

The Sorption and Diffusion of Water in Bismaleimide Resin

INTRODUCTION

In the search for improved matrix resins for high performance composites increasing attention has been paid to polyimides and related materials.¹⁻³ The importance of the interaction of water with the matrix resin of a composite and its effect on physical and mechanical properties was recognized at an early stage in the development of epoxy composites.^{4,5} As part of an ongoing study of water sorption and transport in composite resin materials⁶⁻⁸ results for a commercially available bismaleimide resin are reported on briefly and a comparison made with the Kapton polyimide (E.I. Dupont de Nemours Inc) and the resin MY720 (Ciba-Geigy Ltd).

EXPERIMENTAL

Compimide M751 was kindly supplied by Dr H. D. Stenzenberger (Technochemie GmbH-Verfahrenstechnik). A mould, which gave castings of 3×3 cm was made from two surface-treated glass plates which were separated by a tailored "Teflon", glass-weave skin. The resin powder was dried and compressed into a pellet using a KBr die which could be evacuated. The pellet was placed on the lower plate held at 175°C by being positioned in the open press. The heated top plate, also at $\sim 175^\circ\text{C}$ was carefully positioned over the molten globule and pressure (100-200 psi) applied. The mould was protected from the press by an interlayer consisting of silicone rubber between Teflon, glass-weave sheets. The cure was effected at 180°C for 4 h, 220°C for 2 h, and finally at 250°C for 17 h. Thin films of Kapton were supplied by E. I. Dupont de Nemours Inc., and typical values of film thickness l , density ρ , and glass transition temperature T_g are given in Table I.

The chemical structures of the M751 prepolymer constituents and of Kapton are shown in Figure 1. The chemistry of the curing process for the M751 has already been described in detail.³ Briefly the amino groups of the monomaleimide constituent undergo a Michael addition with the end group double bonds of the bismaleimide constituent to form a linear prepolymer terminated by double bonds. On raising the temperature, the double bonds open and crosslinking occurs through a free radical polyaddition.

Sorption isotherms and rate curves were determined with an electronic vacuum microbalance (Sartorius Instruments Ltd) with small corrections for "blank" sorptions, and vapor pressures were measured with Bell and Howell transducers 4105/00 (0-2.66 cmHg) and 4/327 (0-50 cmHg) as described earlier.⁶

TABLE I
Physical Properties of the Polyimides

	$T_g(^{\circ}\text{C})$	$\rho(\text{g cm}^{-3})^a$	$l(\text{cm})$
Compimide M751	$> 300^b$	1.33	0.013
Kapton	350-450 ^c	1.42	0.0076

^aEstimated from sample weight and dimensions.

^bDynamic Mechanical Thermal Analyser (Polymer Laboratories U.K.) operating at 10Hz and $5^\circ\text{C}/\text{min}$.

^cRef. 9.

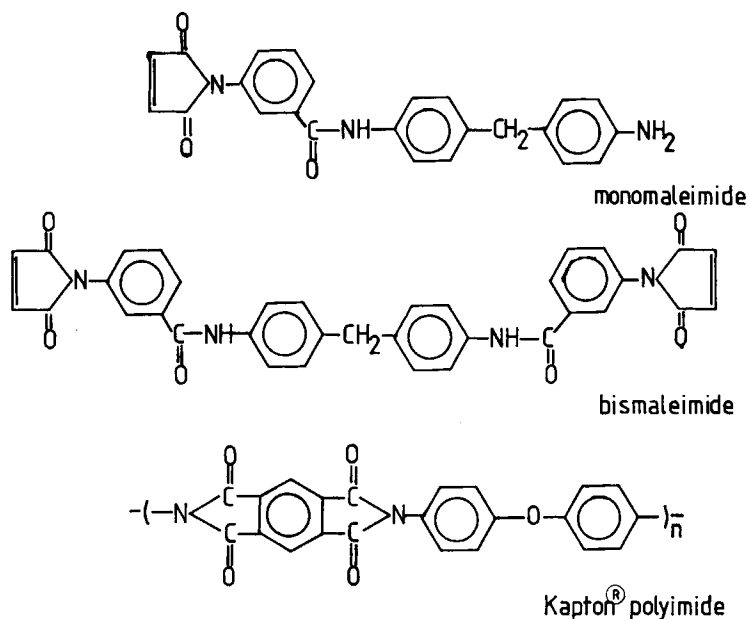


Fig. 1. Compimide M751 and Kapton polyimide constituents.

RESULTS AND DISCUSSION

Sorption

Sorption isotherms for virgin (as prepared) bismaleimide resin were determined at 40, 50, and 60°C in that order and are designated "first" sorptions and are shown in Figure 2. Also shown in Figure 2 is a "second" sorption isotherm at 40°C which was determined on completion of the "first" sorption at 60°C. Each isotherm was measured in the order of increasing vapor activity and the sample was outgassed usually after 2 or 3 isotherm points and before any change of temperature. Regains at unit activity were determined by immersion in liquid water followed by wiping and weighing at 40°C. The error bar in Figure 2 reflects the extent of scatter for a series of 5 measurements. For Kapton only the "first" sorption at 40°C was measured.

The isotherms for both Compimide M751 and Kapton exhibit a Langmuir-type knee at the lower activities consistent with a competitive sorption of the water at a limited number of sites in the network. The exact nature of these sites is open to question, but sorption in microvoids frozen into the glassy matrix and/or at polar sites relatively exposed in microvoids is likely.^{6,7} Similar isotherm shapes have been observed for a number of other polyimide resins and the data for Kapton are in good agreement with those of an earlier study.⁹⁻¹¹

In common with epoxy resins there is both an increase in sorption capacity and a change in isotherm shape at the higher activities accompanying the "second" sorptions.⁶ Although the glass transition temperature of Compimide M751 is greater than 350°C it would appear that there is a significant irreversible relaxation of the network in the presence of water vapor even at temperatures not far removed from ambient. The extent of this hysteresis will depend on the length of time the sample is exposed to water vapor prior to measurement of the "second" sorption and for the present study was approximately one month. The presence of these hysteresis effects precludes a rigorous analysis of the isotherm data, especially the "first" sorptions in terms of heats of sorption and clustering tendencies.¹² The "first" sorptions are virtually independent of temperature indicating an apparent heat of sorption close to the heat of condensation for water. In a recent publication on water sorption in Kapton, differences in the sorption behavior of aged and unaged samples are attributed to a chemical reaction of the sorbed water with components of

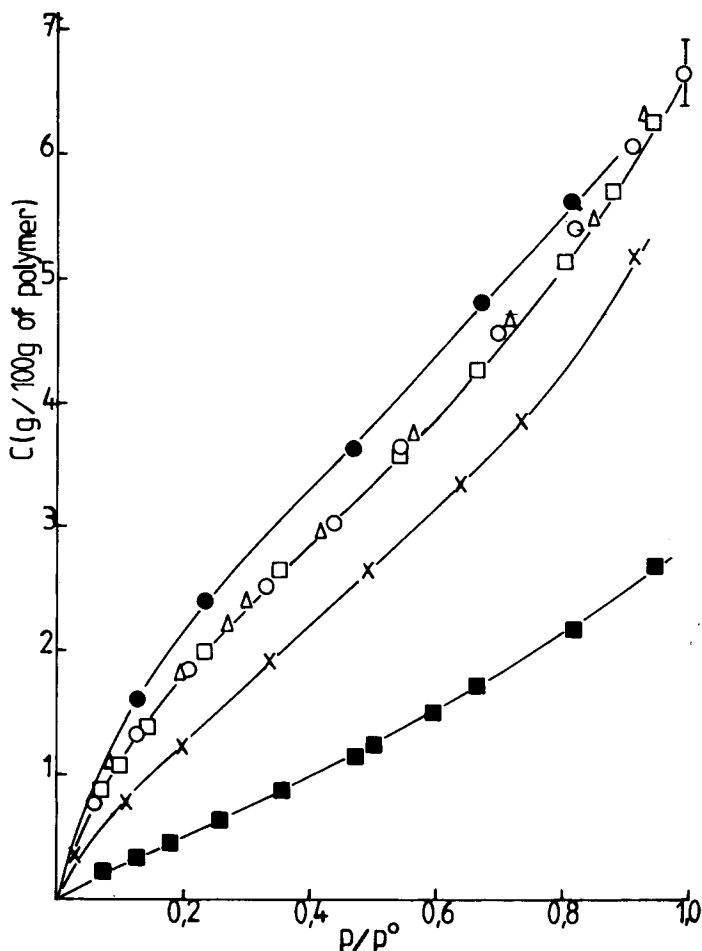


Fig. 2. Sorption isotherms for water. (○), (△), (□), "first" sorptions at 40, 50, and 60°C for Compimide M751; (●) "second" sorption at 40°C for Compimide M751; (×), "first" sorption at 40°C epoxy resin MY720⁷; (■), "first" sorption at 40°C for Kapton polyimide.

the resin during ageing.¹¹ In the present investigation there was no evidence of a significant irreversible component to the sorption for any of the samples, that is of sorbed water not readily removed by outgassing under high vacuum at the isotherm temperature.

The high sorptive capacity of the bismaleimide resin compared with Kapton may be attributed to a larger number of accessible polar sites with the CONH linkage and secondary amines created by the Michael addition as likely candidates. Additional contributory factors may be a comparatively higher microvoid population for the less dense Compimide M751 and/or the presence of paracrystalline regions in Kapton.¹¹ Also included in Figure 2 for comparison is a "first" sorption isotherm for the epoxy resin MY720.⁷

Diffusion

Integral sorption rate curves were determined in the activity range 0-0.9 at 40, 50, and 60°C for Compimide M751 and at 40°C only for Kapton. Typical rate curves for the bismaleimide resin are

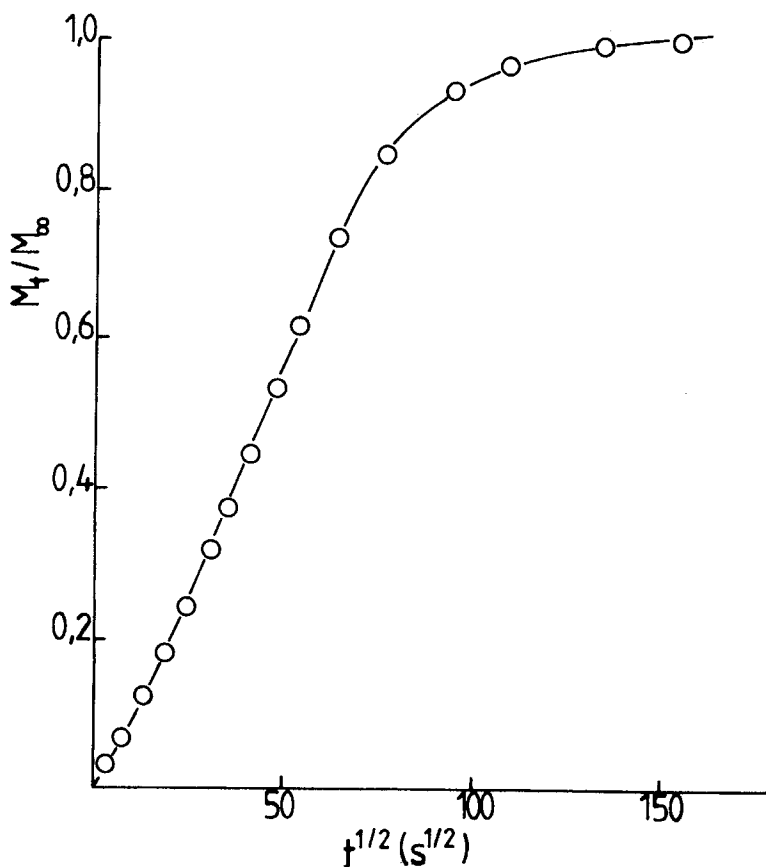


Fig. 3. Sorption rate curve for water in Compimide M751 at 40°C, M_t , M_∞ : amount sorbed at time t and at equilibrium, respectively, with $M_\infty = 2.52$ g/100 g.

shown in Figure 3. These display a slight sigmoid character at short times and at higher activities, indicative of some element of non-Fickian behavior. This non-Fickian behavior is generally attributed to relaxation processes sensitive to the presence of water but changes in the surface temperature accompanying the initial sorption of vapor may also contribute.^{6,7} For Kapton the initial \sqrt{t} region was linear up to fractional regains of ~ 0.7 .

An average diffusion coefficient \bar{D}_s , was obtained from the linear \sqrt{t} region of the rate curve, assuming Fickian behavior, and is shown as a function of concentration in Figure 4. Using the weighted-mean approximation,¹³ the differential coefficient was obtained as a function of concentration and is also shown in Figure 4. For both Compimide M751 and Kapton, D increases with concentration with an indication of a maximum at higher concentrations; in neither case is the concentration dependence strong being weaker for Kapton. Although the bismaleimide resin has a stronger affinity for water the magnitude of the diffusion coefficient for both materials is similar. If only a fraction of the sorbed water is free to diffuse then the effective diffusion coefficient may be represented by $D_m (\partial c_m / \partial c)$ where subscript m denotes mobile species. In the limit $c \rightarrow 0$ this becomes $D_m k_m / k$, where k denotes the limiting Henry's law constant for the overall sorption and k_m that for the dissolved mobile species. Since k is greater for the Compimide M751 and since the effective diffusion coefficients for both resins are similar, then either D_m , or k_m , or both is greater for the bismaleimide resin.

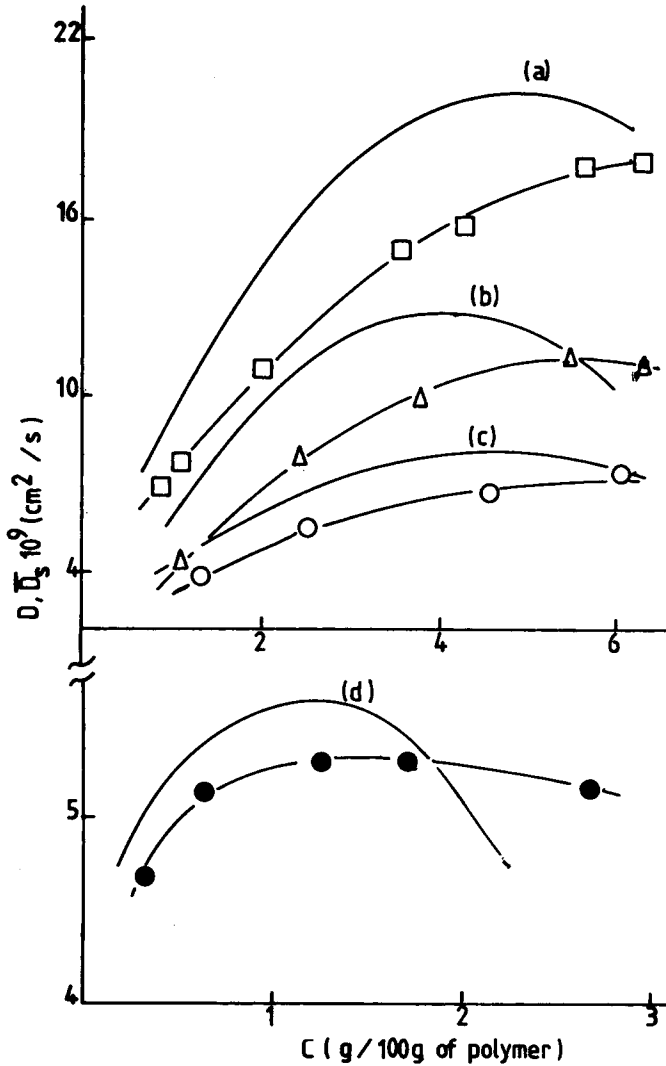


Fig. 4. Concentration dependence of the diffusion coefficients \bar{D}_s and D . (\circ), (Δ), (\square), \bar{D}_s for "first" sorptions at 40, 50, and 60°C for Compimide M751; (a), (b), (c), D for "first" sorptions at 60, 50 and 40°C for Compimide M751; (\bullet), (d), \bar{D}_s and D for "first" sorptions at 40°C for Kapton polyimide.

References

1. K. L. Mittal (Ed.), *Polyimides*, Vol. 1, Plenum Press, New York, 1984.
2. K. L. Mittal (Ed.), *Polyimides*, Vol. 2, Plenum Press, New York, 1984.
3. H. O. Stenzenberger, M. Herzog, W. Romer, R. Scheiblich, and N. J. Reeves, *Br. Polym. J.*, **15**, 2 (1983).
4. J. R. Vinson (Ed.), *Advanced Composite Materials Environmental Effects*, ASTM, STP658, 1978.
5. N. W. Wright, *Composites*, **201**, (July 1981).
6. J. A. Barrie, P. S. Sagoo, and P. Johncock, *J. Memb. Sci.*, **18**, 197 (1984).
7. J. A. Barrie, P. S. Sagoo, and P. Johncock, *Polymer*, **26**, 1167 (1985).

8. P. Johncock, and G. F. Tudgey, *Br. Polym. J.*, **15**, 14 (1983).
9. D. K. Yang, W. J. Koros, H. B. Hopfenberg, and V. T. Stannett, *J. Appl. Polym. Sci.*, **30**, 1035 (1985).
10. E. Sacher, and J. R. Susko, *J. Appl. Polym. Sci.*, **26**, 679 (1981).
11. D. K. Yang, W. J. Koros, H. B. Hopfenberg, and V. T. Stannett, *J. Appl. Polym. Sci.*, **31**, 1619 (1986).
12. B. H. Zimm and J. L. Lundberg, *J. Phys. Chem.*, **60**, 425 (1956).
13. J. Crank, *The Mathematics of Diffusion*, Oxford University Press, Cambridge, 2nd Ed., 1975, pp. 250.

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