in Fig. 5 (for each test solution for four different aluminum filler contents) and in Fig. 6 (for each aluminum filler content for five different test solutions).

The results do not show a significant trend for the effect of aluminum filler content on the apparent moisture diffusivity in epoxy adhesive specimens with some scattering in data. On the other hand, the effect on apparent moisture diffusivity by the salt concentration of the test solution is quite obvious. The rate of diffusion was higher in the test solutions with high salt content (0.5 and 1 M salt solutions) than in those with low salt content (distilled water, 100 and 1000 ppm salt solutions). Diffusivity values ranged from about $3\times10^{-10}\,\text{cm}^2/\text{s}$ in distilled water to about $8\times10^{-10}\,\text{cm}^2/\text{s}$ in 1 M salt solution. It is believed that concentrated salt solutions somehow enhance the formation of microcavities in adhesive materials [24], thereby increasing the rate of moisture diffusion. Diffusivity values as low as $2.18\times10^{-13}\,\text{cm}^2/\text{s}$ [35] and as high as $2.6\times10^{-9}\,\text{cm}^2/\text{s}$ [36] are reported in literature for diffusion of water in epoxy.

The above results indicate that incorporating as much as 50 wt% aluminum filler in the epoxy adhesive does not enhance moisture diffusion into the adhesive. This is a promising result for use of aluminum powder in the epoxy adhesive without adversely affecting its moisture sorption characteristics of the adhesive. It should be noted that in most applications the epoxy-based components has 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.

4. Conclusions

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

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 diffusant adsorbed by the adhesives. This situation is believed to be explained by the reverse osmosis mechanism.

In general, moisture intake decreases as the aluminum filler content increases. This is reasonable because aluminum filler incorporation in the adhesive decreases the available volume for water diffusion.

The aluminum filler content does not affect the moisture diffusion rate in epoxy adhesive significantly but the effect of salt concentration is significant, the higher the salt content in the test solution, the faster the moisture diffusion in the adhesive. Diffusivity values ranged from about $3 \times 10^{-10}\,\mathrm{cm}^2/\mathrm{s}$ in distilled water to about $8 \times 10^{-10}\,\mathrm{cm}^2/\mathrm{s}$ in 1 M salt solution.

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