Absorption of Water in Polyimide Resins and Composites

W. P. PAPLHAM, R. A. BROWN, I. M. SALIN, and J. C. SEFERIS*

Polymeric Composites Laboratory, Department of Chemical Engineering, University of Washington, Seattle, Washington 98195

SYNOPSIS

The effect of temperature, postcure, and fiber orientation on water absorption were examined for Kerimid® 723 bismaleimide resin. The effect of fiber orientation was also examined for Avimid® N and BASF X-5260. Water absorption in Kerimid® 723 was found to have an Arrhenius temperature dependence, depend on degree of postcure, and be independent of fiber orientation. BASF X-5260 water absorption was also found to be independent of fiber orientation. Avimid® N water absorption exhibited a strong dependence on fiber orientation. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Polyimide resins are often used both in the electronic and aviation industries. In aerospace, these resins are candidate matrix systems for high-temperature applications in the engine environment of conventional aircraft and in structural surfaces for supersonic aircraft. A special class of polyimides, bismaleimides, have complete imide rings in the uncured state and crosslink through addition reactions at double bonds found in the imide rings. Other polyimides complete imidization through a condensation reaction, releasing water or alcohol during the cure process.[1] Although these materials are well known for their high thermooxidative stability, little work has been performed investigating other factors relating to composite stability. In the aircraft environment, composites are exposed to water, fuel, and mechanical fluids in addition to extremes in temperature and mechanical stress. These effects are cyclical in nature and may cause more damage to composites than static effects that are often simulated in the laboratory.

Previous work with epoxies has examined the changes in morphology, mechanical properties, and absorption characteristics of epoxy composites exposed to humidity at elevated temperatures.[2-10] To understand the material changes induced by hy-grothermal cycling, it is necessary to examine the absorption behavior. This article concentrates on the effects of temperature, degree of postcure, and fiber orientation on the water absorption behavior of several imide ring matrix systems.

EXPERIMENTAL

The materials examined in this study were Kerimid® 723 neat resin (Rhône-Poulenc), Kerimid® 723/T-300 carbon fiber unidirectional composite prepared in our laboratory (Rhône Poulenc), X-5260/IM7 carbon fiber unidirectional composite (BASF), and Avimid® N/Thornel 650-42 carbon fiber unidirectional composite (E. I. du Pont de Nemours). Kerimid® 723 is an untoughened bismaleimide resin, BASF X-5260 is an interlayer toughened bismaleimide system, and Avimid® N is a high-temperature condensation polyimide system. All neat resin Kerimid® 723 plaques were made by degassing the resin at 80°C in a vacuum and then casting between glass plates. The cure cycle was 1 h at 150°C, followed by 1 h at 200°C. The resin plaques were then removed from the glass, cut, and treated with the appropriate postcure. Both cure and postcure were conducted in air. The neat resin plaques were cut to approximately 40 × 40 mm and were 3 mm thick. Kerimid® 723 carbon fiber unidirectional composite was prepared in an autoclave using a standard vacuum bag. The cure cycle consisted of a 5°C/min ramp to 150°C, a 1-h hold, a 5°C/min ramp to 200°C, followed by
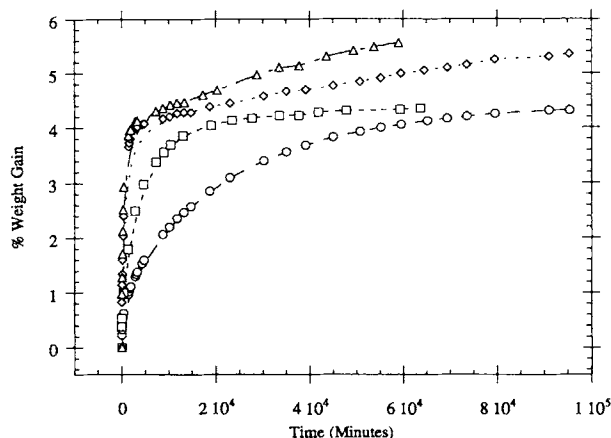

Figure 1 Temperature effect on water absorption: untoughened bismaleimide. (O) 21°C; (□) 52°C; (◇) 90°C; (△) 100°C.

another 1-h hold. The autoclave pressure was 5 bar, and a vacuum was applied until 60°C. The Avimid® N and BASF X-5260 composites were used as supplied.

The effect of temperature on water absorption for Kerimid® 723 resin plaques was examined by placing the samples in water baths maintained at 21 ± 1°C, 52 ± 5°C, 90 ± 1°C, and 100 ± 1°C. The samples were weighed periodically by blotting the samples dry and weighing immediately, minimizing the time out of water. Sample dimensions were measured with a Mitutoyo digital caliper. To examine the effect of postcure on water absorption, three different postcures at different temperatures and durations were applied to the samples. One plaque had no postcure. Samples for evaluating the effect of postcure temperature were postcured for 4 h at either 200, 225, or 250°C, and samples for evaluating the effect of postcure time were postcured at 225°C for either 2, 4, or 6 h. All water absorption was performed at 100°C. Weight and dimension measurements were conducted with the same method as discussed earlier. The effect of the anisotropy inherent in carbon fiber composites was studied using samples with fiber orientations either parallel or perpendicular to the longest dimension of the sample. The samples were approximately 130 × 10 × 3 mm, with the fibers parallel to either the 130-mm or 10-mm dimension. All absorption measurements were made at 52°C. Weight and dimension measurements were made as discussed earlier.

RESULTS AND DISCUSSION

Temperature influenced strongly both the rate of absorption and the degree of water uptake in neat

resin plaques of Kerimid® 723, as can be seen in Figure 1. Two important aspects of the absorption behavior were the deviation from Fick's Second Law, which assumes concentration independent diffusion, and the failure of the samples to reach an equilibrium mass uptake. These samples did not absorb water following Fick's Second Law, whereby the diffusion coefficient is constant and the initial weight gain is proportional to the 0.5 power of time.[11,12] Instead the diffusion coefficient appeared to decrease with time. This indicated that the samples probably experienced a change in morphology that affected diffusion. The long-term absorption behavior indicated changes in the morphology allowing additional water uptake in the form of unbound water. These changes may be attributed to increases in free volume or microvoid/microcrack formation.[2,3,8,13-15] At higher temperatures, this was especially evident. This unbound water may be the cause of the changing diffusion rates.[14,16,17]

Although the absorption behavior deviates from Fick's Second Law, it was assumed that in the initial stages of absorption, any changes in the diffusion coefficient had a negligible effect on absorption. The initial diffusion coefficient was then approximated from the slope of a linear plot of initial weight gain measurements against the square root of time.[18] By plotting the natural logarithm of the diffusion coefficient against inverse temperature (Fig. 2), it was seen that the initial diffusion coefficient could be approximated with an Arrhenius temperature dependence (Eq. 1).

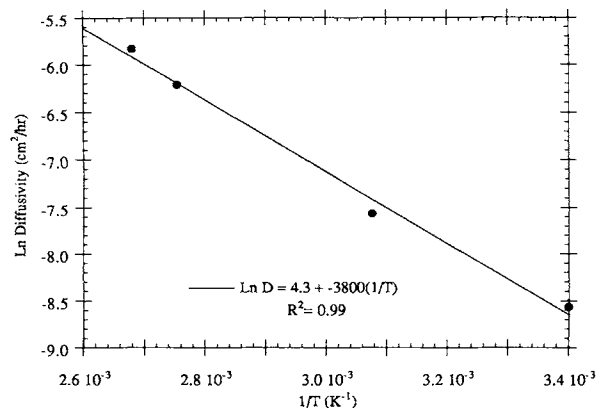$$D = D_R \exp\left[-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_R}\right)\right] \qquad (1)$$

Figure 2 Arrhenius temperature dependence of the diffusion coefficient.

where D is the diffusion coefficient (cm^2/h), D_R is the diffusion coefficient at reference temperature, $(2.08 \times 10^{-4} \, cm^2/h$ at $25°C)$, T is the temperature (K), T_R is the reference temperature (K), E is the activation energy for diffusion $(31.6 \, kJ/mol)$, and R is the gas constant $(8.314 \, J/mol \, K)$.

The measured diffusivities and the diffusivities corrected for deviations due to finite sample dimensions are shown in Table I. The correction for deviations from true one-dimensional diffusion was proposed by Shen and Springer (Eq. 2).[19]

$$D = D_\infty \left(1 + \frac{h}{W} + \frac{h}{L} \right)^2 \tag{2}$$

where D is the apparent diffusion coefficient (cm^2/h), D_∞ is the true 1-D diffusion coefficient (cm^2/h), h is the thickness (cm), W is the width (cm), and L is the length (cm). The values found with this method were probably high due to a thin layer of thermooxidative degradation at the surface from postcure. However, as all samples had the same postcure, the trend maybe assumed to be valid.

The absorption of water was accompanied by swelling. This was significant in that if the material did not swell evenly, internal stresses would be generated. Swelling measurements indicated that after a period of very little dimensional change, the change in dimension was proportional to the weight gain. The early lack of swelling was attributed to the outer swollen resin being constrained by the dry interior. Kerimid® 723 neat resin samples expanded about 0.25% for every 1% of weight gain, as shown in Figure 3. As these systems would gain 5% water or more of their resin weight, the dimensional changes may be significant in large composite parts. Composite samples generally expanded only perpendicular to the fibers, as the unidirectional fibers constrained expansion in the fiber direction. This anisotropic swelling was probably accompanied by internal stresses, which may affect the mechanical stability of the composite system and initiate cracks.
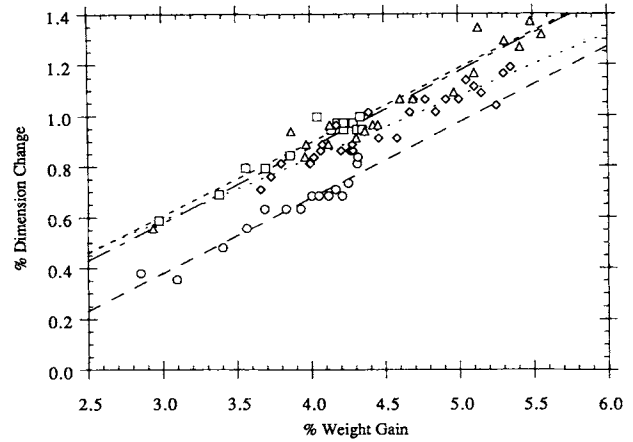

Figure 3   Temperature effect on swelling: untoughened bismaleimide. (O) 21°C; (□) 52°C; (◇) 90°C; (△) 100°C.

Swelling may have had significant mechanical effects even in the neat resin. At both 90°C and 100°C, the neat resin Kerimid® 723 samples demonstrated surface cracking after extended periods of absorption. When these samples were dried at the same temperatures as those in the absorption measurements, there was significant cracking. This cracking was attributed to differential swelling through the thickness due to a water concentration gradient.

In the initial stages of absorption, plaques with greater degrees of postcure had higher rates of absorption. This was evident both for plaques cured at the same temperature for different lengths of time and plaques cured for a given time at different temperatures. On closer examination, it was found that these plaques had a thin, dark layer on the surfaces exposed to air during the postcure. This thin layer of slightly degraded resin may explain the higher diffusion rate due to degradation-induced porosity at the surface. All diffusivity measurements for Kerimid 723® were probably affected in the same manner. To eliminate this problem, the samples should be postcured in an inert atmosphere for absorption measurements.

For longer times of immersion, the rate of absorption slowed dramatically but did not stop. At this point, the rate of absorption was no longer thought to be limited by diffusion but by changes in the material structure which allowed additional water uptake. In this regime, the samples with the lowest degree of crosslinking could accommodate more swelling and thus higher water uptake. This is shown in Figures 4 and 5, where the samples with lower postcures absorbed more water at a higher rate. At very long time periods the samples started losing weight, beginning with the sample with no postcure
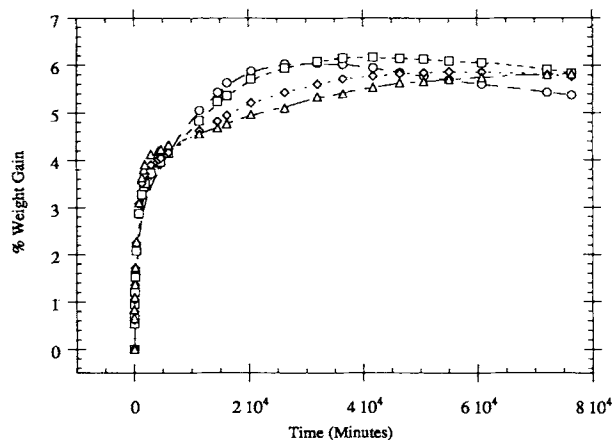
Table I   Temperature Dependence of Diffusion

T (°C)	Diffusivity (cm^2/h)	Geometry Corrected Diffusivity (cm^2/h)
21	$9.55E-05$	$7.10E-05$
52	$1.96E-04$	$1.46E-04$
90	$1.07E-03$	$8.18E-04$
100	$1.30E-03$	$9.86E-04$

Figure 4 Postcure temperature effect on water absorption: untoughened bismaleimide. (O) no postcure; (□) 4 h @ 200°C; (◇) 4 h @ 225°C; (△) 4 h @ 250°C.

Figure 5 Postcure time effect on water absorption: untoughened bismaleimide. (O) no postcure; (□) 2 h @ 225°C; (◇) 4 h @ 225°C; (△) 6 h @ 225°C.

and progressing to higher degrees of postcure. This might have been due to leaching from the sample and/or erosion due to jostling in the boiling water. Some erosion of the sample surfaces was observed. The water used became discolored over time, although the source of this discoloration was not determined. This weight loss must be investigated further. Increasing time and temperature of postcure generally had the same effect on absorption behavior. This indicated that a similar degree of postcure was achieved either by heating for long times at low temperatures or short cure times at high temperatures.

When the fiber orientation effect on absorption was examined, neither bismaleimide exhibited a dependence of diffusion on fiber orientation, although the fiber orientation effect was only examined in-plane (Fig. 6). In the case of out-of-plane diffusion, the interlayers present in the BASF X-5260 system may cause anisotropic absorption. In contrast to the bismaleimide systems, the high-performance polyimide Avimid® N demonstrated a strong dependence of diffusion on fiber orientation. The 90° sample, in which the fibers were perpendicular to the long edge, absorbed water much more rapidly than the 0° sample, in which the fibers were parallel to the longest dimension. This indicated a faster pathway for diffusion along the fiber direction, possibly through the resin/fiber interface. Perhaps more significant was the failure of the 0° and 90° samples to reach the same weight gain eventually. This indicated that the differences were due to more than differences in diffusion rates in different directions. One possibility was that in the 90° sample, the effective length of fiber support was a smaller percentage of the fiber
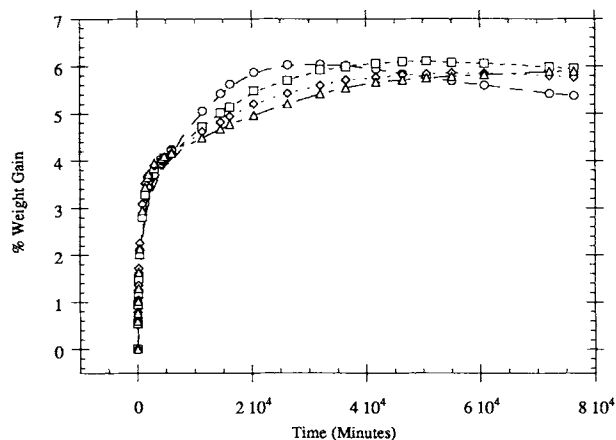
length. This would allow swelling of the resin parallel to the fibers near the fiber tips as well as swelling perpendicular to the fibers.

CONCLUSIONS

Polyimide resins' high affinity for water must be accounted for in evaluations of the long-term environmental stability of polyimide matrix composites used in the aerospace industry. The temperature at which absorption takes place, the degree of postcure, and fiber orientation all had significant effects on the water absorption process. These materials did not reach a steady-state condition, indicating that
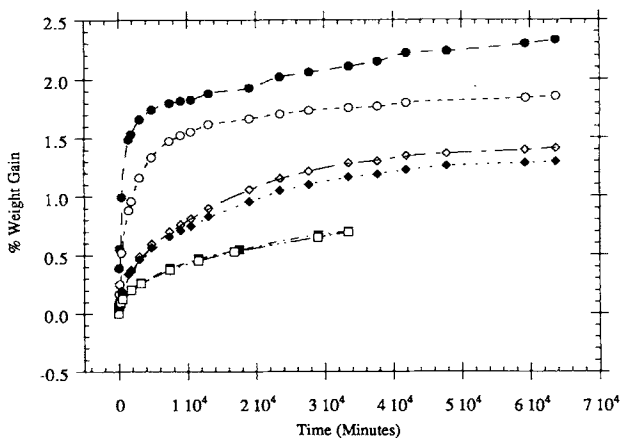

Figure 6 Fiber orientation effect on water absorption. (●) polyimide 90°; (O) polyimide 0°; (◆) untoughened BMI 90°; (◇) untoughened BMI 0°; (■) interlayer toughened BMI 90°; (□) interlayer toughened BMI 0°.

changes in the morphology of the material were occurring. Absorption in Kerimid® 723 was found to be non-Fickian in nature, probably due to morphological changes in the polymer due to the absorption of water. An understanding of the material changes occurring during absorption and desorption will be an important step in determining the durability of these materials in the aircraft environment.

REFERENCES

1. D. A. Tod and S. J. Shaw, *Brit. Polym. J.*, **20**, 397 (1988).
2. A. Apicella and L. Nicolais, *Ind. Eng. Chem. Prod. Res. Dev.*, **20**, 144 (1981).
3. A. Apicella, L. Nicolais, G. Astarita, and E. Drioli, *Polymer*, **22**, 1064 (1981).
4. E. G. Wolff, *SAMPE J.*, **29**, 11 (1993).
5. A. C. Loos and G. S. Springer, *J. Comp. Mater.*, **13**, 16 (1979).
6. E. L. McKague, Jr., J. D. Reynolds, and J. E. Halkias, *J. Appl. Polym. Sci.*, **22**, 1643 (1978).
7. E. L. McKague, Jr., J. E. Halkias, and J. D. Reynolds, *J. Comp. Mater.*, **9**, 2 (1975).
8. C. E. Browning, *Polym. Eng. Sci.*, **18**, 16 (1978).
9. M. J. Adamson, *J. Mater. Sci.*, **15**, 1736 (1980).
10. N. Fried, in *Proceedings of the Fifth Symposium on Naval Structural Mechanics*, Philadelphia, 1967, p. 813.
11. A. Fick, *Ann. Phys.*, **170**, 59 (1855).
12. R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, John Wiley & Sons, New York, 1960, p. 780.
13. G. A. Gordon, *Polym.*, **18**, 958 (1977).
14. J. A. Barrie and B. Platt, *Polym.*, **4**, 303 (1963).
15. W. J. Mikols, J. C. Seferis, A. Apicella, and L. Nicolais, *Polym. Comp.*, **3**, 118 (1982).
16. D. K. Yang, W. J. Koros, and H. B. Hopfenberg, *J. Appl. Polym. Sci.*, **31**, 1619 (1986).
17. H. W. Starkweather, Jr., *Macromol.*, **8**(4), 476 (1975).
18. J. Crank and G. S. Park, in *Diffusion in Polymers*, J. Crank and G. S. Park, Eds., Academic Press, New York, 1968, p. 1.
19. C. H. Shen and G. S. Springer, *J. Composite Mater.*, **10**, 2 (1976).