

Liquid Diffusion into Epoxy Resin Composites

TEJRAJ M. AMINABHAVI, *Department of Chemistry, Karnatak University, Dharwad, India 580003*

Synopsis

Dynamic sorption behavior of four epoxy resin matrix composites derived from fly ash, jute, mica, or vermiculite was studied in water and salt solution at 24°, 35°, and 45°C. The mass of water uptake per mass of sample was determined as a function of time. Diffusion coefficients were higher for distilled water than those for salt solution. The diffusion parameters were computed from the Arrhenius plots and the results analyzed in terms of a Fickian model. The results as obtained from weight gain assays are consistent with the view that the activation energy of diffusion is associated with the energy required to produce a space of sufficient cross-section for the diffusing molecule to pass.

INTRODUCTION

High performance epoxy compounds have been used extensively as matrix materials in making composites.¹⁻⁷ For a successful application of these composites as structural materials, it is useful to know their long-term stability under service conditions. Severe degradation of properties obviously limit their applications and may even lead to unexpected structural failures causing potential loss of life. Despite innumerable research reports on diffusion properties of polymer films,⁸⁻¹⁰ there has been hardly any detailed study on the water diffusion through polymer composites.¹¹⁻¹⁴

The principal objective of this paper is to investigate the diffusion behavior of four different epoxy resin composites for distilled water and salt solution (3.5 wt% NaCl) at three temperatures (24°, 35°, and 45°C). A model developed by Shen and Springer and Loos^{15,16} has been used to predict the diffusion coefficients; activation energies for the process of diffusion were evaluated from the Arrhenius plots. Knowledge of these parameters together with diffusivity and solubility would be useful in considering the outdoor applications of the composites investigated.

EXPERIMENTAL

Specimen Preparation

The epoxy resin used was a Bakelite cycloaliphatic epoxide (ERL-4221) namely, 3,4-epoxyclohexylmethyl-3,4-epoxycyclohexane carboxylate (supplied courtesy of Union Carbide). A NIAX polyol (NIAX LHT-240) specifically, polypropylene oxide triol (m.w. 710) and hexahydrophthalic anhydride were, respectively, used as modifier and hardener. Four polymer composites with different filler systems and composites were prepared by the procedure out-

TABLE I
Data for Slope and Maximum Penetrant Absorption

Composite type	Slope (θ)						M_m (%)					
	Distilled water		Salt solution		Distilled water		Salt solution		Distilled water		Salt solution	
	24°C	35°C	24°C	35°C	24°C	35°C	24°C	35°C	24°C	35°C	24°C	35°C
Jute	4.99	5.82	6.69	5.02	5.76	6.57	12.42	13.80	15.00	14.10	15.01	16.02
Fly ash	4.26	5.37	6.42	5.55	6.25	7.16	11.21	13.20	14.60	15.01	15.82	16.90
Mica	2.93	3.59	4.36	3.29	3.85	4.61	9.11	10.10	11.08	10.45	11.30	12.21
Vermiculite	1.93	2.54	3.09	2.29	2.99	3.58	7.26	8.40	9.23	9.11	10.20	11.21

TABLE II
Diffusion Coefficients and Arrhenius Parameters

Composite type	$D \cdot 10^8$ (cm ² /s)						E_D (kJ/mol)					
	Distilled water		Salt solution		Distilled water		Salt solution		Distilled water		Salt solution	
	24°C	35°C	24°C	35°C	24°C	35°C	24°C	35°C	24°C	35°C	24°C	35°C
Jute	9.2	10.1	7.2	11.3	8.4	9.6	7.92 ± 0.15 ^a	10.96 ± 0.21	11.34 ± 0.14	11.90 ± 0.11	13.92 ± 0.14	17.53 ± 0.33
Fly ash	8.2	9.4	7.8	11.0	8.9	10.2	15.15 ± 0.12	17.41 ± 0.30	8.1	8.1	5.8	5.8
Mica	5.9	7.2	5.6	8.8	6.6	8.1	4.9	4.9	4.9	4.9	4.9	4.9
Vermiculite	4.0	5.2	3.6	6.4	4.9	5.8	4.9	4.9	4.9	4.9	4.9	4.9

^aStandard error at 95% confidence level.

lined previously;³ fillers used were fly ash, jute, vermiculite, and mica. In each case, a 15% resin-hardener mixture was used with 10% of silica and the 75% of the filler material. The resin-hardener and filler mixture with other ingredients, namely, silica was taken into a compression mold to form 2.5×2.5 cm and 0.5 cm thick composites. Pressures up to 2000 psi were used and samples were cured for 28 days at room temperature. Triplicate samples were prepared for each filler type, temperature, and exposure combinations. Temperature fluctuations were within $\pm 0.05^\circ\text{C}$. Sodium chloride (Analar) was used without further purification with double-distilled deionized water.

Immersion / Weight Gain Experiments

Liquid diffusion into the composites was determined using an environmental chamber which controlled the temperature and relative humidity. After drying *in vacuo* at room temperature (for 48 h) the samples were weighed at 24° , 35° , and 45°C and then exposed to a liquid environment by submerging either in distilled water or salt solution using a constant temperature bath. At frequent time intervals (t) the samples were removed, the outer surfaces were dried with a filter paper, the specimens weighed and then placed back into the test chamber. The weight gain as a function of time was measured for all samples at all temperatures until equilibrium was reached. In all cases, triplicate measurements were done; only average values were used in the calculation of percent penetrant content (M_t). The diffusion coefficient, D ,

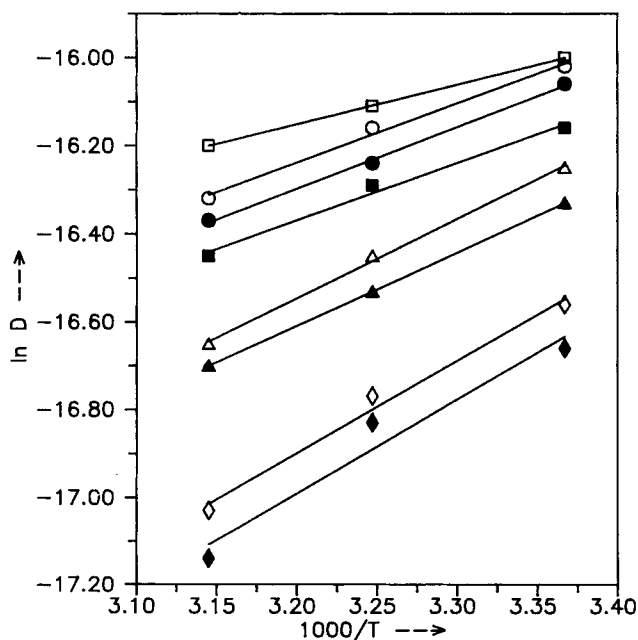


Fig. 1. Arrhenius plot for the diffusion coefficient; Fly ash: (○) distilled water, (●) salt solution; Jute: (□) distilled water, (■) salt solution; Mica: (△) distilled water, (▲) salt solution; Vermiculite: (◇) distilled water; (◆) salt solution.

was calculated^{15,16} from the slopes (θ) of the curves of M_t vs. $t^{1/2}$ using Eq. (1).

$$D = 3.64 \times 10^{-5} \left(\frac{h\theta}{4M_m} \right)^2 (\text{cm}^2/\text{s}) \quad (1)$$

where h is the thickness of the composite and M_m is the percent penetrant at equilibrium. A least-squares fitting was used to obtain the values of θ from which D was calculated. The results are given in Tables I and II.

The temperature dependence of D can be expressed by the Arrhenius relationship:

$$D = D_o \exp(-E_D/RT) \quad (2)$$

where D_o is a constant and E_D is the activation energy for diffusion. Figure 1 depicts plots of $\ln D$ versus $1/T$. Slopes of these lines give values of E_D and their intercepts with the ordinate yield the D_o terms.

RESULTS AND DISCUSSION

The equilibrium percent penetrant content (M_m) was obtained from weight gain assays. Salt solution exhibited a higher absorptivity than distilled water; values of M_m increased continuously with temperature for both penetrants. A quicker equilibrium was attained at room temperature (24°C) than at higher temperatures (35° and 45°C); but all materials reached saturation within 3–4 days from the beginning of the experiment. It is, however, instructive to note that the composites exhibited large variations in their maximum absorptivities; this depended, to a large extent, on the type of filler used in the composite. For instance, high absorptivities observed for jute- or fly ash-containing composites are attributed to their hydrophilic nature. Lower M_m values seen for mica- or vermiculite-filled composites are a result of their water-repelling properties. Activation energy for diffusion (E_D) was calculated from a least-squares fit of the data from the Arrhenius plots, which, with the error analysis, are included in Table II. Of all the composites, the jute-filled composite exhibited higher diffusivities for both distilled water and salt water than the remaining composites. Lowest diffusivities were seen with composites containing vermiculite. Intermediate values were observed with fly ash- or mica-filled composites. In all cases, as expected, distilled water exhibited higher diffusion rates than salt solution.

Energy of activation for diffusion (see Table II) was higher for salt solution than distilled water; the only exception being mica-filled composites. For vermiculite-filled composites, activation energies (~ 17.5 kJ/mol) for both salt solution and distilled water were almost identical, but their diffusivities were not the same. However, for the remaining composites, the activation energies lie within the range of 8–15 kJ/mol.

Experimental evidence and theoretical analysis of liquid diffusion through solid polymers suggest that parameters which affect macromolecular relaxations influence the diffusion mechanism as well.^{17–19} Of particular interest are phenomena related to penetrant diffusion in cross-linked systems having

hydrophilic moieties. In such systems one is usually faced with associated problems related to hydrogen bonding. Additionally, the exposure of composites to either water or salt solution might lead to the formation of microacvities within the composite matrix.^{11,20,21} Composites of both fly ash- and jute-reinforced epoxies exposed to salt water showed slightly higher equilibrium moisture content ($M_m = 17$) than those in fresh water.

The higher diffusion rate exhibited by jute- and fly ash-reinforced composites may be attributed to higher moisture penetration reflected by opening more channels to water molecules. Composite properties may be affected in several ways by liquid absorption. It is known that the absorbed moisture affects the physical and mechanical properties of the cured epoxy material.² Relatively high moisture absorption (i.e., up to 15%) of epoxy resins may be attributed to the presence of hydroxy groups in the epoxy chains attracting polar water molecules. However, the quantitative understanding of the molecular network structure including the average distance between cross-links, the rigidity of the network, the molar mass distribution between cross-links, and the topological heterogeneity of the network structure is still far from satisfactory.

In general, a direct comparison of the present results with those of literature findings is rather difficult because of the nonuniform processing techniques used. However, a few attempts have been made in the past to prepare composites based on jute.^{13,14} Philip^{22,23} tried to modify jute fiber composites by using various resins and also by applying a gel coat or a thin glass fiber/resin layer to improve resistance to environmental degradation (mainly to water). Recently, a number of other studies have been made with composites of jute^{24,25} to see whether a particular variety of jute plant would give rise to a fiber with superior properties. It is interesting to note that a 16% maximum water uptake as observed by Mukherjea et al.¹⁴ for jute/epoxy-modified composites closely parallels to our findings at 45°C (i.e., $M_m = 15\%$). In a recent study by Errede et al.²⁶ concerning water absorption of vermiculite particules in poly(tetrafluoroethylene) composite films, only 5% moisture absorption was observed.

As is well known, D depends not only on the characteristics of the solvent molecule (water) but also on the overall composite characteristics. The size of the penetrant molecule and the availability of free volume for its transport exert a tremendous influence on the diffusivity and water absorption characteristics of the composites.²⁷ As the size of the penetrant increases its displacement depends upon the movement of polymer segments and the availability of voids larger than the penetrant size. Thus, any small change in penetrant size results in a substantial change in diffusivity. When the temperature is increased, the amplitude of the segmental oscillations of the polymer chain also increases, resulting in an increase in the size of voids and thus increased diffusivity.

Additional information on the mechanism of diffusion can be obtained from the variation of transport parameters with temperature as expressed by the Arrhenius equation. The activation energy of diffusion as obtained from such plots (see Fig. 1) is the energy required to complete the unit diffusion process of one mole of a diffusing liquid. Salt solution exhibited higher activation energy of diffusion than distilled water. This increase may be the result of

increased penetrant size (Na^+ or Cl^- ions).²⁸ The increase in activation energy and the proportionate decrease in the diffusion coefficient become greater as the size of the diffusing molecule increases, suggesting that at high crosslink densities there is a tendency for the diffusion medium to act as a valve.²⁹ At any rate, our data are not extensive enough to warrant a deeper analysis of the situation.

Of the composites studied here, jute as a filler did not exhibit promising results because of its high moisture absorptivity and diffusivity. This may be due to the presence of hydroxy functions in jute leading to high water absorption. Even when saw dust, cinder, and coke were used as fillers the water absorptivity was very high (results not presented) and therefore no attempts were made to evaluate the diffusion parameters.³⁰ Developmental work to improve the moisture resistance of some of those composites is necessary before their successful field applications.

The author wishes to thank Patrick E. Cassidy, Southwest Texas State University for his helpful comments and advice on this project. I also thank the administrators of Karnatak University for the sanction of a leave during the summer of 1986.

References

1. T. M. Aminabhavi, P. E. Cassidy, and L. E. Kukacka, *J. Macromol. Sci. Rev. Macromol. Chem. Phys.*, **C22**, 1 (1982-83).
2. T. M. Aminabhavi and P. E. Cassidy, *J. Polym. Mater.*, **2**, 186 (1985).
3. T. M. Aminabhavi, R. C. Patel, and N. S. Biradar, *Mater. Sci. Eng.*, **48**, 199 (1981).
4. E. Stark, A. M. Ibrahim, T. E. Munns, and J. C. Seferis, *J. Appl. Polym. Sci.*, **30**, 1717 (1985).
5. P. Moy and F. E. Karasz, *Am. Chem. Soc. Ser.*, **127**, 505 (1980).
6. Y. Diamont, G. Marom, and L. J. Broutman, *J. Appl. Polym. Sci.*, **26**, 3015 (1981).
7. D. H. Kaeble, *Am. Chem. Soc. Prepr. Pap., Div. Org. Coat. Plast. Chem.*, **43**, 395 (1980).
8. T. M. Aminabhavi, R. W. Thomas, and P. E. Cassidy, *Polym. Eng. Sci.*, **24**, 1417 (1984).
9. B. D. Barr-Howell, N. A. Peppas, and T. G. Squires, *J. Appl. Polym. Sci.*, **31**, 39 (1986).
10. J. Koszinowski, *J. Appl. Polym. Sci.*, **31**, 1805 (1986).
11. M. Narkis and J. P. Bell, *J. Appl. Polym. Sci.*, **27**, 2809 (1982).
12. A. Mazor and L. J. Broutman, *Polym. Eng. Sci.*, **18**, 341 (1978).
13. S. S. Bhatnagar, G. A. R. Khan, and L. C. Verman, Indian Pat. 28,281 and 28,427 (1926).
14. R. N. Mukherjee, S. K. Pal, and S. K. Sanyal, *J. Appl. Polym. Sci.*, **28**, 3029 (1983).
15. C. H. Shen and G. S. Springer, *J. Comp. Mat.*, **10**, 2 (1976).
16. A. C. Loos and G. S. Springer, *J. Comp. Mat.*, **14**, 142 (1980).
17. K. H. G. Ashboo and R. C. Wyatt, *Proc. Roy. Soc. Lond. Ser. A*, **312**, 553 (1969).
18. P. Zadorecki and P. Flodin, *J. Appl. Polym. Sci.*, **31**, 1669 (1986).
19. L. M. Robeson and S. T. Crisafulli, *J. Appl. Polym. Sci.*, **28**, 2925 (1983).
20. R. F. Fedors, *J. Polym. Sci., Polym. Letts Ed.*, **12**, 81 (1974).
21. R. F. Fedors, *Polymer*, **21**, 713 (1980).
22. A. R. Philip, *Reinf. Plas.*, **8**, 306 (1964).
23. A. R. Philip, *Eng. Mater. Des.*, **8**, 475 (1965).
24. A. G. Winfeld, *Plast. Rubber Int.*, **4**, 23 (1979).
25. H. Wells, D. H. Bowen, I. Macphail, and P. K. Pal, *35th Ann. Tech. Conf., RP/C Proc., S. P. I.*, 1980, Sec. 1-F.
26. L. A. Errede, J. D. Stoesz, and L. M. Sirvio, *J. Appl. Polym. Sci.*, **31**, 2721 (1986).
27. A. C. Newns and G. S. Park, *J. Polym. Sci.*, **C22**, 927 (1969).
28. R. M. Barrer and G. Skirrow, *J. Polym. Sci.*, **C10**, 17 (1965).
29. P. E. Cassidy, T. M. Aminabhavi, and J. C. Brunson, *Rubb. Chem. Technol.*, **56**, 357 (1983).
30. T. M. Aminabhavi, unpublished reports.

Received April 30, 1987

Accepted July 16, 1987