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Diffusion of moisture into two-phase polymers

Part 1 *The development of an analytical model and its application to styrene–ethylene/butylene–styrene block copolymer*

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Data are presented for the moisture absorption by a thermoplastic elastomer which consists of a segregated polystyrene glassy phase in a rubbery matrix at 96% relative humidity. The initial stages appear to be Fickian in character but deviate in the final stages. A simple analytical model to describe the diffusion process which occurs in a two-phase resin system has been developed and applied to this system. In this model the moisture absorption characteristics of the dense and less dense phases are determined, and a value for the volume fraction of the dense phase estimated. In Part 2 the analysis is applied to a cured styrenated polyester resin.

1. Introduction

Several authors have monitored moisture absorption and desorption in resins and composite materials. For simplicity most of them have assumed that moisture absorption is a concentration-independent Fickian diffusion process [1–7]. Whilst this model may be applicable to the initial stages of the diffusion process in a wide range of resins and composites it often fails to describe the entire diffusion process. It is evident, therefore, that a more complex model is required to describe the absorption and desorption of moisture in such a system.

In a number of resin systems, whilst the initial stages of moisture absorption would appear to be described using a Fickian approach, it is often found that the final stages show a deviation from Fickian behaviour. Some authors attempt to explain this by means of a Langmuir-type diffusion process [8–11], in which the absorbed material can be divided into mobile and strongly-bound types, whilst others [12, 13] would appear to ignore this fact. Certain resin systems are known to exhibit a two-phase structure, comprising areas of differing density, which may influence the diffusion characteristics of the system as a whole. A typical example of a two-phase polymer is a thermoplastic elastomer, which is the subject of this paper. The implication of this to matrix resins for composites is discussed in Part 2 [14]. In this paper a simple model to describe the diffusion process which occurs in a two-phase resin system is proposed.

The moisture absorption curve for a resin having a two-phase structure is expected to show two important regions (Fig. 1). In Region I there is rapid diffusion of moisture into the resin whereas in Region II the diffusion process is considerably slower. If we assume that the resin consists of a dense phase surrounded by a less dense phase and that the dense phase has a lower diffusion coefficient, then the absorption curve can be interpreted as follows. Region I is attributed to the absorption of moisture into both the dense and less dense phases of the material, whereas Region II is attributed to the absorption of moisture into the dense phase alone. Assuming that initially both phases absorb moisture, but once the less dense phase has reached equilibrium the increase in moisture content of the resin results from absorption by the dense phase alone, then by subtracting the slope of Region II (m_d) from that of Region I (m_x) the slope of the curve corresponding to the absorption of moisture into the less dense phase (m_l) may be obtained (i.e. $m_x - m_d = m_l$). Using a Fickian approach, the diffusion coefficients of the dense phase and the less dense phase can be calculated from these slopes as can the diffusion coefficient of the resin as a whole. It is proposed that from a knowledge of these diffusion coefficients the volume fraction of the dense phase in the system can also be calculated.

2. Experimental procedure

To evaluate the validity of the proposed model it was necessary to use a two-phase polymeric material in which the dense phase is surrounded by the less dense phase. For this reason the thermoplastic rubber Kraton G-1657X (Shell Chemicals UK Ltd) was chosen. The linear A–B–A block-type structure of the Kraton rubber molecule has polystyrene endblocks and an elastomeric midblock. Kraton G-1657X is of the styrene–ethylene/butylene–styrene type (SEBS), in which the styrene/rubber ratio is 13/87 [15] (which is equivalent to a 12% volume fraction of polystyrene). The polystyrene endblocks are associated in rigid domains linked by an elastomeric network.

Thin sheets of Kraton G-1657X, suitable for accurate absorption measurements, were supplied by

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Evode Plastics Ltd., Leicester, UK. Specimens 60 mm × 20 mm were cut from the 2.73 mm thick sheets. These specimens were placed in a vacuum oven and dried to constant weight at 50° C over a period of at least three weeks. This procedure is necessary to ensure that the specimens are completely dry prior to testing.

Dry specimens were exposed to 96% relative humidity at 50° C. This relative humidity was created by the use of a saturated solution of K_2SO_4 and the temperature was maintained by placing the humidity chamber in an air-circulating oven at 50 ± 1° C [16]. The specimens were periodically weighed in order to monitor the moisture absorption of the specimen with time. This procedure was continued until the specimens reached a constant value, which is the equilibrium moisture content (M_∞). The thickness of the specimens when dry and at M_∞ were measured and the amount of swelling was found to be negligible.

3. Results and discussion

Shen and Springer [1] have developed expressions for the diffusion of moisture into fibre-reinforced composite materials. They state that the diffusion coefficient (D_x) for such materials can be calculated from the diffusity of the matrix (D_m), the diffusity of the fibres (D_f), the volume fraction of fibre (V_f) and the orientation of the fibres with respect to the exposed surface. The relationship between D_x and D_m, D_f, V_f and fibre orientation can be established by noting the similarities between thermal conductivity and moisture diffusion. Transfer of heat by conduction occurs by random molecular translation whereas diffusion is a process by which mass is transferred as a result of random molecular motion. Approximations for the thermal conductivities parallel and normal to the fibres have been given by Springer and Tsai [17]. These expressions have been adapted by Shen and Springer [1] to give the diffusion coefficients parallel (D_{11}) and normal (D_{22}) to the fibres as

$$D_{11} = (1 - V_f)D_m + V_f D_f \tag{1}$$

$$\begin{aligned} D_{22} = {} & \left[1 - 2\left(\frac{V_f}{\pi}\right)^{1/2} D_m\right] \\ & + \frac{D_m}{B_D}\left[\pi - \frac{4}{[1 - (B_D^2 V_f/\pi)]^{1/2}} \right. \\ & \left. \times \tan^{-1}\left(\frac{[1 - (B_D^2 V_f/\pi)]^{1/2}}{1 + B_D(V_f/\pi)^{1/2}}\right)\right] \end{aligned} \tag{2}$$

where

$$B_D = 2\left(\frac{D_m}{D_f} - 1\right) \tag{3}$$

Adopting this approach the relationship between D_x and the diffusivity of the dense phase (D_d) the diffusivity of the less dense phase (D_l) and the volume fraction of the dense phase (V_d) for an isotropic two-component system can be established. Behrens [18] derived a general expression for thermal conductivity in two-component systems having orthorhombic symmetry. For spheres in a cubic lattice the expression for thermal conductivity becomes

$$K_x = K_r\left[\frac{(B_x + 2) + 2(B_x - 1)V_f}{(B_x + 2) - (B_x - 1)V_f}\right] \tag{4}$$

$$B_x = \frac{K_f}{K_r} \tag{5}$$

Analogously we can write

$$D_x = D_l\left[\frac{(B_D + 2) + 2(B_D - 1)V_d}{(B_D + 2) - (B_D - 1)V_d}\right] \tag{6}$$

$$B_D = \frac{D_d}{D_l} \tag{7}$$

In this analysis it is assumed that moisture absorption can be described using the one-dimensional case of Fick's second law, and that the diffusion coefficients are independent of the moisture content of the sample so that

$$\frac{\partial c}{\partial t} = D_a \frac{\partial^2 c}{\partial x^2} \tag{8}$$

where c = concentration of diffusing substrate, x = distance through plate thickness, t = time and D_a = diffusion coefficient of the material in the direction normal to the plate surface which can be equated with D_x, D_d or D_l.

Using this assumption the percentage moisture content as a function of time, $M(t)$, can be calculated from the equation

$$M(t) = G(M_\infty - M_i) + M_i \tag{9}$$

where M_i is the initial moisture content of the material, M_∞ is the equilibrium moisture content and G is a time-dependent parameter given by

$$G = 1 - \frac{8}{\pi^2}\sum_{j=0}^{\infty}\frac{\exp[-(2j + 1)^2\pi^2(D_a t/h^2)]}{(2j + 1)^2} \tag{10}$$

which is obtained by integrating the solution to Equation 8 [19] over the plate thickness (h). An analytical approximation for G is given by the expression

$$G = 1 - \exp\left[-7.3\left(\frac{D_a t}{h^2}\right)^{0.75}\right] \tag{11}$$

The one-dimensional case of Fick's second law implies that the material is exposed to the environment on one side only, or on two sides with both sides being parallel. Therefore, for any specimen whose edges do not have a moisture-impermeable coating a correction must be made for the moisture entering through the edges. The correction for "edge effects" in a homogeneous (or isotropic) material, calculated by Shen and Springer [1], states that

$$D_a = D\left(1 + \frac{h}{l} + \frac{h}{n}\right)^{-2} \tag{12}$$

where D = the diffusion coefficient of the material prior to being corrected for edge effects, h = thickness, l = length and n = width.

The weight-gain curve for the absorption of moisture by Kraton G-1657X is given in Fig. 2. By plotting

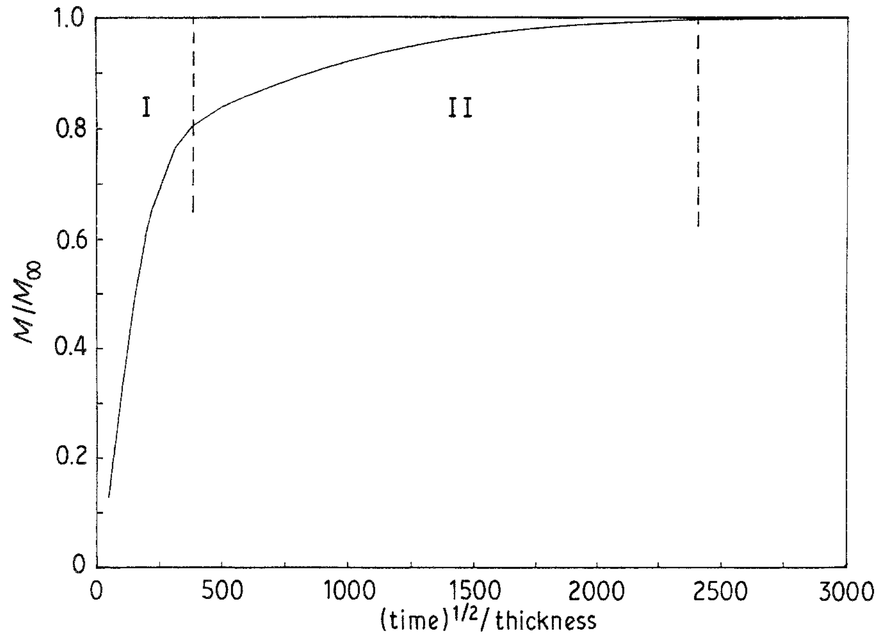

Figure 1 Schematic moisture absorption curve for a resin having a two-phase structure showing absorption into both the dense and less dense phases (Region I) and the dense phase alone (Region II).

$M(t)$ against (time)$^{1/2}$/thickness (Fig. 2) a nominal diffusion coefficient D_x can be calculated from the initial slope (m_x) of the absorption curve in Region I using the equation

$$D_x = \pi\left(\frac{m_x h}{4M_\infty}\right)^2 \tag{13}$$

where M_∞ is the equilibrium moisture content.

Kraton G-1657X is a thermoplastic elastomer consisting of segregated polystyrene domains in an elastomeric matrix. The former has the higher density and is reported to have the diffusion coefficient of a glassy polymer. The values of the diffusion coefficients of the dense and less dense phases D_d and D_l, respectively, can therefore be calculated. To do this it is necessary to determine the equilibrium moisture contents of the dense and less dense phases, M_d and M_l. This has been done by extrapolating the slope of the curve in Region II (m_d) back to the $M(t)$ axis to find the equilibrium moisture content of the less dense phase (M_l) (see Fig. 1). The equilibrium moisture content of the dense phase (M_d) can then be found by subtracting M_l from M_∞. Therefore

$$D_d = \pi\left(\frac{m_d h}{4(M_\infty - M_l)}\right)^2 = \pi\left(\frac{m_d h}{4M_d}\right)^2 \tag{14}$$

and

$$D_l = \pi\left(\frac{(m_x - m_d)h}{4M_l}\right)^2 = \pi\left(\frac{m_l h}{4M_l}\right)^2 \tag{15}$$

The values of D_x, D_d and D_l calculated from Equations 13, 14 and 15, respectively, are sensitive to errors in determining m_x and m_d from the experimental data. In this particular system sufficiently accurate measurements of m_x and m_d can be made, and the theoretical curves in Fig. 4 below can be computed directly. However, it should be recognized that where m_x and m_d cannot be measured sufficiently accurately, as in the case of a cured unsaturated polyester resin [14], an iterative procedure needs to be incorporated into the analysis to determine the values of D_x, D_d and D_l for the material.

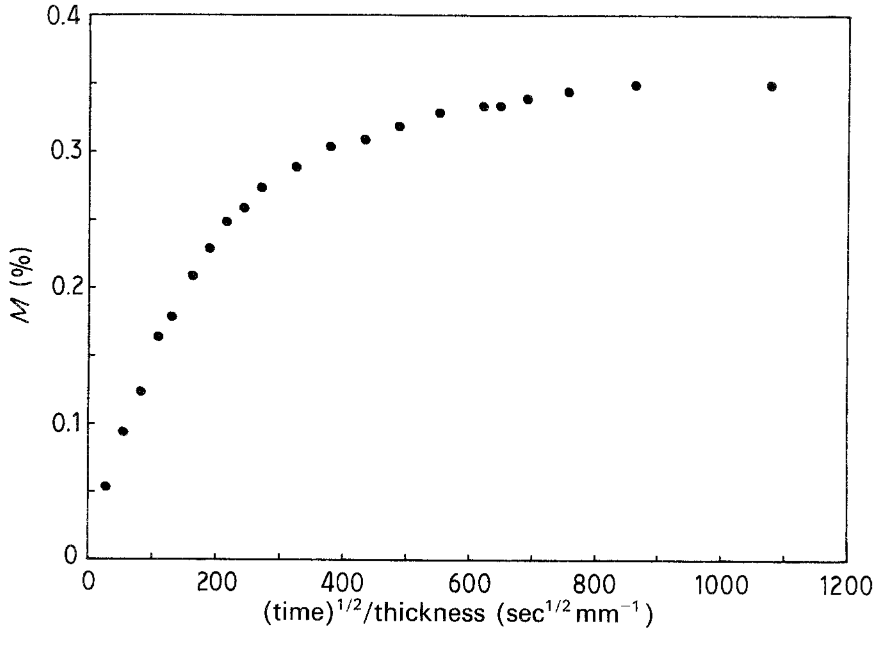

Figure 2 Experimentally determined moisture absorption curve for Kraton G-1657X exposed to 96% relative humidity at 50°C.

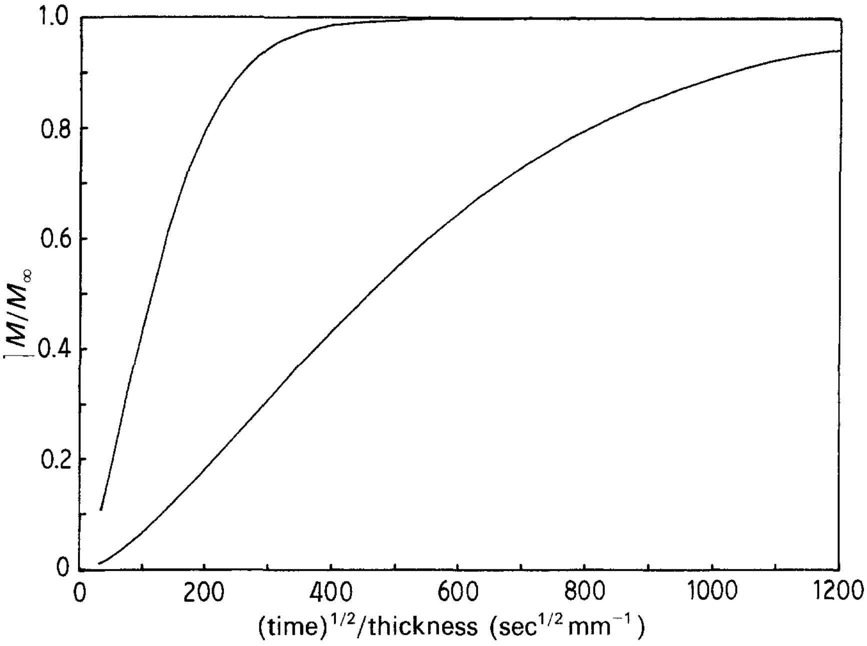

Figure 3 Normalized theoretical moisture absorption curves for the dense and less dense phases in the system.

The values of D_x, D_d and D_l for Kraton G-1657X are given in Table 1 and these values can then be used to calculate V_d from a rearrangement of Equation 6:

$$V_d = \frac{(B_D + 2)[(D_x/D_l) - 1]}{(B_D - 1)[2 + (D_x/D_l)]} \qquad (16)$$

From these values of the diffusion coefficients and equilibrium moisture contents of both phases it is possible to predict the theoretical sorption curves for the material from Equation 9. This is done by normalizing the curves for the dense and less dense phases with respect to their equilibrium moisture contents, and summing in the respective volume fractions. It is implicit in this analysis that both phases begin to absorb immediately upon exposure to the chosen environment. The good fit of the theoretical curve to the experimental data shown in Fig. 4 below demonstrates that this assumption is justified. If, however, this were not the case, and one phase began to absorb after the other, it would be necessary to displace the appropriate sorption curve along the time axis.

This analysis has been applied to the data obtained for Kraton G-1657X, and a normalized sorption curve for each of the phases was constructed from Equation 9, (Fig. 3). For the normalized curve $M_\infty = 1$, and as dry specimens were used $M_i = 0$. Thus Equation 9 becomes

$$M(t) = G = 1 - \exp\left[-7.3\left(\frac{D_a t}{h^2}\right)^{0.75}\right] \qquad (17)$$

The normalized sorption curve for Kraton G-1657X was then predicted from the equation

$$\begin{aligned} M(t) &= V_d G_d + (1 - V_d) G_l \\ &= V_d \left\{1 - \exp\left[-7.3\left(\frac{D_d t}{h^2}\right)^{0.75}\right]\right\} \\ &\quad + (1 - V_d)\left\{1 - \exp\left[-7.3\left(\frac{D_l t}{h^2}\right)^{0.75}\right]\right\} \end{aligned} \qquad (18)$$

The result of this calculation is shown in Fig. 4. It can

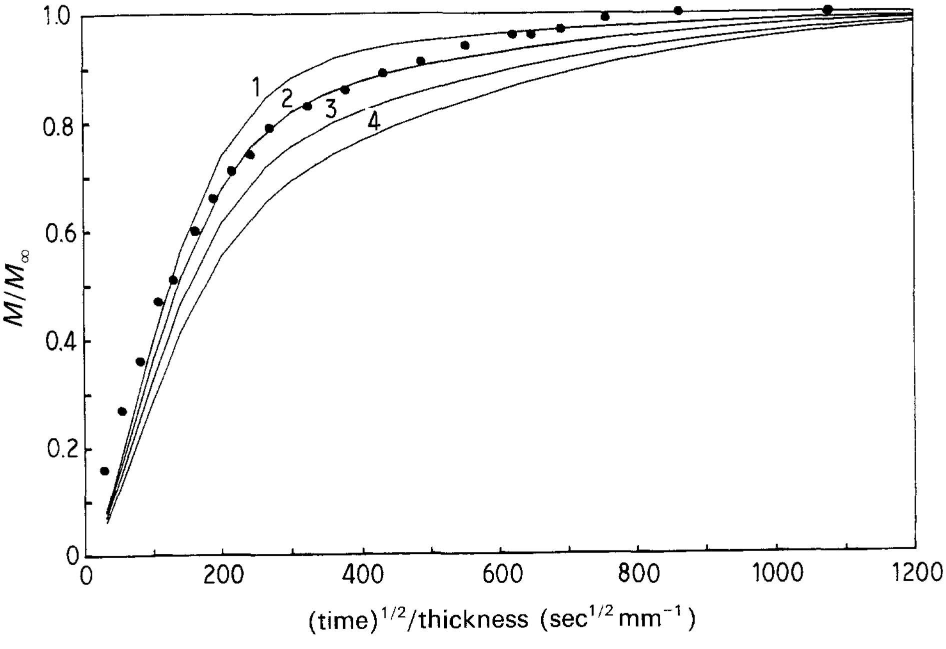

Figure 4 (●) Experimentally determined moisture absorption curve, and theoretical curves for systems with various volume fractions of the dense phase (V_d): (1) 0.10, (2) 0.20, (3) 0.30, (4) 0.40. Coincidence is achieved when $V_d = 0.20$.

TABLE I Moisture absorption data for Kraton G-1657X exposed to 96% r.h. at 50° C

Material	m(% $\text{sec}^{-1/2}$)	M(%)	$D(10^{-6}\,\text{mm}^2\,\text{sec}^{-1})$	V_d^*
Kraton G-1657X (x)	1.49×10^{-3}	0.350	18.88	–
Dense phase (d)	7.43×10^{-5}	0.061	1.55	0.20
Less dense phase (l)	1.41×10^{-3}	0.289	24.93	0.80

*Calculated from D_x and D_l according to Equation 16.

be seen that the experimentally determined value of V_d gives the best agreement with the moisture absorption data.

The value of the moisture diffusion coefficient for the segregated polystyrene phase is found to be $1.55 \times 10^{-6}\,\text{mm}^2\,\text{sec}^{-1}$, which compares favourably with values found in the literature. Lee [20] quotes values for polystyrenes of $2.39 \times 10^{-6}\,\text{mm}^2\,\text{sec}^{-1}$ at 25°C and $1.02 \times 10^{-4}\,\text{mm}^2\,\text{sec}^{-1}$ at 70° C which have been calculated from the permeability data given by Crank and Park [21]. As 70° C is approaching the glass transition temperature T_g of polystyrene (~ 100°C) and is above the relaxation temperature for side-group mobility there may be some change in the absorption characteristics and it is not, therefore, expedient to interpolate a value for the diffusion coefficient at 50° C from these data.

The equilibrium moisture content of polystyrene is generally considered to be low and a value for the equilibrium moisture content of the polystyrene phase in the system of 0.31%, calculated from experimental data ($M_d/V_d \approx 0.31\%$), would seem to confirm this.

The volume of the dispersed polystyrene phase is found by this analysis to be 0.20. The manufacturers report a value of 0.12. Considering the nature of the assumptions employed to assess the volume fraction of dispersed phase from the moisture diffusion characteristics, the close agreement demonstrates the value of this analysis. The analysis assumes that the dense phase in the material is in the form of discrete spheres arranged in a cubic lattice, surrounded by a matrix of less dense material. This implies that the material is isotropic, which is an important consideration when working with finite specimens as it is necessary to apply an "edge effect" correction. It is also assumed that the material is free from voids, inclusions and any other form of inhomogeneity which might influence the diffusion characteristics of the material. During the fabrication of sheets of Kraton G-1657X process oils are added to the rubber, and this may influence the diffusion characteristics of the material. The addition of an oil might explain why the calculated value of $V_d = 0.20$ exceeds the expected value of $V_d = 0.12$ (Table I).

Very little literature exists on methods for determining the volume fractions of the phases present in heterogeneous polymer systems. Optical and electron microscopy in conjunction with staining [22], replication [22] or etching [13, 22, 23] techniques have been used to reveal the microstructure of a variety of polymers, from which the volume fraction can be estimated. This analysis has demonstrated that diffusion data can also be used to estimate the degree of heterogeneity of a polymer or resin. The technique is applied to a study of polyester resins in Part 2 [14].

4. Conclusions

The moisture absorption curve for a two-phase resin system can be described by considering the moisture absorption characteristics of the two phases. Initially both phases absorb moisture, but once the less dense phase reaches equilibrium the increase in moisture content of the resin is due to absorption by the dense phase alone. Using a Fickian approach the diffusion coefficients of the dense and less dense phases can be calculated. From these diffusion coefficients a value for the volume fraction of the dense phase in the material can be calculated.

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References

1. C. H. SHEN and G. S. SPRINGER, *J. Compos. Mater.* **10** (1976) 1.
2. A. C. LOOS, G. S. SPRINGER, B. A. SANDERS and R. W. TUNG, *ibid.* **14** (1980) 142.
3. G. S. SPRINGER, in 'Environmental Effects on Composite Materials", Vol. 1, edited by G. S. Springer, (Technomic, Lancaster, Pennsylvania, 1981) p. 166.
4. C. D. SHIRRELL and J. HALPIN, ASTM STP 617 (American Society for Testing and Materials, Philadelphia, 1977) p. 514.
5. J. M. AUGL and A. BERGER, "The effect of Moisture on Carbon Fiber Reinforced Epoxy Composites I. Diffusion", NSWC/WOL TR-76-7 Naval Surface Weapon Center, White Oak, Silver Spring, Maryland (1976).
6. J. M. WHITNEY, in Proceedings of 18th AIAA/ASME Structure, Structural Dynamics and Materials Conference (1977).
7. *Idem*, in Proceedings of 2nd International Conference on Composite Materials, Vol. 2 (ICCM-Z) edited by B. Noton, R. Signorelli, K. Street and L. Phillips (AIME, Warrendale, Pennsylvania, 1978) p. 1584.
8. P. BONNIAU and A. R. BUNSELL, *J. Compos. Mater.* **15** (1981) 272.
9. J. N. DEWAS, in Compte-rendus des Troisiemes Journees Nationales sur les Composites, JNC -3, Paris (1982) p. 89.
10. J. N. DEWAS and J. P. FAVRE, in Proceedings of 5th International Conference on Composite Materials (ICCM V), edited by W. C. Harrigan, J. Strife and A. K. Dhingra (TMS-AIME, Warrendale, Pennsylvania, 1985) p. 1059.
11. H. G. CARTER and K. G. KIBLER, *J. Compos. Mater.* **12** (1978) 118.
12. M. A. GRAYSON and C. J. WOLF, in Proceedings of 5th International Conference on Composite Materials (ICCM-V), edited by W. C. Harrigan, J. Strife and A. K. Dhingra (TMS-AIME, Warrendale, Pennsylvania, 1985) p. 1463.
13. Y. DIAMANT, G. MAROM and L. J. BROUTMAN, *J. Appl. Polym. Sci.* **26** (1981) 3015.
14. P. M. JACOBS and F. R. JONES, *J. Mater. Sci.* **24** (1989) 2343.
15. "Kraton Thermoplastic Rubber; Typical Properties 1986", SC: 68–86 (Shell Chemical Co., Houston, Texas, 1986).
16. ASTM Designation E104-51, "Standard Recommended Practice for maintaining Constant Relative Humidity by means of

Aqueous Solutions" (American Society for Testing and Materials, Philadelphia, 1971).

17. G. S. SPRINGER and S. W. TSAI, *J. Compos. Mater.* **1** (1967) 166.
18. E. BEHRENS, *ibid.* **2** (1968) 2.
19. W. JOST, "Diffusion in Solids, Liquids, Gases" (Academic, New York, 1960).
20. W. M. LEE, *J. Cellular Plastics* (1973) 125.
21. J. CRANK and G. S. PARK, "Diffusion in Polymers" (Academic, New York, 1968) p. 263.
22. C. B. BUCKNALL, "Toughened Plastics" (Applied Science, London, 1977) p. 39.
23. D. COHN and G. MAROM, *Polymer* **24** (1983) 223.

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