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Free-volume dependent moisture diffusion under stress in composite materials

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A model for the effect of external uniaxial loading on the equilibrium moisture content in unidirectional composite materials is proposed. The model attributes the effect to a change in the free volume of the resin matrix, which is equal to its volume strain. M_∞ of the stressed state is calculated as a function of the stress level, the volume fraction of the fibres and the angle between the applied stress and the fibre direction. Moisture absorption experiments were performed on pure epoxy matrix and on graphite–epoxy composites. The effect of the parameters mentioned above on M_∞ was examined, and excellent agreement was found between the experimental and the calculated values. For stresses which were applied in the direction of the fibres ($\theta = 0°$) the experiment showed that M_∞ decreased with the increase in the stress. We attribute this anomaly to the generation of residual stresses in the composite due to swelling.

Nomenclature

D	diffusion coefficient.
E	Young's modulus.
k	slope of plot of moisture content against square root of time.
M_∞	per cent moisture content in the material in the equilibrium state.
v_f	free volume fraction.
ε	strain.
ϕ	volume fraction.
ν	Poisson's ratio.
ϱ	density.
σ	stress.
θ	angle between fibre and loading directions.
$\Delta V/V_0$	volume strain.

Subscripts

c	composite.
f	fibre.
m	matrix.
x,y,z	axes of the coordinate system.
$0,\sigma$	free and stressed states, respectively.
1,2,3	natural material axes: 1 = longitudinal axis, 2 and 3 transverse axes.

1. Introduction

The subject of moisture penetration into composite materials continues to attract our attention. In particular, we examine the effect of external loading, seeking a theoretical model that interrelates penetration parameters, such as the Fickean diffusion coefficient or the maximum absorption capacity, with the stress level, the angle between the fibre and the loading directions and the fibre volume fraction. Our initial studies concentrated on an empirical characterization of the phenomenon, revealing, for example, that the stress effect is highly dependent on the loading angle, and that this effect may be negative for small angles [1].

Following the experimental observations a theoretical approach was suggested that was based on the calculation of the free-volume change in the stressed state. This corresponded with Fahmy and Hurt's ideas [2], who calculated the free-volume change under stress for an epoxy resin. Assuming that the Fickean diffusion coefficient was related to the free volume by the Doolittle equation, they proposed an expression for the ratio of the diffusion coefficients in the stressed and free states:

$$\ln\frac{D_\sigma}{D_0} = a\left(\frac{1}{v_{f0}} - \frac{1}{v_{f\sigma}}\right) \tag{1}$$

where a is a proportion constant. Implementing these ideas in composite materials, we proposed a model that attributed the effect of external stress on the diffusion coefficient to a change in the free volume of the resin matrix, calculated by subtracting the volume change of the fibres from that of the composites [3]. The latter volume change was calculated through laminate theory equations. The model disregarded any damage-dependent mechanisms such as moisture flow in microflaws in the matrix, or capillary flow along the fibre–matrix interface.

The present paper offers a significant improvement of our model. It presents a more accurate expression for the free-volume fraction in the stressed state, accounting among other parameters for the anisotropy of the fibres. A comparison between the theoretical model and the experimental results shows that the model predicts accurately the change in the maximum moisture absorption capacity, M_∞, under stress.

2. The volume strain of the matrix

Assuming that the effect of stress on moisture penetration reflects free-volume changes, the volume strain of the matrix has to be calculated. Below we present this

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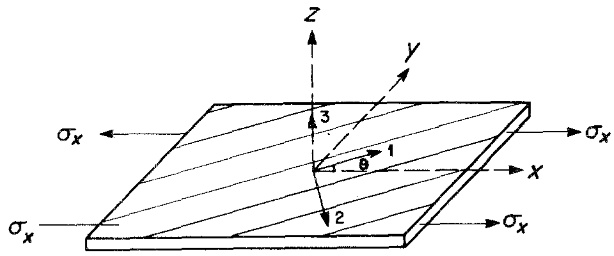

Figure 1 A unidirectional laminate stressed at angle θ with respect to the longitudinal direction.

calculation for a unidirectional composite subjected to an axial stress applied in-plane at an angle θ with respect to the fibre direction. This is shown in Fig. 1, where a plate is situated in the x–y plane, and a stress σ_x is applied in the x direction, forming an angle θ with the fibres.

$(\Delta V/V_0)_m$, the volume strain of the matrix, which is a part of the total volume strain of the stressed composite, is given by

$$(\Delta V/V_0)_c = (\Delta V/V_0)_m \phi_m + (\Delta V/V_0)_f \phi_f \quad (2)$$

Equation 2 is, in fact, a rule of mixtures expression for the volume strain of the composite and is used here instead of the simple sum approximation used in previous papers [4].

The total volume strain of the composite plate may be expressed by the sum of the directional strains

$$(\Delta V/V_0)_c = \varepsilon_{1c} + \varepsilon_{2c} + \varepsilon_{3c} \quad (3)$$

and is given by

$$(\Delta V/V_0)_c = \sigma_x \left[\frac{\cos^2\theta}{E_{1c}} (1 - 2\nu_{12c}) + \sin^2\theta \left(\frac{1}{E_{2c}} - \frac{\nu_{12c}}{E_{1c}} - \frac{\nu_{23c}}{E_{2c}} \right) \right] \quad (4)$$

Further details may be found in the Appendix.

The values of the elastic properties are obtained from the corresponding properties of the constituents and from the fibre volume fraction, ϕ_f. The following relationships are used, which include rule of mixtures and Halpin–Tsai equations [5]

$$E_{1c} = E_m \phi_m + E_{1f} \phi_f \quad (5)$$

$$\nu_{12c} = \nu_m \phi_m + \nu_{12f} \phi_f \quad (6)$$

$$E_{2c} = \left(\frac{1 + \xi\eta\phi_f}{1 - \eta\phi_f} \right) E_m$$

$$\text{where } \eta = \frac{(E_{2f}/E_m) - 1}{(E_{2f}/E_m) + \xi}, \quad \xi = 2 \quad (7)$$

$$\nu_{23c} = \left(\frac{1 + \xi\eta\phi_f}{1 - \eta\phi_f} \right) \nu_m$$

$$\text{where } \eta = \frac{(\nu_{23f}/\nu_m) - 1}{(\nu_{23f}/\nu_m) + \xi}, \quad \xi = 2 \quad (8)$$

The volume strain of anisotropic fibres is calculated in a similar way

$$(\Delta V/V_0)_f = \varepsilon_{1f} + \varepsilon_{2f} + \varepsilon_{3f} \quad (9)$$

$$(\Delta V/V_0)_f = \sigma_x \left[\frac{\cos^2\theta}{E_{1c}} (1 - 2\nu_{12f}) + \sin^2\theta \left(\frac{1}{E_{2f}} - \frac{\nu_{12f}}{E_{1f}} - \frac{\nu_{23f}}{E_{2f}} \right) \right] \quad (10)$$

Further details may be found in the Appendix

The volume strain of the matrix is now calculated by substituting Equations 4 and 10 by Equation 2, as follows

$$(\Delta V/V_0)_m \phi_m = \sigma_x \left\{ \cos^2\theta \left[\left(\frac{1 - 2\nu_{12c}}{E_{1c}} \right) - \phi_f \left(\frac{1 - 2\nu_{12f}}{E_{1c}} \right) \right] + \sin^2\theta \left[\left(\frac{1}{E_{2c}} - \frac{\nu_{12c}}{E_{1c}} - \frac{\nu_{23c}}{E_{2c}} \right) - \phi_f \left(\frac{1}{E_{2f}} - \frac{\nu_{12f}}{E_{1f}} - \frac{\nu_{23f}}{E_{2f}} \right) \right] \right\} \quad (11)$$

3. Experimental procedure

Unidirectional composite plates 0.15 cm thick were prepared from prepregs of graphite fibres (Grafil E/XAS–6K, Courtaulds) and epoxy resin (MY 750/HT 972, Ciba/Geigy) manufactured in our laboratory at various fibre contents. Specimens of 1.0 cm × 10.0 cm were cut at angles of 0, 15, 30, 45, 60, 75 and 90° with respect to the fibre direction.

Tensile stresses were applied by means of a compressed stainless steel spring as shown in Fig. 2, using different spring constants and different compressive strains to control the load. Stressed and unstressed specimens were immersed in distilled water at 90° C, and were removed periodically for weighting and recording of the weight gain. After weighting of a stressed specimen it was returned to the loading device, which was then compressed to the original position, thus correcting for a possible load decrease due to creep of the specimen.

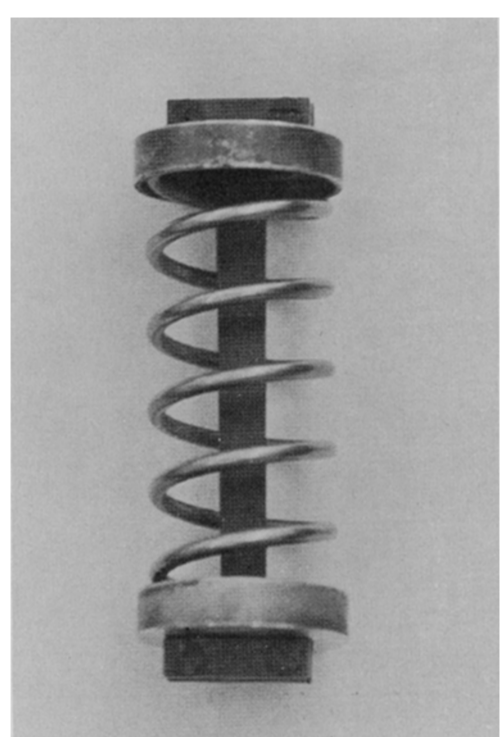

Figure 2 A stressed specimen of graphite–epoxy composite.

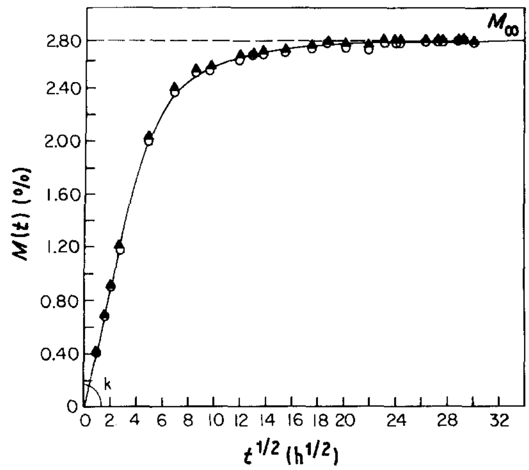

Figure 3 The moisture content as a function of the square root of the exposure time for two expoxy specimens: (○) Specimen 1, (▲) Specimen 2.

4. Results and discussion

4.1. Unreinforced resins

The first experiments were aimed at examining the relation between the free-volume change (in terms of a volume strain) under stress and the change in the moisture absorption. This was carried out by measuring the equilibrium weight gain of pure epoxy specimens loaded and immersed in water as described above. An example of the relative weight gain as a function of the immersed time is given in Fig. 3, while the experimental and calculated values of the equilibrium weight gain are presented in Table I.

The calculated values of M_∞ were obtained as follows. First v_{f0} was calculated from M_∞ of the unstressed specimens by the Equation

$$M_\infty = \frac{\Delta V}{V_0}\frac{\varrho_w}{\varrho_m} = v_{f0}\frac{\varrho_w}{\varrho_m} \qquad (12)$$

The volume strain under stress is given by

$$(\Delta V/V_0)_m = \frac{\sigma}{E_m}(1 - 2\nu_m) \qquad (13)$$

(which is a private case of Equation 11) and is equal to the free-volume change under stress. Finally, M_∞ under stress was calculated from $v_{f\sigma} = v_{f0} + (\Delta V/V_0)_m$ by Equation 12. (The values of E_m and ν_m were 2.5 GPa and 0.35, respectively.)

The calculated and experimental results in Table I are in excellent agreement despite some simplifying assumptions made, taking $\varrho_w = 1\,\mathrm{g\,ml^{-1}}$, disregarding stress decreases due to creep, and neglecting the effect of the clamped specimen ends.

The value of $v_{f0} = 3.16\%$ obtained from the experimental M_∞ by Equation 12 is higher than the value of 2.5% generally quoted for resins in the literature [6]. The first value is in fact the effective free volume accounting for the contributions of defects and voids present in the specimens, and of hygroelastic effects.

In conclusion, it is maintained that the increase in M_∞ under stress can be fully attributed to the increase in the free volume, being equal to the volume strain.

TABLE I The effect of stress on maximum moisture absorption of epoxy resin

σ (MPa)	M_∞ (%) Experimental	Calculated
0	2.66	–
4	2.70	2.70
7	2.71	2.73
10	2.75	2.76

4.2. Unidirectional composites

Experiments with composite materials were utilized for testing the validity of the proposed model, comprising both Equation 11 and the assumption that the volume strain is responsible for the new moisture absorption capacity under stress. Tables II and III contain experimental and calculated M_∞ values for different stress levels and loading angles and for a range of fibre volume fractions. The calculations of M_∞ were carried out by Equations 11 and 14 using the following values: $E_{1f} = 237\,\mathrm{GPa}$, $\varrho_f = 1.81\,\mathrm{g\,cm^{-3}}$, $\varrho_m = 1.19\,\mathrm{g\,cm^{-3}}$, $\nu_m = 0.35$, and the values of $E_{2f} = 13\,\mathrm{GPa}$, $\nu_{12f} = 0.25$ and $\nu_{23f} = 0.40$ obtained from Rogers *et al.* [7]. The temperature effect on these values is insignificant at 90° C [8]; however, the absorbed water is expected to plasticize the epoxy resin and therefore to affect the elastic properties [9]. For simplification this plasticization was not considered.

$$M_\infty = [v_{f0} + (\Delta V/V_0)_m]\frac{\varrho_w}{\varrho_c}\phi_m \qquad (14)$$

TABLE II The effect of stress on maximum moisture absorption of composite materials of $\theta_f \simeq 0.40$

θ(°)	ϕ_f	σ (MPa)	M_∞ (%) Experimental	Calculated
0	0.41	0	1.35	1.35
		50	1.35	1.36
		100	1.28	1.37
15	0.41	0	1.33	1.34
		18	1.36	1.35
		22	1.36	1.35
		26	1.38	1.36
		30	1.43	1.36
30	0.41	0	1.35	1.37
		18	1.44	1.41
		22	1.54	1.41
45	0.37	0	1.47	1.46
		8	1.48	1.50
		12	1.54	1.53
		16	1.61	1.56
60	0.42	0	1.31	1.31
		5	1.34	1.34
		8	1.40	1.36
		11	1.40	1.38
		14	1.42	1.39
75	0.40	0	1.38	1.37
		4	1.41	1.40
		7	1.44	1.42
		10	1.44	1.44
90	0.41	0	1.35	1.35
		4	1.37	1.39
		7	1.38	1.41
		10	1.42	1.43

TABLE III The effect of stress on moisture absorption of composite materials of various fibre contents

θ(°)	ϕ_f	σ (MPa)	M_∞ (%)	
			Experimental	Calculated
30	0.36	0	1.49	1.49
		18	1.58	1.53
		22	1.66	1.54
30	0.46	0	1.20	1.20
		18	1.22	1.23
		22	1.28	1.24
30	0.54	0	0.99	0.99
		18	1.04	1.01
		22	1.05	1.02
60	0.35	0	1.52	1.52
		5	1.53	1.55
		8	1.55	1.57
		11	1.62	1.59
60	0.51	0	1.06	1.07
		5	1.12	1.09
		8	1.11	1.10
		11	1.18	1.11
60	0.59	0	0.87	0.88
		5	0.88	0.89
		8	0.90	0.90
		14	0.94	0.92

Although some individual sets of results exhibit differences, the overall picture that emerges from Tables II and III is one of good agreement between the calculated and the experimental results, as illustrated generally by Fig. 4.

For $\theta = 0°$, however, the calculated values contradicted the decreasing trend exhibited by the experimental results as a function of the stress, in agreement with previously published data [1, 4, 10]. This phenomenon was reconfirmed here by testing additional $\theta = 0°$ specimens as shown in Table IV and Fig. 5. The results in Table IV are average values of a number of specimens for each testing condition the M_∞ values of the stressed specimens being significantly smaller than those of the unstressed specimens at least at the 90% level (by t-test).

A possible explanation for the negative stress effect on the diffusion at $\theta = 0°$ is one that takes into account the residual stresses existing in the composite during swelling. Hahn and Kim [9] have shown that

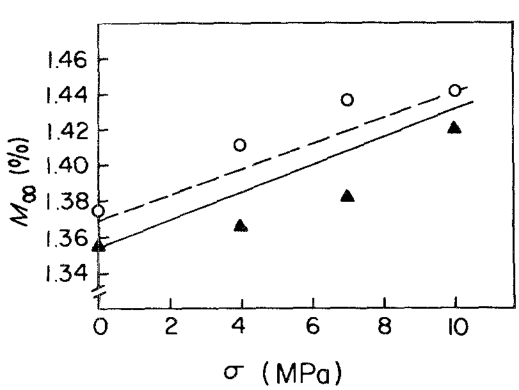

Figure 4 The moisture content in the equilibrium state as a function of stress for specimens loaded at (○) $\theta = 75°$ and (▲) $\theta = 90°$; (——), (---) are the calculated lines.

TABLE IV The effect of stress at $\theta = 0°$ on M_∞

ϕ_f	σ(MPa)	M_∞ (%)
0.36	0	1.55
	60	1.53
0.58	0	1.15
	60	1.12

the transverse compressive residual stresses during moisture absorption of unidirectional graphite–epoxy composites may exceed 70 MPa at the outside surface. Residual stresses are expected to affect the volume strain of the matrix as follows: at $\theta = 0°$ it depends on ν_m by $(\Delta V/V_0) = \sigma_x(1 - 2\nu_m)/E_{1c}$ (Equation 11 for $\theta = 0°$). The value of ν_m may be different in the composite material and in the unreinforced resin. In particular, an effective Poisson's ratio of the matrix should be considered in a situation where a stress is acting at right-angles to a constraint. This, for example, is the case of transverse loading of a unidirectional composite, where the stiffer fibres place a constraint on the tendency of the softer matrix to contract. As a result, the simple rule of mixtures, ignoring this effect, fails to produce an accurate estimate of ν_{21}, and is thus replaced by an expression that takes into account an effective ν_m of $\nu_{eff} \simeq \nu_m(1 + \nu_m)/(1 - \nu_m^2)$ [12]. For an epoxy matrix the effective Poisson's ratio with a transverse constraint is ~0.54.

Assuming that the effect of the residual swelling stresses is to produce a transverse constraint, the volume strain of the matrix is given by $(\Delta V/V_0)_m \simeq -0.08\sigma_x/E_{1c}$ for $\theta = 0°$. The experimental results are of similar order of magnitude and tendency.

The effect of the residual stresses is probably negligible for other values of θ; for those, the volume strain expressed by Equation 11 is a function of additional elastic constants beside ν_m.

The values of v_{f0} used in the calculation of M_∞ were also used to calculate D_σ by Equation 1. The results are not presented here; however, it is pointed out that they did not agree with the experimental D_σ values. It is thought that Fahmy and Hurt's prediction of D_σ by incorporating the Doolittle equation [2] depends on the value of the constant a of Equation 1.

5. Conclusion

In view of the excellent agreement between the experimental M_∞ results and the proposed model we conclude the following:

The equilibrium moisture absorption capacity of composite materials is affected by external stress according to the resultant free volume fraction change which is equal to the volume strain.

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Appendix

A1. The volume strain of the composite material

Hooke's law for orthotropic material (unidirectional

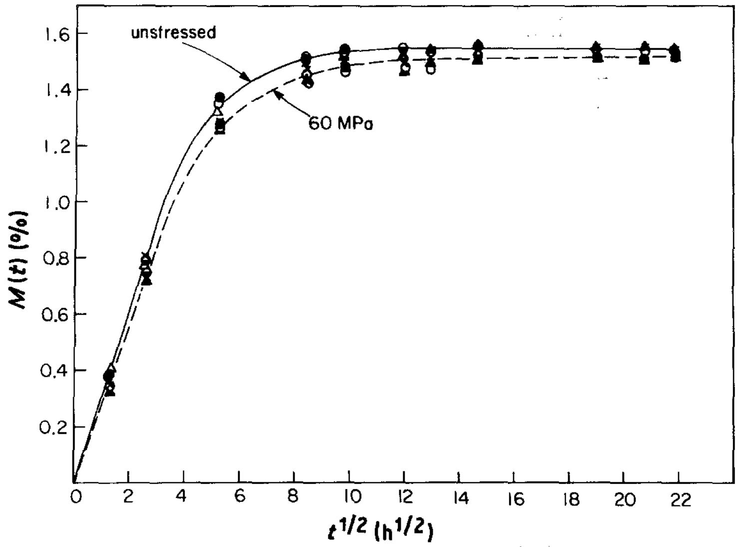

Figure 5 The moisture content as a function of the square root of the exposure time for four unstressed and four stressed (60 MPa) specimens, where $\theta = 0°$.

composite) for an in-plane state of stress ($\sigma_3 = 0$) gives

$$\varepsilon_{1c} = \frac{\sigma_{1c}}{E_{1c}} - \frac{\nu_{21c}}{E_{2c}}\sigma_{2c} \quad \text{(A1)}$$

$$\varepsilon_{2c} = -\frac{\nu_{12c}}{E_{1c}}\sigma_{1c} + \frac{\sigma_{2c}}{E_{2c}} \quad \text{(A2)}$$

$$\varepsilon_{3c} = -\frac{\nu_{13c}}{E_{1c}}\sigma_{1c} - \frac{\nu_{23c}}{E_{2c}}\sigma_{2c} \quad \text{(A3)}$$

If the plane is perpendicular to the "1" axis then $\nu_{13} = \nu_{12}$. Now, consider that the only non-zero stress (Fig. 1) acting on this material is σ_x, then the normal stresses can be calculated by the stress-transformation law

$$\sigma_{1c} = \sigma_x \cos^2\theta \quad \text{(A4)}$$

$$\sigma_{2c} = \sigma_x \sin^2\theta \quad \text{(A5)}$$

Substituting Equations A4 and A5 in Equations A1 to A3 and adding up the three strains, we receive the volume strain of this composite

$$(\Delta V/V_0)_c = \sigma_x\left[\frac{\cos^2\theta}{E_{1c}}(1 - 2\nu_{12c}) + \sin^2\theta\left(\frac{1}{E_{2c}} - \frac{\nu_{12c}}{E_{1c}} - \frac{\nu_{23c}}{E_{2c}}\right)\right] \quad \text{(A6)}$$

where

$$\frac{\nu_{12c}}{E_{1c}} = \frac{\nu_{21c}}{E_{2c}}$$

A2. The volume strain of the anisotropic fibres

The longitudinal (σ_{1f}) and the transverse (σ_{2f}) stresses in the fibres are

$$\sigma_{1f} = \frac{E_{1f}}{E_{1c}}\sigma_{1c} = \frac{E_{1f}}{E_{1c}}\sigma_x\cos^2\theta \quad \text{(A7)}$$

$$\sigma_{2f} = \sigma_{2c} = \sigma_{2m} = \sigma_x\sin^2\theta \quad \text{(A8)}$$

The expressions for the fibre strains (ε_{1f}, ε_{2f} and ε_{3f}) are similar to those of the composite; substituting the appropriate stresses and adding up the three strains results in the fibre volume strain as follows

$$(\Delta V/V_0)_f = \sigma_x\left[\frac{\cos^2\theta}{E_{1c}}(1 - 2\nu_{12f}) + \sin^2\theta\left(\frac{1}{E_{2f}} - \frac{\nu_{12f}}{E_{1f}} - \frac{\nu_{23f}}{E_{2f}}\right)\right] \quad \text{(A9)}$$

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