Study of the interfacial degradation of a glass–epoxy composite during hygrothermal ageing using water diffusion measurements and dynamic mechanical thermal analysis

A. Chateauminois* and L. Vincent
Département Matériaux Mécanique Physique, URA CNRS 447, Ecole Centrale de Lyon, BP 163-69131, Ecully Cedex, France

and B. Chabert and J. P. Soulier
Laboratoire d'Etudes des Matériaux Plastiques et Biomatériaux, URA CNRS 507, Université C. Bernard, Villeurbanne Cedex, France

(Received 5 February 1993; revised 23 May 1994)

The hygrothermal degradation of a glass fibre/epoxy unidirectional composite is investigated by moisture sorption/desorption experiments and dynamic mechanical thermal analysis (d.m.t.a.). At short immersion times, water sorption in distilled water can be satisfactorily described by using Fick's law. The three-dimensional analysis of water diffusion in parallelepipedic samples shows that no significant interfacial capillary flow occurs during the initial Fickian step where water sorption occurs mainly by diffusion through the epoxy network. This conclusion was found to be valid even at the most elevated ageing temperature (90°C). Slow positive deviations from the Fickian behaviour are noticed for long ageing times at 70 and 90°C. They have been found to be correlated to some interfacial debonding, as indicated by an enhanced desorption rate during thermogravimetric analysis (t.g.a.) scans. During these non-Fickian sorption steps, the d.m.t.a. spectra of the aged composite also reveal the progressive appearance of an irreversible broadening of the damping peak associated with the α-relaxation. These processes have been attributed to the occurrence of specific morphological changes and debonding at the interphase during ageing. It is concluded that the hygrothermal degradation of the interface occurs essentially in the non-Fickian sorption steps when the epoxy matrix is close to saturation.

(Keywords: glass–epoxy composite; fibre–matrix interface; hygrothermal ageing)

INTRODUCTION

Polymer matrix composite materials in structural parts of aircrafts or other structures in service may often be exposed to various kinds of environment which involve, in most cases, temperature and humidity. Over the past few years, a great deal of experimental evidence has been accumulated to demonstrate that both physical and mechanical properties of composite materials can be strongly affected during hygrothermal ageing. As a result, environmental effects on the durability of composites became of primary interest for composite designers. However, lifetime predictions in hot/wet environments from accelerated ageing procedures require a basic understanding of the material damage processes. In the case of epoxy matrix composites, the ageing mechanisms fall into two groups.

The first group is related to ageing processes which involve only molecular interactions between water and the epoxy network. Plasticization of the macromolecular network during water diffusion belongs to this category. This well known effect can result in a dramatic decrease in the thermomechanical properties of the composites[1–4], thus limiting their use in a hot/wet environment. In addition to reversible plasticization, some hydrolysis of the epoxy network can induce irreversible losses of properties[5–7]. The specific sensitivity of the fibre/matrix interface to such processes has been pointed out by Hoh *et al.*[8] and Liao[9], who found that the silane coupling agents usually used in the glass sizing were susceptible to hydrolysis in a hot/wet environment.

The second group of hygrothermally induced changes involves macroscopic damage such as material cracking and fibre/matrix debonding. This damage can be considered as a consequence of the molecular processes resulting from water sorption in the epoxy network, and is therefore mainly associated with hydrolysis and/or swelling stresses[10–12]. Cracking and debonding can also modify the mechanisms of water penetration in the

---

* To whom correspondence should be addressed

0032-3861/94/22/4766–09

composite by providing new pathways for moisture ingress. The uptake of moisture and the resulting weakening of the material are then more rapid than those occurring only by molecular diffusion in the matrix. When considering fibre/matrix debonding, reinforcement fibres become susceptible to direct environmental attack. In the case of glass fibres, such direct environmental exposure has been found to induce drastic losses of static properties due to stress corrosion mechanisms[13–15]. Furthermore, microbond experiments[16] have revealed that the interfacial shear strength was strongly affected by water exposure, thus inducing a reduced load transfer ability during mechanical loading.

Whether the considered scale of damage is molecular or macroscopic, it is clear that the fibre/matrix interface is often pinpointed as a weak element in environmental resistance. However, relatively little attention has been paid to the kinetic features of interfacial hygrothermal degradation in relation to water diffusion in the composite. This study also focuses on the kinetics of fibre/matrix debonding and the morphological changes occurring in the interfacial network. An attempt has been made to correlate processes occurring at the macroscopical level (defect nucleation by fibre/matrix debonding) and those occurring at the macromolecular level (morphological and/or structural changes in the interfacial network). Such an approach has proved to be of great relevance in the assessment of the durability of composite materials in a wet environment[17]. Debonding has been investigated by the quantitative analysis of interfacial capillary flows during both moisture sorption and desorption experiments. Macromolecular morphological changes at the interphase have also been studied by dynamic mechanical thermal analysis (d.m.t.a.). Material ageing was performed at different temperatures in order to identify the corresponding damage evolution. In order to ensure precise identification of the effects resulting from interfacial damage, comparative experiments were carried out with the composite material and the unreinforced matrix. It must also be emphasized that only irreversible processes were taken into account, and that reversible plasticization effects will not be considered in this study. Plasticization has been studied elsewhere[18] and no specific effect of the interphase was identified for the composite studied.

EXPERIMENTAL

Material and fabrication of test samples

The matrix of the composite studied here was a bisphenol A epoxy resin and the reinforcement consisted of R-glass fibre roving with a silane sizing. The matrix was obtained from a diglycidyl ether of bisphenol A (DGEBA) resin (Ciba LY556) which had been cured by using a stoichiometric amount of 4,4′-diaminodiphenylmethane (DDM) hardener (Ciba HT972). The reinforcement was a high mechanical performance P9HT R-glass roving (1600 tex) supplied by Vetrotex. Fibres were coated with γ-aminopropyltriethoxysilane (A1100) as a coupling agent; the other sizing components are DGEBA prepolymers and amine acetates.

Unidirectional plates (1 and 2 mm thick) were fabricated by filament winding. The impregnation of the glass roving was performed at 65°C without using any solvent. The resin impregnated strand was continuously wound around a rotating steel plate heated by radiating panels. The strand was shifted at each rotation and the winding thread was chosen in order to avoid the overlapping of the strands in each lay-up. Due to the selection of an appropriate rotation speed for the plate, the glass fibres were able to be weakly tightened to maintain an accurate aligning of the glass fibres. At the end of the winding step, two counter moulds were applied to each face of the steel plate for the curing.

The cure cycle was 3 h at 80°C followed by 3 h at 175°C. This procedure resulted in a fully crosslinked resin with a T_g of 175°C, as measured at 3 Hz by dynamic mechanical thermal analysis (see below). The volume fraction of fibre was 0.48 ± 0.02, with the void content being less than 1%. Unreinforced matrix specimens were also obtained by pouring the epoxy resin between two mould plates treated with release agent. The cure cycle was identical to that selected for the composite.

Moisture sorption test procedure

The plates were cut into specimens of various lengths (5, 7.5, 10 and 20 mm) and constant widths (20 mm) by using a diamond coated slitting wheel. These different specimen sizes were selected in order to evaluate interfacial capillary diffusion by taking into account edge effects (see below).

Prior to immersion, the as-cast specimens were dried in a vacuum oven at 70°C until they reached a constant weight (a process which took ~2 weeks). This preconditioned state was then used as a reference for the measurement of the water uptake during immersion.

Samples were immersed in distilled water at various temperatures, i.e. 30, 50, 70 and 90°C. At appropriate intervals, they were removed, surface dried and then weighed to within 0.1 mg with a Mettler AE100 analytical balance. The relative weight gain, M_t, is expressed as a percentage of the initial weight of the sample. Five specimens were taken for each immersion temperature and sample geometry.

Thermogravimetric analysis (t.g.a.)

Moisture desorption after water ageing was investigated by thermogravimetric analysis. A Dupont thermogravimetric analyser (Model 951) was used to measure the weight loss of wet material when it was heated at a controlled heating rate ($2°\mathrm{C\,min^{-1}}$) from 30 to 250°C, with the experiments being performed under a helium flow. As for the sorption experiments, the weight losses were expressed as percentages of the dried material. The test specimen geometry was $5 \times 5 \times 1$ mm.

Dynamic mechanical thermal analysis (d.m.t.a.)

The dynamic mechanical thermal analysis of the material was performed on a Polymer Laboratories Mark II viscoelasticimeter equipped with a bending head. The sample was sinusoidally strained in a single cantilever mode. A 16 μm dynamic displacement amplitude was selected and tests were carried out in the isothermal mode. During temperature steps in the glass transition range, $\log E'$ and $\tan\delta$ were measured at different frequencies, ranging from 0.1 to 10 Hz. Off-axis analysis was performed in order to enhance the matrix and interface viscoelastic response. The angle between the fibre direction and the sample axis was set at 30°.

The d.m.t.a. experiments were carried out in both the non-aged and the aged state. Prior to analysis, the aged specimens were redried in a vacuum oven at room

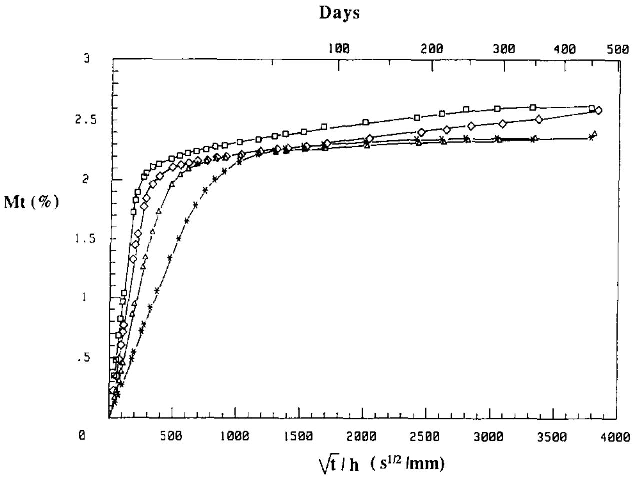

Figure 1 Relative weight gain of the unreinforced epoxy matrix *versus* time of immersion in distilled water at different temperatures: (*) 30°C; (△) 50°C; (◇) 70°C; (□) 90°C

temperature until they reached a constant weight (this took ~2 months). It was found that whatever the ageing temperature, the changes in the weights of the aged and subsequently redried specimens were within 0.1% of their initial weights. It can therefore be concluded that no significant loss of material occurred during ageing. This redrying of the aged specimens was performed in order to eliminate the reversible plasticization effects due to the sorbed water molecules. Thus, only irreversible changes which occurred in the epoxy network were analysed by d.m.t.a..

RESULTS AND DISCUSSION

Initial sorption tests at different temperatures

Primary sorption experiments were first carried out in order to obtain an overall view of the sorption behaviour at the different selected temperatures. This first phase of the investigation determined the moisture content dependency with time and temperature over 400 days.

The sorption behaviour of the unreinforced epoxy matrix is shown in *Figure 1*. The relative weight gain M_t is plotted *versus* the square root of the immersion time (normalized to the thickness h of the sample). At each immersion temperature, two parts can be distinguished on the sorption curves as follows:

(1) At shorter times, the moisture content increases linearly at first, and then reaches a pseudo-equilibrium state. The water uptakes at this pseudo-equilibrium state are approximately the same whatever the immersion temperatures being considered. Such features are characteristic of a thermally activated Fickian sorption behaviour, as reported by Cranck[19]. Water is then considered to remain in a single free phase, and is driven to penetrate the resin by the water concentration gradient.

(2) At longer times, a slow positive deviation from the Fickian pseudo-equilibrium state occurred. These non-Fickian water uptakes increase with immersion temperature. Such continuous slow absorption processes have been reported by numerous authors, and can be attributed either to slow relaxation processes of the glassy epoxy network[20–23], or to the filling of hygrothermally induced voids[24–26].

Similar features can be noted for the composite (*Figure 2*). The water uptakes in the non-Fickian part of the sorption curves is also dependent on the ageing temperature. It must be emphasized that a microscopic examination of polished sections of the composite specimens did not reveal any cracking of the matrix for the immersion times being considered. As a result, the observed non-Fickian behaviour of the composite cannot be attributed to the filling of hygrothermally induced cracks in the matrix. At 90°C, these non-Fickian water uptakes represent 24% of the total weight gain, instead of 15% for the unreinforced epoxy matrix: non-Fickian behaviour thus occurs to a greater extent in the case of the composite.

The water uptake of the composite at a given temperature can be assumed to take into account two components:

(i) the water uptake of the matrix itself, which has been found to be temperature dependent due to either relaxation or microvoid nucleation, as mentioned above;

(ii) a specific water uptake at the fibre/matix interface if some debonding occurs.

When no debonding is induced, a theoretical moisture content, M_t^*, of the composite can be estimated from the water content of the unreinforced matrix, assuming that the composite obeys a mixture rule for sorption:

$$M_t^* = \phi_f M_t^f + \phi_m M_t^m \qquad (1)$$

where ϕ is a mass fraction and the subscripts (and superscripts) m, f, and c refer to matrix, fibre and composite respectively. The fibres sorbed relatively little water and M_t^f was neglected. In equation (1), the assumption is made that the water uptakes of the composite matrix and the unreinforced matrix are the same. This hypothesis has been found to be valid at both 30 and 50°C, where the experimental and calculated weight gains of the composite are very similar (*Table 1*). Moreover, this good fit to the mixture rule indicates that no significant water uptake occurred by fibre/matrix debonding at temperatures of 30 and 50°C.

On the other hand, it can be noted that the experimental weight gains of the composite at 70 and 90°C are somewhat above those obtained from the mixture rule.

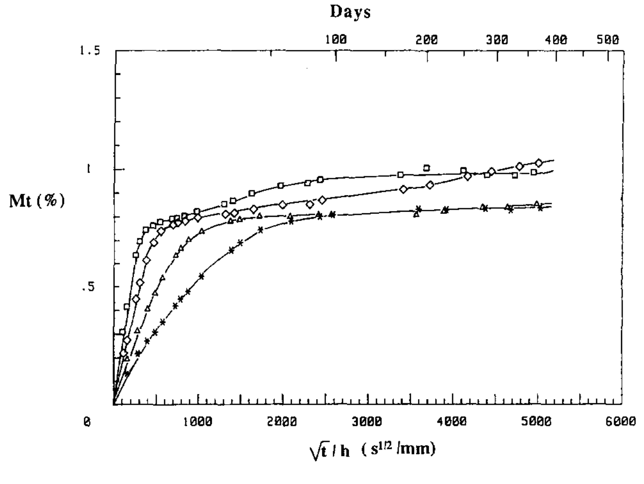

Figure 2 Relative weight gain of the composite *versus* time of immersion in distilled water at different temperatures: (*) 30°C; (△) 50°C; (◇) 70°C; (□) 90°C

Table 1 Calculated (from equation (1)) and experimental weight gains of the composite after immersion in distilled water for 400 days

Temperature (°C)	Experimental M_t (%)	Calculated M_t^* (%)
30	0.84	0.82
50	0.86	0.83
70	1.03	0.89
90	1.02	0.91

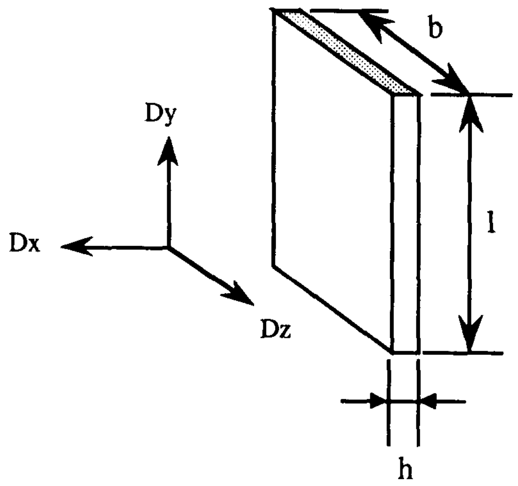

Figure 3 Test specimen geometry and components of the diffusion coefficient in Cartesian coordinates: note that the glass fibres used in this study are parallel to the y-axis

The temperature dependence of the composite water content can no longer be predicted only from a knowledge of the sorption behaviour of the epoxy matrix at the considered temperatures. These experimentally high M_t values for the composite at 70 and 90°C must then be interpreted by considering some additional effects, such as the filling of hygrothermally induced voids at the debonded fibre/matrix interface.

Therefore, there is some suggestion of interfacial degradation and debonding upon water ageing at high temperatures. As a result, new pathways for the moisture ingress could be provided by such interfacial damage, which modifies the overall sorption process. An attempt was also made to investigate the occurrence of capillary flow at the fibre/matrix interface. During the Fickian sorption steps, this can be performed by evaluating the moisture flow through the cut edges of the parallelepipedic samples, as described below.

Evaluation of interfacial diffusion during Fickian sorption steps

Theoretical basis. Fick's second law of diffusion has been widely used to describe the uptake of moisture by composite materials. One-dimensional analytical solutions have been discussed by Shen and Springer[27] for the moisture content in a thin composite plate. These are based on the following relationship:

$$\frac{dC}{dt} = D_x \frac{d^2C}{dx^2} \tag{2}$$

where C is the water concentration, D_x is the diffusivity normal to the surface, i.e. in the x-direction, and t is the diffusion time. In the case of isotropic thin plates ($h \ll l$ and $h \ll b$ on *Figure 3*), the moisture entering the parallelepipedic specimen through the edges can be neglected. D_x can then be experimentally obtained from the initial slope of the M_t *versus* $\sqrt{t}$ curve:

$$D_x = \pi\left(\frac{h}{4M_m}\right)^2\left(\frac{dM_t}{d\sqrt{t}}\right)^2 \tag{3}$$

where M_m is the equilibrium weight gain. If moisture flow through the lateral faces can no longer be neglected, edge corrections must be introduced in order to compute D_x from the sorption curves.

Using the short term solution of the one-dimensional Fick's law, Shen and Springer[27] derived the following relationship:

$$M_t = \frac{4M_m}{h\sqrt{\pi}}\sqrt{t}\left(\sqrt{D_x} + \frac{h}{l}\sqrt{D_y} + \frac{h}{b}\sqrt{D_z}\right) \tag{4}$$

where D_x, D_y and D_z are the diffusion coefficients in the x, y and z directions.

This equation was obtained by making the assumption that the water flows through each sample face are additive. This is only valid at short times, when the interactions between the six faces of the parallelepiped can be neglected. For longer times, the kinetics can be computed by using the three-dimensional solution of Fick's law :

$$\frac{M_t}{M_m} = 1 - \left(\frac{8}{\pi^2}\right)^3 \sum_{m=0}^{\infty}\sum_{n=0}^{\infty}\sum_{p=0}^{\infty} \frac{\exp(-tq_{m,n,p})}{(2m+1)^2(2n+1)^2(2p+1)^2} \tag{5}$$

with

$$q_{m,n,p} = \frac{\pi^2}{4}\left[D_x\left(\frac{2m+1}{h/2}\right)^2 + D_y\left(\frac{2m+1}{l/2}\right)^2 + D_z\left(\frac{2m+1}{b/2}\right)^2\right] \tag{6}$$

where m, n *and* p are integers.

From equation (4) an overall diffusion coefficient, D , can be defined as follows:

$$D = D_x\left(1 + \frac{h}{l}\sqrt{\frac{D_y}{D_x}} + \frac{h}{b}\sqrt{\frac{D_z}{D_x}}\right)^2 \tag{7}$$

In the case of an isotropic material, such as the unreinforced epoxy matrix, $D_x = D_y = D_z$, which implies that:

$$D = D_x\left(1 + \frac{h}{l} + \frac{h}{b}\right)^2 \tag{8}$$

For a unidirectional composite $D_x = D_z$ and equation (7) can be written in the following form:

$$\sqrt{D} = \sqrt{D_x}\left(1 + \frac{h}{b}\right) + \frac{h}{l}\sqrt{D_y} \tag{9}$$

Thus, for specimens of different lengths, but with a constant thickness and width, a plot of $\sqrt{D}$ *versus* h/l should yield a straight line with slope $\sqrt{D_y}$ and intercept $\sqrt{D_x}(1 + h/b)$. A similar, but simplified method has been successfully used by Pollard *et al.*[28] to evaluate D_x and D_y in glass/polyester composites. In our case, a knowledge of the D_y/D_x ratio will provide some information on the occurrence of preferential diffusion along the fibre direction during Fickian sorption steps.

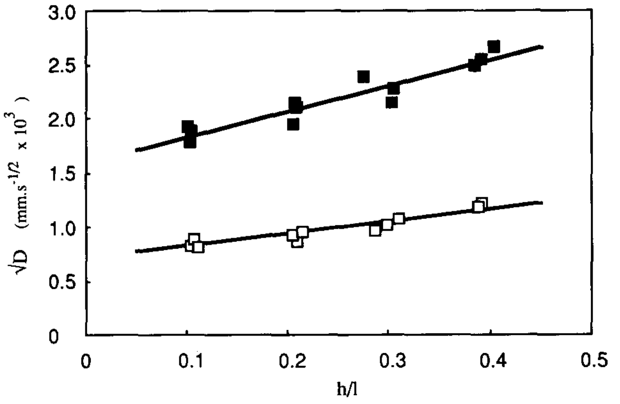

Figure 4 The square root of the apparent diffusion coefficient D *versus* the h/l ratio, for the composite immersed in water at different temperatures: (□) 50°C; (■) 90°C

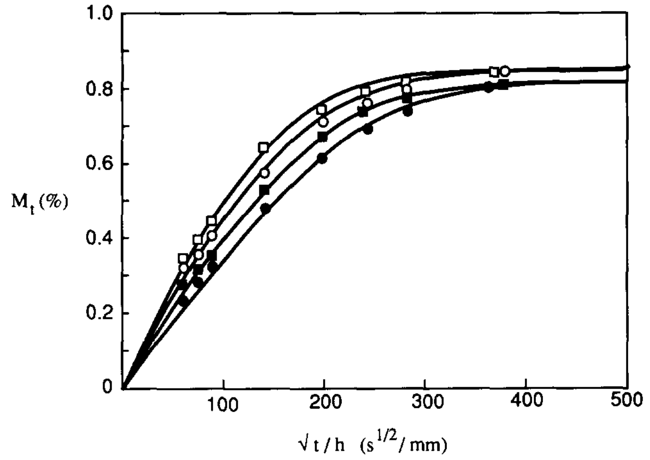

Figure 5 Three-dimensional water diffusion in the composite immersed at 90°C for different values of l: (□) 5 mm; (○) 7.5 mm; (■) 10 mm; (●) 20 mm. Solid lines correspond to the three-dimensional diffusion kinetics computed from equations (5) and (6)

Three-dimensional diffusion at 50°C and 90°C. Composite test specimens of different lengths (see above) were immersed in water at 50 and 90°C. For each geometry, the overall diffusion coefficient D was measured from the slope of the initial linear part of the sorption curves. In *Figure 4*, $\sqrt{D}$ has been plotted *versus* the h/l ratio. A linear straight line is effectively obtained, and D_x and D_y can be computed from equation (9). From these calculated values, the water sorption kinetics were calculated by using equations (5) and (6). Examples of the sorption curves obtained at 90°C are reported in *Figure 5*, showing the good agreement between the computed kinetics and the experimental data.

It is of interest to compare the D_y/D_x ratio to the theoretical values derived from thermal or electrical analogies. The most widely used expressions give[27]:

$$\frac{D_y}{D_x}=\frac{(1-V_f)}{(1-2\sqrt{V_f/\pi})} \tag{10}$$

where V_f is the fibre volume fraction. It must be emphasized that this expression implies that no preferential diffusion occurs at the fibre/matrix interface. An enhanced sorption rate due to capillary flow at the interface would thus result in a mismatch between the theoretical D_y/D_x ratio and the experimental one.

From the fibre volume fraction, we obtained a D_y/D_x theoretical value which was equal to 2.3, which is close to the experimental value (see *Table 2*). It follows from this result that, in this particular type of composite, there is no capillary or preferential diffusion at the fibre/matrix interface during the Fickian steps of water sorption. This conclusion remains valid at 90°C, where the D_y/D_x ratio remains unchanged. Although many authors have pointed out interfacial capillary flows, this emphasizes the good water resistance of the interface studied during the initial Fickian step, where water sorption occurs mainly by diffusion through the epoxy network.

Desorption behaviour

Thermogravimetric analysis of the aged specimens was performed after 400 days of immersion, i.e. during the non-Fickian diffusion step. The experiments were directed towards providing information on the desorption behaviour of the composite and the unreinforced matrix after isothermal water ageing at increasing temperatures.

The weight losses of the aged matrix during a temperature scan from 30 to 250°C are reported in *Figure 6a*. Below 150°C, the desorption curves remain the same

Table 2 Values of the components of the diffusion coefficient, parallel (D_y) and perpendicular (D_x) to the fibre direction

Temperature (°C)	D_x (mm^2 s^{-1})	D_y (mm^2 s^{-1})	D_y/D_x
50	4.5×10^{-7}	13×10^{-7}	2.9
90	2.1×10^{-6}	5.8×10^{-6}	2.7

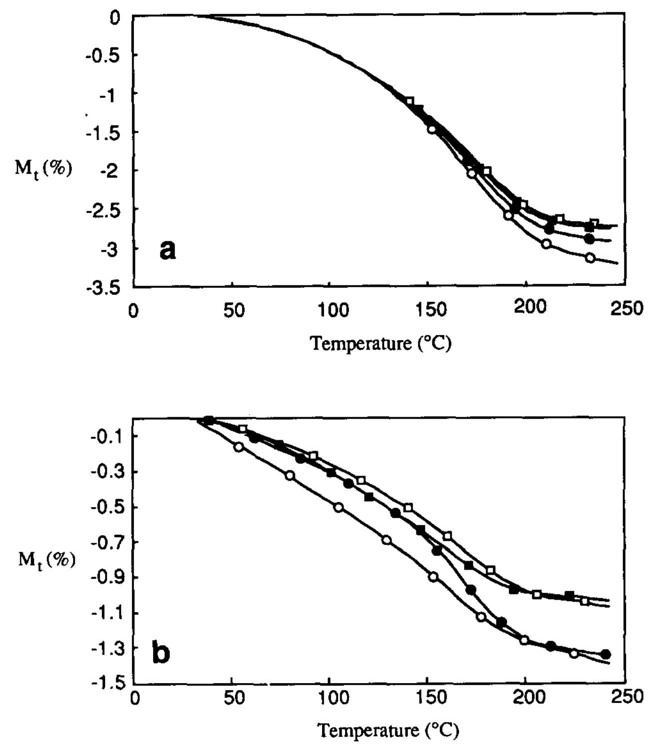

Figure 6 Thermogravimetric analysis curves of the unreinforced matrix (a) and the composite (b) after 400 days of ageing in distilled water at various temperatures: (□) 30°C; (■) 50°C; (●) 70°C; (○) 90°C (temperature scan rate = 2°C min^{-1})

Table 3 Comparison between the amount of sorbed water during an isothermal immersion and the corresponding amount of desorbed water at 250°C during a t.g.a. scan (for a composite and unreinforced matrix, both after 400 days of ageing)

Ageing temperature (°C)	Dynamic weight loss, t.g.a. scan (%)		Isothermal weight gain (%)	
	Composite	Matrix	Composite	Matrix
30	1.04	2.74	0.84	2.35
50	1.07	2.77	0.86	2.42
70	1.35	2.93	1.03	2.53
90	1.40	3.22	1.02	2.66

whatever the ageing temperature. In the case of the matrix specimens aged at 70 and 90°C, a shift of the t.g.a. thermograms toward higher weight losses can be noted above 150°C. This increase can be related to the higher initial water content of the specimens aged at these temperatures (see *Figure 1* where $t = 400$ days). Moreover, it must be noted that the weight losses from the t.g.a. scans, measured at 250°C, are greater than the initial water content of the aged material (*Table 3*). This could be due to some thermal degradation of the sample at the elevated temperature, or to the desorption of low-molecular-weight species, as reported by Netravali *et al.*[6].

The t.g.a. thermograms of the aged composite are reported in *Figure 6b*. Increased weight losses at 70 and 90°C can be associated with the higher initial water content of the specimens, as was the case for the unreinforced matrix (*Table 3*). However, ageing at 90°C resulted in a significant change in the shape of the t.g.a. thermogram when compared to the curves obtained for the other ageing temperatures. Increased amounts of desorbed water can be measured from the beginning of the t.g.a. scan at room temperature. This enhanced desorption rate is specific to the composite, as no change in the desorption behaviour of the cast resin was observed below 150°C. It is therefore clear that isothermal water ageing at elevated temperature induced a specific change in the desorption behaviour of the composite and this indicates the occurrence of some microstructural damage.

In order to quantify these changes in the desorption behaviour, an attempt has been made to compute the diffusion coefficient under the non-isothermal conditions encountered during the t.g.a. scan. The assumption was made that the desorption behaviour obeyed Fick's law, as was the case for the initial sorption steps. Furthermore, no significant thermal gradient was supposed to occur in the specimen during the temperature scan for the low heating rate being considered (2°C min^{-1}). The unidirectional Fick's law under anisothermal conditions can thus be written as follows:

$$\frac{\mathrm{d}C}{\mathrm{d}t} = D(t)\frac{\mathrm{d}^2C}{\mathrm{d}x^2} \tag{11}$$

where $D(t)$ represents the change in the diffusion coefficient with time during the temperature scan. By considering the variable change $\mathrm{d}\psi = D(t)\mathrm{d}t$, suggested by Cranck[19], equation (11) can be rewritten in the following manner:

$$\frac{\mathrm{d}C}{\mathrm{d}\psi} = \frac{\mathrm{d}^2C}{\mathrm{d}x^2} \tag{12}$$

After the 400 day period of water ageing, the specimens are close to saturation and the moisture can therefore be supposed to be uniformly distributed throughout the samples at the beginning of the temperature scan. Due to the helium flow in the t.g.a. oven, the water concentration at the specimen edges can also be regarded as equal to zero. The corresponding boundary conditions are:

$$C = C_i \quad \text{for} \quad -h/2 < x < h/2 \quad \text{and} \quad \psi = 0 \tag{13}$$

$$C = 0 \quad \text{for} \quad x = \pm h/2 \quad \text{and} \quad \psi \geqslant 0 \tag{14}$$

These boundary conditions are identical to those obtained by replacing ψ by t in the boundary conditions taken for isothermal diffusion. It is thus possible to apply to equation (12) the approximate solution proposed by Shen and Springer[27] for isothermal diffusion:

$$\frac{M_t}{M_i} = \exp\left[-7.3\left(\frac{\psi}{h^2}\right)^{0.75}\right] \tag{15}$$

where M_i is the initial water content, as measured at the end of the 400 days of isothermal ageing preceding the t.g.a. scan. At each time t, ψ can thus be computed from a knowledge of M_t, M_i and the thickness h:

$$\psi = \left(\frac{\ln M_i - \ln M_t}{7.3}\right)^{1.33} h^2 \tag{16}$$

From the values of ψ, an average diffusion coefficient D_a can be calculated at a given time (i.e. temperature) interval:

$$D_a = \frac{1}{t}\int_0^t D(t')\,\mathrm{d}t' = \frac{\psi}{t} \tag{17}$$

The values obtained for D_a after soaking the composite at 50°C have been reported in the form of an Arrhenius plot in *Figure 7*. Similar plots were obtained for the cast resin. The curve can be subdivided in two linear parts, with a cross-over point at around 160°C, which indicates a change in the temperature dependency of the desorption rate. The diffusion processes are dependent on the cooperative motions of the macromolecular chains[29] and it can therefore be assumed that this change is due to the increase in molecular mobility occurring through the glass transition of the epoxy network. It can also be noted that the cross-over point temperature is close to the T_g of the dry material, as measured by a differential scanning calorimetry (d.s.c.) scan ($T_g = 163$°C). However, a more

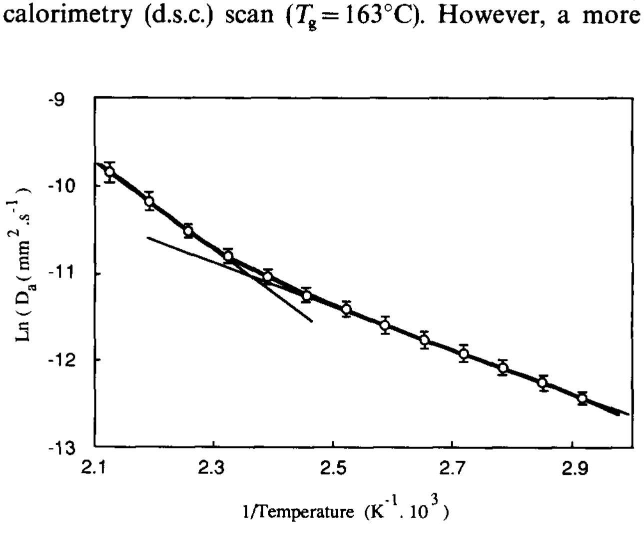

Figure 7 Arrhenius plot of the average diffusion coefficient D_a during a t.g.a. temperature scan, for a composite aged 400 days at 50°C

Table 4 Evolution of the activation energy of the average diffusion coefficient D_a with immersion temperature, for both unreinforced matrix and composite after 400 days of ageing

Immersion temperature (°C)	E_a[a] (kJ mol^{-1}) Unreinforced matrix	Composite
30	29	23
50	29	21
70	28	16
90	27	12

[a] Errors are within ±2 kJ mol^{-1}

accurate comparison between the T_gs of the wet material, as measured by t.g.a. and d.s.c., is not possible. Different specimen sizes would effectively result in different desorption rates during the temperature scan, which in turn would induce a different plasticization state in the glass transition zone.

In the glassy state, the activation energy of D_a was computed in the range 70–110°C (*Table 4*). No significant evolution can be noticed for the unreinforced matrix, thus confirming that the desorption behaviour of the epoxy network remains unchanged whatever the ageing temperature. On the other hand, a significant decrease of the activation energy of the composite occurred after soaking at 70 and 90°C. This evolution can be interpreted by considering that water desorption from the composite involved two processes:

(i) the thermally activated desorption of water molecules from the epoxy network;
(ii) the capillary flows that occur along hygrothermally induced cracks in the matrix and/or at the fibre/matrix interface. Such processes will result in enhanced desorption rates due to the increased area/volume ratio in the cracked material.

The analysis of the desorption kinetics of the cast resin revealed that no significant change occurred, even after ageing at elevated temperatures. The changes in the desorption behaviour of the composite specimens aged at 70 and 90°C can thus be attributed to the occurrence of capillary flows, rather than to a change in the desorption behaviour of the epoxy network. However, the microscopic examination of polished sections of the specimens did not reveal the occurrence of any cracking of the composite matrix. Capillary flows could therefore be attributed mainly to preferential moisture flow along the hygrothermally debonded interfaces. These processes can be supposed to present a low activation energy when compared to the desorption of water molecules from the epoxy network. As a result, the decrease of D_a after ageing at 70 and 90°C can be interpreted by considering an increased contribution of interfacial flow to the overall desorption processes. This result suggests that an enhanced interfacial weakening occurred above 50°C, i.e. during the non-Fickian sorption steps. It must be noted, however, that these conclusions are opposed to those which have been drawn from the analysis of interfacial water sorption during the Fickian diffusion steps (see above). These contradictory results can be explained by considering that interfacial degradation presents a time-dependent rate. During the initial (i.e. Fickian) sorption steps, water diffusion involves mainly molecular diffusion in the epoxy network, without any significant interfacial flow. On the other hand, non-Fickian water uptakes at long immersion times are associated with interfacial debonding, as revealed by the enhanced desorption rate during the t.g.a. scans. The interfacial degradation thus appears to result from the preliminary sorption of water in the epoxy matrix.

Dynamic mechanical behaviour

Further investigations of this interfacial degradation were carried out by dynamic thermomechanical analysis. By measuring the dynamic mechanical properties of the non-aged material, a baseline was established for the subsequent study of ageing effects.

Typical plots of log E'' and log E' in the α-transition zone of the composite are shown in *Figure 8*. Since the samples were fully crosslinked, similar spectra are obtained during a second isothermal test. The height of the log E'' peak remained constant whatever the frequency, thus showing the linear viscoelastic behaviour of the composite. The time–temperature superposition principle is illustrated by the shift of the viscoelastic spectra to higher temperatures with increasing frequencies.

The log E'' spectra of the aged material were analysed after 200 days of immersion at 90°C followed by re-drying. It can be noted that water ageing of the composite resulted in an irreversible broadening of the α-transition associated with the glass transition (*Figure 9*, top), especially at the lower frequencies (0.1 and 0.33 Hz). These changes are specific to the composite;

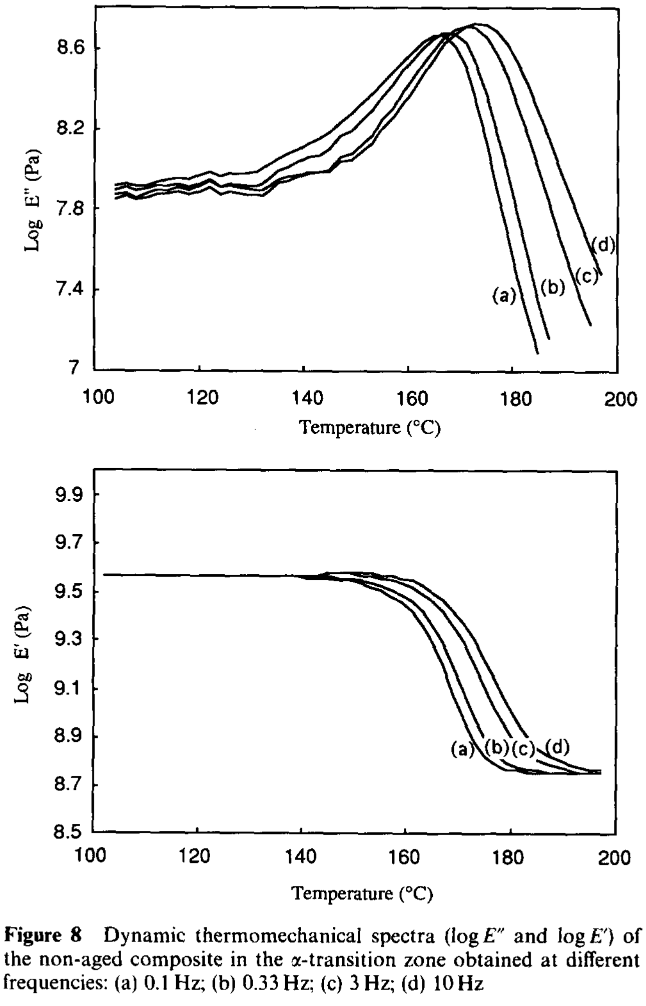

Figure 8 Dynamic thermomechanical spectra (log E'' and log E') of the non-aged composite in the α-transition zone obtained at different frequencies: (a) 0.1 Hz; (b) 0.33 Hz; (c) 3 Hz; (d) 10 Hz

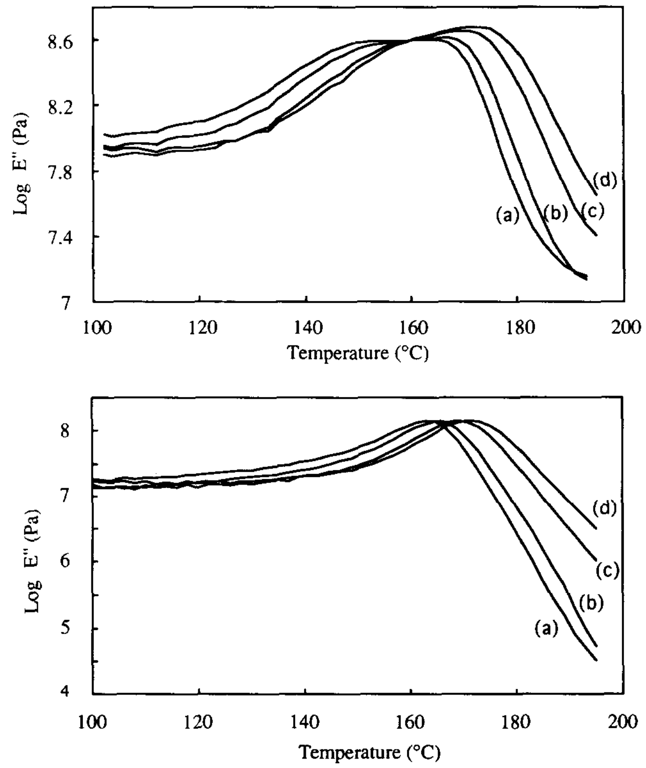

Figure 9 Dynamic thermomechanical spectra (log E'') of the composite (top) and the unreinforced matrix (bottom) after immersion for 200 days at 90°C in distilled water obtained at different frequencies (the aged specimens were re-dried prior to analysis): (a) 0.1 Hz; (b) 0.33 Hz; (c) 3 Hz; (d) 10 Hz

such a broadening was not observed in the case of the aged unreinforced resin (see *Figure 9*, bottom).

This broadening of the log E'' peak shows that hygrothermal ageing at 90°C results in a change in the distribution of the relaxation times associated with the α-transition. As the specimens were dried prior to analysis, these changes cannot be attributed to a plasticization effect. Moreover, it must be emphasized that the evolution of the shape of the relaxation peaks is not associated with any decrease in the rubbery modulus (*Table 5*). Since the rubbery modulus is related to the epoxy network crosslink density[30], it can thus be concluded that no significant decrease in the matrix crosslink density occurred during ageing.

Similar trends were observed to a more limited extent after 200 days of ageing at 70°C , but were never seen at 30 and 50°C. The broadening of the α-transition is thus specific to the composite which has been aged at the most elevated temperatures (70 and 90°C). A possible explanation for the change in the distribution of relaxation times would involve a specific evolution of the macromolecular network at the fibre/matrix interphase and/or debonding during ageing. Although it is not possible to identify these processes from a chemical point of view, they would affect the interface sufficiently to modify the relaxation processes associated with the α-transition. It must be noted that a similar broadening and even a splitting has been reported by studying the β relaxation of glass/epoxy composites exposed to boiling water[31]. Furthermore, the assumption of a specific interfacial relaxation after ageing at 70 and 90°C is consistent with the t.g.a. experiments, which also revealed an enhanced interfacial weakening at the same temperatures.

The kinetics of the log E'' broadening at 90°C was investigated by viscoelastic analysis of the composite at different ageing times, i.e. 7 days (which corresponds to the end of the Fickian sorption step), plus 100 and 200 days (non-Fickian sorption step). The data presented in *Figure 10* clearly indicate that a progressive broadening of the log E'' peak occurred during the non-Fickian sorption step when the epoxy matrix was close to saturation. Furthermore, it must be emphasized that this result is consistent with the conclusions drawn from the sorption experiments and thermogravimetric analysis which showed that interfacial debonding occurred during non Fickian sorption steps. There is also some indication of a correlation between the fibre/matrix debonding occurring on the macroscopic scale and the hygrothermally induced morphological changes at the interphase, which occur on the macromolecular scale. A more comprehensive treatment of this relationship relies, however, upon a more accurate analysis of the fibre/matrix debonding, which is presently being pursued.

CONCLUSION

Two distinct steps have been identified during hygrothermal ageing of the glass/epoxy composite studied in this work. The first of these is associated with Fickian diffusion at short times. From evaluation of the component of the diffusion coefficient along the fibre direction, it can be concluded that no significant capillary flow occurred at the fibre/matrix interface during this first stage. Diffusion thus involves only molecular diffusion of the water molecules through the epoxy matrix.

Table 5 Elastic rubbery modulus (log E') of the unreinforced matrix before and after 200 days of ageing (measured at 3 Hz and 180°C)

Immersion temperature (°C)	Log E'^{a} (Pa)
Non-aged	7.63
30	7.66
50	7.63
70	7.61
90	7.59

^{a}Errors are within ±0.05

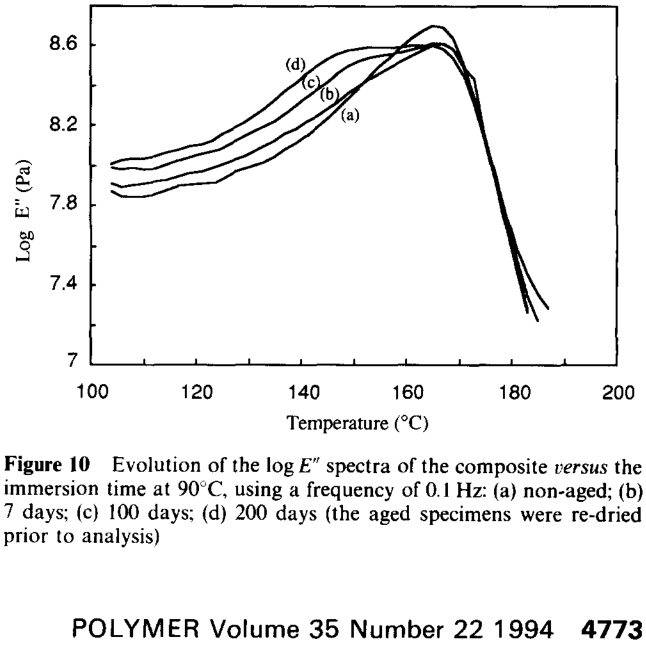

Figure 10 Evolution of the log E'' spectra of the composite *versus* the immersion time at 90°C, using a frequency of 0.1 Hz: (a) non-aged; (b) 7 days; (c) 100 days; (d) 200 days (the aged specimens were re-dried prior to analysis)

At longer times, a second step was identified in relation to non-Fickian diffusion behaviour. During this stage, both debonding and morphological changes occur at the interface, since the epoxy matrix is close to saturation. The significant increase in the desorption rates was interpreted by considering capillary flow along the debonded interfaces after ageing at 70 and 90°C. In addition, d.m.t.a. spectra revealed the irreversible occurrence of a broadening of the α-transition after water exposure at 70 and 90°C. These specific evolutions of the thermomechanical behaviour were interpreted in terms of morphological changes and/or debonding at the interface during non-Fickian steps.

Major changes in desorption and thermomechanical behaviour occurred between 50 and 70°C, thus suggesting a temperature limit for hygrothermal interfacial damage. From the kinetic analysis of these processes, it can be concluded that molecular diffusion through the epoxy matrix is the rate controlling process for the interfacial weakening of the composite being considered.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the support for this study by the CNIM (Constructions Industrielles de la Méditerranée, Toulon, France).

REFERENCES

1 McKague, E. L., Reynolds, J. D. and Halkias, J. E. *J. Appl. Polym. Sci.* 1978, **22**, 1643

2 Keenan, J. D., Seferis, J. C. and Quinlivan, J. T. *J. Appl. Polym. Sci.* 1979, **24**, 2375

3 Peyser, P. and Bascom, W. D. *J. Mater. Sci.* 1981, **16**, 75

4 Barton, J. M. and Greenfield, D. C. L. *Br. Polym. J.* 1986, **18**, 51

5 Netravali, A. N., Fornes, R. E., Gilbert, R. D. and Memory, J. D. *J. Appl. Polym. Sci.* 1985, **30**, 1573

6 Netravali, A. N., Fornes, R. E., Gilbert, R. D. and Memory, J. D. *J. Appl. Polym. Sci.* 1986, **31**, 1531

7 Luoma, G. A. and Rowland, R. D. *J. Appl. Polym. Sci.* 1986, **32**, 5777

8 Hoh, K. P., Ishida, H. I. and Koenig J. L. *Polym. Compos.* 1990, **11**, 192

9 Liao, Y. T. *Polym. Compos.* 1989, **10**, 424

10 Menges, G. and Gitshner, H. W. in 'Proceedings of the Third International Conference on Composite Materials (ICCM/3)' (Ed. A. R. Bunsell), Vol. 3, Pergamon, Oxford, 1980, p. 25

11 Cairns, D. S. and Adams, D. F. *J. Reinf. Plast. Compos.* 1983, **2**, 239

12 Bouadi, B. and Sun, C. T. *J. Reinf. Plast. Compos.* 1989, **8**, 40

13 Bascom, W. D. *J. Adhes.* 1970, **2**, 161

14 Metcalfe, A. G. and Schmitz G. K. *Glass Technol.* 1972, **13**, 5

15 Aveston, J., Kelly, A. and Sillwood J. M. in 'Proceedings of the Third International Conference on Composite Materials (ICCM/3)' (Ed. A. R. Bunsell), Vol. 1, Pergamon, Oxford, 1980, p. 556

16 Gaur, U. and Miller, B. *Polym. Compos.* 1990, **11**, 217

17 Chateauminois, A., Chabert, B., Soulier, J. P. and Vincent, L. *Composites* 1993, **24**, 547

18 Chateauminois, A., Chabert, B., Soulier, J. P. and Vincent, L. in 'Proceedings of the Eighth International Conference on Composite Materials (ICCM/8)' (Eds S. W. Tsai and G. S. Springer), 1991, p. 16-E

19 Cranck, J. 'The Mathematics of Diffusion', Oxford University Press, Oxford, 1975

20 Johncock, P. and Tudgey, G. F. *Br. Polym. J.* 1983, **15**, 14

21 Wong, J. C. and Broutman, L. J. *Polym. Eng. Sci.* 1985, **25**, 521

22 Wong, J. C. and Broutman, L. J. *Polym. Eng. Sci.* 1985, **25**, 529

23 Apicella, A. and Nicolais, L. *Adv. Polym. Sci.* 1985, **66**, 190

24 Carfagna, C. and Apicella, A. *J. Appl. Polym. Sci.* 1983, **28**, 2881

25 Brettle, J., Brewis, D. M., Comyn, J., Cope, B. C., Goosey, M. T. and Hurditch, R. D. *Int. J. Adhes. Adhes.* 1983, **3**, 189

26 Jones, F. R., Shah, M. A., Bader, M. G. and Boniface, L. in 'Proceedings of the Sixth International Conference on Composite Materials (ICCM/6)' (Eds F. L. Matthews, N. C. R. Buskell, J. M. Hodgkinson and J. Morton), Vol. 4, Elsevier, Amsterdam, 1987, p. 443

27 Shen, C. H. and Springer G. S. in 'Environmental Effects on Composite Materials' (Ed. G. S. Springer), Technomic, Lancaster, PA, 1981, p. 15

28 Pollard, A., Bagott, R., Wostenholm, G. H., Yates, B. and George, A. P. *J. Mater. Sci.* 1989, **24**, 1665

29 Barrie, J. A. in 'Diffusion in Polymers' (Eds J. Cranck and S. Park), Academic, London, 1968, p. 259

30 Murayama, T. and Bell, J. P. *J. Polym. Sci. Polym. Phys. Edn* 1970, **8**, 437

31 Williams, J. G. *J. Mater. Sci.* 1987, **17**, 1427